The Metal-Insulator Transition of NbO$_2$: an Embedded Peierls Instability

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Results of first principles augmented spherical wave electronic structure calculations for niobium dioxide are presented. Both metallic rutile and insulating low-temperature NbO$_2$, which crystallizes in a distorted rutile structure, are correctly described within density functional theory and the local density approximation. Metallic conductivity is carried to equal amounts by metal $t_{2g}$ orbitals, which fall into the one-dimensional $d_{||}$ band and the isotropically dispersing $e_g^*$ bands. Hybridization of both types of bands is almost negligible outside narrow rods along the line X–R. In the low-temperature phase splitting of the $d_{||}$ band due to metal-metal dimerization as well as upshift of the $e_g^*$ bands due to increased $p$-$d$ overlap remove the Fermi surface and open an optical band gap of about 0.1 eV. The metal-insulator transition arises as a Peierls instability of the $d_{||}$ band in an embedding background of $e_g^*$ electrons. This basic mechanism should also apply to VO$_2$, where, however, electronic correlations are expected to play a greater role due to stronger localization of the 3d electrons.

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Despite intense work over decades the metal-insulator transition (MIT) of VO$_2$ has remained a matter of controversy. This is related to the simultaneous occurrence of a structural transformation from the high-temperature rutile phase to a distorted monoclinic structure, which is characterized by (i) pairing of the high-temperature rutile phase to a distorted monoclinic structure, which is characterized by (i) pairing of the metal atoms within chains parallel to the rutile $c$ axis and (ii) their lateral zigzag-like displacement. Electronic states near the Fermi energy are of mainly $V^{3+}$ character. They separate into the $d_{||}$ band, which mediates V–V overlap along the metal chains, and the remaining $e_g^*$ bands. At the transition, splitting of the $d_{||}$ band and upshift of the $e_g^*$ bands due to increased metal-oxygen overlap produce a finite band gap. This basic mechanism should also apply to VO$_2$, where, however, electronic correlations are expected to play a greater role due to stronger localization of the 3d electrons.

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For this reason, a complete and widely accepted picture of the rutile-related transition metal dioxides has not yet emerged.

Here we present first principles electronic structure calculations for NbO$_2$. These are the first calculations at all for the insulating phase and the first calculations for rutile NbO$_2$, which used the experimental crystal structure. Both phases are correctly described within density functional theory (DFT) and the LDA. The results strongly support the band theoretical point of view of the MIT as arising predominantly from a Peierls-type instability of the rutile phase.

Evidence for the MIT being driven by strong metal-metal bonding was first inferred from the small and almost temperature independent paramagnetic susceptibility below the transition temperature as well as from the enhanced thermal expansion of the $c$ lattice parameter just above $T_c$. Additional support came from strong decrease of $T_c$, nonlinear variation of $c$, and crossovers of the magnetic susceptibility to Curie-Weiss behaviour on substitution of Ti for Nb, which destroys the metal-metal bonding.

According to neutron-diffraction experiments the bct structure of insulating NbO$_2$ has 16 formula units per cell, space group $I4_1/a$ ($C_{4h}$), and lattice constants $a \approx 2\sqrt{2}a_R$ and $c \approx 2c_R$, where $a_R = 4.8464$ Å and $c_R = 3.0316$ Å are the rutile lattice parameters. The two different Nb-Nb distances of 2.7 and 3.3 Å as arising from the metal-metal pairing along the rutile $c$ axis deviate considerably from the rutile value $c_R$. In addition, the zigzag-like in-plane displacement of niobium atoms parallel to either the [110] or [110] direction of the rutile subcell leads to a variation of Nb–O distances between 1.91 and 2.25 Å, which deviate from the high-temperature values of 2.00 and 2.08 Å. Critical scattering observed above $T_c$ at the
tetragonal wave vector $q_P = (1/4, 1/4, 1/2)$ pointed to a 
soft phonon mode, which, however, could not be clearly 
identified \[23\]. Yet, using a shell model, Gervais and Kress were able to reveal softening of a $P$ point 
phonon with a displacement pattern consistent with the 
low-temperature structure \[23\].

Room-temperature UPS and XPS experiments re-
vealed a 9 eV wide occupied group of bands, which falls 
into the 1 eV wide Nb 4$d$ bands just below $E_F$ and a 
6 eV wide group of O 2$p$ bands at higher binding en-
ergies \[26\]. The room temperature optical band gap was 
estimated to about 0.5 eV \[2\]. By and large, photoem-
issi on data agree with band structure and Xa cluster 
calculations \[15, 16, 24\], which, due to the complex-
ity of the low-temperature structure, only addressed to 
the rutile phase. Only Sasaki et al. accounted for the 
bct structure by studying Nb$_2$O$_{10}$ clusters with either 
short or long Nb-Nb distance and deduced a band gap of 
0.68 eV; however, oxygen positions were not relaxed and 
the same value for all Nb-O distances used \[16\]. Finally, 
calculated Fermi surfaces and generalized susceptibilities 
agreed with experiment in that they could not find a 
soft-mode instability \[15, 23\].

The present calculations were performed using the 
scalar-relativistic augmented spherical wave (ASW) 
method \[29\]. Both the LDA and the generalized gradi-
ent approximation were applied with essentially no differ-
ces in the electronic structure. Crystallographic data 
as given by Bolzan et al. \[22\] and Pynn et al. \[23\] were 
used. In order to account for the loose packing of the 
crystal structures empty spheres, i.e. pseudo atoms with-
out a nucleus, were included to model the correct shape 
of the crystal potential in large voids. Optimal empty 
sphere positions and radii of all spheres were automatic-
ally determined \[30\]. As a result, three and 14 in-
equivalent empty sphere types with radii ranging from 
0.96 to 2.49 $a_B$ were included in the rutile and bct cell, 
respectively, keeping the linear overlap of niobium and 
oxygen spheres below 18.5%. The basis set comprised 
Nb 5$s$, 5$p$, 4$d$ and O 2$s$, 2$p$ as well as empty sphere 
states. Brillouin zone sampling was done using an in-
creased number of $k$ points ranging from 18 to 1800 and 
12 to 552 points within the respective irreducible wedge.

Partial densities of states (DOS) resulting from calcula-
tions for the rutile and bct structures are displayed in 
Fig. 1. The gross features are similar in both phases. 
Three groups of bands are identified. While bands in the 
energy range from $\approx -9$ to $-3$ eV are dominated by 
O 2$p$ states, the two higher lying groups at and above 
the Fermi energy derive mainly from Nb 4$d$ orbitals. All 
other states play only a negligible role in the energy inte-
gral shown. Crystal field splitting causes nearly complete 
energetical separation of the Nb 4$d$ bands into two groups 
of $t_{2g}$ and $e_g$ symmetry. Contributions of the O 2$p$ and 
Nb 4$d$ states to the upper two and the lower group, re-
spectively, are indicative of covalent bonding.

Our results for insulating and metallic NbO$_2$ are in 
good agreement with the photoemission experiments \[26\] 
and the previous calculations \[13, 16, 24\]. Differences 
with the latter could be traced back to the fact that these 
calculations were not self-consistent or, due to lack of 
crystallographic data, used a rutile structure obtained 
from symmetrizing the bct structure.

The results for both phases differ with respect to the 
energetical position of the O 2$p$ group of bands as well as 
the shape of the $t_{2g}$ partial DOS. In Fig. 2 these DOS are 
further separated into their symmetry components. To 
this end orbitals were transformed to a local coordinate 
system with the $z$ and $x$ axis parallel to the apical axis 
of the local octahedron and the rutile $c$ axis, respectively 
\[17\]. While the $d_{x^2-y^2}$ (≡ $d_{||}$) and $d_{yz}$ states mediate 
$\sigma$-type $d$-$d$ overlap along the rutile $c$ and $a$ axes, respec-
tively, the $d_{xz}$ states account for $\pi$-type overlap across 
the chains. Note that the latter two orbitals combine 
into the $e_g$ states. The $t_{2g}$ groups of bands are displayed in 
Fig. 1, where the $d_{xz}$ bands are highlighted by bars with 
widths proportional to the $d_{x^2-y^2}$-contribution to 
the respective wave function. Thus, states with vanishing 
bars are of pure $e_g$ character (apart from small $e_g^*$ as
FIG. 2: Partial $t_{2g}$ DOS of (a) metallic and (b) insulating NbO$_2$ (per f.u.).

FIG. 3: Weighted band structure of (a) metallic and (b) insulating NbO$_2$ (see text).

well as O 2p contributions).

Most striking in Fig. 2(a) is the nearly perfect one-dimensional dispersion of the $d_{x^2-y^2}$ bands parallel to the rutile c axis, i.e. parallel to the niobium chains, which gives rise to the pronounced double peak structure in the partial DOS, Fig. 2(a). In contrast, dispersion of the $e_g^\pi$ bands is of the same order in all directions. This leads to the single broad structure of the $d_{x^2}$ partial DOS, while the $d_{yz}$ states fall into two maxima due to the aforementioned inplane d-d overlap. The DOS at $E_F$ is comprised from similar contributions from all three $t_{2g}$ orbitals explaining the rather isotropic electrical conductivity. Note that, except for the bands along the line X-R, the $d_{||}$ states hardly hybridize with the $e_g^\pi$ states and thus coupling between both types of bands is mainly via charge conservation. For this reason, the $d_{x^2-y^2}$ band may be regarded as a one-dimensional band in a three-dimensional embedding background of $e_g^\pi$ bands.

On going to insulating NbO$_2$ two distinct changes occur. i) The previously one-dimensional $d_{x^2-y^2}$ band is split into bonding and antibonding branches due to Nb-Nb dimerization within the chains. As a consequence, the separation of the two peaks in the $d_{x^2-y^2}$ partial DOS has increased by more than 1 eV and the contributions in between have been considerably reduced. ii) The $e_g^\pi$ states experienced energetical upshift by $\approx$ 0.5 eV due to increased p-d overlap, causing almost complete depopulation of these orbitals. This is due to the much reduced Nb-O distances arising from the zigzag-like displacement of the Nb atoms. However, the lateral displacements also affect the inplane metal-metal bonding. For this reason, the two peak structure of the $d_{yz}$ partial DOS has vanished and both $e_g^\pi$ partial DOS have become more similar. Taken together these changes lead to complete separation of the low lying $d_{x^2-y^2}$ bands from the $e_g^\pi$ states, which gives rise to a band gap of 0.1 eV. This value was determined from checking band extrema on a 16 $\times$ 16 mesh within the Brillouin zone. Note that the hybridization between both types of bands is still negligible.

To conclude, the electronic structures of both metallic and insulating NbO$_2$ are well described within DFT and LDA. The near $E_F$ electronic structure of metallic NbO$_2$ consists of two very weakly hybridizing types of $t_{2g}$ bands, namely, $d_{||}$ states with one-dimensional dispersion parallel to the Nb chains and isotropically dispersing $e_g^\pi$ bands. In the low-temperature structure Nb-Nb dimerization splits the $d_{||}$ band into bonding and antibonding branches, whereas the $e_g^\pi$ states shift to higher energies.
due to reduced Nb-O distances. Since coupling between both types of bands is still by charge conservation rather than hybridization, the insulating state is interpreted as due to a Peierls instability of the $d_{\parallel}$ bands in an embedding reservoir of $\epsilon_g^T$ electrons.

The results complement previous work on VO$_2$ as well as MoO$_2$, and give rise to a unified picture for the early transition metal dioxides, which explains (i) destabilization of the rutile structure and (ii) the metal-insulator transition of the $d^3$ members. Since the 4$d$ bands are broader than the 3$d$ bands metal-metal bonding is stronger in the fourth row dioxides this leading to the higher transition temperature of NbO$_2$ as compared to VO$_2$. In contrast, the absence of a gap in LDA calculations for the latter compound might be indicative of a considerable amount of electronic correlations. Here, a combination of LDA and dynamical mean field theory as recently successfully applied to V$_2$O$_3$ might be more appropriate.

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