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STUDY OF THE PHYSICAL, MECHANICAL AND ELECTRONIC PROPERTIES IN VOLUME OF WO_3

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Abstract

In this work, we studied the mechanical and electronic properties of the WO3 cubic phase using Density Functional Theory (DFT) with the Generalised Gradient Approximation (GGA). The results obtained for the mechanical properties following geometric optimisation show that the crystalline parameter a(A)=3**.835863** for a volume V(A^3)=56**.4403** . The elastic constants obtained are such that **C11=579.5320, C12=29.0545 C44=70.**54350 confirm the stability of the cubic phase of WO3 with the modulus of compressibility B(Gpa)= **212.5470** and the Young's modulus E(Gpa)=369**.0477.** We obtained a Debye temperature of **558.5640 K** and showed that cubic WO3 exhibits anisotropy for the transverse propagation mode in the [100] and [110] directions. For the lectronic structure, we obtained a gap equal to 0.642 eV. These results from the classical DFT are in good agreement with the theoretical results obtained by the GGA+U approximation (U Hubbard parameter)..

Keywords: Tungsten Trioxide, Band Structure, Density of States, Elastic Constants, Elastic Moduli, Debye Temperature, Band Structure, Density of States.

1. INTRODUCTION

Depending on their extraction sources, the tungsten compounds obtained have various properties used in several fields (metallurgy, chemistry, etc.) making tungsten a very indispensable element in materials science and medicine, as shown in Table ***1***.

Table 1: Tungsten compounds and uses

Compound	Chemical formula	Uses
Ammonium tungstate (APT)	$(NH_4)W\ O_{1241}\ .5H\ O_2$	*Important intermediate traded product. Also used for luminophores, catalysts, absorbent gels and in porcelain.*
Ammonium meta tungstate (AMT)	$W\ O_{1239}\ .3\text{-}4H\ O_2$	*Catalysis, in particular for petroleum hydrocarbons*
W trioxide	WO_3	*Production of metallic W, tungsten carbide used for yellow pigments (paint) and catalysts*
W blue oxide	WO_{3-x}	*Variable composition, mixture of several W oxides and hydrogen or ammonium bronzes*
Tungstic acid	$H_2\ WO_4$	*Luminophore pigments, oil additives*
W hexachloride	WCl_6	*Used for depositing tungsten wire on ceramics, graphite and metals, fluxing agent in welding: catalysis*
W hexafluoride	WF_6	*Semiconductor manufacturing*
Sodium tungstate	$Na_2\ WO_4$	*Preparation of organic pigments, dyes and catalysts; Medical research*
Calcium tungstate (scheelite)	$CaWO_4$	*Luminophore for cathode ray tubes, lasers and fluorescent tubes*
Main chemical compounds of W roskill, 2009		

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The different crystallographic forms are simply the result of the influence of temperature leading to irregularity in the WO_3 lattice, which is favoured by the ability of tungsten to stabilise at different oxidation levels and the nature of the distortion between the atoms. Mass tungsten oxides have been the subject of much research in recent years, with investigations focusing on determining the sub-oxide phases formed after the reductive treatment of tungsten trioxide and its reducibility.

Table 2 shows some of the sub-oxides likely to form after reduction of the WO3 system:

Table 2: The different WO3 phases and their stability ranges [1] [2]

Structure	Structure	temperature	a (A)^o	b (A)^o	c (A)^o	α	β	γ
δ-WO₃	Triclinic	-40-17 C ^{o}	*7.31*	*7.52*	*7.69*	*88.8^o*	*90.9^o*	*90.9^o*
γ-WO₃	Monoclinic	17-320 C ^{o}	*7.30*	*7.54*	*7.69*	*90^o*	*90.9^o*	*90^o*
β-WO₃	Orthorhombic	320-720 C ^{o}	*7.34*	*7.57*	*7.75*	*90^o*	*90^o*	*90^o*
α-WO₃	Tetragonale	720 C ^{o}	*5.25*	*5.25*	*3.92*	*90^o*	*90^o*	*90^o*
h-WO₃	Hexagonal	metastable	*7.30*	*7.30*	*7.80*	*90^o*	*90^o*	*120^o*
c-WO₃	*cubic*	*stable*	*3.8*	*3.8*	*3.8*	*90^o*	*90^o*	*90^o*

The Groupe de Recherche sur les Propriétés Mécaniques et physico-Chimiques des Matériaux at the Faculté des Sciences et Techniques de l'Université Marien NGOUABI has already carried out experimental and simulation studies using the Embedded Atom Method (EAM) on the mechanical properties of tungsten trioxide and its growth on a supersubstrate in the presence of potassium ***[3]- [5]*.**

The theory presents us with a series of experimental results, but sometimes the physical mechanisms used to understand the results escape us; it is with this in mind that this **DFT-based** study is carried out. In order to understand the basis of the calculations, in this work we study the physical, mechanical and electronic properties of the cubic phase of WO3 in the GGA approximation.

2. METHODOLOGY

This work is a simulation of the physical and mechanical properties of the cubic phase of WO3 using DFT with the Generalised Gradient Approximation (GGA).

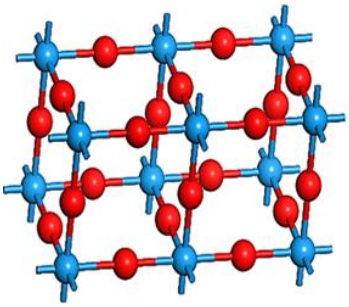

Fig 1: Tungsten Trioxide 2x1x1 Cubic Phase

In this work, the cut-off energy ***[6]*** of the plane wave is taken as E_{cut} = 571 eV, the k-point integral in the Brillouin zone is fixed at 1×1×1 and the self-consistent convergence method is used to optimise the cubic WO3 structure.

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For the various stages of the calculation, we set the parameters of the pseudo potential (numerical). For the geometrical optimisation we used the Perdew-Burke-Ernzerhof (PBE) pseudo potential, which enabled us to calculate the crystalline parameters; Perdew-Burke-Ernzerhof (PBEsol) for solids was used to evaluate the elastic constants.

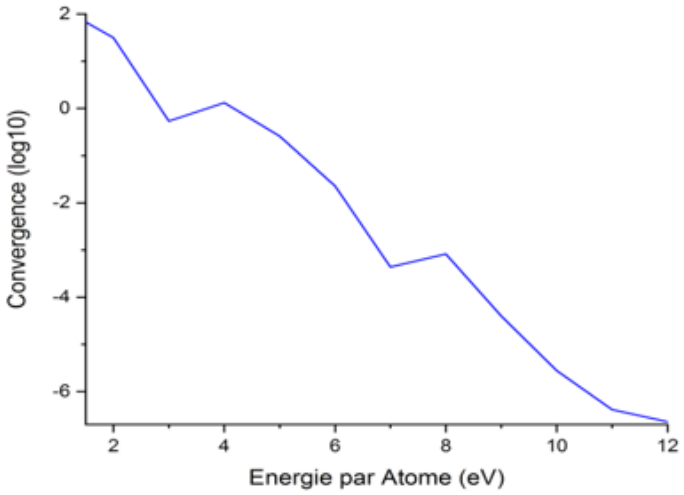

Fig 2 :Optimisation-convergence by iteration

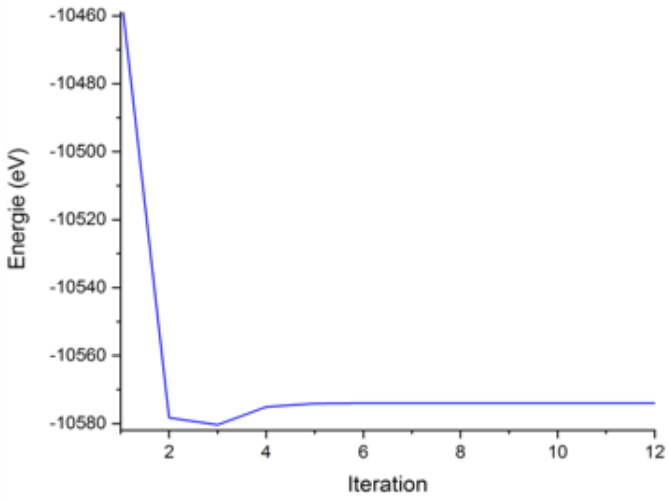

Fig 3: Iteration-based energy optimisation

3. RESULTS

In this work, we present results relating to crystalline parameters, mechanical properties and electronic properties such as DOS and PDOS, as well as thermodynamic properties obtained using DFT.

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3.1 Crystalline parameters

The crystalline parameters are presented in Table ***IV-1*** below for the cubic phase of tungsten trioxide calculated with the DFT. The results obtained are close ***[7]*** to the theoretical values with a margin of error of **2%** for the crystalline parameter a=b=c=3*.8358 A*.

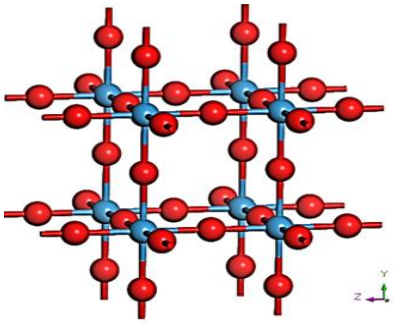

Fig 4: cubic tungsten trioxide

Table 3: Crystalline parameters of WO3

Parameters	Our study	experimental
a=b=c(A)	*3.8358*	*3.73*
α=β=γ	*90.00*	*90.00*
Volume(A)^3	*56.4403*	*/*
d_{W-O} (A)	*1,98*	*1.85*

3.2 Mechanical properties

Mechanical properties are interpreted in terms of elastic constants and functional elastic moduli. Mechanical properties are essential parameters for predicting the elastic properties and mechanical stability of materials.

The mechanical properties of the cubic structure of tungsten trioxide were calculated and compared with experimental results. We have shown that WO3 is very stable, this stability being verified by the condition given by the elastic constants $C_{12} - C_{22} > 0$.

3.2.1 Elastic constants

The elastic and mechanical properties of solids reflect their reactions to certain external factors. In the simplest case, these factors are mechanical actions: compression, traction, bending, impact and torsion. In addition to mechanical actions, they can be thermal, magnetic, etc. These properties are determined primarily by the bonding forces between the atoms or molecules that make up a solid.

When subjected to a stress, a crystal will deform linearly with respect to this stress, provided that the deformation generated is small. When the stress is removed, the material reversibly returns to its standard state. This behaviour is observed in all materials and is known as "elastic".

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In order to understand mechanical stability, we studied the elastic constants at ambient pressure of cubic WO3phase. The cubic system is characterised by three independent elastic moduli: ***C11*, *C12* and *C44***.

For elements with a cubic structure, the criterion for predicting structural stability is as follows:

$$\boldsymbol{C_{11} - C_{12} > 0,\ C_{11} > 0,\ C_{44} > 0,\ C_{11} + 2C_{12} > 0}$$

However, the matrix linking the deformations and the elastic constants is represented by the following relationship:

$$\begin{pmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{pmatrix} = \begin{pmatrix}C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16}\\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26}\\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36}\\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46}\\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56}\\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}\end{pmatrix}\begin{pmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{pmatrix}$$

- The constant $\boldsymbol{C_{11}}$ is a measure of the resistance to deformation produced by a stress applied to the (100), (010) and (001) planes in the <100> directions (length elasticity).
- $\boldsymbol{C_{44}}$ represents the measure of resistance to deformation in the case of a shear stress applied to the (100), (010) and (001) planes along the diagonals (shape elasticity).
- $\boldsymbol{C_{12}}$ has no simple physical interpretation, but these linear combinations with C_{11} give us the compression modulus *B* and the shear modulus *G*.

The elastic constants for the cubic structure of WO3 have been calculated and are presented in the table 4:

Table 4: Elastic constants, comparison with theory and experiment [8].

Symbols	Our work (Gpa)	Theoretical(Gpa)
C11	*579.5320 +/-2.904*	*546*
C12	*29.0545 +/-1.223*	*35*
C44	*70.5435 +/-1.748*	*71*
C11-C12	***550,4775***	***511***

Using these data, we were able to compare the elastic constants with each other and with the theoretical and experimental data, which we show in the following fig 5:

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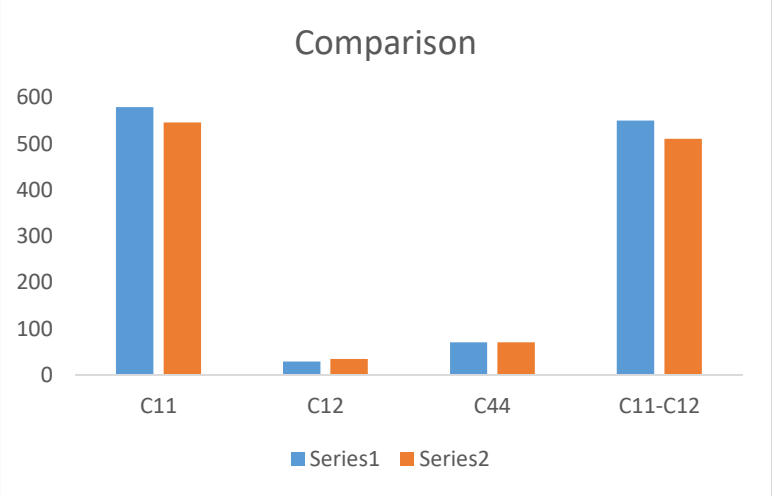

Fig 5: Comparison of elastic constant

Series 1 (blue) represents our work, series 2 (orange), the order of magnitude is well defined by $C_{11} > C_{12}$ translates the stability of the WO3 cubic structure.

3.2.2 Elastic modules

In this section we present the corresponding elastic moduli in various Reuss, Hill and Voigt systems.

These moduli reflect the rigidity and flexibility of the material against external excitations, and the direction of the resulting deformation or stress. They are also referred to as elastic coefficients, which are none other than the engineer's moduli for the properties of nanomaterials.

First, we give the mathematical relationships between Young's modulus, compression modulus, Poisson's ratio and shear modulus with the elastic constants.

- The modulus of compression **B** is defined as the ratio of hydrostatic pressure to the fractional change in volume produced by this pressure (volume elasticity).
- The second modulus ***G*** is the resistance to deformation produced by a shear stress applied to the plane (110) in the direction [110].
- The elastic moduli (Bulk modulus **B**, Shear modulus **G** and Young's modulus **E**) are estimated using the **Voigt-Reuss-Hill** method. Generally, the greater the B, the greater the resistance of the material to change in volume.

The table below shows all the elastic moduli in different systems of approach for a cubic crystallographic structure.

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Table 5: Mathematical expressions of elastic moduli for a cubic structure

$E = \frac{9BG}{3B+G}$	$\nu = \frac{3B - E}{6B}$	$B = \frac{C_{11} + 2C_{12}}{3}$
$G_v = \frac{C_{11} - C_{12} + 3C_{44}}{5}$	$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}$	$G = \frac{G_R + G_V}{2}$
$B_{Hill} = \frac{1}{2}(B_{Reuss} + B_{Voigt})$	$B_R = B_R = \frac{1}{3}(C_{11} + 2C_{12})$	$G_{Hill} = \frac{1}{2}(G_{Reuss} + G_{Voigt})$

The results obtained from the expressions of the previous moduli of cubic WO3 are presented in the table 6:

Table 6: Elastic moduli of cubic WO3 [9]

Size	Symbols	Voigt (Gpa)	Reuss (Gpa)	Hill (Gpa)
Bulk modulus	B	212.54702	212.54702	212.54702
Shear modulus (Mu blade)	G	152.42160	100.41497	126.41829
Lambda blade	λ	110.93262	145.60371	128.26817
Young modulus	γ	369.04771	260.25955	316.50483
Fish ratio	ε	0.21061	0.29592	0.25182

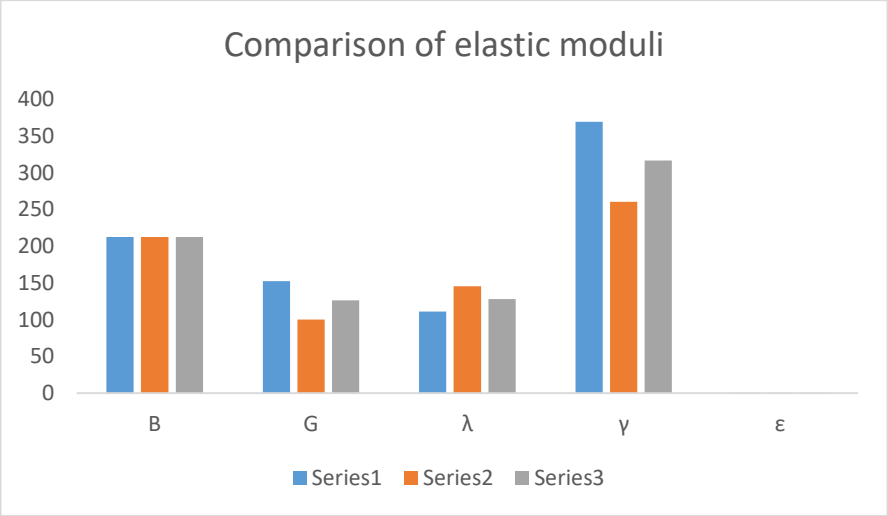

Fig 6: comparison of elastic moduli

3.3 Thermodynamic properties: debye temperature and propagation speed

In this section we present the results for the Debye temperature and the wave propagation velocities in the [100], [110] and [111] directions. The results are presented in the table below

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Table 7: Debye temperature and propagation speed

Physical properties	Values
Bulk modulus (GPa)	212.5470 +/- 1.266
Compressibility (1/GPa)	0.0047
Elastic Debye temperature K	**558.5641**
Averaged sound velocity	4533.4815

The calculated Debye temperature is around 558.56408K, which is close to the value found by Xing Liu and Hui-Qing Han.

3.3.1 Wave propagation speed

We have calculated the velocities of propagation of the longitidunal wave Vp, according to the compression Vp, thermal vm.

The speed relationships are given by the following expressions :

$$v_s = \sqrt{\frac{G_i}{\rho}}\ ;\ v_p = \sqrt{\frac{B_i + 4G_i/3}{\rho}}\ ;$$

Table 8: wave propagation speed

Dimensions	System		
	voight	Hille	Reuss
vs	4770.13	4350,27	4770,13
vp	7889,24	7553,05	7201,23
vm	5273,514	4830,871	4328,308

We have therefore shown that the direction of longitidunal propagation is much more important than the other two ***[10]***.

3.3.2 Anisotropy

We have calculated the longitidinal and transverse propagation velocities for the WO3 phase in the [100], [110] and [111] directions, which we present in the table below with expressions of the velocities relative to the directions.

Table 9: propagation speed and mode

Management	Mode of propagation	expression	value
[100]	**Longitudinal**	$\boldsymbol{v_1 = \sqrt{C_{11}/\rho}}$	**9314,24015**
[100]	Transversal	$v_2 = \sqrt{C_{44}/\rho}$	3249,6546
[110]	**Longitudinal**	$\boldsymbol{v_3 = \sqrt{(C_{11} + C_{12} + 2C_{44})/2\rho}}$	**7490,8226**
[110]	Transversal	$v_4 = \sqrt{C_{44}/\rho}$	3249,6546
[110]	Transversal	$v_5 = \sqrt{(C_{11} - C_{12})/2\rho}$	6418,942
[111]	**Longitudinal**	$\boldsymbol{v_6 = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3\rho}}$	**6774,8290**
[111]	Transversal	$v_7 = \sqrt{(C_{11} - C_{12} + C_{44})/3\rho}$	5566,743

Longitudinal wave propagation in the [100] direction is the most important, while transverse wave propagation in the [100] and [110] directions are equivalent and therefore have the same properties, i.e. anisotropy. In addition to these differences, we

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can also note that the long-term propagation speeds of the wave in the **[110] and [111]** directions **are close.**

3.4 Electronic Structure

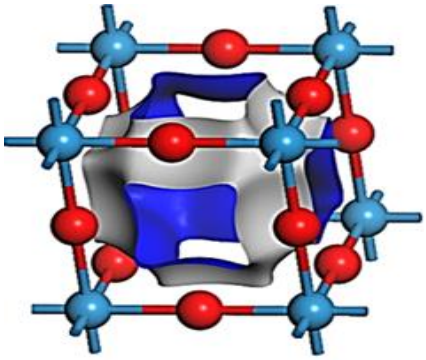

Fig.7: Cubic Phase Density of WO3

In this section we present the results on the electron structure of the WO_3 cubic phase, the band structure and the density of states have been calculated. The values given by the theory are in the range 0.3-0.6ev for the gap*.*

3.4.1 Band structure

We carried out a study of the band structure, and the calculations gave us a gap of 0.642eV. On the figure, we note the red dotted line representing the Fermi level, in order to verify the property of the semicondictors for cubic WO3.

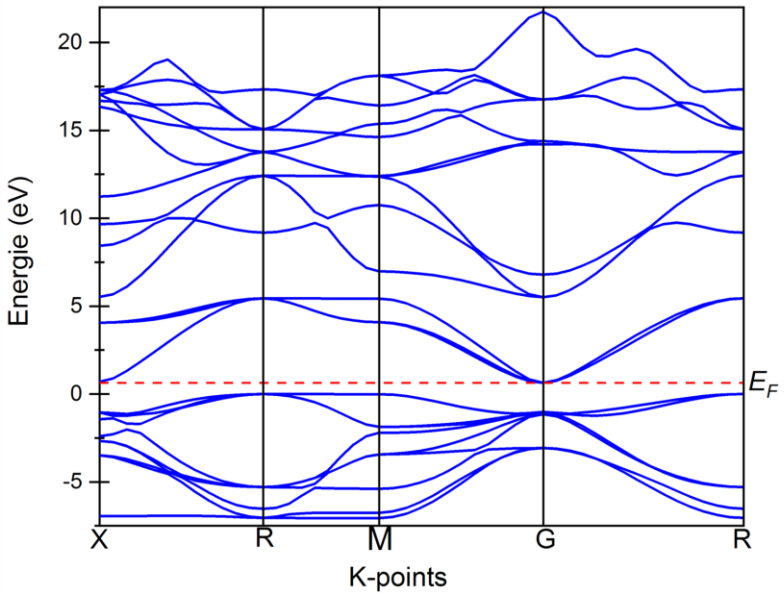

Fig 8 : Bande Structure of WO3 cubique

We can see that at the R point, WO3 reaches a value very close to the fermi level and that at the G point it reaches the minimum value.

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3.4.2 Density of DOS states

Here we show the Total Density of States of cubic WO3, reflecting the electronic contribution of the s, p and d sublayers.

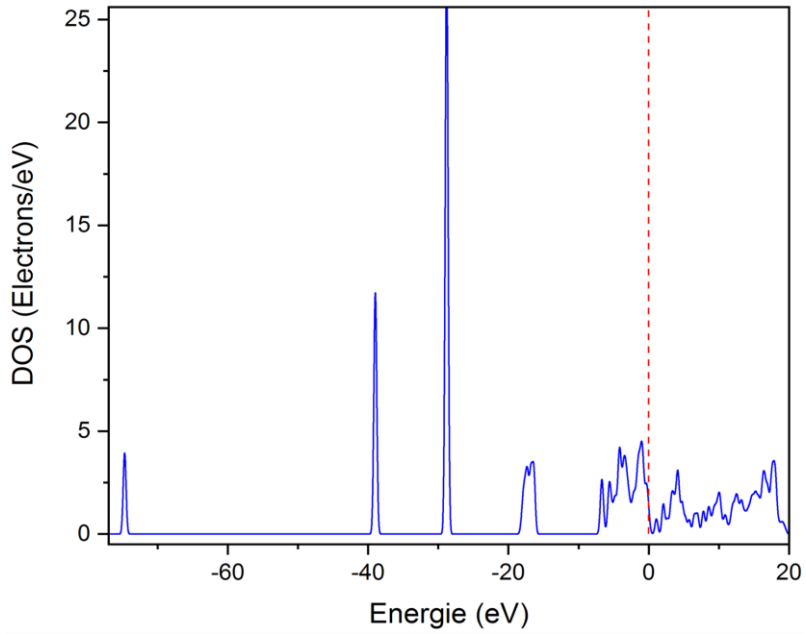

Fig 9: Density of states of cubic WO3

We can restart our study around -20 to 20, a zone in which we observe hybridizations characterized by a series of spikes.

- ✓ *The first hybridisation is reached around the point (-17.3; 3.17eV)*
- ✓ *The second hybridisation is reached around the point (-4.1; 4.18eV)*
- ✓ *The third hybridisation is reached around the point (4.17; 3.1eV)*

3.4.3 Study of the electronic population of WO3

Here we present the electronic distribution and the different charges in the sub-layers of the WO3 composite elements, namely tungsten and oxygen.

Table 10: Distribution of electronics and charges

Coumpound	Charge Spilling	species	Mliken atomic populations					Muliken charge	Formal ionic charge	Effective valence	Hirrshfeld charge	Effective valence
			s	p	d	f	total					
WO3	4.34	O	2.00	5.98	0.00	0.00	7.98	-1.98	-2	**0.02**	-0.26	**1.74**
		W	2.00	6.00	0.00	14.00	22.00	6.00	4	**-2**	0.78	**3.22**

Compound	bond	n^u	p^u	d^u
WO3	W-O	3	-0.65	1.91793
	O-O	3	-0,10	2.71236

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4. CONCLUSION

This work is the result of a simulation study of cubic-type tungsten trioxide using the Density Functional of States (DFT) without using the Hubbard parameter. The results obtained in this work are in good agreement with the theory; the generalised gradient approximation (GGA) as a pseudo potential was largely sufficient during these calculations to obtain significant results on the mechanical and electronic properties. Although the Hubbard parameter is an additional corrective term, the basic approximations are sufficient, in the case of tungsten trioxide, for a DFT study.

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