

VO₂: A Novel View from Band Theory

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(Received 18 February 2011; published 29 June 2011)

New calculations for vanadium dioxide, one of the most controversially discussed materials for decades, reveal that band theory as based on density functional theory is well capable of correctly describing the electronic and magnetic properties of the metallic as well as both the insulating M_1 and M_2 phases. Considerable progress in the understanding of the physics of VO₂ is achieved by the use of the recently developed hybrid functionals, which include part of the electron-electron interaction exactly and thereby improve on the weaknesses of semilocal exchange functionals as provided by the local density and generalized gradient approximations. Much better agreement with photoemission data as compared to previous calculations is found and a consistent description of the rutile-type early transition-metal dioxides is achieved.

DOI: [10.1103/PhysRevLett.107.016401](https://doi.org/10.1103/PhysRevLett.107.016401)

PACS numbers: 71.20.-b, 71.30.+h, 71.70.-d

The metal-insulator transition (MIT) of stoichiometric VO₂ at ambient pressure [1] has been a matter of ongoing controversy for decades. The issue attained its fundamental character from the discovery of a structural distortion occurring at the same temperature (340 K) as the MIT [2,3]. Since then, discussion has focused on resolving the hen-and-egg problem of identifying the driving force of the combined electronic-structural transition. The latter is from the high-temperature rutile phase to the low-temperature monoclinic, so-called M_1 phase. The distortions occurring at the transition are characterized by metal dimerization parallel to the rutile c axis and a zigzaglike antiferroelectric shift of the V atoms perpendicular to this axis out of the center of the surrounding O octahedra. In a simple molecular-orbital picture these structural changes affect mainly the V $3d$ t_{2g} -derived states, which in the rutile phase straddle the Fermi energy and have similar band occupations [3,4]. Yet, due to the peculiarities of this structure with its characteristic octahedral chains parallel to the c axis, the t_{2g} states naturally fall into the $d_{||}$ orbitals and the so-called π^* orbitals, which show a quasi-one-dimensional and rather three-dimensional dispersion, respectively [5]. Response to the structural changes occurring at the transition to the M_1 phase is diverse. While the $d_{||}$ bands split into occupied bonding and empty antibonding states, the π^* states experience energetic upshift leading to their depopulation [3,4]. As a consequence, a band gap opens between the bonding $d_{||}$ and the π^* bands. An alternative interpretation, emphasizing the electronic origin of the MIT, assigns the splitting of the $d_{||}$ bands in the insulating phase rather to strong electronic correlations, which are screened by the π^* electrons in the metallic phase [6].

Still, the matter was complicated by the discovery of two additional insulating phases, namely, the monoclinic M_2 and the triclinic T phase occurring in doped samples or under uniaxial pressure, which suppresses the zigzaglike shift in half of the octahedral chains [7]. In the M_2 phase,

these chains still show metal dimerization, while in the remaining chains the dimerization is lost in favor of quasi-one-dimensional antiferromagnetic ordering. The T phase is intermediate between the two monoclinic phases as, compared to the M_2 phase, the dimerized chains start to zigzag and the zigzag chains start to dimerize until both chains are identical and the M_1 phase is entered. Of course, the observation of the M_2 phase reinitiated the debate about the driving force of the phase transitions and questioned especially the interpretation in terms of particular structural changes underlying the molecular-orbital picture.

A somewhat related but more academic aspect of the debate is the question as to what extent band theory would be able to correctly describe and understand the MIT and the role of electronic correlations. This discussion has its roots in the spectacular failure of calculations based on density functional theory within the local density (LDA) or generalized gradient approximation (GGA) to reproduce a finite band gap in the single-particle spectrum obtained from the monoclinic structures [5,8]. Furthermore, from the existence of the $S = \frac{1}{2}$ -Heisenberg chains characterizing the M_2 phase as well as the fact that, due to simple electrostatic arguments connecting the pairing on one chain to the antiferroelectric shift on the neighboring chains, the M_1 and T phases may be regarded as superpositions of two M_2 -type distortion patterns with equal and unequal amplitude, respectively, Rice, Launois, and Pouget concluded that all insulating phases of VO₂ must be of the Mott-Hubbard type and are not accessible by band theory [9]. Indeed, LDA calculations for the M_2 phase, while leading to an antiferromagnetic ground state, missed the insulating gap like for the M_1 phase [5]. This failure could be cured by LDA + U calculations (U is the Coulomb repulsion parameter), which, however, resulted in antiferromagnetic insulating ground states also for the M_1 and the metallic rutile phase [10]. So far, these latter two phases could be correctly reproduced only by GW calculations

and combinations of LDA with the dynamic mean-field theory [11–14]. Nevertheless, a correct consistent description of the metallic rutile as well as both insulating monoclinic phases using a parameter-free methodology has not yet emerged.

Here, the results of renewed calculations as based on density functional theory are presented. In contrast to previous work the present investigation builds on the use of the recently developed class of hybrid functionals, which have already proven to allow for a strikingly improved description of semiconductors and insulators [15,16]. Yet applications of these new tools to materials, which are regarded as strongly correlated, are still rare due to the high computational demand [15]. The present work demonstrates that density functional theory in combination with hybrid functionals is well capable of generating an insulating gap in the single-particle spectrum of both the M_1 and M_2 phases and of properly describing the antiferromagnetic ordering on the Heisenberg chains of the latter. These results shed new light onto the discussion of the role of the relevant correlations, since hybrid functionals primarily aim at improving on the exchange part of the LDA or GGA, while leaving the correlation functional unaltered.

The calculations were performed using density functional theory as implemented in the *ab initio* total-energy and molecular-dynamics program VASP (Vienna *ab initio* simulation program) developed at the Universität Wien [17]. The exchange-correlation functional was considered at the level of the GGA [18]. In addition, calculations as based on the recently developed hybrid functionals were performed. Within the framework of the generalized Kohn-Sham scheme [19] these functionals combine the exchange functional as arising from the LDA with the nonlocal Hartree-Fock expression. In the present work, the functional proposed by Heyd, Scuseria, and Ernzerhof (HSE) was used [20]. In this approach, the short-range part of the exchange functional is represented by a (fixed) combination of GGA and Hartree-Fock contributions, while the long-range part and the correlation functional are described by the GGA only. The single-particle equations were solved using the projector-augmented wave (PAW) method [21,22] with a plane-wave basis with a cutoff of 400 eV.

In a first step, the metallic rutile phase was considered. Structural data were taken from the work of McWhan *et al.* [23] in order to be consistent with previous calculations [5]. Partial densities of states (DOS's) as emerging from spin-degenerate calculations are displayed in Fig. 1. Two groups of bands are recognized. While the fully occupied bands derive mainly from the O 2*p* states, the group of bands straddling the Fermi energy are dominated by the V 3*d* states. V 3*d* and O 2*p* contributions showing up in the energy range, where the respective other orbitals dominate, result from hybridization between these states. The nearly perfect octahedral crystal field splits the V 3*d* levels into weakly π -bonding t_{2g} states ranging from -0.8 to $+1.8$ eV and strong σ -bonding e_g bands, which are found

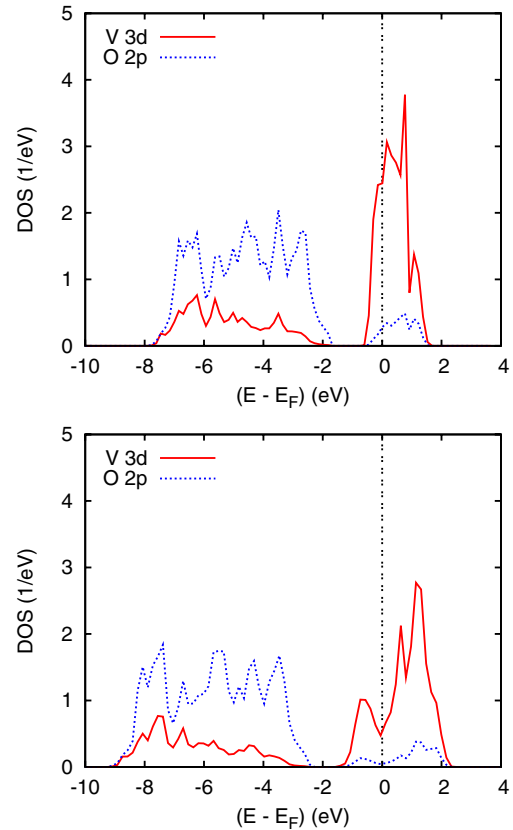


FIG. 1 (color online). Partial DOS of rutile VO_2 as calculated using the GGA (top) and the HSE (bottom) functional.

at higher energies but not shown here. The GGA results as displayed in the upper panel of Fig. 1 are very similar to the partial densities of states as arising from previous LDA calculations [5,8].

The HSE results given in the lower panel of Fig. 1 deviate substantially from those obtained by the GGA. While retaining their shape, the O 2*p* partial densities of states experience 10% broadening and energetic downshift by about 1 eV. In contrast, the width of the V 3*d* states almost doubles, leading to an occupied bandwidth of about 1.5 eV and a pronounced peak near -0.75 eV in much better agreement with experiment than the GGA results. In particular, photoemission finds an occupied bandwidth of about 1.5 eV for the V 3*d* band centered at about -1 eV [24,25].

For the monoclinic M_1 phase, crystal structure data by Longo and Kierkegaard were used [26]. Partial densities of states as arising from GGA calculations are shown in the upper panel of Fig. 2. As for the rutile structure, these results closely resemble those of previous calculations [5,8]. Again, the bands fall into O 2*p* and V 3*d* dominated groups well below and at the Fermi energy. Although the V 3*d* states display a sharp dip at E_F , the calculations still reflect the above mentioned failure of LDA or GGA to reproduce the insulating band gap of the monoclinic phase. According to the band structure displayed in the upper panel of Fig. 3 the metallic behavior results from small semimetalliclike overlap of the characteristic double band

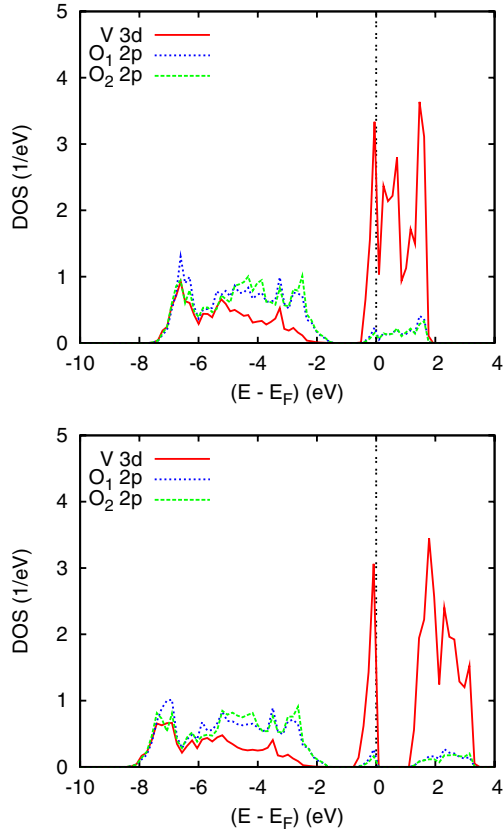


FIG. 2 (color online). Partial DOS of M_1 -VO $_2$ as calculated using the GGA (top) and the HSE (bottom) functional.

ranging from -0.5 eV to slightly above the Fermi energy with the almost empty higher lying bands. Yet, as has been discussed in detail previously, strong orbital ordering is obtained, since the occupied double band derives mainly from the $d_{||}$ states, whereas the π^* states are found mostly above E_F [5]. This is in striking contrast to the rutile phase, where LDA calculations yield very similar occupations of the t_{2g} bands with only small hybridization between the $d_{||}$ and π^* states [5]. Thus, the MIT is accompanied by strong orbital switching, as has been confirmed by most calculations as well as by recent x-ray-absorption spectroscopy measurements [27].

The situation changes drastically on turning to the hybrid functional calculations. According to the partial densities of states displayed in the lower panel of Fig. 2, the previously slightly overlapping groups of bands are pulled apart and an insulating band gap of ≈ 1.1 eV is opened between the bonding $d_{||}$ bands and the empty π^* states. The bonding $d_{||}$ bands form a sharp peak at about 0.75 eV below the center of the gap, again in good agreement with photoemission experiments, which find the V 3d band of about 1 eV width at a binding energy of about 1 eV [24,25,28]. The band structure shown in the lower panel of Fig. 3 reveals a clear separation into fully occupied and empty bands. Furthermore, we note the striking similarity to the GGA bands as concerns both widths and shapes, the main difference being the rather rigid band shift.

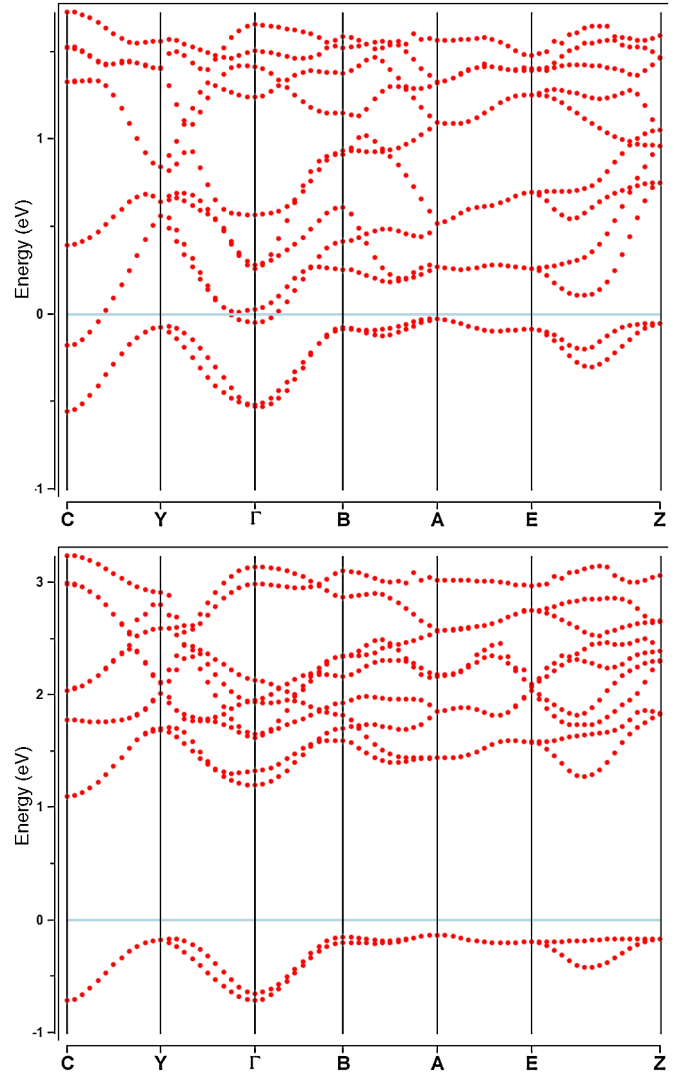


FIG. 3 (color online). Electronic bands of M_1 -VO $_2$ as calculated using the GGA (top) and the HSE (bottom) functional.

Finally, spin-polarized antiferromagnetic calculations were performed for the M_2 phase. Here, crystal structure data as given by Marezio *et al.* were used [7]. While previous LDA calculations resulted in a stable antiferromagnetic ground state with local magnetic moments of $\approx 0.5\mu_B$ mainly carried by the V 3d $d_{||}$ states, the insulating behavior could not be reproduced [5]. In contrast, the present HSE calculations lead to V magnetic moments of $1.0\mu_B$ and an optical band gap of about 1.2 eV. This is easily seen in the band structure shown in Fig. 4. Analysis of the corresponding partial densities of states reveals strong polarization of the vanadium atoms in the antiferroelectrically distorted chains, whereas polarization of the dimerizing vanadium atoms is almost negligible.

To conclude, band theory as based on density functional theory is well capable of correctly describing the metal-insulator transitions of VO $_2$ provided that the appropriate exchange-correlation functional is used. In particular, while LDA and GGA fail to account for the insulating behavior of

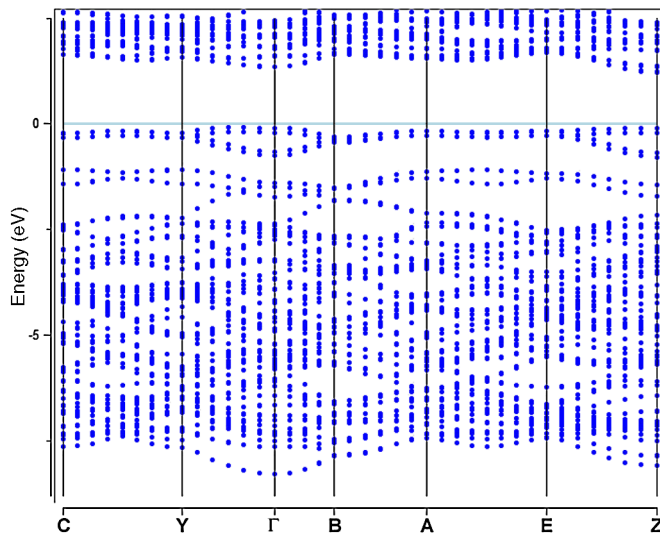


FIG. 4 (color online). Electronic bands of M_2 -VO₂ as calculated using the HSE functional.

the low-temperature phases, the recently proposed hybrid functionals lead to a finite band gap for both the M_1 and M_2 phases and the antiferromagnetic ordering observed for the latter. In addition, much better agreement with photoemission data has been found. Our results put VO₂ in line with the metal-insulator system NbO₂ and metallic MoO₂, which both display the same structural distortions and have already been successfully described within density functional theory [29–31]. We are not aware of any other theory that has provided a consistent and successful description of the structural distortions of the rutile-type early transition-metal dioxides as well as the MIT's of the d^1 members. Finally, the present study sheds new light on the old discussion about the predominant influence of either structural distortions or electronic correlations as no further interactions beyond those covered by density functional theory and the Hartree-Fock exchange have to be introduced. However, recent experimental studies indicate that the insulator-to-metal transition is initiated by rearrangements of the electronic system [32]. A theoretical understanding of these data is the subject of current research.

I am particularly grateful for vivid discussions with and support from K.-H. Höck, T. Kopp, J. Mannhart, M. Marsman, P. Saxe, P.C. Schmidt, M. Stephan, and E. Wimmer. The calculations were performed using Material Design's MedeA computational environment as well as the computational facilities of Materials Design. This work was supported by the DFG through TRR 80 and by the BMBF through Project No. 03SF0353B.

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