

Oxygen vacancies in vanadium dioxide: A DFT + V studyOskar Leibnitz , Peter Mlkvik ,* Nicola A. Spaldin , and Claude Ederer *Materials Theory, Department of Materials, ETH Zürich, Wolfgang-Pauli-Strasse 27, 8093 Zürich, Switzerland*

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We present a density-functional-theory (DFT) study of the effects of oxygen vacancies on the structural and electronic properties of vanadium dioxide (VO_2). Our motivation is the reported suppression of the metal-insulator transition by oxygen vacancies and the lack of a clear consensus on its origin. We use the DFT + V method with a static intersite vanadium-vanadium interaction term, V , to calculate the properties of the oxygen-deficient metallic rutile and insulating monoclinic M1 phases of VO_2 on the same footing. We find that oxygen vacancies induce local distortions in the M1 phase, but do not destroy the dimerization usually associated with the insulating behavior. In spite of this, we find that the M1 phase becomes metallic as a result of the partial filling of the conduction band due to a rigid-band-like doping effect.

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I. INTRODUCTION

The metal-insulator transition (MIT) in vanadium dioxide (VO_2) has been proposed for a variety of applications, from memristive devices [1,2], ultrafast electronics [3,4], to energy-efficient windows [5,6]. In order to fully realize the application potential of VO_2 , the MIT temperature, T_c , as well as the transition hysteresis, and order of magnitude change in resistivity, should ideally be reliably tunable. Besides epitaxial strain [7–10] and doping [11–14], oxygen vacancies (O_V 's), one of the most frequent point defects, have been studied extensively for their potential to mediate such tuning. In this work, we computationally investigate the effects of oxygen vacancies on the main VO_2 phases.

The MIT in VO_2 is accompanied by a structural transition, from a high-temperature rutile (R) phase to a low-temperature monoclinic (M1) phase, at $T_c = 340$ K [15,16]. The transition involves V-V dimerization along the tetragonal c axis coupled to lateral displacements, causing a doubling of the unit cell, resembling a Peierls instability. In the R phase, $3d^1$ V^{4+} ions situated in distorted VO_6 octahedra have partially filled a_{1g} and e_g^π states, resulting from a splitting of the t_{2g} manifold. In the dimerized M1 phase (Fig. 1), the a_{1g} band is further split into occupied bonding and unoccupied antibonding states [17], while the e_g^π levels shift upward, resulting in a narrow insulating gap. Besides these Peierls effects, Mott-Hubbard correlation effects are needed for a full description of the physics of VO_2 [18–26], and a dual Peierls-Mott mechanism appears to provide the most appropriate description of the MIT in VO_2 [27–30].

Numerous studies consistently show that increasing oxygen vacancy concentration suppresses the insulating state of VO_2 . Oxygen vacancies lower the T_c even when strain effects are excluded [31–35]. Field-switching experiments reveal a corresponding decrease in the critical voltage [36], and O_V 's can modify or even eliminate hysteresis [37,38]. Isotope-labeled oxygen studies directly confirm that these effects arise from oxygen vacancies [33]. Quantifying the vacancy concentration remains difficult, with most studies offering only qualitative comparisons, such as different vacuum annealing times [39]. X-ray photoemission spectroscopy provides rare quantitative estimates, reporting $\delta = 0.07$ – 0.20 in $\text{VO}_{2-\delta}$ after annealing in low-oxygen environment [37,40].

Despite this phenomenological consensus, the literature diverges on the nature of the physics underlying the change in T_c , with two main interpretations emerging. First, several studies suggest that oxygen vacancies stabilize the R structure below the T_c of the stoichiometric phase. Xu *et al.* [40] observed a softening of Raman modes associated with the M1 phase and a lowering of the structural transition temperature in thin films of $\text{VO}_{1.92}$. The proposed explanation is a weakening of the V-O hybridization and the V-V dimerization by the electrons donated by the vacancy. Kim *et al.* [41] similarly observed a reduction in the structural transition temperature, but attributed it to a weakening of the V-V dimers by oxygen-vacancy-induced compressive strain. Zhang *et al.* [36] report Raman mode softening at a temperature below T_c and linked it to a stabilization of the R phase due to the dopant electrons. Matsuda *et al.* [42] showed spectroscopic evidence of a confinement of the V-V pairing to nanodomains within an undimerized R-like VO_2 structure at room temperature, consistent with partial rutile phase stabilization due to oxygen deficiency. Guo *et al.* [43] reported a decrease in T_c with Ar-plasma irradiation in VO_2 nanobeams and linked it to oxygen-vacancy-induced stabilization of the R phase; however, no experimental phase characterization was performed. Passarello *et al.* [44] demonstrated that ionic liquid gating induces oxygen vacancy formation and stabilizes the R structure down to 270 K. The retention of R symmetry was confirmed

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spectroscopically and attributed to a combination of vacancy-driven lattice expansion and epitaxial clamping of the in-plane lattice constants by the TiO_2 substrate used.

The second interpretation common in the literature is the emergence of a metallic M1 phase. This phase has been observed through pump-probe spectroscopy and reported in nonequilibrium studies on photoexcited VO_2 [45,46]. A variety of other studies support the stabilization of such a metallic M1 phase in oxygen-deficient VO_2 . Li *et al.* [47] observed a vacancy-induced metallic M1 phase in VO_2 nanobeams and associated it with orbital-selective carrier doping. Schrecongost *et al.* [48–50] demonstrated reconfigurable nanoplasmonic devices based on metallic M1 phases patterned via oxygen vacancy or free carrier injection using atomic force microscopy, attributing the metallicity to the associated carrier injection. The monoclinic nature of the observed phase is confirmed using micro x-ray diffraction and electron diffraction. Vacuum annealing experiments reveal a metallic M1 phase, confirmed by hardening of Raman-active V-V modes, dimer stabilization, and robust room-temperature metallicity, and attribute it to changes in electronic correlations and a shortening of V-V bonds [39].

Angle-resolved photoemission spectroscopy (ARPES) [51] and other spectroscopic studies [37,52,53] also attempt to elucidate how oxygen vacancies affect the MIT in VO_2 , but overlapping spectral features and increased disorder associated with adding oxygen vacancies make it difficult to unambiguously pinpoint any orbital effects responsible for the observed lowering of T_c .

The effect of oxygen vacancies has also been studied using first-principles methods. Several DFT + U studies [31,39,54,55] report a metallic M1 phase as the ground state of VO_2 , even at low vacancy concentrations, though their interpretations vary. Guo *et al.* [43] found partial filling of the conduction band in an oxygen-deficient M1 structure and deduced a stabilization of the R phase from this result, although they do not explicitly calculate the nonstoichiometric R structures. Chen *et al.* [56] also only studied the oxygen-deficient M1 phase, finding weaker V-V dimerization from which the authors inferred a total dedimerization into an R phase under larger oxygen concentrations. Lee *et al.* [22] considered heterostructures of oxygen-deficient and stoichiometric VO_2 and constructed a two-dimensional energy phase space describing the electronic correlation and the structural V-V dimerization. Their model exhibited a global energy minimum at high electronic correlation and large dimerization (insulating M1), but also a local minimum at low correlation and large dimerization, which they identified with the metallic M1 phase stemming from the oxygen-deficient state stabilized by the presence of the underlying stoichiometric VO_2 . Ganesh *et al.* [57] used dynamical mean-field theory (DMFT) and diffusion Monte Carlo to argue for the suppression of the MIT due to a vacancy-induced reduction of the partial a_{1g} orbital polarization in the R structure. This reduces the dimerization tendency, hence stabilizing the R phase. Their findings support the existence of a quasicritical threshold for vacancies above which the MIT is fully suppressed, linking it to experimental observations of a critical vacancy concentration [37]. In addition, the authors calculated the optical band gap in M1 $\text{VO}_{2-\delta}$ and observed its reduction down to zero depending

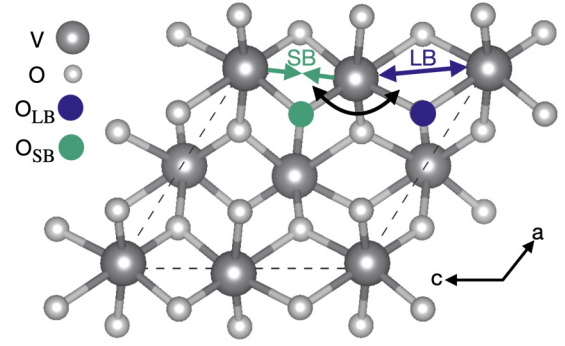


FIG. 1. Crystal structure of the M1 phase in the M1 primitive cell (dashed line). Green and blue arrows indicate the short and long bonds (SB and LB, respectively) along the c direction. V (O) atoms are shown in (light) gray. Inequivalent oxygen sites in the M1 structure (O_{SB} and O_{LB}) are indicated in green and blue, respectively.

on the vacancy position, effectively observing a metallic M1 phase.

In summary, while the literature consistently describes a suppression of the MIT in oxygen-deficient VO_2 , decisively different interpretations of the underlying physical effects exist. Computationally, no existing study adequately captures both the structural and electronic effects across the R and M1 phases within a unified framework. A comprehensive approach is therefore highly desirable to make a conclusive statement about the mechanism of MIT suppression in $\text{VO}_{2-\delta}$.

Recently, in Ref. [58], we demonstrated that incorporating a static intersite interaction term within the DFT + V method enables efficient, accurate, and unbiased treatment of both the M1 and R phases on the same footing. The application of the DFT + V approach to VO_2 is motivated by the observation that in advanced cluster DFT + DMFT calculations of the M1 phase, an on-site interaction gives rise to an essentially frequency-independent intersite self-energy [27], which is well approximated by a simple static vanadium-vanadium intersite potential [28,59–62]. The work of Ref. [58] builds on this idea by using the DFT + V method, which is readily implemented in the QUANTUM ESPRESSO density-functional theory (DFT) package [63–66]. In particular, as shown in Ref. [58], an identical treatment of all pairs along the dimerization direction in both R and M1 phases of VO_2 leads to the correct energy balance between the two phases and opens a gap in the M1 phase, agreeing well with previous studies using more advanced methods [25,27,30,61]. The DFT + V approach also avoids certain shortcomings encountered within the DFT + U approach for VO_2 , such as the opening of a gap in the R phase [67], at a much lower computational cost compared to using, e.g., hybrid functionals [68–70].

Accordingly, in this work, we study the phase stability and electronic structure in $\text{VO}_{2-\delta}$ using the DFT + V method.

II. COMPUTATIONAL DETAILS

In our calculations, we use different periodic cells, all based on the unit cell of the low-symmetry M1 structure, i.e., a doubled primitive cell of the high-symmetry R structure (Fig. 1). We use the experimental lattice parameters of

the R phase [71] and neglect the monoclinic strain and the expansion of the c lattice parameter in the M1 phase relative to R, which have a negligible effect on the resultant electronic structure [58]. We do not perform volume relaxations, as we aim to describe the dilute limit of oxygen vacancies in VO_2 .

In this basic unit cell, a single oxygen vacancy results in $\text{VO}_{2-\delta}$ with $\delta = 0.25$, i.e., defect concentration of 12.5%, and one oxygen vacancy appearing every two vanadium atoms along c under periodic boundary conditions. To decrease the O_V periodicity, we construct a $2 \times 2 \times 2$ supercell of the stoichiometric primitive M1 unit cell, so that a single O_V corresponds to $\delta \approx 0.03$ and a defect concentration of 1.5625%, with one O_V appearing every four vanadium atoms along c under periodic boundary conditions. We additionally study a $1 \times 1 \times 5$ supercell elongated along the c direction, with $\delta = 0.05$, resulting in a larger O_V spacing along the V chains.

While all oxygen sites are symmetry equivalent in the R phase, the dimerization breaks this symmetry, leading to two distinct oxygen sites in the M1 phase. We label the sites adjacent to the short dimerized bond and long nondimerized bond as O_{SB} and O_{LB} , respectively (corresponding to OI and OII from Ref. [57]), and we examine three different oxygen-deficient structures, R-O, M1- O_{SB} , and M1- O_{LB} .

All DFT + V calculations are performed using the QUANTUM ESPRESSO (QE 7.3 and 7.4) package [63–65]. The exchange-correlation energy is approximated using the Perdew-Burke-Ernzerhof (PBE) generalized gradient functional [72,73]. Ultrasoft pseudopotentials, which include the V 3s and V 3p semicore states in the valence manifold are sourced from the GBRV library [74]. Convergence tests establish 70 Ry as a suitable kinetic energy cutoff for the plane-wave basis set describing the Kohn-Sham wave functions and the kinetic energy cutoff for the charge density is set to 12×70 Ry. A Γ -centered $6 \times 6 \times 8$ $\mathbf{k}$ -point grid is used for the primitive cell and scaled down according to the reduction in Brillouin zone size in supercell calculations. The energy is converged to a tolerance of 5×10^{-8} eV between iterations. Electronic occupations are treated using Gaussian smearing with a width of 10^{-3} Ry to facilitate convergence while maintaining an effectively insulating occupation profile. Atomic positions are relaxed to a force tolerance of 10^{-3} Ry/bohr using the Broyden-Fletcher-Goldfarb-Shanno algorithm.

Following Ref. [58], we use the DFT + V method [75,76] to introduce a static intersite correlation correction in all calculations throughout this work. Importantly, the V term does not correspond to a Coulomb interaction between vanadium atoms, but rather to a hybridization correction ultimately stemming from on-site correlation effects [27]. We therefore treat the intersite interaction parameter V as an empirical quantity modifying the corresponding effective hopping amplitudes. We set $V = 1$ eV, which yields the experimental energy ordering of the R and M1 VO_2 phases, and ensures a band gap opening in the M1 phase. We find good agreement between the obtained band gap of approximately 0.4 eV and the experimental optical gap of about 0.5–0.6 eV [77–80]. The specific value of the V correction is directly related to the size of the relevant bonding-antibonding splitting in the M1 phase and hence also has a direct quantitative effect on the energy balance between the R and M1 phases. Previously [58], we have shown that values of V in the range of 1–2 eV

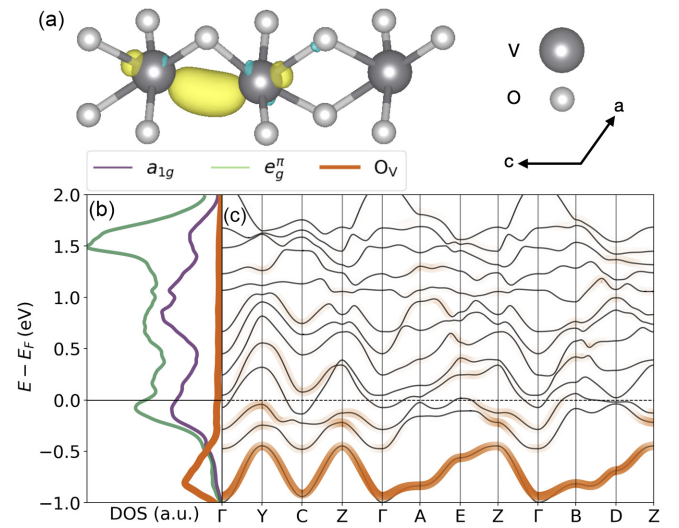


FIG. 2. (a) Details of the primitive cell M1- O_{SB} vacancy WF. Yellow and blue colors indicate positive and negative phases, respectively; V (O) atoms are shown in (light) gray. (b) PDOS of the primitive cell with purple (green) colored lines indicating the a_{1g} (e_g^{π}) WF. O_V is shown in orange. (c) Band structure of the primitive cell M1- O_{SB} with the O_V contribution shown in orange.

provide a good account of both phases of VO_2 . Practically, we apply the correction to 3d projectors on all neighboring V-V pairs along the c direction. The energy correction due to the intersite interaction, V , both depends on and modifies the intersite occupation, $n_{\times}$, where usually the trace (indicative of intersite same-orbital interactions) captures the majority of the intersite occupation.

We construct maximally localized Wannier functions (WFs) [81] using the WANNIER90 code [82]. To construct the localized orbitals most relevant for understanding the MIT behavior, we select a subspace of V- t_{2g} -dominated bands located around the Fermi level. There are 12 t_{2g} bands corresponding to three states for each of the four vanadium atoms in the stoichiometric primitive cell [see the energy range in Figs. 2(b) and 2(c)]. Hence, we initialize one of each t_{2g} -type projectors at each vanadium site, as well as including an additional s -type projector at each vacancy site (for motivation, see the discussion later and Refs. [83,84]).

The BANDUPPY package [85–87] is used to compute unfolded band structures from supercell wave functions, using the unfolding formalism [88,89]. Here, the irreducible set of supercell $\mathbf{k}$ points is mapped, *unfolded*, onto a larger set of primitive cell $\mathbf{k}$ points. A spectral weight, $A(\mathbf{k}, E)$, a momentum-resolved primitive-cell representation of the electronic structure at each $\mathbf{k}$ point, is then computed directly from the supercell plane-wave data without requiring a separate primitive-cell calculation.

III. RESULTS AND DISCUSSION

We start by considering a primitive cell of M1- O_{SB} $\text{VO}_{2-\delta}$ with a single vacancy. Although this cell describes a defect arrangement with relatively short periodicity (O_V every two vanadium atoms along c), it nevertheless serves as a first demonstration of the behavior of O_V in $\text{VO}_{2-\delta}$.

TABLE I. Relative energies of the different structures of VO_2 and $\text{VO}_{2-\delta}$, for $\delta \approx 0.03$. $\Delta E = E - E_{\min}$, with $E_{\min}$ taken from the respective minimum energy structure.

Geometry	Structure	ΔE (meV/f.u.)
Stoichiometric	R	75.55
Stoichiometric	M1	0
Unrelaxed	R-O	74.9
Unrelaxed	M1- O_{SB}	3.7
Unrelaxed	M1- O_{LB}	0
Relaxed	R-O	32.27
Relaxed	M1- O_{SB}	0.06
Relaxed	M1- O_{LB}	0

In Figs. 2(b) and 2(c), we show the projected density of states (PDOS) and the band structure of the relaxed primitive cell M1- O_{SB} structure. We observe an emergence of an additional band within the energy range of the t_{2g} manifold (centered around -0.7 eV) compared to the stoichiometric structure [Figs. 8(a) and 8(b)]. This feature appears consistently across all oxygen-deficient configurations presented in this work. In fact, if we initialize a Wannier function at the vacancy position, we find that this orbital maps almost completely onto the separated band [see the vacancy contribution in orange in Figs. 2(b) and 2(c)], and cannot be directly attributed to any other manifold in the full band structure. The resultant WF is highly localized in space (with spread comparable to those of the t_{2g} WFs), stretching between the neighboring vanadium atoms across the SB [Fig. 2(a)]. Notably, the vacancy state is also strongly localized in energy.

We note that no clear a_{1g} bonding-antibonding splitting is visible in the PDOS in Fig. 2(b), and there is also a relatively large occupation of the e_g^π orbitals, unlike the stoichiometric case shown in Figs. 8(a) and 8(b). However, since this small cell is not very representative, we do not analyze this any further. We mainly include these results to introduce the vacancy WF, which is most prominent in the small cell with high vacancy concentration. Due to the short periodicity resulting from the small size of the primitive cell, we focus the remainder of our analysis on larger supercells.

A. Fixed atomic positions

We first consider unrelaxed supercells, where we remove an oxygen atom but otherwise keep the atomic positions fixed, to assess the purely electronic impact of an oxygen vacancy.

In Table I, we show the energy difference (ΔE) between the different VO_2 and $\text{VO}_{2-\delta}$ phases and configurations. In the unrelaxed, fixed-geometry case, the R-O structure remains significantly disfavored (see middle rows in Table I), with energy difference similar to stoichiometric VO_2 (top rows in Table I). Both monoclinic configurations exhibit lower total energies, with the M1- O_{LB} slightly favored over the M1- O_{SB} structure.

To better understand the effects of the vacancy, we investigate the electronic effects, and specifically the intersite occupation as a quantity representing the V-V bonding. In Figs. 3(a) and 3(b), we show the trace of the intersite occu-

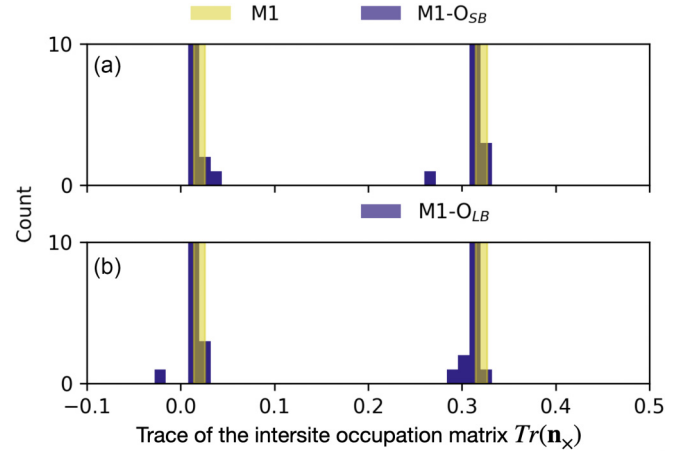


FIG. 3. The trace of the intersite occupation matrix, $\text{Tr}(n_x)$, for neighboring V-V pairs along c in (a) the M1- O_{SB} and (b) the M1- O_{LB} structures (blue) compared to stoichiometric M1 values (yellow).

pation matrix, $\text{Tr}(n_x)$, for all neighboring V-V pairs along the c direction in both stoichiometric VO_2 and $\text{VO}_{2-\delta}$ (yellow and blue lines, respectively). For M1 VO_2 , $\text{Tr}(n_x)$ yields two values, corresponding to short and long distances between vanadium atoms, and hence large and small values of the electronic overlap.

Upon introduction of a vacancy, the distribution of $\text{Tr}(n_x)$ values for both M1 configurations remains close to those of the stoichiometric reference values. In each case, there is only a single data point with significantly different $\text{Tr}(n_x)$ corresponding to the vanadium pair adjacent to the vacancy, either on the short (M1- O_{SB}) or on the long (M1- O_{LB}) bond between nearest neighbors [at 0.27 in Fig. 3(a) and at -0.02 in Fig. 3(b), respectively]. The reduction of this $\text{Tr}(n_x)$ value in the M1- O_{SB} configuration already indicates a suppression of hybridization between nearest-neighbor orbitals by the presence of the vacancy, even without structural relaxation. Notably, this reduction is rather small, highlighting that the dimerization in VO_2 largely stems from a direct V-V overlap rather than oxygen atoms mediating the V-V intersite interaction.

The unperturbed nature of the majority of V-V pairs except for those closest to the vacancy indicates the high localization of the vacancy effects in the M1 structures.

In Figs. 4(a) and 4(e), we show the PDOS corresponding to the V t_{2g} subspace and the vacancy WF for the M1- O_{SB} and M1- O_{LB} configurations, together with the corresponding unfolded band structures in Figs. 4(b) and 4(f), respectively. Similar to the case of the primitive cell, the electronic structures exhibit a strongly localized vacancy state appearing just below the Fermi level, E_F [see orange peak in Figs. 4(a) and 4(e)], but no other major changes compared to stoichiometric VO_2 [Figs. 8(a) and 8(b)]. The unfolded band structure confirms the presence of an energetically isolated intragap state, with a very weakly visible band seen close to the conduction band at the C point in Figs. 4(b) and 4(f). Crucially, the phase remains insulating with a very small gap. The R-O configuration [Figs. 4(i) and 4(j)] remains similar to that of stoichiometric R VO_2 [Figs. 8(c) and 8(d)], remaining

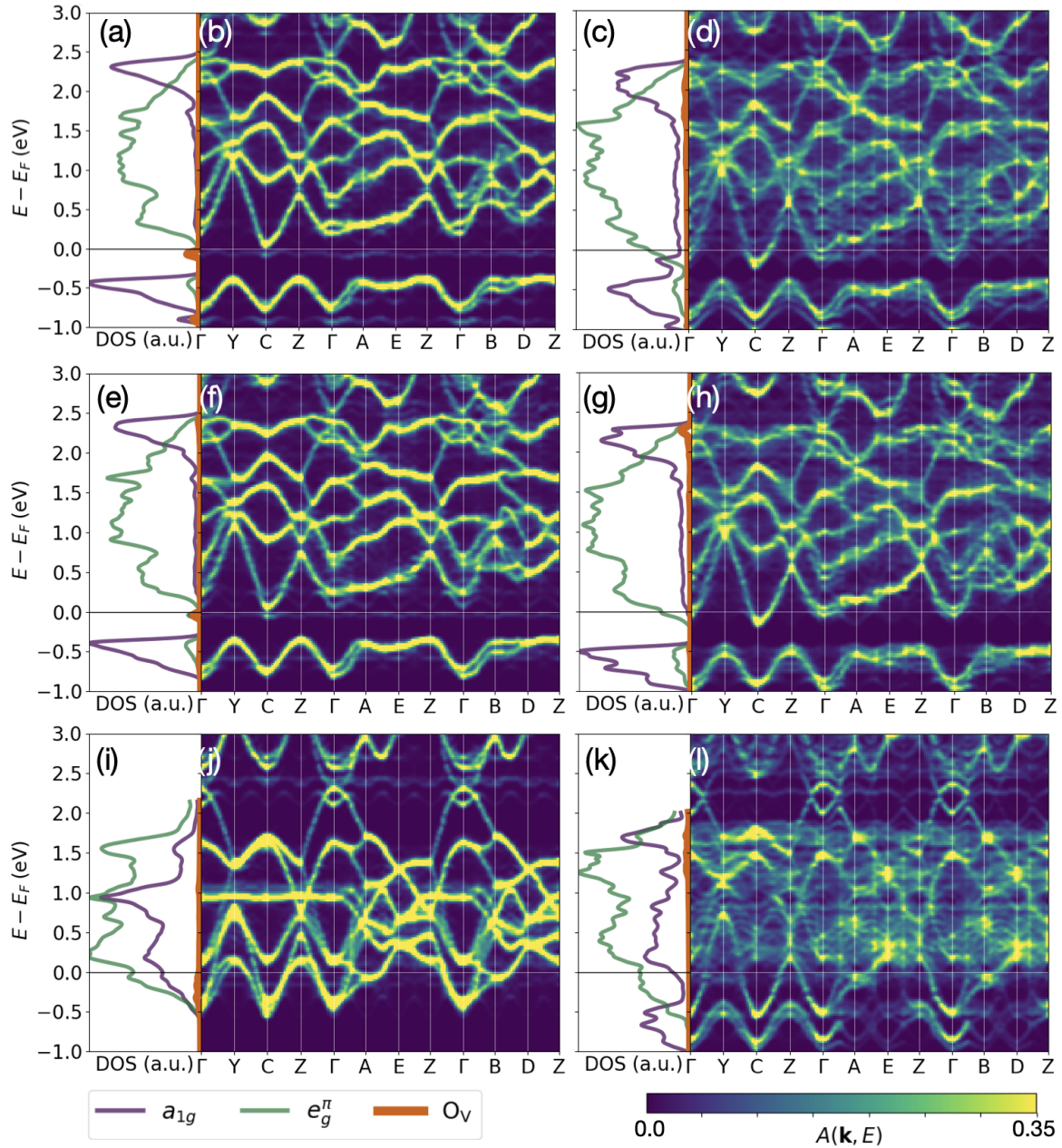


FIG. 4. Unfolded band structures and PDOS of the (a)–(d) M1-O_{SB}, (e)–(h) M1-O_{LB}, and (i)–(l) R-O configuration before [panels (a), (b), (e), (f), (i), and (j)] and after internal relaxation [panels (c), (d), (g), (h), (k), and (l)]. Colors in the PDOS denote orbital character: purple (a_{1g}), green (e_g^π), and orange (O_V). Colors in the band diagram denote spectral weight $A(\mathbf{k}, E)$ of the unfolded band structure.

metallic, with highly coherent unfolded band structure and a broad vacancy peak just below E_F .

B. Relaxed atomic positions

After internal relaxation, the energy difference between the dimerized and nondimerized phases is drastically reduced. The high-temperature R phase is stabilized relative to the stoichiometric configuration, from 75.55 to 32.27 meV/f.u. (Table I, bottom). This finding is consistent with the observed persistence of the R structure to lower temperature. The M1-O_{LB} and the M1-O_{SB} structures are now almost identical in energy, with a very small preference for the M1-O_{LB} structure.

The small energy difference between the two vacancy configurations makes both configurations plausible in real systems.

In Figs. 5(a)–5(c), we show the distribution of nearest-neighbor V-V distances as a measure of the structural changes. In yellow, we show the short and long nearest-neighbor V-V distances of the stoichiometric relaxed M1 structure (at 2.50 and 3.24 Å), and in green those of the R structure (at 2.85 Å).

Both monoclinic structures [Figs. 5(a) and 5(b)] display only relatively small and localized structural perturbations. The majority of V-V distances deviate by less than 0.2 Å from the stoichiometric distances. The M1-O_{LB} configuration maintains clear alternation of short and long V-V bonds

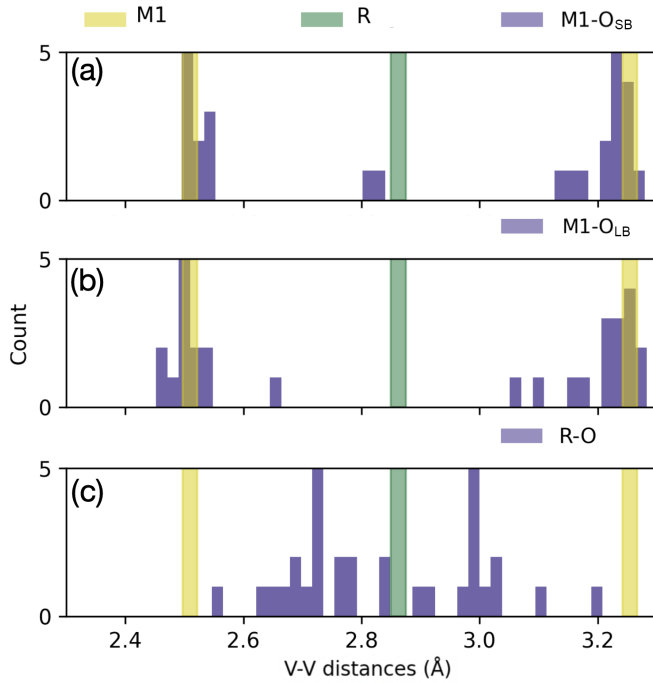


FIG. 5. Nearest-neighbor V-V distances (purple) in the internally relaxed (a) M1-O_{SB}, (b) M1-O_{LB}, and (c) R-O structures. The stoichiometric reference values for M1 and R are shown in yellow and green, respectively.

centered around the stoichiometric values, indicating a persistent dimerized ground state. In M1-O_{SB}, larger deviations are observed along the oxygen-deficient chain, including compressions and elongations relative to the dimerized reference. Since the dimerized structures have been shown to be the lower-energy structures, the small energetic preference for the O_{LB} vacancy location could be explained by the energetic preference for the more unperturbed, i.e., dimerized, M1-O_{LB} structure.

In contrast to the M1 configurations, in the R-O configuration [Fig. 5(c)], V-V distances are perturbed throughout the whole cell and range broadly from 2.5 to 3.2 Å. This variation occurs without discernible spatial correlation, indicating strong interchain communication of vacancy-induced structural effects in the R phase. A possible explanation of this striking difference compared to the M1 symmetry is the reduced degree of on-chain hybridization (i.e., bonding singlet states), making the R structure more susceptible to interchain perturbations. Notably, the R-O structure does not relax into either of the lower-energy oxygen-deficient structures, indicating this phase to be a local minimum configuration.

Although some V-V distances in M1-O_{SB} approach the characteristic R V-V distances [Fig. 5(a), at around 2.8 Å], we do not interpret this as a structural transition to the R phase, as has been proposed elsewhere [37,56]. First, as we have just seen, the R-O structure does not feature any tendency to dimerize. Second, the strongly perturbed, R-like bond lengths present in the M1-O_{SB} configuration are in fact localized strictly on the vacancy chain, with no evidence of dedimerization in adjacent chains.

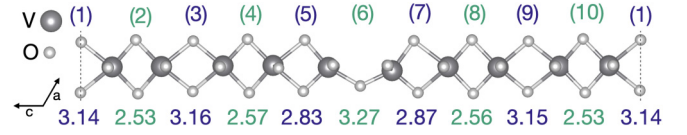


FIG. 6. The ten-atom vanadium chain in the relaxed M1-O_{SB} structure of the $1 \times 1 \times 5$ cell (dashed lines) with bond lengths (in Å) for the initial long (blue) and short (green) V-V bonds. O_V lies on bond (6). V (O) atoms are shown in (light) gray.

To further rule out global dedimerization as a result of oxygen deficiency, we additionally consider a $1 \times 1 \times 5$ supercell (VO_{2- δ} with $\delta = 0.05$) containing a periodicity across ten atoms within the vanadium chains (see Fig. 6), as opposed to the four-atom periodicity along c in the $2 \times 2 \times 2$ supercell. We perform an internal relaxation of the M1-O_{SB} structure in this supercell and investigate the resultant bond lengths, labeled (1)–(10).

In this structure, we confirm that upon the introduction of a vacancy [at position (6)], we only observe significant changes in bond lengths directly adjacent to the vacancy [(5) and (7)]. In fact, due to the presence of the vacancy, we observe an elongation of the SB hosting the vacancy to 3.27 Å from the stoichiometric 2.50 Å, and a compression of the surrounding LB bond lengths to 2.83 and 2.87 Å from the stoichiometric 3.24 Å. Dimerization remains intact throughout the rest of the chain.

These results suggest that the appearance of R-like distances should be interpreted as a localized structural feature induced by the vacancy, rather than an indication of a global structural transition away from the dimerized state.

We now consider the electronic structure of the relaxed configurations. In Figs. 4(c) and 4(g), we show the PDOS, together with the corresponding unfolded band structure [Figs. 4(d) and 4(h)] of the relevant states around the Fermi level in M1-O_{SB} and M1-O_{LB}, respectively, similar to Figs. 4(a), 4(b), 4(e), and 4(f).

Focusing first on the M1-O_{LB} configuration, comparing Figs. 4(g) to Fig. 4(e), we see that upon relaxation, the vacancy state (orange) empties and shifts upward to approximately 2.3 eV above the Fermi level, effectively donating two electrons to the conduction band. Despite the local lattice distortions, the bonding a_{1g} band remains narrow and well separated from the conduction band [see the a_{1g} peak in Fig. 4(g)]. The doped system behaves electronically as an almost undisturbed host retaining its original band gap between the bonding a_{1g} and the higher-lying bands [Fig. 4(h)], with metallicity emerging from the conduction band filling resembling a rigid band doping, rather than from defect-induced states or band rehybridization.

The M1-O_{SB} configuration [Figs. 4(c) and 4(d)] shows a similar shift of the vacancy state, with a less rigid response to the distortions, leading to more incoherent weight in the unfolded band structure. The doping electrons populate mostly the e_g^π states, even though the bonding a_{1g} states get broadened and smear out the gap, indicating a slight departure from the clean band-filling picture observed in M1-O_{LB}. In contrast, in the R-O configuration [Figs. 4(k) and 4(l)],

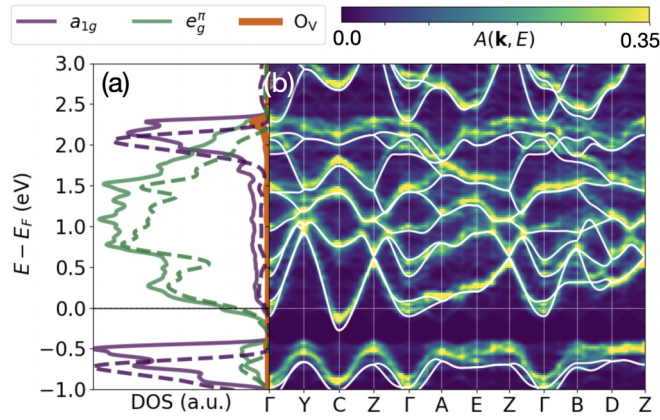


FIG. 7. (a) PDOS of the relaxed M1-O_{LB} structure with purple (green) lines indicating the a_{1g} (e_g^π) orbital. O_V is shown in orange. Dashed lines correspond to the background charge method with total charge set to -0.25 . (b) Unfolded band structure of the relaxed M1-O_{LB} structure shown in color denoting the spectral weight $A(\mathbf{k}, E)$. Band structure corresponding to the background charge method with total charge set to -0.25 is shown in white lines.

the more delocalized lattice distortions lead to a broader t_{2g} manifold and a rather incoherent unfolded band structure. The vacancy state forms a diffuse peak well above E_F , while an almost split-off a_{1g} feature appears below. However, no stable electronic motif emerges, and the phase remains high in energy.

C. Comparison with background charge doping

To further analyze the effects of oxygen vacancies, we now utilize the background charge method; i.e., we consider a stoichiometric primitive M1 unit cell, which we structurally relax with an added electron filling of -0.25 elementary charges, corresponding exactly to the number of electrons added by one oxygen vacancy in the $2 \times 2 \times 2$ supercell. This extra charge is then compensated in the calculation by adding an equivalent homogeneous positive background charge. In Figs. 7(a) and 7(b), we compare the resulting PDOS and band structure with those of the relaxed, slightly lower in energy, M1-O_{LB} configuration from Figs. 4(g) and 4(h).

First, we note that, compared to the stoichiometric M1 structure [Figs. 8(a) and 8(b)], the band structure obtained from the calculation with added electrons essentially corresponds to a rigid shift of the Fermi level upward in energy, i.e., the behavior of the system under the background charge method strongly resembles a rigid band doping. In particular, we observe no tendency for structural dedimerization, also reflected in the clearly separated a_{1g} peaks in Fig. 7(a).

Comparing now to the M1-O_{LB} structure, we can again observe a strong resemblance of the corresponding band structures and confirm the simple conduction band filling, as mentioned earlier. Indeed, we observe an excellent agreement between the shifted conduction band due to the oxygen vacancy and the background charge; i.e., a rigid doping (note particularly the energy range between 0 and 2 eV). These bands specifically correspond to the nondimerizing e_g^π states

[green in Fig. 7(a)]. On the other hand, there is a slight shift of the a_{1g} bands relative to the e_g^π conduction bands between the two methods [see the discrepancy around -0.5 and 2 eV in purple in Fig. 7(a)], while the bonding-antibonding splitting of the a_{1g} states remains very similar.

These results directly show that the effect of the oxygen vacancies can, to a good approximation, be interpreted as a rigid doping of the conduction band, formed mainly by the e_g^π states, while the overall structure, and in particular the V-V dimerization, remains relatively unperturbed. This is especially true in the M1-O_{LB} structure, where the rigid band approximation holds most accurately.

IV. SUMMARY AND OUTLOOK

In summary, we have investigated the influence of oxygen vacancies on the structural and electronic properties of the rutile R and monoclinic M1 VO₂ phases using DFT + V. Our results demonstrate that the dimerized M1 structure remains energetically favored in the presence of oxygen vacancies, although the energy penalty for dedimerization is reduced relative to stoichiometric VO₂. This finding aligns with the experimentally observed reduction of the structural transition temperature between the R and M1 phases in VO_{2- δ} compared to VO₂.

Specifically, our findings suggest a dual mechanism of the MIT suppression: structurally, through a lowered structural phase transition temperature, and electronically, via vacancy-electron doping of the conduction band. Analysis of relaxed oxygen-deficient structures shows that vacancies induce locally constrained distortions without promoting global dedimerization. Electronically, vacancies introduce defect states below the Fermi level in unrelaxed structures, which become depleted upon structural relaxation and transfer their electrons into the conduction band. This results in a partially filled conduction band and a metallic ground state in the monoclinic phase, regardless of vacancy position, identical to the observed carrier doping effects [48]. The electronic response agrees very well with a calculation with an added background charge and closely follows a rigid band doping model of the conduction band e_g^π states, highlighting the intrinsic robustness of the M1 structure against vacancy-induced perturbations. Notably, the fact that the dimerization appears unaffected by the doping of the e_g^π states indicates agreement with a Peierls picture hosting essentially decoupled electronic degrees of freedom between the dimerizing and nondimerizing orbitals.

Whether electron delocalization and conduction band injection persist under stronger electron correlation remains an open question, warranting further study either via explicit vacancy-site correlation treatments such as through on-site Hubbard terms applied to vacancy orbitals [90] or via DFT + DMFT techniques [83,84]. In particular, albeit computationally demanding, it would be interesting to see whether the stability of the essentially decoupled electronic degrees of freedom between the Peierls-active and Peierls-inactive orbitals would remain intact with added on-site correlation effects within DFT + DMFT. Notably, oxygen vacancies have previously been linked to a weakening of electronic correlations, measured by, for example, a decrease of the a_{1g} orbital

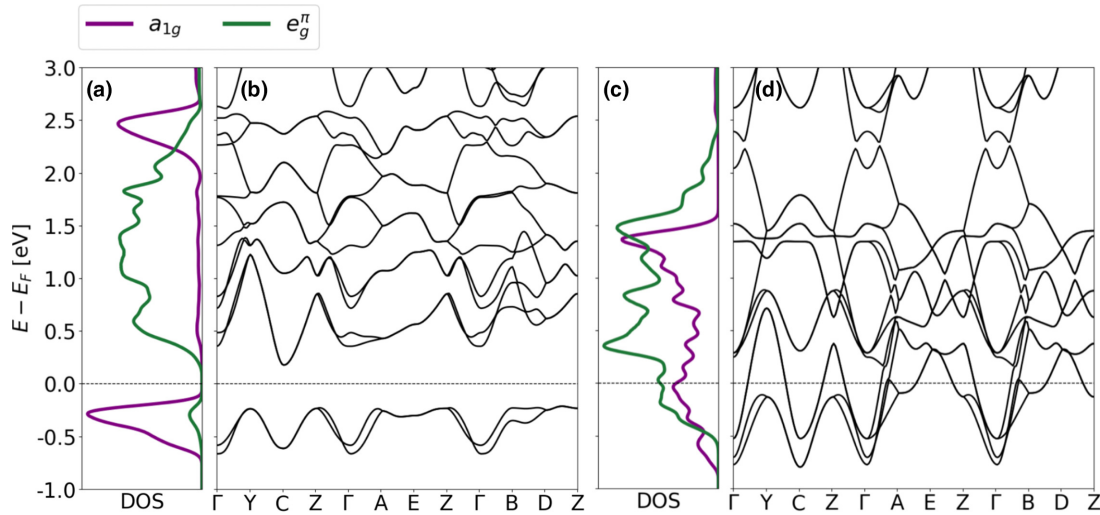


FIG. 8. PDOS and band structures for the stoichiometric M1 [panels (a) and (b)] and R [panels (c) and (d)] internally relaxed structures using $V = 1$ eV, with a_{1g} and e_g^π PDOS in purple and green, respectively.

polarization in the R phase [57]. In particular, a more explicit treatment of correlation effects could also address a possible formation of local magnetic moments induced by the oxygen vacancies, and their subsequent effects on the physics observed here.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [91].

APPENDIX: STOICHIOMETRIC R AND M1 STRUCTURES

In Fig. 8, we show the PDOS and band structures for the stoichiometric M1 and R structures.

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