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Study of the Structural and Electronic Properties of MgO in the Wurtzite Phase Using the Density Functional Theory

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The ab initio pseudopotential method is based on Density Functional Theory (DFT), in which the Generalized Gradient Approximation (GGA) according to the scheme described by Perdew-Burke-Ernzerhof (PBE) and the Local Density Approximation (LDA) according to the scheme described by Ceperly-Alder (CA) are used. The method is implemented using the Siesta program to investigate the structural and electronic properties of the wurtzite (B4) phase of magnesium oxide (MgO) compound. Indeed, it is a useful method to predict the crystal structure of MgO. Actually, the calculated structural parameters of this compound are consistent with the available experimental data, so these results can be considered as a good prediction. Both the lattice constants and band gap at zero pressure are found to be in agreement with previous theoretical and experimental results. Besides, the binding energy is verified and compared with previous work. Electronic properties, especially the Total Density of States (TDOS) and Partial Density of States (PDOS), also show that the contribution of the oxygen atom to DOS in the region close to the Fermi level is significant. Comparison of the calculated lattice parameters and all electronic properties with the available experimental values reveals the compatibility between them. These results are in broad agreement with experimental results.

Keywords: Density functional theory (DFT), Siesta, MgO, Structural properties, Electronic properties.

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1. INTRODUCTION

MgO compound has become one of the main oxides as demonstrated by theoretical and experimental works in recent years. It is a white solid metal found in the lower layers of the Earth and an important component of these inner layers, where the pressure is about 140 GPa. Therefore, its structure changes significantly compared to natural pressure. Indeed, this is how it gained its geophysical importance [1].

MgO is type II-VI, which consists of an ionic bond between magnesium and oxygen atoms. It is one of the basic compounds included in industrial sciences, as it has a band gap of 7.833 eV [2]. In addition, it has various applications such as insulators, medicines, cement, etc. It can crystallize in several phases, most of which are in B1, B3 and B4 forms. Different experiments were carried out to study these phases that form thin layers deposited on metal substrates [3].

This compound was chosen for the study because it is non-toxic, unlike other oxides. In addition to that, it can be used in the manufacture of some household items. MgO has been reported in numerous theoretical and experimental studies [4, 5], where its electronic and structural properties for B1 and B2 phases were investigated by Chang and Cohen [4] using the semi-potential method within the LDA. As well as the work of Causa et al., [5] is based on the study of the structural properties and stability of phases in which MgO is present using the Hartree-Fock theory.

In a few previous studies, the cohesion energy of MgO was searched. This study is interested in finding the binding energy using two different approximations. For example, Chang and Cohen [4] calculated the cohesion energy theoretically and experimentally, and Jaffe et al. [6] also did the same for both MgO and ZnO in different phases, namely B4, B3, B2 and B1, using the LDA and GGA approximations. The main objective of the current work is to study the B4 phase of MgO oxide and find its cohesion energy and properties.

2. THEORETICAL METHOD OF CALCULATION

The calculation method is based on the structural and electronic properties of wurtzite MgO. Actually, it is necessary to use the Full Potential Linearized Augmented Plane Wave (henceforth FP-LAPW) method for the results to be precise. The latter is then applied on the basis of Density Functional Theory (DFT) following the Siesta code [7]. Ceperly-Alder of the Local Density Approximation (LDA) and Perdew-Burke-Ernzerhof of the Generalized Gradient Approximation (PBE-GGA) [8] are used to calculate the exchange correlation effect. In our study, the kinetic cut-off energy for plane waves of 250 eV and k-point mesh parameters of 3×3×1 were used in accordance with Monkhorst-Pack. The total energy was converged to less than 5×10^{-5} eV per atom, while the maximum ionic Hellmann-Feynman force per atom was approximately less than 0.05 eV/A. Actually, we had to increase the k-points to 6×6×3 for obtaining more accurate results.

3. RESULTS AND DISCUSSION

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3.1 Primary Cell Structure

The lattice constants of MgO have been verified many times over several decades [9]. The stable primary cell structure of MgO is wurtzite B4, a compact hexagonal shape characterized by the $P63_{mc}$ group and lattice constants estimated as $a = b = 3.283$ Å, $c = 5.095$ Å, $\alpha = 90.03°$, $\beta = 90.037°$and $\gamma = 119.90°$ [10]. Each primary cell of MgO consists of four atoms, each two Mg atoms occupy positions (0, 0, 0) and (1/3, 2/3, 1/2). As far as O atoms are concerned, they occupy the implantation positions (0, 0, μ) and (1/3, 2/3, μ), where μ is an internal variable of the wurtzite structure, which determines the bond length between Mg and O atoms. The variable μ is determined as follows:

$$\mu = \frac{1}{4} + \frac{c^2}{3a^2}, \quad (1)$$

where a and c are the cell constants.

The calculations in this study depend on the Siesta program, which was used to calculate the primary cell constants of MgO. The results are given in Table 1.

Table 1– Comparison of the primary cell constants of MgO with theoretical and practical results

		a (Å)	c (Å)	μ (Å)	c/a
Our results	GGA	3.327	5.025	1.011	1.510
	LDA	3.288	5.004	1.220	1.521
Theoretical work following GGA method		3.308 [11]	5.074 [11]	0.386 [11]	/
		3.281 [12]	5.136 [12]	0.393 [12]	/
		3.310 [13]	5.123 [13]	0.391 [13]	1.547 [13]
Theoretical work following LDA method		3.252 [11]	5.027 [11]	0.391 [11]	/
		3.322 [09]	/	0.391 [09]	1.546 [09]
		3.249 [14]	5.277 [14]	0.391 [14]	1.547 [14]
Experimental work		3.283 [10]	5.095 [10]	0.388 [10]	1.552 [10]

Using DFT and the Siesta program, we were able to calculate the primary cell constants, and then using the GGA to find the values 3.327 Å for the constant a and 5.025 Å for the constant c. The values of 3.288 Å and 5.004 Å were recorded for the previous constants using the LDA, respectively.

It is noted that these results largely correspond to the applied theoretical results [10-14] shown in Table 1. In addition, the percentage of error in the obtained values was calculated. Assuming that they are compared with the experimental values that were taken as a reference, we found that the error value was estimated to be 1.34 % for the constant a and 1.37 % for the constant c with GGA. The error value with LDA was estimated to be 0.15 % for the constant a and 1.79 % for the constant c. Based on that, it seems that the calculated error values are small, indicating that the method adopted in the calculation is logical and reasonable.

3.2 Magnesium Oxide Formation Energy

The formation energy of MgO was calculated for each Mg-O pair using the following relationship:

$$E_C = E_T[MgO] - E_T[Mg] - E_T[O], \quad (2)$$

where E_T[MgO] is the total energy of MgO in the solid state, E_T[Mg] is the total energy of the free Mg atom, E_T[O] is the total energy of the free O atom, Ec is the formation energy.

The results of calculating the formation energy of MgO are shown in Table 2.

The obtained value of MgO formation energy to bind each Mg-O pair was 5.8120 eV with LDA and 5.7694 eV with GGA. Both results are very close to the experimental results obtained in [17].

Table 2– Formation energy of the Mg-O pair

Formation energy of the Mg-O pair	
Our results	Another theory's results
GGA: 5.7694 eV	GGA: 7.692 eV [15]
LDA: 5.8120 eV	LDA: 9.769 eV [15]
GGA: 11.5389 eV/pair	GGA: 10.05 eV/pair [09]
LDA: 11.6240 eV/pair	GGA: 10.85 eV/pair [16]
	Experimental result: 7.52 eV [17]

3.3 Electronic Properties of the Compound

3.3.1 Structure of Energy Bands

The Brillouin region is chosen to study the primary structure in order to find the electronic properties of the matter. Fig. 1 shows the Brillouin region related to the hexagon. It is worth noting that the study of properties on this region can be generalized later to MgO.

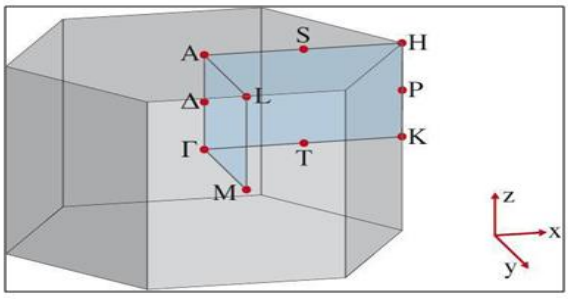

Fig. 1 – Brillouin region of a wurtzite crystal

DFT and GGA were used to determine the band gap of MgO. This method is also relied upon because it is one of the most suitable methods for studying the electronic structures of materials. The energy band structure of MgO was calculated for the above obtained lat-

tice constants ($a = 3.327$ Å, $c = 5.025$ Å, $\beta = 90.037°$, $\alpha = 90.03°$, $\gamma = 119.90°$). The structure of energy bands of MgO is shown in Fig. 2.

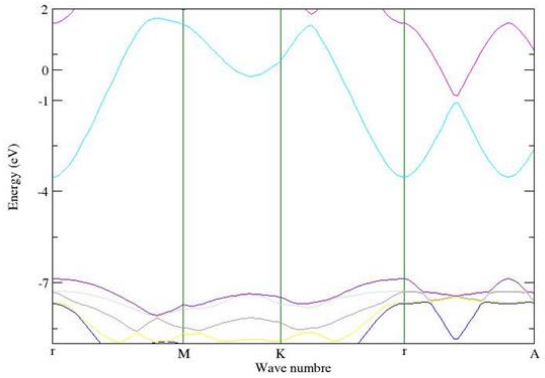

Fig. 2 – Energy band structure of the MgO wurtzite phase

It is noticeable in Fig. 2 that the highest peak of the valence band and the lowest peak of the conduction band are on the same line passing through the point *K*. This explains that MgO has a direct gap estimated at 3.27 eV. The following values refer to the band gap calculated with GGA and compared to other theoretical results, as shown in Table 3.

We note that the value of the band gap obtained using this theory is close to the theoretical results listed in Table 3. Our calculated results for the structure of energy bands by the GGA method are smaller than the experimental ones. This indicates that it does not provide very accurate results. Unfortunately, we found that the band gap calculated by GGA is lower compared to the experimental results. Even if we use LDA, the value of the energy band will also be less than the experimental value. It is well known that GGA reduces the calculated band gap compared to the experimental value, so the calculated values remain the lower estimate of the true values of the band gap.

Table 3 – Band gap E_g (eV) compared to theoretical and experimental results

Used method	Band gap E_g (eV)	
	GGA	LDA
Our results	3.27	/
Other results	3.8913 [11]	3.607 [11]
	4.408 [18] 4.45 [19] EV-GGA [19] 5.42	/ 5.05 [20]
Experimental results	7.833 [14] 3.48 [12]	

3.3.2 Electronic Density of States

To determine the reason for the existence of states that formed both the valence and conduction bands and to understand the nature of interactions between atoms of the studied compound, the Total Density of States (TDOS) and Partial Density of States (PDOS) for the MgO compound are analyzed using GGA and LDA, as shown in Fig. 3 and Fig. 4, respectively.

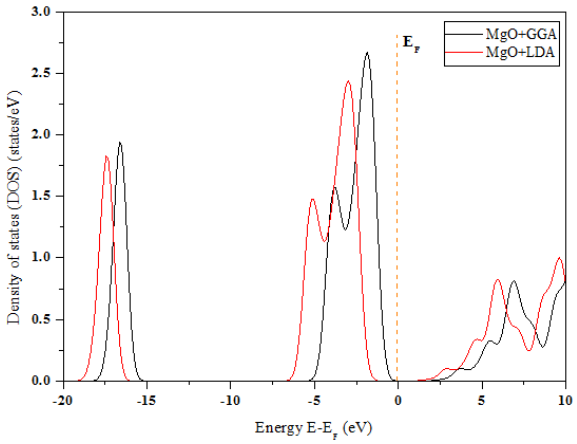

Fig. 3 – TDOS for MgO with GGA and LDA

Fig. 3 shows that the calculated TDOS for MgO has high values with GGA and LDA in the region close to the Fermi level. The value of TDOS for MgO with GGA is higher than the one with LDA. This means that the valence band is rich in electrons.

At the Fermi level, we note that the highest value of TDOS for MgO with GGA is 2.8 states/eV, followed by a lower value with LDA estimated at 2.5 states/eV in the same region. The two TDOS curves for MgO with GGA and LDA in the conduction band near the Fermi level are almost identical and have a TDOS value of 1.0 states/eV in an energy field ranging from 6-7.5 eV.

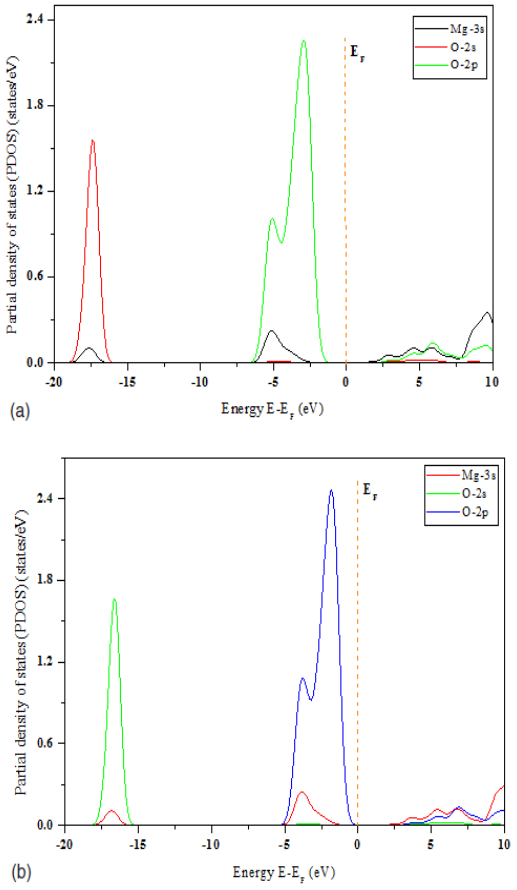

Fig. 4 – PDOS for MgO with (a) GGA and (b) LDA

In this study, PDOS for the MgO compound is calculated and explained in detail to understand the movement of electrons that are close to the Fermi level. Before this, we need to know PDOS for Mg and O, contributing to the formation of TDOS for MgO in the solid state. Fig. 4a shows PDOS for MgO with GGA and Fig. 4b shows PDOS for MgO with LDA.

It appears from Fig. 4 that the two curves have the same overall shape, so we can say that the presence of DOS values in the valence band region is due to the basis of the 2*p* orbital of the O element and the 3*s* orbital of the Mg element. Therefore, the *p* orbital of the O element and *s* orbital of the Mg element are responsible for DOS in the region of the valence band. We also note the emergence of a station near the Fermi level with an energy of – 2.5 eV for the O-2*p* station and another for Mg-3*s* at a value of – 3.5 eV. The O-2*s* station is almost non-existent, which helps in the fast movement of electrons from the valence band to the conduction band when MgO is exposed to external stimulation such as light. PDOS peaks were recorded in the conduction band, which seem to have the same oscillatory values at Mg-3*s*, O-2*p* and O-2*s* stations.

4. CONCLUSIONS

The use of DFT, GAA and LDA enabled us to calculate the ground state properties of the wurtzite (B4) phase of the MgO compound, which has high stability in comparison with other phases.

Due to the great compatibility between the previous theoretical and experimental results and our results regarding the calculation of the primary cell constants for the wurtzite phase, as well as the determination of the binding energy of MgO, the DFT method and the use of the Siesta program are among the most effective ways to predict the general properties of the ground state of the MgO compound. In addition, our calculations show that the O-2*p* orbital significantly contributes to PDOS values near the Fermi level, followed by a lower contribution from the Mg-3*s* orbital. Our results also confirm that MgO has a direct band gap of 3.27 eV.

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Дослідження структурних та електронних властивостей фази вюрциту MgO з використанням теорії функціоналу щільності

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Ab initio метод псевдопотенціалу заснований на теорії функціоналу щільності (DFT), в якій використовуються наближення узагальненого градієнта (GGA) за схемою, описаною Perdew-Burke-Ernzerhof (PBE), і наближення локальної щільності (LDA) за схемою, описаною Ceperly-Alder (CA). Метод реалізовано за допомогою програми Siesta для вивчення структурних та електронних властивостей фази вюрциту (B4) сполуки оксиду магнію (MgO) і є корисним для прогнозування кристалічної структури MgO. Фактично розраховані структурні параметри даної сполуки узгоджуються з наявними експериментальними даними, тому отримані результати можна вважати хорошим прогнозом. Виявлено, що як параметри решітки, так і ширина забороненої зони при нульовому тиску узгоджуються з попередніми теоретичними та експериментальними результатами. Крім того, отримана енергія зв'язку порівнюється з результатами попередньої роботи. Електронні властивості, особливо загальна гус-

тина станів (TDOS) і часткова густина станів (PDOS), також показують, що внесок атома кисню в DOS в області, близькій до рівня Фермі, є значним. Порівняння розрахованих параметрів решітки та всіх електронних властивостей з наявними експериментальними значеннями виявляє узгодженість між ними. Ці результати в цілому узгоджуються з результатами експерименту.

Ключові слова: Теорія функціоналу щільності (DFT), Siesta, MgO, Структурні властивості, Електронні властивості.