

Accurate Band Gaps of Correlated Transition-Metal Oxides from MedeA[®]-VASP with Hybrid-Functionals

The electronic structures of the metallic and insulating phases of VO₂ are calculated using density functional theory and modern hybrid functionals as recently implemented in MedeA[®]-VASP. Strongly contrasting previous calculations as based on local or semilocal approximations, which missed the insulating behavior of the low-temperature phase, these new calculations accurately reproduce the optical band gap and thus bring to an end a fifty-year old controversy on the origin of the metal-insulator transition of VO₂.

Keywords: Transition-metal oxides, vanadium dioxide, metal-insulator transition, electron correlations, optical band gap, MedeA[®], VASP, hybrid functionals

Background

The metal-insulator transition (MIT) of stoichiometric VO₂ at ambient pressure has been the subject of ongoing dispute since its discovery in the 1950s [1,2]. Occurring at a technologically interesting temperature of 340 K this MIT is connected with a change in resistivity of several orders of magnitude. Interestingly, it is also closely tied to a structural transition from the high-temperature rutile structure to a low-temperature monoclinic M₁ structure, which deviates from the former by a pronounced V-V dimerization parallel to the rutile c-axis and a zigzag-like antiferroelectric displacement of the V atoms perpendicular to this axis.

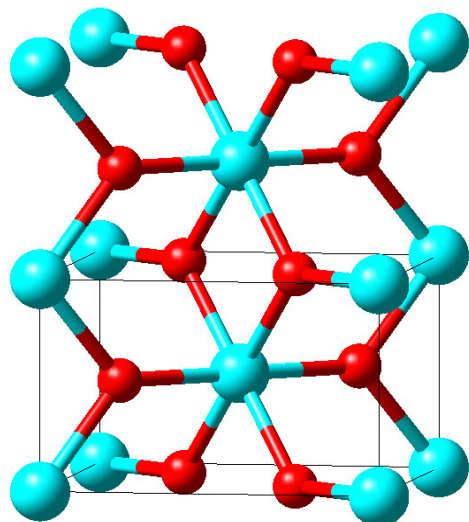


Figure 1. High-temperature rutile structure of VO₂. Vanadium and oxygen atoms are given in cyan and red, respectively.

In Fig. 1, two unit cells of the rutile structure with the characteristic VO₆ octahedra and the vertical V-atom chains are displayed. In the monoclinic M₁ structure shown in Fig. 2 the unit cell is doubled and the vanadium atoms in the chains are dimerized as well as horizontally shifted off the octahedral centers.

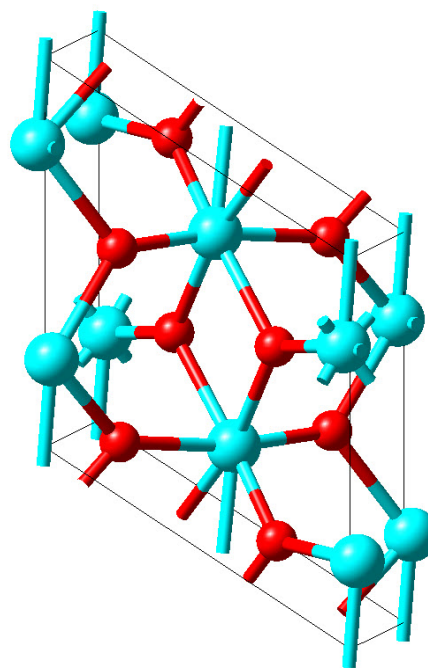


Figure 2. Low-temperature monoclinic M₁ structure of VO₂. Vanadium and oxygen atoms are given in cyan and red, respectively.

As has been worked out in detail by Goodenough, these atomic motions can be nicely translated into energetic shifts and splittings of the relevant V 3d and closely related O 2p states. In doing so, Goodenough was indeed able to provide a qualitative understanding of the MIT within the framework of an orbital or band picture [3,4]. This was soon after questioned by Mott

and coworkers, who were convinced that strong electron correlations play a dominant role for the MIT and regarded the structural changes rather as an amendment [5]. Indeed, first principles calculations as based on density functional theory and the local density or generalized gradient approximation just missed the insulating behavior and resulted in a semimetal-like overlap of the valence and conduction bands [2,6]. Finally, the situation became even more complicated by the discovery of the additional low-temperature insulating M_2 phase with a slightly different pattern of the structural distortions and long-range magnetic ordering, which even more fired up the debate [7]. Again, density functional theory together with a semilocal approximation failed to correctly capture the insulating behavior [2].

This application note demonstrates the outstanding capability of the MedeA[®] software environment with modern hybrid functionals as implemented in VASP [8] to accurately describe both the metallic and insulating phases of correlated electron materials and thereby to settle the long-standing dispute on the origin on the MIT of the cornerstone material VO_2 [9].

Method of Calculation

While density functional theory is an exact theory for the ground state its practical application requires the specification of the unknown exchange-correlation functional. Local and semilocal approximations such as the local density approximation (LDA) and the generalized gradient approximation (GGA) have proven to be perfectly suited for describing metals but are well known to underestimate or in some cases even miss the optical band gap of semiconductors and insulators. Recent developments to overcome this weakness led to the so-called hybrid functionals, which combine the local exchange with non-local contributions as known from Hartree-Fock theory. This approach has turned out to yield very accurate band gaps for a vast number of semiconductors but had not been systematically applied to materials with so-called strong electronic correlations [10]. Specifically, in the present context we use the hybrid functional proposed by Heyd, Scuseria, and Ernzerhof (HSE).

Computed Results

The calculations were performed for both the metallic high-temperature rutile phase and the insulating low-temperature monoclinic M_1 phase. The partial densities of states (DOS) calculated for the rutile phase using the GGA and HSE functional are displayed in Fig. 3.

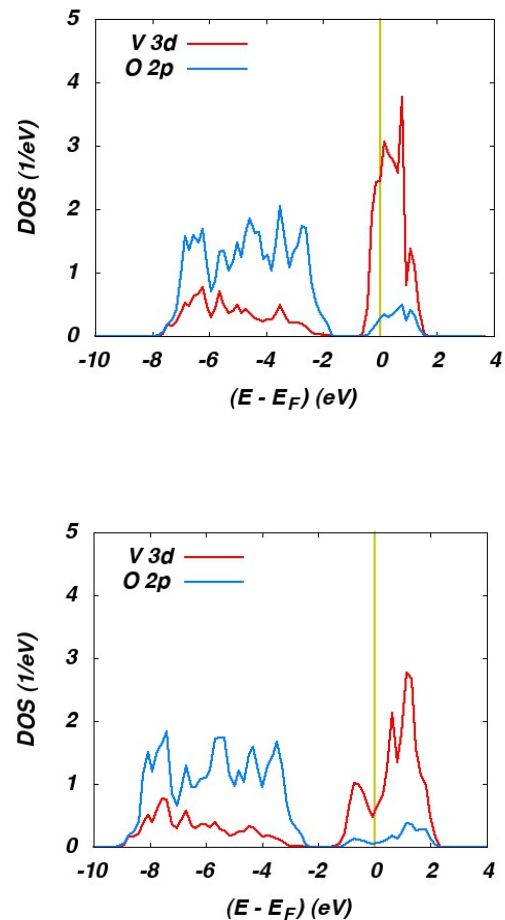


Figure 3. Partial DOS of rutile VO_2 as calculated using the GGA (top) and the HSE (bottom) functional.

The O 2p and V 3d states (with small admixtures from the respective other type of orbital due to hybridization of these states) are easily recognized well below and at the Fermi energy. Both functionals result in metallic behavior in accordance with the experimental findings. However, use of the hybrid functional leads to a much larger width of the V 3d bands in much better agreement with photoemission data.

The corresponding partial DOS for the monoclinic M_1 phase are displayed in Fig. 4. Again, the O 2p and V 3d states are well separated for both functionals. Yet, GGA and HSE result in completely different behavior. While the GGA leads to metallic behavior as clearly indicated

by the presence of electronic states at the Fermi energy (see the blue arrow), the HSE calculations reproduce the observed optical band gap indicated by the blue arrow.

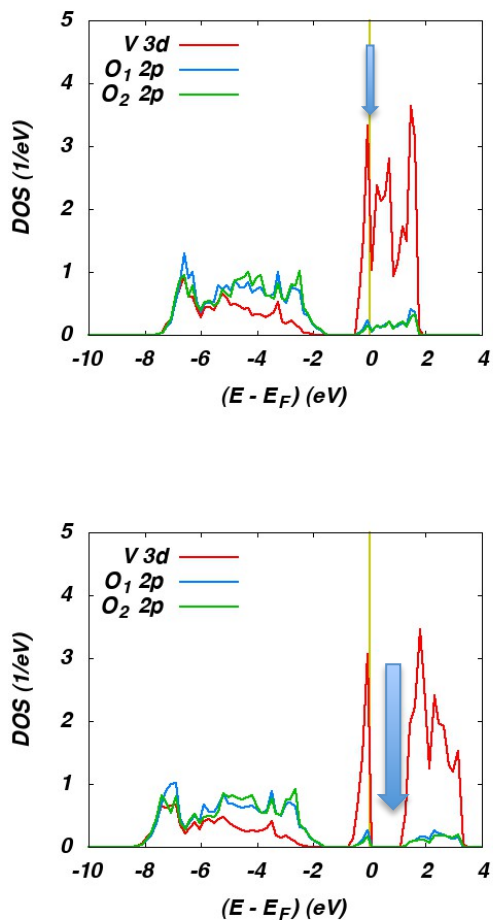


Figure 4. Partial DOS of M_1 -VO₂ as calculated using the GGA (top) and the HSE (bottom) functional.

Finally, spin-polarized antiferromagnetic calculations were performed for the insulating M_2 phase. While for this phase, GGA calculations likewise had failed to reproduce the insulating behavior, HSE calculations were successful in obtaining the optical band gap and well localized magnetic moments at the vanadium sites, thus impressively underlining the striking progress offered by the hybrid functionals.

Conclusion

First principles calculations using the recently developed hybrid functionals have been demonstrated to be well capable of fully describing the insulating

phases of VO₂, which is one of the key representatives of the broad class of so-called electronically correlated materials, and also to allow for a deeper understanding of the origin of the metal-insulator transition. The latter is shown to be intimately connected to the structural changes occurring at the phase transition.

MedeA[®] Modules Employed in this Example

The present calculations were performed with the MedeA[®] platform using the following integrated features and modules:

- The standard MedeA[®] framework including crystal structure builders and geometric analysis tools
- The MedeA[®]-VASP interface
- The MedeA[®] JobServer and TaskServer

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