# The metal-insulator phase change in vanadium dioxide and its applications

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# The metal-insulator phase change in vanadium dioxide and its applications

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#### ABSTRACT

Vanadium dioxide is an unusual material that undergoes a first-order Metal–Insulator Transition (MIT) at 340 K, attracting considerable interest for its intrinsic properties and its potential applications. However, the nature of MIT has not been fully determined. Variants of density functional theory (DFT) have been widely used to study the MIT in pure and doped VO<sub>2</sub>. A full description of MIT is complicated by several related factors such as V–V dimerization, magnetic properties, and spin correlations. Each of these requires careful attention. In this Perspective, we explain why DFT fails, introduce a spin-pairing model of MIT, and propose a new way to estimate the transition temperature. We then use the method to study the doping and alloying process. Finally, we give an overview of some applications of MIT. This work aims to provide insight into and stimulate more research studies in this promising field.

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#### I. INTRODUCTION

Vanadium dioxide (VO<sub>2</sub>) undergoes a first-order metal-insulator transition (MIT) at around 340 K,<sup>1</sup> in which a dramatic change in electronic conductance and optical properties occurs within a few femtoseconds.<sup>2–4</sup> In pure VO<sub>2</sub>, the high-temperature phase has a rutile structure or "R" phase, while the low-temperature phase is monoclinic (M<sub>1</sub>). This temperature-induced MIT can also be accessed by applying voltage or stress.<sup>10</sup>

The MIT makes VO<sub>2</sub> a material of great interest for various applications in low-power electronics, steep-slope transistors, neuromorphic computing, RF components, and sensors or large area coatings like smart windows,<sup>5–11</sup> which are illustrated in Sec. IV. A second point is that the transition temperature ( $T_C$ ) of 340 K is somewhat non-optimum, too high for smart windows but too low for many electronic applications. Thus, it is useful to be able to tune  $T_C$ up or down by alloying with other metal oxides. Therefore, theoretical modeling of the MIT is necessary for these applications. A key question is whether structural or electronic transition is the primary cause of MIT.<sup>12</sup> We aim to provide insights into this question.

Density Functional Theory (DFT) has been widely used to describe different phases of pure and doped VO<sub>2</sub>. At first, Local Density Approximation (LDA) was used to calculate the electronic structure of VO2. But it gives a zero bandgap for the lowtemperature M1 phase.13 Adding some nonlocal exchange functional appears to solve the problem,<sup>14-21</sup> but leaves ground state energy errors.<sup>21</sup> In this Perspective, we pay special attention to the magnetic properties in the DFT calculation. We perform non-spin-polarized DFT calculations to study the electronic structure of each phase and find metallic rutile (R) and insulating M1 phases. However, experiments show that VO<sub>2</sub> is magnetic in each phase.<sup>22-25</sup> Experiments show that the R phase is Curie-Weiss paramagnetic, while the M1 phase is Van Vleck paramagnetic. The problem with spin-polarized DFT is that it cannot obtain V-V dimerization in the M1 phase. The reason DFT fails is the lack of enough correlation rather than exchange to describe the two-body effect of spin dimers. Therefore, hybrid functionals are not favored. We introduce a spin-pairing model that is consistent with experiments describing the MIT mechanism. Then, we perform noncollinear spin-polarization calculations of the paramagnetic phases.

The calculation estimates a transition temperature of 341 K in pure  $VO_2$ , which is near the experimental value. Finally, we use the model to predict transition temperature and electronic structure of doped  $VO_2$ . There are some complex post-DFT methods introduced shortly for calculating the electronic density of states and magnetic structure. The novel aspects of this Perspective are to provide a basis for DFT-like calculations of the electronic structure and total energy difference of each phase, to allow multi-atom models of pure and alloy supercell structure as the basis for future device modeling.

#### **II. CRYSTAL STRUCTURES**

The structural transition of vanadium dioxide at the transition temperature has already been noted. The crystal structures are shown in Fig. 1. The high-temperature form rutile (R) has a tetragonal cell containing two formula units. This lattice has only one type of vanadium and oxygen site in each cell, with a symmetry of  $P4_2/mnm$ . A chain of vanadium atoms in this phase is separated by 2.86 Å along the c direction.<sup>26–28</sup>

At the MIT, the adjacent vanadium atoms in a chain move vertically toward each other with rotations to form a quasi-1D Peierls distortion and two types of oxygen sites, giving the low-temperature  $M_1$  phase with a lattice symmetry of  $P2_1/c$ . The primitive cell of  $M_1$  is twice the primitive cell of R along the chain direction, with a V–V dimer length of 2.62 Å and a inter-dimer separation of 3.12 Å.<sup>27,28</sup>

Besides these two phases, there are several intermediate structures caused by doping or uniaxial stress.<sup>22,23,29–31</sup> Among them, the most important phase is  $M_2$  with C2/m symmetry, where half of the vanadium chains are dimerized. Its primitive cell has two kinds of vanadium, paired and unpaired, and three kinds of oxygen. Nuclear magnetic resonance (NMR) and EPR find that



**FIG. 1.** Left: Schematic diagram of vanadium site dimerization for  $M_1$  and  $M_2$  phases and its absence in the rutile phase, with doubling the primitive rutile cell along with Oz in  $M_1$  and  $M_2$ . The dashed green lines show the lattices of  $M_1$  and  $M_2$ .  $M_2$  has a magnetic moment of one Bohr magneton in each unpaired V. Right: DFT + U relaxed structure of each phase, and the calculation details are given in Sec. III B.

there is a magnetic moment of one Bohr magneton on each V in the unpaired chain,  $^{22-25}$  as in Fig. 1.

There are also tetragonal phases other than R called A,  $B^{30,31}$  with symmetry  $P4_2/ncm$ , I4/m. The phase diagram is complicated, while the mechanism of the phase transition can vary. Here, we focus on the R to  $M_1$  transition.

## III. DFT WITH NONLOCAL EXCHANGE-CORRELATION FUNCTIONALS

The electronic structure of R and M1 phases was first calculated by Wentzcovitch et al.<sup>13</sup> using LDA. It fails to give an insulating state for the M1 phase. To provide enough short-range interaction to split the  $d_{\parallel}$  orbital, an option is to add nonlocal exchange to the density functional. Eyert<sup>15</sup> uses the Heyd, Scuseria, and Ernzerhof (HSE) hybrid functional for this, which creates a gap in the M<sub>1</sub> state. We can compare this with adding a Hubbard U term to the density functional such as in generalized gradient approximation (GGA). GGA + U requires less computation time than HSE while correcting the correlation part rather than the exchange part. Thus, GGA + U is more capable of describing VO<sub>2</sub>. Note that all calculations done in Sec. III A and by Eyert<sup>15</sup> or Wentzcovitch et al.<sup>13</sup> are non-spin-polarized. In Sec. III B, we outline spin-polarized calculations. In Sec. III C, we illustrate the MIT mechanism by a spin-pairing model that is beyond DFT. In Sec. III D, we suggest a way of describing the paramagnetic system. In Sec. III E, we provide some results for doped VO<sub>2</sub>. In Sec. III F, we discuss some post-DFT methods.

#### A. Non-spin-polarized calculations using GGA + U

We study the electronic structures of the R and M<sub>1</sub> phases using DFT + U for U = 0–5 eV plotted in Fig. 2(a). The calculation is performed using the CASTEP package<sup>36</sup> with the GGA-PBE functional, ultra-soft pseudopotentials,  $5 \times 5 \times 5$  Monkhorst-Pack grid k-points, and a cutoff energy of 340 eV. The structures of all phases are relaxed until the residual force is under 0.03 eV/Å, without any constraints. The data in the shaded zone in Fig. 2(a) are those close to experimental values. For a large U, the R phase is no longer a local minimum, but instead a local maximum. Therefore, a very large U > 5 eV is unrealistic in this case. We adopt U = 0.90 eV in the electronic structure calculations. The calculations of R and M1 are spin-unpolarized in nature, which also means non-spin-polarized. For M2, we use spin-polarized calculations as there is an AFM order for the half-unpaired V, which is consistent with the experiment,  $^{22-25}$  as shown in Fig. 1. In Fig. 2(b), we obtain M<sub>1</sub> and M<sub>2</sub> phases with bandgaps and a metallic R phase. In the partial density of states (PDOS) of M<sub>1</sub>, there are a pair of non-spin-polarized electrons in each dimer, occupying one d band in the VBM peak. There are nine empty d bands mixed with parallel and vertical d orbitals.

The calculated and experimental lattice parameters<sup>27–33</sup> are listed in Table I. The theory and experimental values are similar. We also calculate the dimer lengths in  $M_1$  and  $M_2$  for various U, all close to experimental values and insensitive to U, unlike the bandgap of  $M_1$  and the enthalpy change. We also calculate the phonon spectra using the final displacement method. Figure 3(c)



**FIG. 2.** (a) Enthalpy change of MIT and bandgaps vs Ueff, the experimental value is in dashed horizontal red and blue line, and the shade zone includes the data of DFT + U that are close to the experimental values.<sup>34,35,37</sup> Among them, Ueff = 0.90 eV is chosen to plot the (b) PDOS of Rutile, M1, and M2. (c) Phonon Density of States of R and M1 phase with  $U_{eff}$  = 0.90 eV. There are states at the negative energy region in R phase, meaning that R is an unstable phase while M1 is stable.

**TABLE I.** Experimental<sup>27–33</sup> and DFT + U (U = 0.90 eV) calculated lattice constant of VO<sub>2</sub> phases. Note that for M<sub>2</sub>, the lattice constant of the conventional cell rather than the primitive cell is shown.

	Rutile		$M_1$		M <sub>2</sub>	
	Exp	DFT + U	Exp	DFT + U	Exp	DFT + U
а	4.55	4.58	5.38	5.37	9.06	9.25
b	4.55	4.58	4.53	4.56	4.52	4.61
с	2.86	2.76	5.73	5.60	5.80	5.80
V–V			2.62	2.47		2.42
dimer						
α	90.00	90.00	90.00	90.00	90.00	90.01
β	90.00	90.00	122.65	121.87	90.00	90.01
γ	90.00	90.00	90.00	90.00	91.85	93.43

plots the phonon density of states of R and  $M_1$ . The R phase is unstable, so it has some negative phonon frequencies.

So far, it appears that GGA + U can describe  $VO_2$  with a spin-unpolarized method. However, magnetic moments have been observed experimentally. We next discuss the problem of the spin-polarized calculations of  $M_1$  and find a magnetic ground state with lower energy than the non-spin-polarized  $M_1$ .

#### B. The problem of magnetism

By switching on spin polarization, there are two main choices of long-range magnetism: ferromagnetic order (FM), where all magnetic moments align in the same direction, and anti-ferromagnetic order (AFM), where adjacent magnetic moments are aligned oppositely. There are several DFT studies on spin-polarized  $VO_2$ .<sup>16–21</sup> Among them, Mellan *et al.*<sup>18</sup> present a complete study of



**FIG. 3.** Potential-energy surface (eV/VO<sub>2</sub>) and bandgap (eV) as a function of dimerization  $\delta$  (Å), which is the difference in d(V – V) between consecutive pairs of cations along the rutile c axis. Values are shown for nonmagnetic (NM), antiferromagnetic (AFM), and ferromagnetic (FM) orderings, and for a range of d electron on-site Coulomb interaction strengths. Reproduced with permission from T. A. Mellan *et al.*, Phys. Rev. B **99**, 064113 (2019). Copyright 2019 American Physical Society.

the energy levels of NM (non-spin-polarized), FM, and AFM  $VO_2$  with different dimerization lengths, using GGA + U, as shown in Fig. 3.

R phase is undimerized, while the  $M_1$  phase should have a finite dimerization  $\delta$ . However, if U is added to create a correlation part, the "non-spin-polarized" or non-magnetic (NM) state is no longer the most stable phase. By forcing the electrons to pair, NM becomes less stable than FM or AFM. One may conclude that VO<sub>2</sub> should be FM or AFM. However, long-range magnetism like FM and AFM were already excluded by the experiment. Additionally, both FM and AFM, as calculated by DFT + U, favor an undimerized structure, shown in Fig. 3 by red and blue data, whereas experiments clearly show dimers. Neither GGA + U nor HSE can give the experimental transition enthalpy of 44 meV/FU (formula unit)<sup>21,34,35</sup> of Fig. 4 with the spin-polarized calculation. Thus, we now study the magnetism problem from the viewpoint of many experimental reports of the 1970s on VO<sub>2</sub>.

## C. The role of spin correlation in the metal-insulator transition

Figure 4(a) shows the magnetic susceptibility vs temperature dependence using the Faraday method, redrawn from Pouget *et al.*<sup>24</sup> A step has been observed at the transition temperature. The curve varies as ~1/T above 340 K, indicating that the rutile phase is paramagnetic (PM), following the Curie–Weiss Law. Below 340 K, the magnetic susceptibility is independent of temperature, showing that the M1 phase is not FM or AFM. The phase transition has an enthalpy change of 44 meV/FU and is a first-order transition, unlike the conventional second-order Landau ferromagnetic–paramagnetic transition. Besides, the Mössbauer data of Kosuge<sup>38</sup> show



**FIG. 4.** (a) Schematic diagram of spins in the R and  $M_1$  phases. R is paramagnetic with random spin directions. It is suggested that the spins in  $M_1$  dimers may also have random spin directions but with spins within dimers aligned, shown joined by a red curve. (b) Magnetic susceptibility of pure VO<sub>2</sub> and 5% Nb-doped VO<sub>2</sub> vs temperature compared. The high-temperature R phase is Curie–Weiss paramagnetic, whereas the low-temperature M1 phase is a singlet dimer (Van Vleck paramagnet). Reproduced with permission from J. P. Pouget *et al.*, J. Phys. Chem. Solids **33**, 1961 (1972). Copyright 1972 Elsevier.

an absence of AFM order in the  $M_1$  phase. We concluded that the system is spin-polarized for all temperatures, but there should also be no long-range magnetic order at any finite temperature. An unpaired electron in each V cannot vanish with only structural deformation. Pouget<sup>24</sup> doped VO<sub>2</sub> by Nb. NbO<sub>2</sub> is rutile in its natural form and is NM. The curve should be unchanged with Nb doping, by presuming the absence of spin in  $M_1$  phase. However, it is not. The magnetic susceptibility in the low-temperature region depends on the temperature, similar to the paramagnetic dispersion. Kosuge and Berglund suggest that  $M_1$  is also paramagnetic, but Van Vleck paramagnetism. The Van Vleck paramagnetism can be derived from the second-order perturbation theory to the ground state.<sup>39</sup> It contributes a weak, positive, and temperature-independent magnetic susceptibility, as shown in Fig. 4(b).

We now suggest a spin-pairing model. An ideal pure VO<sub>2</sub> in the M1 phase is 100% dimerized. This means that each unpaired electron in V is strongly correlated to another unpaired electron inside the dimer, with the same magnetic moment magnitude but the opposite direction, giving a quantum singlet state. The singlet state has a good quantum number of  $L = L_1 + L_2 = 0$ , so it contributes to no Curie-Weiss magnetic susceptibility as it is  $\sim \frac{\sqrt{J(J+1)}}{\tau}$  , and a second-order Van Vleck paramagnetism arises. Above the transition temperature, the dimer breaks up, so the magnetic moments are no longer paired, and each of them has an angular moment of  $L = \frac{1}{2}\hbar$  and a random direction, contributing to the Curie-Weiss paramagnetism. Doping with Nb breaks the dimers, so Nb releases some spins to act as paramagnets in the lowtemperature phase. When the doping ratio reaches 50%, the step vanishes, so there is no MIT and it is Curie-Weiss paramagnetic in all temperature ranges.

The  $M_1$  phase is described by the quantum Monte Carlo method as a "non-magnetic singlet state" consisting of spin dimers due to strong intradimer coupling and weak interdimer coupling.<sup>12</sup> It is called "dynamic singlet state" in the language of dynamic mean-field theory (DMFT).<sup>41</sup> The term "dynamic" can be interpreted as the random direction of spins, while the term "singlet" means the magnetic moments inside the dimer are strongly correlated to have opposite directions. Therefore, the dimer forms a local non-spin-polarized system. We emphasize that this quantum singlet state is not AFM, it can have magnetic entropy from the random spin directions, whereas AFM and FM have long-range order, without magnetic entropy. Figure 4(a) shows a schematic diagram of this singlet state in rutile.

With the model in Fig. 4(a), a picture of MIT emerges. At high temperature, the spin coupling is as weak as ~50 meV/FU,<sup>39</sup> the magnetic moments are randomly oriented, as is in Curie– Weiss paramagnetic order. The overlap of electron orbitals allows an electron to hop between sites, giving it a metallic state. As the temperature falls below 340 K, the V–V dimer forms with a strong intradimer coupling of ~440 meV, resulting in spin pairing. The two sites within the dimer share electrons, so the hopping between these two sites is large. However, the electron cannot hop outside the dimer. Therefore, M<sub>1</sub> is an insulating state. The dimerization causes a large rearrangement in the hopping, although the average hopping value is constant during MIT.<sup>40</sup> The dimerization and spin pairing happen simultaneously within the experimental limit.<sup>41</sup>

Apart from the explanation of MIT, there are other key experiments worth mentioning. The excitation energy across the correlation gap has been measured by resonant inelastic x-ray scattering<sup>42</sup> showing the dominance of correlation over exchange. Laverock *et al.*<sup>43</sup> pointed out that electron correlation is central to MIT, after observing a monoclinic-like metallic phase in strained VO<sub>2</sub> heated on M<sub>1</sub>. Huffman *et al.*<sup>19</sup> conclude that the energy gap is insensitive to the dimerization in M<sub>2</sub> chains. Wegkamp *et al.*<sup>44</sup> find instantaneous bandgap collapse in the photo-excited state of M<sub>1</sub>.

The ultrafast renormalization causes a depairing of the spins even when the dimer is preserved. Spin pairing is of long range. The collective length has been measured in the on-top VO<sub>2</sub>/ W-doped VO<sub>2</sub> layer.<sup>45</sup> Light W doping can decrease the  $T_C$  of VO<sub>2</sub>. Therefore, there should be two separate MITs for each layer. By shrinking the thickness of both layers to 15 nm, Yajima *et al.*<sup>45</sup> found a two-step to one-step phase change, meaning both layers start MIT at the same temperature, in between their separate temperatures. Budai *et al.*<sup>46</sup> illustrate the critical role of anharmonic lattice dynamics in phase competition. Cavalleri *et al.*<sup>47</sup> show that the atomic arrangement of the R phase is necessary to form the metallic state, even if the correlated d band is highly hole-doped.

Another important question is the entropy contribution due to the spin pairing. We use the model in Fig. 4(b). The entropy of a system is given by

$$S = -k_B \sum_{i} P_i \log P_i, \tag{1}$$

where  $P_i$  is the probability of the *i*th microstate. In a paramagnetic system, the normalized probability density function is  $p(\theta, \varphi) = \frac{\sin \theta}{4\pi}$ . In the "singlet state," the spins inside the dimer are correlated, so the entropy decreases to half. The change of the entropy per FU during MIT is

$$\Delta S = \frac{1}{2} S_{PM} = -\frac{1}{2} k_B \int p(\theta, \varphi) \log \left[ p(\theta, \varphi) \right] d\varphi d\theta = 1.42 k_B, \quad (2)$$

with experimental transition temperature, the enthalpy change contribution from the spin disorder of  $\sim$ 42 meV, which is almost the same as the experimental enthalpy change. Therefore, spin entropy contributes most of the enthalpy change at the MIT.

To estimate the transition temperature, Zheng and Wagner<sup>12</sup> calculate the FM, AFM, and AFM (intra) energies to extract the spin coupling factor J of the intradimer, interdimer, and interchain cases. Then, they run simple Monte Carlo calculations for both R and M<sub>1</sub> cases to obtain the magnetic susceptibility vs temperature dependence based on the Ising model. The curves match well with the results of Kosuge<sup>38</sup> and Zylbersztejn and Mott<sup>48</sup> results. Then, a range of transition temperatures can be seen. Here, we proposed a simple way with only mean-field theory to estimate the transition temperature based on the spin-pairing model.<sup>49</sup> The inter-chain exchange interactions were estimated earlier to be less important, based on the strong distance dependence of J.<sup>49</sup> Thus, by ignoring the interdimer and interchain spin correlations, the system can be simplified into a two-body problem. The dimer Hamiltonian can be written as

$$H_{dimer} = -J\hat{s}_1 \cdot \hat{s}_2,\tag{3}$$

where J is the intradimer exchange coupling factor. The transition temperature is given by the mean-field theory,

$$T_C = -\frac{J}{2k_B} = \frac{2\Delta E}{3k_B}.$$
 (4)

where  $\Delta E$  is the enthalpy change of the MIT. It is also the energy split of the singlet state, which is (3/4) *J*. It gives a reasonably good result of 342 K.<sup>49</sup>

#### D. DFT + U calculated paramagnetic VO<sub>2</sub>

DFT is unable to capture this spin-pairing model entirely because the singlet state is based on the two-body correlations, whereas DFT simplifies the case to a single-body Hamiltonian, which has an exact form and puts the many-body parts into the exchange-correlation term, which lacks an exact form. Therefore, the dimer arises from the many-body effect beyond DFT. This problem can be tackled by post-DFT methods like quantum Monte Carlo DMFT. Although DFT cannot find the correct magnetic ground state as easily as geometric structures, we can use the experimental structure and then fix the spin configuration of the PM and singlet states.

In Ref. 49, we showed that DFT + U can describe the Curie– Weiss PM alignment of the R phase using the noncollinear spins with a random spin direction on each V site. Therefore, a large supercell is necessary to describe these random directions. We tried supercells from 12 atoms to 768 atoms, generating a set of spherically distributed spin directions as randomly as possible, and did the electronic relaxation. DFT + U was able to give a good PM state with a spin of one Bohr magneton on each V and with the relaxed configuration remaining PM. For  $M_1$ , we checked that the electronic structure of the singlet state is equivalent to AFM. AFM is a special case of this singlet paramagnetism where all spins have a long-range alignment. The electronic structures of AFM and singlet PM are identical as they have the same mechanism of bandgap



**FIG. 5.** PDOS of VO<sub>2</sub> in the R and M<sub>1</sub> phases. The rutile supercell has 216 atoms. This supercell is enough to produce an experimental enthalpy change and a metallic phase. Reproduced with permission from H. Lu *et al.*, Phys. Chem. Chem. Phys. **22**, 13474 (2020). Copyright 2020 Royal Society of Chemistry.

opening, which is to stop electrons hopping between the nearest neighbor. We calculated the enthalpy change and found that with a larger supercell and more random spin fixes, the enthalpy changes to approach the experimental situation, as in both metallic R and insulating  $M_1$ , as shown in Fig. 5.<sup>49</sup>

In summary, there are two different low-cost ways to describe a bandgap in DFT, DFT+U, and hybrid functionals. These methods act differently. The U term is a repulsion of two electrons of opposite spin on the same site and is related to correlation. Hybrid functionals add back a fraction (a "mixing parameter") of non-local Hartree-Fock exchange into the density functional and represent exchange, while correlation is included in the DFT term. Hybrid functional methods like B3LYP,<sup>50</sup> HSE,<sup>51</sup> or screened exchange<sup>52</sup> are effective at correcting the bandgap error for typical semiconductors with standard parameters. One of the earliest examples, B3LYP, fitted gaps for various semiconductors with its standard parameters.  $^{50}\ \mathrm{HSE}^{51}$  was regarded as a success for VO2 as it was one of the first such methods to obtain a bandgap.1 However, more recently, its bandgap using such parameters was seen to be too large<sup>49</sup> in that there is no reason to reduce the HF mixing parameter for VO<sub>2</sub>.

GGA + U acts more on the correlation terms of bandgap correction. Its origins are in the models of localized magnetic impurities in metals. It is now often used to shift the energies of d or f states of low dispersion also in semiconductors to fit excitation spectra. Now, although GGA + U has a more empirical background, it may represent the origin of the bandgap of VO<sub>2</sub> more correctly.

#### E. Doping and alloying

Light or heavy doping/alloying is often used to study the MIT mechanism and applications. Doping is useful to vary the transition temperature, to lower  $T_C$  for smart window coatings, and to raise  $T_C$  for steep slope transistors or RF devices. It is often desired to change the transition temperature and bandgap. Experimentally, VO<sub>2</sub> can be doped with elements.<sup>23–25,29,53–57</sup>  $T_C$  increases for Ge and Si doping, while it decreases for Mg, Fe, Nb, W, Al, Fe, and Ga doping.

The doping ratio should be below 7% as heavy doping reduces the resistivity ratio at the MIT. It is easy to understand this with the spin-pairing model. A single defect in a dimer will release a conductive V, so the low-temperature phase is less insulating, whereas a single defect is also a scattering center that scatters electrons in the high-temperature phase and makes it a bad metal. Therefore, using a dopant to change the transition temperature is not ideal.

We now try to extend the spin-pairing model to the lightly doped case. The most abundant case should be a single-site substitution, while it can also be a double substitution (two V atoms in a dimer are each replaced by a dopant). We start with the simplest case, Ge doping. Pure GeO<sub>2</sub> is a rutile insulator in its natural form so that Ge doping is just a replacement of V with little deformation of oxygen. Therefore, Ge is just a spin vacancy and contributes no states near the Fermi level, as shown in Fig. 6. Since the transition temperature is proportional to the strength of the spin-exchange coupling factor *J* inside the dimer,<sup>49</sup> we can calculate the enthalpy



FIG. 6. Atomic structure of Ge and Ga doped VO<sub>2</sub>. Oxygen: red; vanadium: gray; germanium: green; gallium: pink; fivefold vanadium where spin vanishes: black.

change of Ge-doped VO<sub>2</sub> and derive  $T_C$  using

$$T_{CX} = T_C \frac{\Delta E_X}{\Delta E(1-n)},\tag{5}$$

where  $T_C$  is the transition temperature of pure VO<sub>2</sub> (340 K in bulk),  $T_{CX}$  is  $T_C$  in the alloy, and *n* is the density of spin vacancies (impurities). For single defects, *n* is the doping ratio. For a double substitution, *n* is the density of dimer vacancies. The calculated PDOS is in Fig. 7(a).

We then consider a more complicated case. If a dopant is not sixfold like Ge or Nb or Si, there are O vacancies at the defect sites. Also, if the dopant ion like Mg has a fixed valence that differs from V, there is a vacancy. For each Mg substitution, there is one O vacancy. For each Al, Ga substitution, there is half an O vacancy.



FIG. 8. Structure, spin configuration, and PDOS of 20% MgO alloying VO<sub>2</sub>, with fivefold V sites. Reproduced with permission from H. Lu *et al.*, Phys. Rev. Mater. 3, 094603 (2019). Copyright 2019 American Physical Society.

We run those dopant calculations with the AFM configuration for convenience. Both phases have different structures than Ge-doped VO<sub>2</sub>. The oxygen vacancy causes a local deformation and a fivefold V site marked black in Fig. 8. The fivefold V site as in V<sub>2</sub>O<sub>5</sub> has a closed shell with no spin. Therefore, there are two dimer vacancies on one defect site. The formula above is still valid, but *n* is the density of the dimer vacancies, not the doping ratio.

The most complicated cases are W, Fe, and Cr doping. These oxides are magnetic but have different magnetic orderings. Apart from the J factor between V, we also need to calculate the J factor between V and the dopant and the J factor between dopants. The formula Eq. (3) is no longer valid, and one must calculate the transition temperature from the Hamiltonian, which is more than a two-body problem and beyond the scope of the present methods. Also, experiments have found that new phases  $M_2$  and T exist in the low-temperature region.



**FIG. 7.** (a) PDOS of 2.08% Ge-doped VO<sub>2</sub> in both phases. Reproduced with permission from H. Lu *et al.*, Phys. Chem. Chem. Phys. **22**, 13474 (2020). Copyright 2020 Royal Society of Chemistry. (b) Transition temperature vs doping ratio from the calculations (small rounded dots) and experimental data (big square dots). <sup>53–57</sup>

In Fig. 7(b), we show the trend of transition temperature vs doping ratio for several dopants. The calculated data match well with the experimental data from Refs. 53-56. One possible explanation for this trend is that the dopant changes the dimer lengths near the defect sites and, therefore, also changes the *J* factor.

We also consider the heavy doping (n > 10%) case where our MIT model breaks down and new phases occur. MgO is a nonmagnetic highly ionic oxide. The radius of Mg is large compared with that of V. We found that heavy Mg doping immediately brings about the M<sub>2</sub> phase and the AFM configuration. If n > 20%, there will be a reconstruction for MgO–VO<sub>2</sub> alloys. The alloys have a fivefold V and a larger bandgap than doped VO<sub>2</sub> with AFM-ordered domains,<sup>17</sup> as shown in Fig. 8.

#### F. Post-DFT methods

Since DFT is not enough to describe the strong correlation effects inside dimers, beyond-DFT methods must be used. The first-principle quantum Monte Carlo method can describe two-body correlation in the dimer.<sup>40</sup> Dynamic mean-field theory (DMFT) is widely acknowledged as a strong tool for the strongly correlated, many-body system. The cluster DMFT method enables one to add spatial dependence to the impurity self-energy. It is more computationally demanding, but it successfully proposes the mechanism of MIT and introduces the idea of dynamic V–V singlet pairs in M<sub>1</sub> as well as the temperature-dependent bandgap in M<sub>1</sub>, as shown in Fig. 9.<sup>58–60</sup> A parameter-free GW method is claimed to include correlation effects in both the R and the M<sub>1</sub> phases.<sup>61</sup>

#### **IV. APPLICATIONS**

 $VO_2$  has various proposed uses, as a large-area reflective surface or "smart window" for environmental control in buildings,<sup>5,57</sup> for optical (infrared) switching elements, and as a switchable micro-



**FIG. 9.** DFT + DMFT-based total (black dashed line) and projected DOS of (a) the R and (b)  $M_1$  phases of VO<sub>2</sub>. Reproduced with permission from W. H. Brito *et al.*, Phys. Rev. Lett. **117**, 056402 (2016). Copyright 2016 American Physical Society.

electronic component, for steep-slope devices or RF components. As a smart window material, the optimum transition temperature  $T_C$ would be just above room temperature, such as 310 K, or below the 340 K of pure VO<sub>2</sub>. For a microelectronic device, the optimum transition temperature would be above 370 K or more so that the device could be operated over a reasonable range of conditions. In both cases,  $T_C$  should be modified from that of pure VO<sub>2</sub> by alloying to shift its  $T_C$ . This is why the control of  $T_C$  by alloying is so useful for applications.

Various alloying elements will lower  $T_{C}$ , such as Cr, but very few will raise  $T_{C}$ . Ge is one of the few able to raise  $T_{C}$ . Ga will also raise  $T_{C}$ , but its compositional range is less than that of Ge, perhaps because of its different valence.

#### A. Thin film deposition

Three main techniques have been used to deposit the thin films of VO<sub>2</sub>, sputtering, pulsed laser deposition (PLD), and atomic layer deposition (ALD).<sup>62-66</sup> There are also solution methods, not discussed here. Most early experiments on VO<sub>2</sub> films were carried out on single crystalline samples grown by solution-phase or vacuum techniques. PLD is favored for the deposition of films of controlled stoichiometry, relevant to vanadium oxides with its multiple valences.<sup>67,68</sup> However, PLD is more suitable for thin films of small areas. Sputtering is favored for a larger area deposition as desired. For both sputtering and PLD, it is found that the quality of the MIT in terms of  $I_{\rm on}/I_{\rm off}$ and also the width of the hysteresis window depends on the grain size, according to Brassard *et al.*<sup>69</sup> for sputtering and Jian *et al.*<sup>7</sup> for PLD (Fig. 10). This suggests that the disturbed bonding at grain boundaries reduces the resistivity range and sharpness of their phase transition.

More recently, ALD has become the favored method for film deposition for micro-electronics, particularly for conformal, pinhole-free oxide films of uniform thickness and ease of doping. For ALD, the typical precursor is TEMAV (tetrakis ethyl methyl amino vanadium), and the oxidant is water or ozone.<sup>3,62–66,71</sup> The precursor TEMAV already possesses the tetravalent V site. The resultant film is then annealed to 450–500 °C with the pressure of O<sub>2</sub> of  $10^{-3}$  Pa to crystallize VO<sub>2</sub>, densify the film, and remove hydration layers. The composition of the resultant film is checked by Raman spectroscopy<sup>71,72</sup> for evidence of the M<sub>1</sub> crystal structure and V impurities of other valences. The characterization of VO<sub>2</sub> deposited by ALD was described in Refs. 62–64.

It was found possible to plot grain size vs film thickness, the resistivity ratio,  $\rho$ , at the MIT, and the MIT width or sharpness vs grain size on a common scale for each of the three key deposition methods, sputtering, ALD, and PLD.<sup>69–71</sup> This was shown to be possible because the film properties depended primarily on the grain size, which, in turn, was controlled by the common annealing or sintering process, and not by the particular deposition process itself.<sup>71</sup> The grain boundaries are a dominant cause of gap states in the films that degrade the semiconducting or metallic behavior of the grains in either phase, which accounts for the reduction of  $\rho$ . Thus, as each deposition method gives similar films, ALD has strong advantages given its ease of alloying, changing precursors, conformal growth, and thickness control.



**FIG. 10.** Plot showing the variation in the (a) grain size vs thickness, (b) resistivity ratio between the M1 and the R phases, and (c) the MIT width for VO<sub>2</sub> thin films as a function of their average grain size, for each of the three deposition methods,  $^{69-71}$  to show the similarity of their polycrystalline materials. Reproduced with permission from D. Brassard, S. Fourmaux, M. Jean-Jacques, J. C. Kieffer, and M. A. El Khakani, Appl. Phys. Lett. **87**, 051910 (2005). Copyright 2005 AIP Publishing LLC.

#### **B. Smart windows**

One of the earliest applications to be considered is smart windows, in which the reflectivity of windows increases as the local temperature exceeds a certain value. However, the  $T_C$  of 340 K for pure VO<sub>2</sub> is a little too high and would benefit from tuning. To achieve this, Granqvist *et al.*<sup>54</sup> alloyed various metal oxides such as MgO with VO<sub>2</sub> to decrease  $T_C$ . The underlying mechanism of this tuning is given in the behavior of alloying in Sec. IV E. This allows the preferred oxide to be chosen by first-principles methods as well as experiments.

The *Tc* of other MIT systems is given by Ramanathan *et al.*<sup>3</sup> However, most of these systems are not suitable for alloying with VO<sub>2</sub> to vary its  $T_C$ .

#### C. Steep-slope devices

Modern microelectronic FETs are reaching the end of the roadmap of dimensional scaling according to Moore's law. Presently, scaling is mostly constrained by the power density of microprocessors,<sup>73</sup>  $fCV^2$ , where *f* is the switching speed, *V* is the supply voltage, and *C* is the gate capacitance. This is limited by the subthreshold slope of the gate switching characteristic of MOSFETs, the intrinsic thermal limit to *S* of kT · ln10 = 60 mV/decade. The three main technological contenders to overcome this intrinsic limit are tunnel FETs,<sup>73–79</sup> negative capacitance gate FETs,<sup>79–83</sup> and MIT FETs.<sup>9,10</sup>

Tunnel FETs rely on a tunneling barrier for cutting off the thermal distribution of electrons at the potential barriers for injection.<sup>73,74</sup> Tunnel FETs have been made of III–V heterojunctions and more futuristically by heterojunctions containing transition metal dichalcogenides. The main disadvantage of tunnel FETs is that while they make a steeper slope, they have a lower ON current density than a normal FET (Fig. 11), so the advantage is less than expected. A limiting factor with implementing tunnel FETs has been in creating heterojunctions with a low enough defect density, to having the steep-slope behavior occur at high working currents, not near cutoff. The best tunnel FETs are presently in III–V nanowire devices that are less constrained by lattice matching.

The second technology of interest for steep-slope devices is using ferroelectric  $HfO_2$  to give a negative differential gate capacitance.<sup>79-83</sup> Ferroelectricity was discovered in the  $P_{cb2}$  phase of  $HfO_2$ , one of the few oxides that are stable in direct contact with Si. It is widely studied especially in  $(Hf, Zr)O_2$  alloys. After some years of argument about whether this effect existed at all, there are now considerations of how charge trapping due to grain boundaries and oxide defects might limit the device switching speed and how to simulate their performance. There is also concern about how thin the gate oxide layer can be, given the dead layer effect of



FIG. 11. The I-V curve of MOSFET (gray), tunnel FET (red), and MIT FET (blue).

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depolarization of ultra-thin ferroelectric layers and, thus, on whether these devices can be scaled to realistic devices.  $^{82}$ 

The MIT in VO<sub>2</sub> can provide very steep subthreshold slopes of order 3-4 mV/decade, much less than the thermal limit.<sup>9,10</sup> The problem with MIT devices is the operating characteristic and the hysteresis (Fig. 11). Switching occurs at a significant DC offset voltage, and there is also a large hysteresis in the turn-on and turn-off curves, incompatible with standard CMOS characteristics. Thus, it is presently difficult to adapt the concept of a VO<sub>2</sub> switch into a practical device with a low operating voltage and compatible with other devices.

#### D. Neuromorphic computing devices

The bistable switching characteristics of the VO<sub>2</sub> MIT have been of interest as a key circuit element of neuromorphic devices, a key component. These devices are used for data processing and image recognition. ALD deposited VO<sub>2</sub> switches have been used recently in the coupled oscillator variant of neuromorphic circuits. They have also been used for two-terminal memory in a crossbar array.<sup>8,11,84</sup>

Previous interest in using ALD  $VO_2$  for two-terminal nonlinear resistors as selector devices on non-volatile ovonic or resistive random-access memories was discontinued.<sup>64</sup>

#### E. Reconfigurable RF switches

Recently, there has been progress in the fabrication of electrically reconfigurable RF switches. These allow the circuit layout of RF components to be controlled by the application of a DC voltage rather than a mechanical switch.<sup>85–87</sup> This is particularly useful in controllable RF filters. VO<sub>2</sub> can be deposited on SiO<sub>2</sub>, Si, or GaN for this purpose.

#### V. SUMMARY AND OUTLOOK

We investigate the density functional studies of VO<sub>2</sub> and the mechanism of the phase transition. The argument of the nature of MIT has existed for 50 years, about whether it is Peierls transition or Mott transition. Part of the problem is clear now and more works are encouraged to verify our model, which is consistent with the experimental observation. This model points out the spin correlation inside the V–V dimer is the main reason for the MIT. Since the spin–orbital coupling effect in VO<sub>2</sub> can be ignored, we believe that the electron transition and phonon transition can be decoupled, which has been done in the experiments. The electronic transition is the cause of the MIT, not the structure transition. However, it is impossible to completely separate the entangled structural and electronic effects.

From the perspective of application,  $VO_2$  attracts extensive attention as a promising material in multiple devices and fields, including smart windows, steep slope devices, low-power devices, and even neuromorphic computing.<sup>88,89</sup> The characteristics of the pure  $VO_2$  are not so ideal for those applications unless necessary amendments of the material properties such as transition temperature and the bandgap are made. Therefore, it is of vital importance to tune these parameters for the future application of  $VO_2$ . Theoretically, the nature of MIT is primarily the electronic transition with our spin-pairing model, from which the enthalpy change and the transition temperature can be derived. DFT can produce a realistic enthalpy change by using a noncollinear spin calculation. However, "no dimer" in the spin-polarized calculation is the primary problem to be solved in the future. Many-body physics should be included to describe the entanglement between dimerization and spin correlation.

DFT is still considered as the foundation of advanced methods and can provide valuable insight into the MIT process in VO<sub>2</sub>. Treating the system as non-magnetic with a proper nonlocal exchange coefficient can help obtain reasonable lattice parameters, electronic structures, a stable rutile phase, and a dimerized M<sub>1</sub> phase, whereas spin-polarized calculation cannot do so. However, the magnetic ground state of VO2 is not non-magnetic. DFT cannot identify the magnetic ground in the rutile and M1 phases with correct energy levels. DFT + U and hybrid functional can improve the results, but the correct energy levels cannot be reproduced. The magnetic ground state of the high-temperature rutile is Curie-Weiss paramagnetic, where the magnetic moment of each V is randomly oriented, while in the low-temperature phase, dimers form and spins inside the dimer are strongly correlated, forming a correlated singlet state.<sup>49</sup> The singlet state is the origin of MIT. To simulate the paramagnetic state using DFT, the noncollinear spin calculation is performed and helps obtain reasonable electronic structures and an enthalpy change. The transition temperature can be derived using a simple dimer Hamiltonian. Currently, the spinpairing model lacks experimental evidence. A future experimental task is to identify the magnetic ground states and spin correlations of each phase of VO<sub>2</sub>.

The low cost and feasibility of DFT enable it to be the only method available for large supercells necessary for most band engineering methods such as doping and interface. The doped VO<sub>2</sub> is also considered using the noncollinear spin calculation. The transition temperatures of doped VO<sub>2</sub> are calculated to match well the experiments. Moreover, heavily doped VO<sub>2</sub> and VO<sub>2</sub>-metal oxide alloys are also introduced. Alloying and doping might be the most effective ways to tune the properties of MIT in VO<sub>2</sub>. The wellstudied dopants are Ti and Cr. It is worthwhile to introduce other elements for better performance. Strain will be introduced during the fabrication and packaging process. The interface is inevitable in devices and it could affect both the structural and electronic properties during the MIT process. More phases arise due to doping, alloying, interface, strain, etc.

There are post-DFT methods proposed, because DFT is not enough to describe the strongly correlated electrons inside dimers, which is necessary to accurately describe the MIT process. But all these methods still require DFT wavefunction as their input. Most of them still require DFT relaxed atomic structures, because force is not accessible in most of the methods.<sup>52</sup> A more accurate DFT level calculation can still greatly improve the post-DFT process. The quantum Monte Carlo method is by far the most accurate method and has been widely used as a benchmark for DFT calculations.<sup>11</sup> However, it can only treat a limited number of atoms, which makes it almost impossible to describe doped VO<sub>2</sub> systems. DMFT has been attracting increasing interest to describe strongly correlated systems such as VO<sub>2</sub>, because it is using the same variational principles as DFT. However, it is not suitable for open-shell systems and it does need some fitting parameters from experiments. The GW method can be parameter-free, but it cannot describe the strong correlation and needs help from the Hubbard model to deal with quite a few transition metal oxides. These methods can provide more information about the coupling of electronic and atomic structure effects, but the computational cost is still much higher than DFT. The advancement in these methods could provide a better description of electronic structures in complex VO<sub>2</sub> structures such as doping and interface.

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#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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