Band gap and partial density of states for ZnO: Under high pressure

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Abstract

In this work, the effect of pressure on the electronic band structure, partial density of states (PDOS), and the band gap of the four phases of ZnO, namely B4 (wurtzite), B3 (zinc-blende), B1 (rocksalt) and B2 (CsCl-type), has been investigated using the plane-wave pseudo-potential code CASTEP with three different schemes: the generalized gradient approximation (GGA) in the latter approach Perdew–Burk–Ernzerhof (PBE) with and without spin–orbit (SO) coupling, the new hybrid exchange–correlation functional named B3LYP functional and Hartree–Fock + Local Density Approximation (HF + LDA). These schemes are employed in order to treat the exchange–correlation effects. In addition, we will illustrate how the orbital motion of crystal electrons is affected by spin–orbit (SO) coupling. To our knowledge, this is the first theoretical study reported on ZnO using the B3LYP method. Our investigation shows that the increase of the pressure causes the nature of the band gap to change from direct to indirect. The mechanism responsible for this change of band structure is analyzed. The wide band gap of the B4 (wurtzite) phase at \( p = 0 \) as determined by the precedent methods is 3.221 and 3.222 eV (PBE) with and without spin–orbit (SO) coupling, respectively, 9.186 eV (HF + LDA) and 2.451 eV (B3LYP). The first two approaches provide the best agreement with the experiments. The band gap of B3 (zinc-blende), B1 (rocksalt) and B2 (CsCl-type) and the strong contribution of d orbitals of Zn atoms on the structure of the bands will be discussed. The SO coupling effect on the band structure for all phases is presented. This effect on the electronic properties of the various phases of ZnO in particularly for the B3 (zinc-blende), B1 (rocksalt) and B2 (CsCl-type) phases at high pressures are not well-known. The aim of this work is to improve the DFT band gap error by introducing different schemes and therefore this study is important for future experimental work on this potential semiconductor material. In this study we have shown the effect of SO coupling on the bands structure of ZnO as a function of pressure, and analyzed the mechanism of this effect. The understanding of spin–orbit coupling related phenomena is very important in both fundamental research and in applications of semiconductors systems.

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1. Introduction

Zinc oxide (ZnO) is considered to be a promising material in a wide range of applications ranging from optoelectronics to the fields of catalysis and gas sensors. It is a wide direct band gap semiconductor 3.44 eV [1] of great interest for the development of new applications in photonics and piezoelectricity. ZnO is a semiconductor that belongs to the II-VI family, and is known as the zincite. It crystallizes in the form of wurtzite hexagonal compact type, which corresponds to the space group P6\(_3\)mc. ZnO is an interesting example of an area where the interaction of d (Zn: 3d) states with anion valence states (mainly O: 2p) is important. In addition, ZnO occurs naturally as a mineral and its high pressure phases are considered in a geological approach [2,3]. Due to its technological importance in various fields (photovoltaic, optical coating, catalysis, ceramics, etc.) the electronic properties of ZnO have been the subject of several theoretical studies in recent years. Surprisingly, theoretical understanding of the electronic structure of this supposedly simple s, p semiconductor turns out to be rather challenging.

When stress is applied to a semiconductor, the deformation of the crystal results in shifts and splitting of the energy levels, so the external pressure and strain are thus powerful tools to study the band structure of semiconductors.

The quasi-particle calculations within the conventional G_0W_0 approach [4,5] gives a band gap of 2.44 eV [6], which is more than 1 eV smaller than the experimental result of about 3.6 eV [7,8] after correcting for the lattice effects. Two recent LDA/GW calculations...
gave an even smaller gap of 2.12 eV, although this value is increased to about 3.2 eV by subsequent self-consistent GW calculations [9]. Recently H. Dixit et al. [10] represented the quasi-particle band structure of ZnO in its B3 (zinc-blende) and B1 (rocksalt) phases at the $\Gamma$ (0,0,0) point, and made calculations within the GW approximation. This approach gives a good description for the band structure. Aryasetiawan and Gunnarsson [20] have shown that the GW calculation is capable of giving good electronic structure for both extended as well as localized semi-core states.

Zakharov et al. [21] have reported plane-wave GW method for a number of II-VI compounds. They simply treated the d electrons as core electrons and deliberately carried out their GW calculation. They obtained very good results for the anion p valence bands and for the band gap energies but no assertion concerning the d-band positions could be made.

C.L. Dong et al. [22] reported X-ray absorption (XAS) and X-ray emission spectroscopy (XES) experimental studies of nanostructured ZnO in zincite structure (wurtzite), in parallel with calculations using local density approximation (LDA) and LDA + U approach [22].

It is well-known that in some cases the LDA and GGA calculations yield to a band gap that is smaller than the one determined experimentally. The band gap problem in DFT associated with LDA and GGA has been reported previously [14–16], and it was argued that this problem is the underlying reason for not obtaining satisfactory agreement between the values determined by experiments. A possible, although slightly unsatisfactory, method to avoid this problem is to introduce a scissors operator, as the one of Levine and Allan [17] and as discussed by Gonze and Lee [18]. Note that the scissors operation, a linear shift of the calculated results, has been used to correct the calculated band gaps with the standard band gap of ZnO (3.37 eV), because the density functional theory leads to an underestimation of the band gap in the case in which the correlation of excited electrons is ignored [19,20–23]. In our calculations with PBE approach, the values of the scissor in the phase B4 (wurtzite) is chosen to be 2.48 eV (GGA). For all these reasons, it is desirable to have a rigorous framework for understanding the electronic properties of this compound. Consequently, analysis of the electronic band structure and partial density of states are essential to explore the electronic properties of this material system. It is worth pointing out that the electronic properties at high pressures, and in particularly the values of the band gap and the partial density of states for the B2 (CsCl-type), are not well-known in the literature.

2. Computational details

The calculations carried out of in this work are based on the density functional theory (DFT) using the CASTEP program package [25]. Exchange and correlation effects were treated using the generalized gradient approximation (GGA) as parameterized by Perdew-Burk-Ernzerhof (PBE) [11], Hartree–Fock + Local Density Approximation (HF + LDA) [26] and hybrid functional B3LYP [24].

![Fig. 1. Band structures for ZnO in both B4 and B3 phases.](image-url)
Magnetic systems can be studied by carrying out spin-polarized DFT calculations with CASTEP. This setting is recommended for transition metal oxides, certain inorganic surface studies, and metallic systems containing magnetic elements (Zn, Fe, Co, Mn, ...). The calculations were performed using different wave functions for different spins; use the same orbitals for alpha and beta spins.

Spin polarized CASTEP calculations are normally carried out with a variable magnetic moment. This procedure, however, does not guarantee finding the lowest energy state. DFT solutions can converge to a variety of local minima, so that the metastable states are found. The most commonly obtained solutions correspond to high spin ad low spin states. The state generated by CASTEP depends on the initial magnetic configuration, since the solution is likely to converge to the nearest local minimum rather than to the global minimum. There are two ways of defining the initial magnetic configuration: either specify the total magnetic moment per unit cell, which gets uniformly distributed over the space, or provide detailed information on the absolute values and direction (up or down) of the spins for each atom in the unit cell. The former method can be used for relatively simple systems where only two solutions are expected (magnetic and non-magnetic). The latter method, which specifies the spin state of the atoms in the system, is more general and gives much more flexibility.

The calculations were performed in the plane-wave basis, using both Vanderbilt ultra-soft pseudo-potentials [12] and the norm-conserving pseudo potentials [27]. In this computational work, only the valence band electrons of the Zn (3d^{10}, 4s^2) and O (2s^2, 2p^4) are considered for PBE. The cut-off energy for the plane wave expansion is 380 eV. Calculations are carried out for the full band-structure, the partial density of the states (PDOS) and the band gap along several high symmetry directions.

The Brillouin zone sampling was performed using the 10 \times 10 \times 10 and 9 \times 9 \times 6 set of Monkhorst–Pack mesh [13] division of the reciprocal unit cell for cubic and hexagonal structure,
respectively. The sequence of ionic movements and electronic minimizations is commonly referred to as geometry optimization and can be continued until a specified convergence of the total energy is reached. The self-consistent calculations are considered to converge when the total energy of the system is stable within $10^{-6}$ eV/atom.

### 3. Results and discussion

#### 3.1. Electronic band structures and partial density of states in B4 and B3 phases

The calculated electronic band structures and the partial density of states of B4 and B3 at $p = 0$ and 3 GPa, respectively, along the principal high-symmetry directions in the first Brillouin zone are shown in Figs. 1 and 2. The observed direct band gaps ($\Gamma - \Gamma$) with the different schemes, are in excellent agreement with the experimental and recent theoretical values reported in References [28–31]. The transition between the two bands can take place with minimal energy and without change of wave vector. This will allow the absorption and the emission of the light in a way much more effective than in indirect gap materials [32].

In Figs. 1 and 2, it can be seen that the valence band for B4 phase at three different schemes can be divided into two regions: the lower parts of valence bands are dominated by O 2s states, and the upper parts are originated mostly from the cation Zn 3d states hybridized with the anions O 2p states. This result is in excellent agreement with that reported in Ref. [33]. These figures; show that the motion of electrons is characterized by energy bands $E_n(k)$ with band index $n$ and wave vector $k$. Here also, the SO coupling has a very profound effect on the energy band structure $E_n(k)$. The two different values of gap ($E_{gap(SO)} - E_{gap}$ = 0.001 eV) indicate that has a SO interaction caused by structural inversion asymmetry of ZnO in B4 structure, where extra degrees of freedom provided by electron spin are involved. We think that it would be possible in the future to control and tune the spintronic properties by the application of pressure on spintronic devices and materials such ZnO in B4. It was predicted by Fujita et al. [34], and confirmed by later spin polarized DFT calculations [35], that the instability due to the high density of states at the Fermi energy is removed by forming an antiferromagnetic or ferromagnetic ground state, lifting the degeneracy of the $p$-bands by opening a band gap in the band structure. This intrinsic magnetic ground state might be interesting for applications in spintronic devices. The coupling suggests that a spin-degenerate level can be split by spin-orbit (SO) coupling into levels with spin up (alpha) and spin down (beta).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The gap value and the valence Band width (eV) for ZnO in B4 (wurtzite), B1(rocksalt) and B2 (CsCl-type) phases.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our results</td>
<td>GGA</td>
</tr>
<tr>
<td>B4 (wurtzite)</td>
<td>Direct gap $\Gamma - \Gamma$</td>
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<tr>
<td></td>
<td>VB width</td>
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<tr>
<td>B3 (zinc-blende)</td>
<td>Direct gap $\Gamma - \Gamma$</td>
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<td>VB width</td>
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<tr>
<td>B1(rocksalt)</td>
<td>Indirect gap L–$\Gamma$</td>
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<td>VB width</td>
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<tr>
<td>B2 (CsCl-type)</td>
<td>Indirect gap X–$\Gamma$</td>
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<td>VB width</td>
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</table>

<sup>a</sup> Ref. [3].
<sup>b</sup> Ref. [28].
<sup>c</sup> Ref. [29].
<sup>d</sup> Ref.[6].
<sup>e</sup> Ref. [9].
<sup>f</sup> Ref. [43].
<sup>g</sup> Ref. [4].
<sup>h</sup> Ref. [42].
<sup>i</sup> Ref. [41].
<sup>j</sup> Ref. [42].
<sup>k</sup> Ref. [31].
<sup>l</sup> Ref. [33].
<sup>m</sup> Ref. [46].
<sup>n</sup> Ref. [47].
<sup{o</sup> Ref. [48].
<sup>p</sup> Ref. [49].

In Figs. 1 and 2, it can be seen that the valence band for B4 phase at three different schemes can be divided into two regions: the lower parts of valence bands are dominated by O 2s states, and the upper parts are originated mostly from the cation Zn 3d states hybridized with the anions O 2p states. This result is in excellent agreement with that reported in Ref. [33]. These figures; show that the motion of electrons is characterized by energy bands $E_n(k)$ with band index $n$ and wave vector $k$. Here also, the SO coupling has a very profound effect on the energy band structure $E_n(k)$. The two different values of gap ($E_{gap(SO)} - E_{gap}$ = 0.001 eV) indicate that has a SO interaction caused by structural inversion asymmetry of ZnO in B4 structure, where extra degrees of freedom provided by electron spin are involved. We think that it would be possible in the future to control and tune the spintronic properties by the application of pressure on spintronic devices and materials such ZnO in B4. It was predicted by Fujita et al. [34], and confirmed by later spin polarized DFT calculations [35], that the instability due to the high density of states at the Fermi energy is removed by forming an antiferromagnetic or ferromagnetic ground state, lifting the degeneracy of the $p$-bands by opening a band gap in the band structure. This intrinsic magnetic ground state might be interesting for applications in spintronic devices. The coupling suggests that a spin-degenerate level can be split by spin-orbit (SO) coupling into levels with spin up (alpha) and spin down (beta).
In a free atom, spin–orbit interaction can lift the degeneracy of states with the same orbital (spatial) wave function but with opposite spins. In solids, however, such a splitting can be forbidden due to crystal symmetry. This example illustrates how the orbital motion of crystal electrons is affected by spin–orbit (SO) coupling.

Datta and Das [36] have proposed a new type of electronic device where the current modulation arises from spin precession due to the spin–orbit (SO) coupling in a narrow-gap semiconductor, while magnetized contacts are used to preferentially inject and detect specific spin orientations. Recently, extensive research aiming at the realization of such a device has been under way [37].

A close attention to the electronic band structures and the PDOS at zero pressure, reveal that these are divided into four groups: three being occupied and one unoccupied. In the PBE formalism the lowest band has an energy in the range -18.00 to -17.75 eV. This can be attributed to the levels O: 2s. These results agree with the experimental value measured by L. Ley et al. [38] and those reported in [39]. The band immediately above is a narrow band with a width in the range -5.7 to -5.6 eV. The highest level in energy of the band between -4.8 and -4.125 eV arises mainly from the levels Zn: 3d. On the other hand, the low energy level from -5.50 to -5.375 eV corresponds to a strong hybridization of the levels Zn: 3d and O: 2p. Both O: 2p and Zn: 3d wave functions are strongly localized, and the O: 2p states are very energetically close to the Zn: 3d states, which implies a significantly strong interaction between O: 2p and Zn: 3d. These findings are in good agreement with those of J.E. Jaffe and Hess [40]. The last occupied band, which has an energy from -0.375 to 0.00 eV and its maximum is located at $\Gamma (0,0,0)$, is rather broad and corresponds to the valence band. The levels of this band result from the levels O: 2s, 2p and Zn: 4s, 4p. The conduction band (unoccupied) has a width of 3.45 eV. The bottom of the conduction band, which consists especially of zinc states, has a minimum around the point $\Gamma (0,0,0)$. This means that ZnO in the B4 phase is a univalent semiconductor [41].

Figs. 1 and 2 are shown that the electronic band structure of B3 is divided into four groups, three being occupied and one unoccupied. The lowest band, which is from -17.72 eV to -17.00 eV (PBE), originates mainly from the levels O: 2s. The band immediately above is a very narrow band of width from -5.925 to -4.70 eV (PBE). It can be seen that the low levels are intermediate between -4.50 and -4.24 eV (PBE). This under-band corresponds to a strong hybridization of the levels Zn: 3d and O: 2p. On the other hand, the highest energy levels in this band are from -4.2 to -4.15 eV (PBE).
These levels are mainly resulting from the levels Zn: 3d. The third occupied band (valence band), which is intermediate between –3.90 and 0.00 eV (PBE), is the broadest band as compared to the others. It is worth pointing out that the electronic properties of the B3 phase are not well known in the literature. This means that these new results will be of great importance to researchers working on ZnO semiconductors.

As shown in Table 1, the wide band gap in the B4 phase at P = 0 is ~3.222 eV (PBE) with and without SO coupling, respectively, 9.186 eV (HF + LDA) and 2.451 eV (B3LYP). We note that, our results obtained with PBE and B3LYP agree with experimental data [42], and are very close to that reported in Refs. [6,9,20,28,31,33,43–46]. However, our results attained by the (HF + LDA) method are closer to those calculated by J.E. Jaffe et al. [3]. We also note that, our results concerning the total valence band are very close to those calculated in Refs. [33,45,46].

Calculations were performed for the electronic band structure, the partial density of the states and the band gap of B3 versus
the wave vector \( \mathbf{k} \) in the first Brillouin zone at the points of high symmetry at \( p = 3 \) GPa. The results are illustrated in Table 1, which show that the band gap is always with the same value of \( \sim 3.095 \) eV (PBE) with and without SO coupling. This value is close to the determined experimental value of 3.27 eV \([30]\), and the 3.47 eV value calculated by GW approach reported in \([10]\). According to our results the phenomenon of SO coupling does not affect the band gap value in the case of zinc-blende structure which has a center of inversion but gives rise to a spin splitting of the bulk energy dispersion. This is well known from early theoretical studies \([50]\). In addition, this has been observed experimentally by analyzing the Shubnikov–de Haas effect in uniaxially strained bulk InSb \([51]\) and by detecting the precession of the spin polarization of electrons photoexcited from a GaAs layer \([52]\). But our results \( \sim 6.456 \) eV (HF + LDA) and \( \sim 4.693 \) eV (B3LYP) are larger than the experimental value \([30]\) and with those recently calculated in references \([31,46–48]\).

### 3.2. Electronic band structures and partial density of states in B1 and B2 phases

The results of the investigation of the electronic band structures, the partial density of the states and the band gap in both B1 and B2 phases are shown Figs. 3 and 4, respectively. As can be observed for B1 phase, the maximum of the valence band occurs at point \( \mathbf{k} \), which is the border of the first Brillouin zone along the [111] direction, and the minimum of the conduction band is at \( \Gamma \) (0,0,0). These two points have different wave vectors \( \mathbf{k} \). From this finding one can conclude that the band gap in these phases is indirect. The indirect band gap of B1 phase is \( \sim 2.60 \) and 2.56 eV (PBE) with and without SO coupling, respectively. Our results agree well with the experimental value of 2.45 eV \([28]\), and the recent calculated values of 2.93 and 1.683 eV \([31,46]\). According to the calculations of the partial density of the states of B1 phase, the energies bands are divided into four groups: three being occupied and one unoccupied. The lower band has a very narrow band width from \(-16.214(-16.0) \) eV to \(-13.0(-14.0) \) eV (PBE), with and without SO coupling, respectively. This sub band is assigned to levels O: 2s. But the band immediately above from \(-7.95(-8.0) \) eV to \(-7.0(-6.0) \) eV (PBE), with and without spin–orbit (SO) coupling, respectively, corresponds to a strong hybridization of levels Zn: 3d and O: 2p.

According to our calculations, the third occupied band (valence band), which is intermediate between \(-4.57(-5.80) \) and \(1.57(0.8) \) eV (PBE), with and without SO coupling, is the result of the spin–orbit interaction that causes a change in the sub bands energy. We note that this sub band resulting from levels O: 2p and Zn: 4p is above the Fermi level. The valence band for beta spins (spin down) orientation is partially filled while there is a gap in the density of states for the other alpha spin (spin up) orientation. This results in a conducting behavior for only electrons in the beta spin orientation which constitutes the majority. For this reason we believe that ZnO in B1 phase becomes a half-metal.

Experimental investigations of the electronic properties of the B2 phase at high pressure are limited. Consequently, the aim of this part of the work is to understand the electronic band structure, partial density of states and the band gap under high pressure. Fig. 3 illustrate the results obtained at \( p = 265 \) GPa. As can be seen in this figure the maximum of the valence band occurs at point \( \mathbf{k} \) which is at the border of the first Brillouin zone along the [100] direction, whereas the minimum of the conduction band is at point \( \Gamma \) (0,0,0). This means that the band gap is indirect (\( \Gamma–\Gamma \)). This indicates that B2 is an indirect semiconductor with a band gap of \( \sim 2.405 \) eV and 2.410 eV (PBE) without and with SO coupling, respectively, and also show the effect of spin–orbit (SO) coupling on the band structure. We believe that ZnO in B2 phase becomes a half-metal. Although this finding does not agree with the work reported in Ref. \([31]\), our result for the valence band is in excellent agreement with the calculations of Reference \([31,46]\). It is worth mentioning here that so far there are no experimental data available that could verify these calculated results.

### 3.3. Effect of pressure on the band gap in B4 and B3

The value of the gap constitutes an essential parameter for the choice of semiconductors in the fabrication of electronic devices based on ZnO. Despite of this importance, very little experimental work is reported on the effect of pressure on the band gap of this semiconductor material. For this reason a systematic study of the evolution of the band gap with pressure from 0 to 10 GPa and from 3 to 8 GPa has been carried out for B4 and B3, respectively. The obtained results (PBE) are shown in Fig. 5 where a polynomial evolution for B4 and linear one for B3 are noted and given by the following equations, respectively:

\[
E_g(p) = 3.22101 + 0.00543p + 0.000566p^2 \\
E_g(p) = 3.08654 + 0.00071p
\]

### 4. Conclusion

These work calculations using the plane-wave pseudo-potential code CASTEP with three different schemes: the parameterized generalized gradient approximation Perdew, Burke and Ernzerhof functionals PBE with and with SO coupling, Hartree–Fock + Local Density Approximation (HF + LDA), and the B3LYP functional. The pressure dependence of the electronic band structures, PDOS and the band gap are investigated from 0 to 300 GPa. This investigation demonstrated four remarkable phenomena that manifest themselves as a function of pressure: (i) an increase of the pressure causes a change of the electronic band structures and affect both the value and the nature of the band gap from a direct gap (\( \Gamma–\Gamma \)) in the B4 phase with a value of wide gap 0 is \( \sim 3.222 \) and 3.221 eV (PBE) with and without SO coupling, respectively, 9.186 eV (HF + LDA) and 2.451 eV (B3LYP) at \( p = 0 \), and B3 phases to an indirect gap (\( \Gamma–X \)) for B1 and \( \Gamma–L \) for B2; (ii) the values of the band gap for the four phases are generally close to that in theory and experiment; (iii) our results prove that the band gap in both B4 and B3 phases have a polynomial and linearly evolution with the increase of pressure, respectively; (iii) the effect of SO coupling in the band structures and partial density of ZnO in B4, B1 and B2 phases is clear.
References