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A First-Principles Study of the Electronic and Structural Properties of γ-TaON

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The geometric and electronic structure of the recently found new polymorph of tantalum oxynitride, γ-TaON, and its structural stability were studied quantum-chemically at the density functional level. Results obtained by complementary quantum-chemical techniques with wavefunctions either expanded in atom-centered functions or in plane waves were compared, having employed pure density-functional functionals within the generalized gradient approximation as well as density-functional/Hartree−Fock hybrid methods. In particular, several plausible anion distributions were investigated and, in accordance with Pauling's second rule, it was found that the configuration in which nitrogen occupies crystallographic sites with highest coordination numbers is the most stable one. Theoretically generated local structural parameters were used to improve the accuracy of the experimentally derived information. The bonding situation in the most stable configuration was investigated by an analysis of the density of states.

1. Introduction

While the properties of a large number of extended oxides and, to a lesser extent, nitrides are well-known and a multitude of technological applications has been established in the past,[1,2] oxynitride materials have become a field of growing interest only within the past decade.[3−5] The properties of oxynitrides are mainly influenced by the amount of nitrogen incorporated in the oxide, and this leads, for example, to decreasing band gaps,[6] thereby offering the opportunity to synthesize tailor-made colored pigments[7] or dielectric compounds[8] by changing the anionic components. Moreover, oxynitrides show potential for the purpose of catalysis.[9,10]

The archetypal oxynitride of tantalum, β-TaON, is known to crystallize in the baddeleyite structure type with a Ta coordination number of seven and an ordered anionic sublattice.[11−13] Another proposed polymorph, dubbed α-TaON, could be falsified via quantum chemical methods,[14] while a possible high-pressure phase with 9-fold metal coordination adopting the cotunnite structure was predicted by two independent groups.[15,16] Recently, we reported the synthesis of a new TaON polymorph referred to as γ-TaON,[17] which crystallizes in the monoclinic $VO_2(B)$ structure with space group $C2/m$ (see Figure 1). In γ-TaON, the tantalum atoms experience 6-fold coordination and thus, in accord with the pressure-coordination rule as proposed by Neuhaus,[18] its molar volume is larger than in β-TaON. The structure consists of layers linked by the vertices of Ta(O,N)−octahedra; within the layers, the octahedra are joined by their edges.

The $VO_2(B)$-type structure includes four different anion sites with coordination numbers 2, 3, 3, and 4, respectively. From Pauling's second rule,[19] it follows that the 2-fold coordinated anion sites should be occupied by O and the 4-fold coordinated anion sites by N, whereas no prediction can be made for the 3-fold coordinated sites. Because quantum-chemical techniques have been successfully applied to investigate the structure and stability of various hypothetical TaON polymorphs,[20] these methods are suitable to investigate the stability of different anion configurations in γ-TaON. In this communication, we compare the calculated electronic and structural properties of the new compound γ-TaON, which were obtained with complementary theoretical approaches.

2. Computational Details

In the present study, a combination of several quantum-chemical methods was employed. Structure optimization of bulk γ-TaON was performed from first-principles with the Vienna ab initio simulation package (VASP)[21,22] using both ultrasoft pseudopotentials (USPP) of Vanderbilt type[23] and projector-augmented waves (PAW)[24,25] with a kinetic energy cutoff of 490 eV; the crystal orbitals were expanded in plane waves. Exchange and correlation terms were described by the generalized gradient approximation (GGA) functionals of Perdew and Wang[26] and of Perdew, Burke, and Ernzerhof,[27] respectively. The Brillouin zone was sampled with a $4 \times 8 \times 16$ Monkhorst−Pack grid,[28] resulting in 128 irreducible k points.

To investigate the influences of the exchange−correlation potential and the various basis sets on the computed results, we also performed bulk structure optimizations with the crystalline-orbital program CRYSTAL03.[29] Here, the Bloch functions are expanded in atom-centered contracted Gaussian functions. As done in our previous study touching upon the stability of different TaON polymorphs,[20] the following basis sets were used: [Xe]311G21d for tantalum where the inner electrons are replaced by the Hay−Wadt small-core effective core potential,[30] 8-411G* for oxygen, and 7-311G* for nitrogen.

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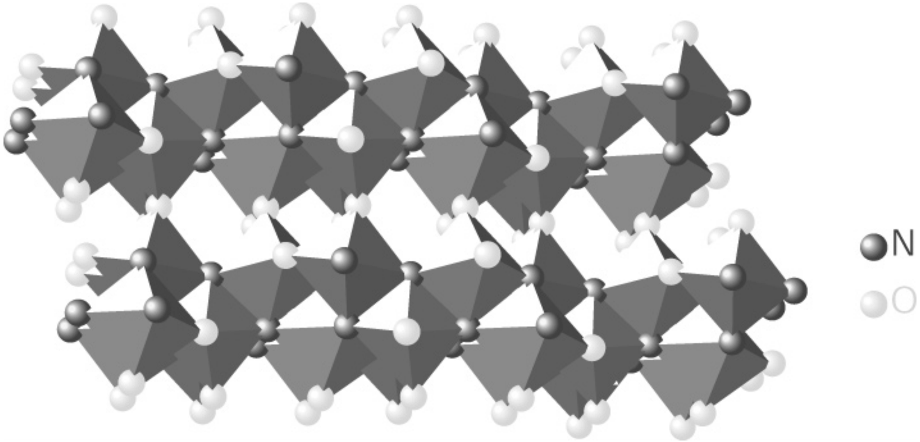

Figure 1. Coordination polyhedra around Ta in γ-TaON with the theoretically predicted anion distribution.

TABLE 1: Structural Parameters of γ-TaON after Rietveld Refinement[17] [a]

		atom (coordination)	site	*x*	*y*	*z*
space group	*C*2/*m* (12)	Ta1(6)	4*i*	0.3063(2)	0	0.2010(4)
a (Å)	12.9508(4)	Ta2(6)	4*i*	0.6037(3)	0	0.2074(5)
b (Å)	3.87854(8)	X1(2)	4*i*	0.383(2)	0	0.507(5)
c (Å)	6.7077(2)	X2(3)	4*i*	0.154(2)	0	0.206(5)
β (deg)	107.444(2)	X3(3)	4*i*	0.457(4)	0	0.159(6)
		X4(4)	4*i*	0.867(3)	0	0.185(6)

[a] The anion sites are labeled with X1−4.

TABLE 2: Relative Energy ΔE (kJ/mol) of Different N/O Configurations in γ-TaON as a Function of the Quantum-chemical Method; Crystal-PW Values with Increased Number of *k* Points and Augmented Ta Basis Set are Given in Parentheses

	N sites	PW1PW	CRYSTAL-PW	USPP−PW	PAW-PW	PAW-PBE
a	X3, X4	0	0	0	0	0
b	X2, X4	20	18(14)	21	18	18
c	X1, X4	42	38(40)	7	8	8
d	X2, X3	54	46(46)	31	26	26
e	X1, X3	62	56(63)	21	19	20
f	X1, X2	79	69(71)	37	32	32

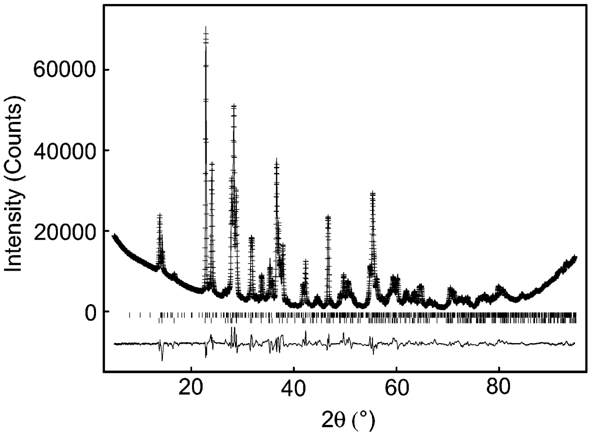

Figure 2. Rietveld refinement plot for γ-TaON with β-Ta_2O_5 as a side phase. The residual values are $R_{wp} = 0.089$, $R_p = 0.055$, and $R_F = 0.039$.

Likewise, the previously used Hartree−Fock/density functional theory (DFT) hybrid method PW1PW was used in the CRYSTAL calculations. To do so, electron correlation was described by the Perdew−Wang functional,[26] while the exchange potential consists of a 20% Hartree−Fock and a 80% Perdew−Wang functional contribution. In fact, our previous study[20] was characterized by a quantitative agreement between the CRYSTAL-PW1PW and PAW-PW results when it comes to the relative stability of the baddeleyite, rutile, anatase, and fluorite phases of TaON. For this reason, we used the same combination of complementary methods to study γ-TaON. For another comparison with the previous VASP approach, additional pure DFT calculations employing the Perdew−Wang functional were performed. An 8 × 8 × 8 Monkhorst−Pack grid consisting of 150 points in the irreducible Brillouin zone was applied. The integral thresholds were decreased by a factor of 10 compared to the standard settings.[29] Larger *k* point sets, smaller integral thresholds, and increased basis sets for tantalum were also considered in convergence test calculations. In the latter calculations, the Ta basis set was augmented with diffuse sp and d shells.

3. Experimental

γ-TaON was synthesized by the ammonolysis of β-Ta_2O_5 with dry ammonia at a flow rate of ≈10 L/h and a reaction temperature of 850 °C. Ammonolysis reactions were performed in a resistance-heated tube furnace equipped with a sintered corundum tube of 50 mm inner diameter. The ammonia gas (3.8, Messer−Griesheim) flow rate was regulated with a needle valve. The oxide precursor (200 mg, Ta_2O_5, 99.99%, Sigma−

TABLE 3: Calculated Fractional Coordinates for γ-TaON, Given for the Most Stable Anion Distribution[a]

		x						*y*	*z*					
	site	PW1PW	CRYSTAL	USPP	PAW-PW	PAW-PBE	average		PW1PW	CRYSTAL-PW	USPP-PW	PAW-PW	PAW-PBE	average
Ta1	4*i*	0.3115	0.3107	0.3110	0.3116	0.3120	**0.3114(5)**	**0**	0.1968	0.1948	0.1942	0.1938	0.1940	**0.195(1)**
Ta2	4*i*	0.6026	0.6028	0.6024	0.6024	0.6020	**0.6024(3)**	**0**	0.2080	0.2088	0.2063	0.2080	0.2080	**0.2078(8)**
O1	4*i* (X1)	0.3624	0.3600	0.3586	0.3604	0.3600	**0.360(1)**	**0**	0.4934	0.4924	0.4931	0.4928	0.4930	**0.4929(3)**
O2	4*i* (X2)	0.1364	0.1316	0.1347	0.1343	0.1340	**0.134(2)**	**0**	0.2135	0.2120	0.2109	0.2110	0.2110	**0.212(1)**
N1	4*i* (X3)	0.4452	0.4450	0.4458	0.4460	0.4460	**0.4456(4)**	**0**	0.1338	0.1357	0.1372	0.1373	0.1370	**0.136(1)**
N2	4*i* (X4)	0.7576	0.7581	0.7586	0.7585	0.7590	**0.7584(5)**	**0**	0.1464	0.1474	0.1475	0.1477	0.1480	**0.1474(5)**

[a] The uncertainty values for the averaged parameters (bold type) denote the mathematically derived standard deviations by averaging over the individual theoretical parameters.

TABLE 4: Calculated Optimized Lattice Parameters for γ-TaON, Given for the Most Stable Anion Distribution[a]

	a (Å)	*b* (Å)	*c* (Å)	β (deg)
PW1PW	12.998	3.862	6.722	107.41
CRYSTAL-PW	13.091	3.903	6.770	107.49
USPP-PW	13.133	3.881	6.736	107.62
PAW-PW	13.187	3.890	6.766	107.64
PAW-PBE	13.195	3.891	6.768	107.62
average	**13.12(7)**	**3.89(1)**	**6.75(2)**	**107.56(9)**

[a] The uncertainty values for the averaged parameters (bold type) denote the mathematically derived standard deviations by averaging over the individual theoretical parameters.

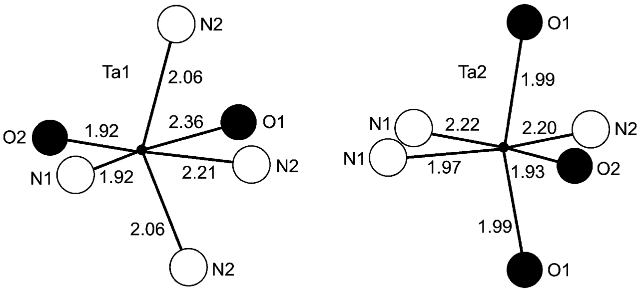

Figure 3. Calculated (averaged) Ta−O and Ta−N distances (Å) in γ-TaON; see also text.

Aldrich) was placed in a small alumina boat inside the furnace tube. The maximum yield of γ-TaON (≈85wt %) was obtained with a duration of 5 h. Here, the additional phases are β-TaON and Ta_2O_5. More severe synthetic conditions, namely a higher gas-flow rate, higher temperature, or longer reaction time only result in the formation of β-TaON and Ta_3N_5. Using softer synthesis conditions, no nitridation was observed.

The products were characterized by powder X-ray diffraction (XRD, Siemens D5000) with Cu Kα1 radiation (λ = 1.5405 Å) and in situ high-temperature XRD (STOE STADI-P, graphite heated furnace) with Mo Kα radiation (λ = 0.7093 Å). The crystal structure was determined by direct methods with the program EXPO[31] and refined by the Rietveld method using powder data (GSAS);[32] The quantitative N/O analysis was performed by hot gas extraction (LECO TC-300/EF-300 N/O analyzer).

4. Discussion

Rietveld refinements of X-ray powder diffraction data (Figure 2) lead to approximate structural parameters as summarized in Table 1. Within the primitive unit cell of the $VO_2(B)$-type structure, there are four different anionic sites labeled as X1 to X4. Unfortunately, it is impossible to distinguish these in terms of O and N atoms on the basis of the X-ray diffraction data. Structural optimizations and total-energy calculations were therefore performed from first-principles for all six possible distributions of the two O and the two N atoms over these four sites. Not too surprisingly, it turns out that, in the most stable structure, oxygen occupies the 2-fold coordinated sites, while nitrogen is placed on the 4-fold coordinated sites, as given in Table 2. This most fundamental result is obtained with all quantum-chemical methods, and it is in perfect agreement with Pauling's second rule.[19] Remarkably, however, exchanging the occupation of the anionic sites leads to different sequences in total energy, and these depend on the theoretical method used. The results from the Hartree−Fock/DFT hybrid method PW1PW

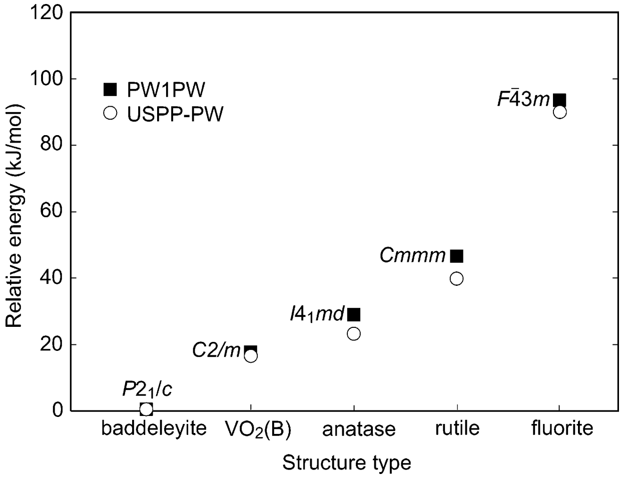

Figure 4. Atomization energies of $VO_2(B)$-type γ-TaON in its most stable anion distribution compared with other structure types,[20] calculated with the PW1PW method (boxes) and with USPP-PW (circles).

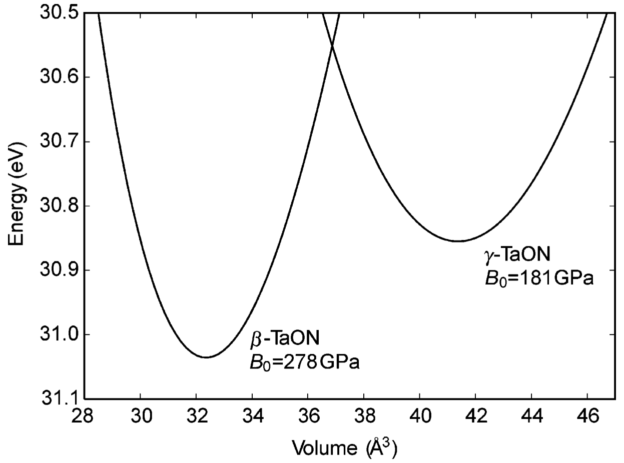

Figure 5. Energy and volume per formula unit for the β- and γ-phase of tantalum oxynitride, calculated with PAW-PBE.

TABLE 5: Theoretically Calculated Interatomic Distances (Å) in γ-TaON[a]

	average	PW1PW	CRYSTAL-PW	USPP-PW	PAW-PW	PAW-PBE
Ta1−N1	**1.917(6)**	1.908	1.911	1.922	1.923	1.922
Ta1−O2	**1.922(9)**	1.905	1.928	1.919	1.928	1.931
Ta1−N2 (2×)	**2.055(6)**	2.044	2.061	2.051	2.059	2.059
Ta1−N2	**2.214(8)**	2.211	2.229	2.205	2.213	2.213
Ta1−O1	**2.36(3)**	2.312	2.389	2.352	2.376	2.379
Ta2−O2	**1.932(6)**	1.921	1.940	1.932	1.933	1.933
Ta2−N1	**1.970(9)**	1.955	1.984	1.966	1.971	1.972
Ta2−O1 (2×)	**1.985(4)**	1.978	1.983	1.985	1.989	1.989
Ta2−N2	**2.20(2)**	2.174	2.188	2.204	2.217	2.219
Ta2−N1	**2.22(2)**	2.195	2.233	2.207	2.228	2.229

[a] The uncertainty values for the averaged parameters (bold type) denote the mathematically derived standard deviations by averaging over the individual theoretical parameters.

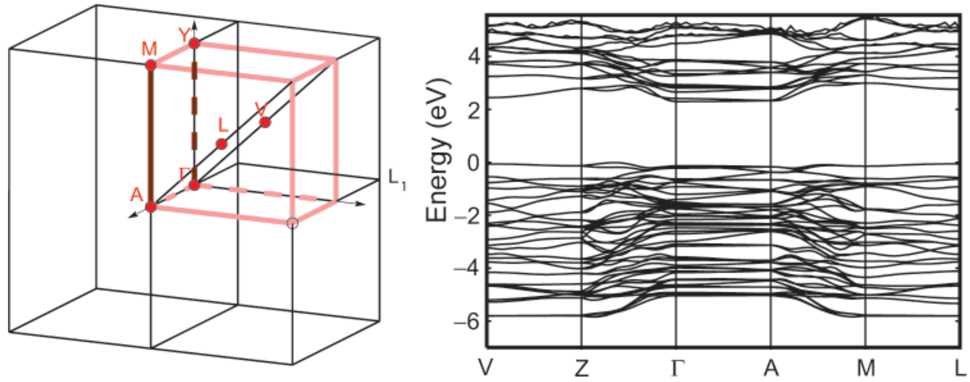

Figure 6. Brillouin zone of space group *C*2/*m* (left) and band structure of γ-TaON (right), calculated with PAW-PBE.

suggest that the stability decreases with decreasing coordination numbers for the nitrogen anions. In contrast, the plane wave methods favor both oxygen anions to experience 3-fold coordination. Moreover, the energy differences between the various anion permutations are much smaller than those calculated with PW1PW, independent from both functional and pseudopotential. This finding is different from our previous study of TaON polymorphs,[20] where the relative energies of CRYSTAL-PW1PW and PAW-PW were similar.

To test the effect of the exchange-correlation functional, we also applied the Perdew−Wang functional with CRYSTAL03, and we also increased the Ta basis set and the number of *k* points. The comparison of CRYSTAL-PW1PW and CRYSTAL-PW in Table 2 shows that both methods follow the same trend of stability for the N positions, namely (X3,X4) > (X2,X4) > (X1,X4) > (X2,X3) > (X1,X3) > (X1,X2). Increasing the numerical precision of the CRYSTAL-PW calculations does not have a significant influence on the relative energies. Because the Perdew−Wang functionals used in the CRYSTAL and VASP calculations are identical, the different order of stability obtained with VASP, (X3,X4) > (X1,X4) > (X2,X4) ≈ (X1,X3) > (X2,X3) > (X1,X2), must be a direct consequence of the different kinds of basis set. Further investigations of the influence of technical parameters in the calculations on the relative stability of the less stable ordering variants are required to identify the reason for this discrepancy.

Continuing the investigations dealing with the occupation of the anionic lattice sites, we also calculated partially ordered as well as fully disordered anion distributions using a supercell approach. It turns out that partially ordered structures, such as X1 = X2 = X3 = X4, are at least 30 kJ/mol less stable if compared with the most stable ordered anion distribution, and thus they are as unfavorable as the most unstable ordered variant.

The optimized fractional coordinates of the atoms in the most stable structure are given in Tables 3 and 4. While the results from the various theoretical methods are relatively close to each other, in particular, for the spatial parameters, the agreement between calculated and measured lattice parameters is not perfect, but this is explainable by the fact that the experimental sample contained by-phases of β-TaON (17%) and Ta_2O_5 (6%), leaving some structural details still unresolved. Thus, a complete description of the structure is as yet only possible using the theoretical results.

Figure 3 presents the $Ta(O,N)_6$ octahedra drawn with the averaged positional parameters from Table 3. The average distances Ta−O and Ta−N are slightly larger in the $Ta1(O,N)_6$ octahedron in all calculations, simply because of the higher coordination number of the anions compared with the $Ta2(O,N)_6$ octahedron. A similar situation is found in VO_2(*B*) and TiO_2-(*B*). The interatomic distances as they are obtained with the various theoretical methods are summarized in Table 5.

From the quantum-chemical point of view, it is obvious that γ-TaON is indeed a metastable polymorph, and it is clearly more stable than some of the previously investigated structure types such as anatase and rutile (Figure 4). The lower stability compared with β-TaON is only about 20 kJ/mol. Attempts to distort the lattice symmetry did not result in more stable structures but resulted in a regular energy−volume function (Figure 5), which can be easily fit to the Birch−Murnaghan equation of state.[33] Compared with its baddeleyite-type polymorph (bulk modulus B_0 = 278 GPa with PAW-PBE), the bulk modulus of γ-TaON (B_0 = 181GPa, see Figure 5) is significantly lower, which can be traced back to the smaller average coordination number in the VO_2(*B*)-type structure, which also causes a higher equilibrium volume.

To gain further insight to the electronic properties of the compound, it is reasonable to consider the band structure and density of states. γ-TaON turns out to be a semiconductor with a band gap around 2 eV (compare with Figure 6). It is impossible to make a statement on the exact size of band gaps using a ground-state method such as density functional theory, so it is better to recalculate the band structure with the PW1PW method, which is known to reproduce band gaps with a higher accuracy than other first-principles methods.[34] This is basically due to a reduction of the self-interaction error in DFT by the incorporation of exact exchange. The relative contribution of Hartree−Fock exchange to the hybrid functional has been chosen as a free parameter[34] in order to reproduce bulk properties such as binding energies, lattice parameters, and optical band gaps. In Figure 7, the total and projected density of states (DOS) of the most stable γ-TaON structure (see Table 2, *a*) is presented. Similar to what has been found for the oxynitride of zirconium,[35] the orbitals in the upper part of the valence band are dominated by contributions from nitrogen 2p. The nonzero partial DOS of tantalum within the occupied region indicates a partially covalent nature of the bonding in TaON. The lower part of the conduction band essentially consists of Ta 5d orbitals. The calculated band gap of γ-TaON (2.9 eV) at PW1PW level is slightly larger than that of Zr_2ON_2.[35] By interpreting the calculated differences of one-electron levels as an approximation to optical transitions, defect-free γ-TaON is predicted to be colorless.

5. Conclusions

Independent from the quantum-chemical method used, the present calculations give evidence that the proposed structure of the new polymorph γ-TaON is indeed metastable and only about 20 kJ/mol less stable compared to the ground-state

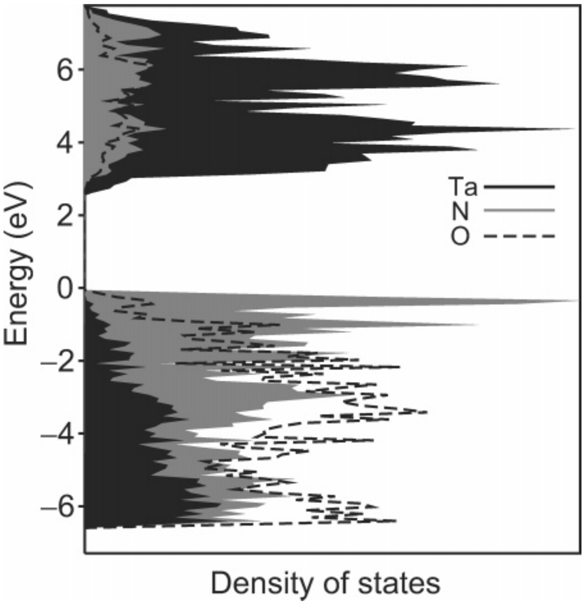

Figure 7. Total and projected density of states of the most stable γ-TaON structure as obtained with PW1PW.

β-polymorph. Because of the 6-fold coordination of the Ta ions in the VO_2(*B*) structure type, γ-TaON has a larger cell volume per formula unit than in its baddeleyite-type polymorph. Consequently, the bulk modulus is much lower. The most stable anion distribution is the one according to Pauling's second rule, with the oxygen anions occupying the 2-fold coordinated anion sites and the 4-fold anion sites being occupied by nitrogen. The electronic structure is similar to that of another oxynitride, Zr_2ON_2, with large contributions from nitrogen orbitals in the upper valence band and tantalum orbitals in the lower conduction band.

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