The electronic structure of tantalum (oxy)nitrides TaON and Ta$_3$N$_5$


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Detailed results of ab initio band structure calculations for tantalum (oxy)nitrides (TaON and Ta$_3$N$_5$) are reported. The calculations are performed within the framework of density functional theory (DFT). We compare results obtained with the molecular dynamics pseudopotential (PP) approach of the Vienna Ab initio Simulation Program (VASP) and the Full Potential Linearized Augmented Plane Waves method (FP-LAPW) using the WIEN97 program. In agreement with neutron diffraction measurements, we show an ordering of the anions in TaON. The calculations also show that the valence band is composed mainly of the anion 2p orbitals hybridized with Ta 5d states. For TaON the top of the valence band is dominated by N 2p states. The bottom of the conduction band is mainly composed of Ta 5d states. Both TaON and Ta$_3$N$_5$ are semiconductors with calculated indirect band gaps of respectively 1.8 and 1.1 eV (VASP calculations) and 2.0 and 1.2 eV (WIEN97 calculations). Optical diffuse-reflectance spectra show an energy gap of 2.08 eV for Ta$_3$N$_5$.

1. Introduction
In recent years, oxynitrides have become a rapidly growing field of interest.1–3 Many oxynitrides are formed by introduction of nitrogen into the anionic (oxygen) network. The consequent increase of negative charge can be compensated with cationic substitutions.4 These materials may have new physical properties. For example, the replacement of O by N may adjust the color of some oxynitrides containing 4d and 5d transition metals and these oxynitride materials have potential as safe pigments or transition for these and related materials.

2. Details of the calculation method
For the sake of comparison, two types of calculations, both within the Density Functional Theory (DFT) approach, were carried out. On the one hand, we used the ab initio total-energy and molecular dynamics program VASP (Vienna Ab initio Simulation Program), developed by the Institut für Theoretische Physik of the Technische Universität Wien (who also supplied the pseudopotentials) 19–21 Vanderbilt-type ultra-soft pseudopotentials22 were used for Ta, O and N and non-linear core corrections3,24 were applied for Ta. The Kohn–Sham functional of ref. 25. The Brillouin zone (BZ) was sampled using the Monkhorst–Pack grid, 26 resulting in 80 k-points in the irreducible part centered at Γ. Tests on denser k-point meshes showed that this sampling is adequate. Calculations were also performed for the tantalum nitride Ta$_3$N$_5$ for the sake of comparison. Knowledge of the electronic structure of both compounds is very useful to gaining an understanding of the colour and the corresponding optical transition for these and related materials.

Four Ta atoms as the nearest neighbors, while N2 is coordinated to three Ta atoms. The Ta–N distances range from 1.96 to 2.24 Å and are similar to those in TaON. Until now there has been no report on the electronic and optical properties of tantalum oxynitride. This paper presents the results of self-consistent first-principles calculations for the crystal structure and electronic structure of β-TaON within DFT. Calculations are also performed for the tantalum nitride Ta$_3$N$_5$ for the sake of comparison. Knowledge of the electronic structure of both compounds is very useful to gaining an understanding of the colour and the corresponding optical transition for these and related materials.
sampling is not affected. This procedure was repeated several times in order to give a set of total energies as a function of cell volume. From this the equilibrium volume and bulk modulus were obtained by a fit to a Murnaghan equation of state. Only electronic structure calculations have been performed for the tantalum nitride Ta\textsubscript{3}N\textsubscript{5} using the experimental lattice parameters and coordinates of atoms, as shown in Table 2. For the oxynitride TaON, structure optimizations are performed and the electronic structure is calculated using the optimized lattice parameters and coordinates of atoms.

On the other hand, calculations were also carried out with the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method implemented in the WIEN97 code. In the LAPW method, the unit cell is divided into two types of regions, the atomic spheres centered upon nuclear sites and the interstitial region between the nonoverlapping spheres. Inside the atomic spheres, the wave functions are replaced by atomic-like functions, while in the interspheres region the wave function of a Bloch state is expanded in plane waves. The local density approximation of Perdew and coworkers was used together with the Perdew–Burke–Ernzerhof GGA potential. The maximum value in the expansion of the basis set inside atomic spheres was 10 for the computation of the muffin-tin matrix and 4 for the nonmuffin-tin matrix element. The convergence of the basis set is controlled by a cutoff parameter $R_{\text{mt}}k_{\text{max}}$ where $R_{\text{mt}}$ is the smallest atomic sphere radius in the unit cell and $k_{\text{max}}$ is the magnitude of the largest $k$ vector. Self consistency was carried out on a 72 $k$-point mesh in the irreducible Brillouin zone for Ta\textsubscript{3}N\textsubscript{5} and a 112 $k$-point mesh for TaON. All the WIEN97 calculations were performed with the experimental crystal structures of Ta\textsubscript{3}N\textsubscript{5} and TaON.

### 3. Results and discussion

#### 3.1. Electronic structure of Ta\textsubscript{3}N\textsubscript{5}

We begin by considering tantalum nitride Ta\textsubscript{3}N\textsubscript{5}. Fig. 3a shows the Brillouin zone (BZ) for Ta\textsubscript{3}N\textsubscript{5} with space group $Cmcm$. The dispersion of the electron bands calculated with the VASP and the WIEN97 codes are shown in Fig. 4a and b, respectively.

The partial and total density of states (DOS) computed with both methods are almost identical. Therefore, only the VASP DOS curves are shown in Fig. 5.

### Table 1

Calculated parameters and coordinates of the atoms in $\beta$-TaON using the PP method as compared with the experimental results. The calculated bulk modulus is also included.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>4(e)</td>
<td>0.2939</td>
<td>0.0461</td>
<td>0.2153</td>
</tr>
<tr>
<td>A1(N)</td>
<td>4(e)</td>
<td>0.4437</td>
<td>0.7565</td>
<td>0.4863</td>
</tr>
<tr>
<td>A2(O)</td>
<td>4(e)</td>
<td>0.0627</td>
<td>0.3264</td>
<td>0.3464</td>
</tr>
</tbody>
</table>

$\beta$-TaON: space group: $P_{2_1}/c$.

### Table 2

Lattice parameters and coordinates of the atomic position for tantalum nitride (Ta\textsubscript{3}N\textsubscript{5}).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta1</td>
<td>4(c)</td>
<td>0</td>
<td>0.1971</td>
<td>$\frac{1}{4}$</td>
</tr>
<tr>
<td>Ta2</td>
<td>8(f)</td>
<td>0</td>
<td>0.13455</td>
<td>0.55906</td>
</tr>
<tr>
<td>N1</td>
<td>4(c)</td>
<td>0</td>
<td>0.76322</td>
<td>$\frac{1}{4}$</td>
</tr>
<tr>
<td>N2</td>
<td>8(f)</td>
<td>0</td>
<td>0.04701</td>
<td>0.11049</td>
</tr>
<tr>
<td>N3</td>
<td>8(f)</td>
<td>0</td>
<td>0.30862</td>
<td>0.073378</td>
</tr>
</tbody>
</table>

Ta\textsubscript{3}N\textsubscript{5}: space group $Cmcm$, $a=3.8862$, $b=10.2118$, $c=10.2624$ Å.
−12.6 eV (the Fermi level is set at the top of the valence band), are mainly composed of N 2s states. The 2s states of the N2 ions, with a peak at the upper part of the band, are different from the other two N ions (N1 and N3). This is due to the different coordination: every N2 ion has three Ta neighbors while N1 and N3 ions are coordinated by four Ta atoms. There is a gap of about 5.6 eV between the N 2s states and the bottom of the valence band. The valence band is mainly composed of N 2p states (Fig. 4b and 5). However, the density of Ta 5d states is high all over the valence band, which indicates a strong covalent interaction between Ta and N. The bottom of the conduction band is mainly composed of Ta 5d states. The top of the valence band is along the C–X line and the bottom of the conduction band is at Y in the BZ. Therefore, the compound is an indirect semiconductor with an energy gap of about 1.1 eV (VASP) and 1.2 eV (WIEN97) as shown in Table 3. The direct energy gap at C is about 1.4 eV for both programs.

Samples of Ta3N5 have the colour of bordeaux wine red. From the measured optical diffuse-reflectance spectra an energy gap of about 2.1 eV is obtained. This is in reasonable agreement with the calculated value of the direct gap, as it is well known that electronic structure calculations within GGA generally underestimate the energy gap.

### Table 3 Comparison between the calculated indirect gaps and experimental (optical) values for the tantalum compounds (*estimated value). The calculated values in parentheses are the direct energy gap at C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Exp./eV</th>
<th>Colour</th>
<th>Calculated results/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta2O5</td>
<td>4.1–4.4</td>
<td>white</td>
<td>—</td>
</tr>
<tr>
<td>TaON</td>
<td>&gt;2.1*</td>
<td>green</td>
<td>1.8 (2.0) 2.1 (2.2)</td>
</tr>
<tr>
<td>Ta3N5</td>
<td>2.1†</td>
<td>bordeaux red</td>
<td>1.1 (1.4) 1.2 (1.4)</td>
</tr>
</tbody>
</table>

3.2. Crystal structure of TaON

The first question about the structure of TaON is the occupation of the O/N anions at the sites A1 and A2, i.e. the distribution of O/N in the structure as suggested in the literature. VASP calculations with the same lattice parameters and a relaxed symmetry (space group P1) were performed for four different kinds of occupations: (a) 4 N at A1 and 4 O at A2; (b) 3 N and 1 O at A1, and 3 O and 1 N at A2; (c) 2 O and 2 N at A1 and A2; and (d) 4 O at A1 and 4 N at A2. The calculations include optimization for both lattice parameters and coordinates of atoms for every configuration. The VASP calculations confirmed the ordered O/N occupation for TaON, that is, A1 is fully occupied by N atoms and A2 fully occupied by O atoms, which has an energy about 1 to 2 eV lower than the other kinds of occupations. This is understandable because nitrogen ions prefer to be four-coordinated, while oxygen ions would prefer to have three neighbors. This result is in agreement with the refinement of the structure with neutron diffraction measurements. Table 1 lists the results of...
optimization of lattice parameters and coordinates of the atomic positions. The agreement between the calculated coordinates of the atoms and the experimental results is excellent. The minimum in the total energy curve gives an equilibrium volume of 129.46 Å³, close to the experimental data (127.16 Å³). Such results are typical for the GGA approximation. By fitting the calculated data points to the Murnaghan equation of state, we obtained a bulk modulus of 278 GPa. This value is larger than the experimental value of 185 GPa of the partially stablised (monoclinic) zirconia ZrO₂. There are no data about the bulk modulus for the tantalum oxides and (oxy)nitrides. The only experimental value we found is 575.8 GPa for TaN.

3.3. Electronic structure of TaON

Fig. 3b shows the BZ for β-TaON. The dispersions of the electron bands calculated with the VASP and the WIEN97 codes are shown in Fig. 6a and b, respectively. As in the case of Ta₃N₅, both types of calculations give very similar results and therefore, only the VASP DOS curves are shown in Fig. 7.

The lowest bands, with energy in the range from −18.4 to −17.3 eV (the Fermi level is set at the top of the valence band), are mainly of O 2s states. The upper part of the O 2s band, there are two bands, which are very localized with a bandwidth of less than 0.2 eV, as shown in Fig. 6 and 7. A gap of about 2.7 eV exists between the O 2s and the next (N 2s) band. The N 2s states have a splitting with a bandwidth of about 2.0 eV, which is narrower than that in Ta₃N₅ (about 3.0 eV), but broader than the O 2s band (about 1.0 eV). The gap between the N 2s band and the valence band (band near the Fermi level) is about 6 eV, close to that of Ta₃N₅ (Fig. 5). The valence band is mainly composed of O 2p and N 2p states (Fig. 6b) hybridized with Ta 5d states. Both the O 2p and N 2p states are

Fig. 6 Dispersion of the energy bands for TaON: (a) VASP calculations; (b) WIEN97 calculations. The thickness of the lines is proportional to the contribution of the 5d Ta states (left), 2p O states (middle) and 2p N states (right).

Fig. 7 Partial and total density of states for TaON (VASP calculations). The Fermi level is at 0 eV.
all over the valence band. But the top part of the valence band is dominated by N 2p states. The top of the valence band is at Γ of the BZ, while the bottom of the conduction band is not at Γ, but at B. Therefore, the compound is an indirect-gap semiconductor with a calculated energy gap of 1.8 eV (VASP) and 2.1 eV (WIEN97). The direct gap at Γ is about 2.0 eV (VASP) and 2.2 eV (WIEN97). The lower part of the conduction band is mainly composed of Ta 5d states.

There is no report about experimental determination of the energy gap of TaON. This compound is generally reported to be green coloured.10–18 Assuming that this colour does not originate from impurities or non-stoichiometry, this colour indicates the existence of several absorption peaks in the visible spectrum. From the comparison of the experimental and theoretical band gaps of Ta3N5 (see above), we suggest the TaON experimental band gap to be significantly larger than 2.1 eV. Further experimental investigations on the physical properties of TaON are in progress.

The experiments showed an energy gap of 4.1 to 4.4 eV for the white oxide Ta2O5.18,37 Table 3 compares the calculated results and experimental (optical) gaps for the tantalum compounds. It is shown that with increasing content of nitrogen the energy gap of the tantalum compounds decreases.

4. Conclusions

First-principles calculations were performed for TaON and Ta3N5 by using two different computer codes within DFT (the molecular dynamics VASP program and the FP-LAPW WIEN97 program). Both types of calculations provide very similar results. The VASP calculations show that the O/N atoms in TaON are ordered, in agreement with the neutron diffraction results. Both types of calculations show that with increasing the content of nitrogen the energy gap of tantalum compounds decreases. The calculated indirect energy gap is 1.1/1.2 eV for Ta3N5 and 1.8/2.1 eV for TaON. The calculated direct gap at Γ is 1.4 eV for Ta3N5 and 2.0/2.2 eV for TaON as shown in Table 3. The optical diffuse reflectance spectra show an energy gap of about 2.1 eV for Ta3N5.

References

27 F. D. Murnaghan, Proc. Natl. Acad. Sci. USA, 1944, 30, 244.