Journal of New Technology and Materials
JNTM
Vol. 04, N°01 (2014)143-146

OEB Univ. Publish. Co.

Theoretical approach by the ADF-Band of electronic properties in oxides. Part I: ZnO

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Received: 30 April 2014, accepted 26 May 2014

Abstract:

The ADF-Band (Amesterdam Density Fonctional), based on the Density Functional Theory (DFT), which is one of the most common methods used in ab-initio calculations in periodic systems such as polymers, thin films and crystals. Modeling of crystalline oxides state, at the nanoscale, through optimization of the crystalline structure. Computational calculation by the ADF-Band provides the opportunity to confirm the crystal structure and determine their electronic properties such as: the Energy gap (Eg), the Fermi level (E_F), the structure of the bands in the first Brillouin zone, the character and the nature of(B.C) , (B.V) bands and the charge transfer in the oxides .

Keywords:ADF-Band,Energy gap,Fermi level,optimization,electronic bands,chargestransfer.

1. Introduction

Among the oxides,ZnO hasgained substantial interest in the research community. It isa II-VIbinary compound semiconductor, n-type and crystallize in either cubic zinc blende or hexagonalwurtzite structure where each anion is surrounded by fourcations at the corners of tetrahedron.A tetrahedral coordination is typical of sp^3 covalent bonding .The iconicity of ZnO resides at the borderline between covalent and ionic semiconductor.ZnO is economical and has technical applications such as Photo-catalytic, the sensitive thin layer gas, varistors, LED diodes, spinotronics components, nanolasers....[1].

In our work, the ZnOcrystal, withwurtzite hexagonal structure [2], was modeled by using the ADF-Band program[3-4-5-6].We have employed the density-functional theory (DFT) using two different approximations, namely,the local-density approximation (LDA) and the generalized gradient approximation (GGA), in the exchange-correlation function to calculate the total energy and electronic structure of ZnO.Computational calculations allowed to:

(i) Optimize the geometry of the structure.
(ii) Represent the electronic bands, the first Brillion zone, the nature and character of the bands.
(iii) Plot the density of electronic states (DOS) with the Fermi level energy and Gap band.
(iv) View the charge transfer, which reveals partial character in the oxide.

2. Computational details

2-1- Optimization of ZnOcrystalline Structure

a)-Creation of a unitcell:thestructure selected has a hexagonalwurtzite unit cell with two lattice parameters a=3.24 Å and c=5.21Å, in the ratio of c⁄a=√(8/3)=1.63, and belongs to the space group of $P6_3mc$. The value of the parameter u (defined as the length of the bond parallel to the c axis in units of c) is 0.375 in an ideal wurtzite structureand deviation from that is probably due to lattice stability and iconicity such as zinc antisites and oxygen vacancies[7].

b) - Geometrical optimization: after optimization, we obtain the energy formation as a function of the number of unit cell. A new values of unit cell parameters are calculated at the equilibrium cohesive energy.

2-2-Electronic bands structure

a)-Bands diagram :the diagram is constituted by the plot of E (k) where the wave vector (k) takes its values on the first Brillouin zone (Fig.1).

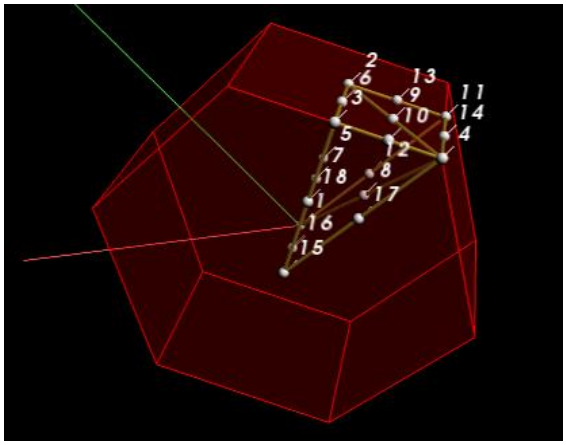

Fig.1: Path visualizationof the First Brillouin Zonewith k-points numbersof wurtzite structure.

b)-Bands nature: Fermi level is represented by a redline. The bands bellow E_F form the valence band (B.V) and whose above it form the conduction band (B.C)

c)-Bands character:With the function 'Double Isosurface (+, -)' we select the lowest and the highest energy band (occupied state) and the lowest energy band (unoccupied /virtual state).

2-3- Electronic density of state

a)-With 'DOS'function, we obtain the plot of the density of states in terms of energy.

b)-To view the contribution to the bands, we use 'addgraph'subfunctionand select Oxygen or Zinc atom.

2-4-Charges transfer

The charges transferis determined by the 'density deformation'functionand represented by'cuts plane (+/-)'subfunction.

3. Results and Discussions

3-1) By using a convergence criterion equal to 0.001 (example) for one unit cell and teen unit cell, we obtainthe plot of energy formation. The optimized energy appears as -0.5747 a.u and -0.5787a.u as it is shown in the figure1 and figure2 respectively.

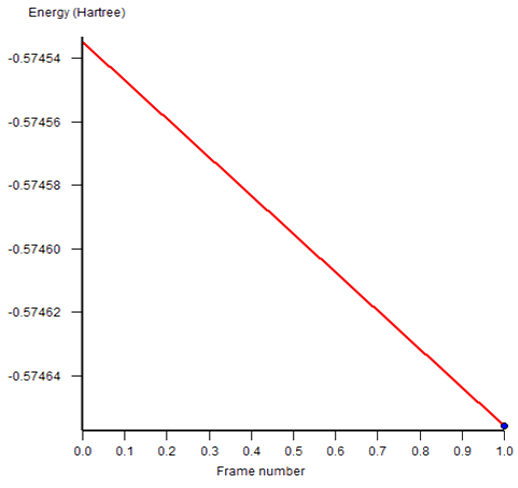

Fig.2: Energy of formation forone unit cell.

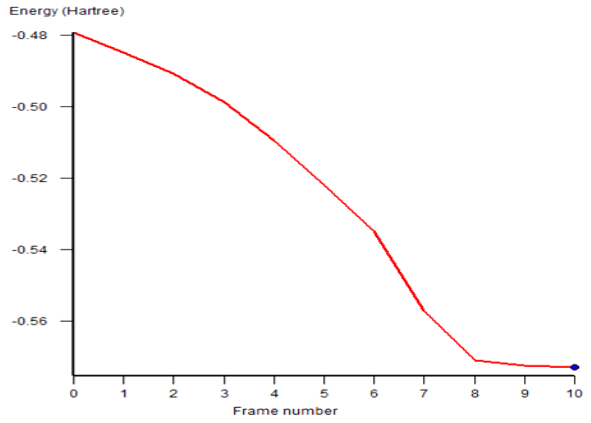

Fig.3: Energy of formation for a fragment (ten unit cells).

3-2) The bandwhose energies are between the values $E_F \pm 0.75$ a.uare represented with a number of energy values equal to 300.

The diagram band (Fig.4) shows that:

-ZnOmaterial is n-type semiconductor,anisotropic and with a direct gap.

-The valence band is constitutedby nine bands (which come from the occupied orbital) double degenerate at unique k-point1 (Γ/k=0,0,0).

-The conduction band is constituted by five bands,which come from the unoccupied / virtual orbitals.

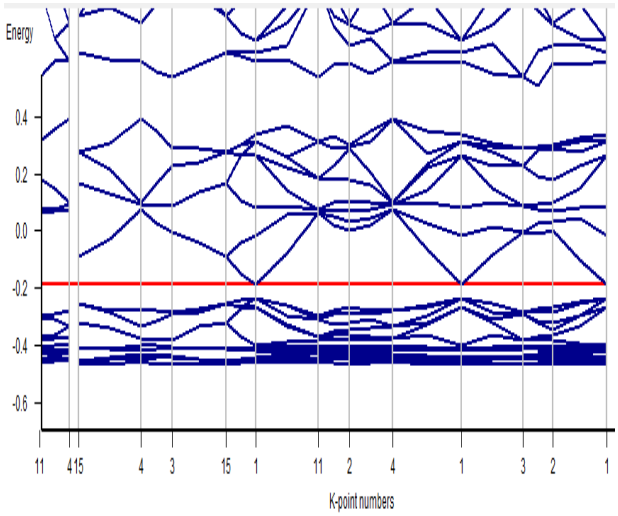

Fig.4 :Diagram band of zinc oxide(ZnO).

-Tovisualizethe character of the valence band, weselect the lowest band of occupied statek=(0,0,0) (Fig.5) and highest band of occupied statek=(0,0.8,0.8) (Fig.6). For the conduction band, we selectonly the lowest band of unoccupied/virtual state k=(0,0,0)(Fig.7).

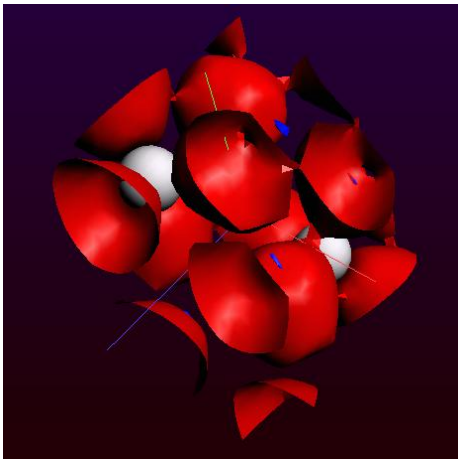

Fig.5: 2s-orbital of Oxygen atom.

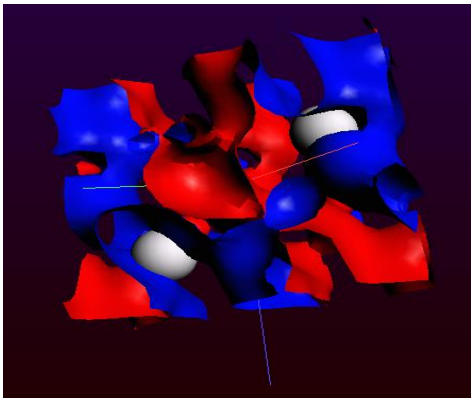

Fig.6: 2p-orbital of Oxygen atom.

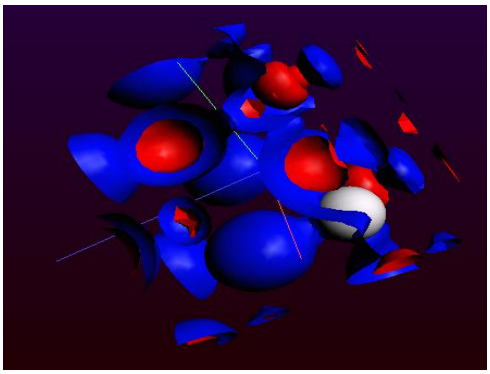

Fig.7:4s-orbital of Zinc atom.

3-3) From the band gap information (fig.4):

The standardLDA(VWN) and GGA(BLYP-D) calculations underestimate the ZnO band gap to be as low as E_g^{LDA}=1.304eV and E_g^{GGA}=1.550eV, as opposed to E_g^{exp}=3.37eV. This is due to the fact that the d-electrons are in the valence band are properly taken into account and isin good agreement with the literature [7].

The plot of the density of states in terms of energy is shown by Fig.8.

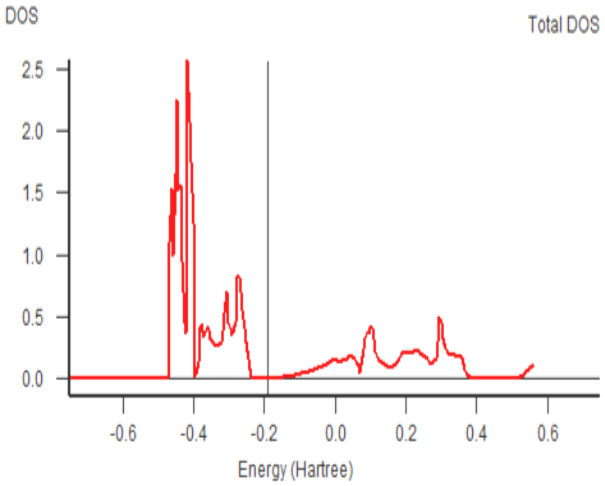

Fig.8: Total density of states In ZnO bulk.

To view the contribution to the bands (Fig.8), we select the Oxygen atom and obtain the Figure 9, which shows that the major contribution to conduction band (C.B) comes from Zinc atoms and the major contribution to valence band (B.V) from Oxygen atoms.

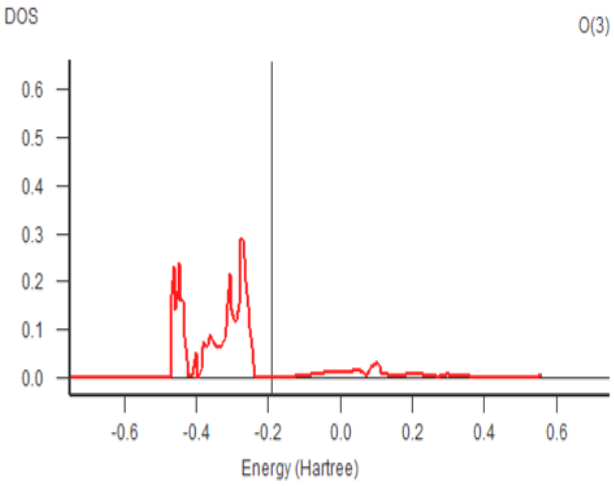

Fig.9: Density of States of Oxygen atoms in ZnO bulk.

3-4) TheFig(III-4-1) -Charge transfer inZnO (Fig.10)shows that a charge is added (blue color) near the Oxygen and removed (red color) from the Zinc atom.

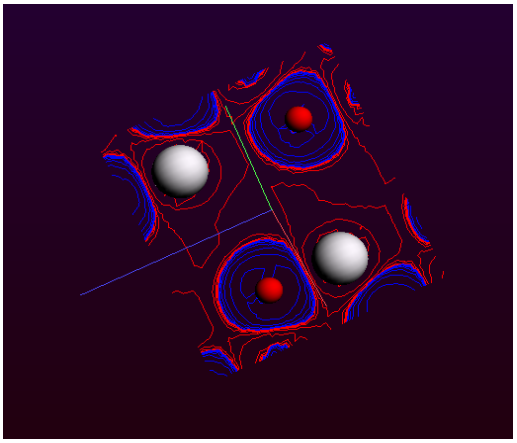

Fig.10: Charge map of the charge density in ZnO.

The amount of charge is only about 0.33. This is of corse due to the fact that the 2p-Oxygen orbital overlaps quite significantly with the Zinc region (Fig.11).

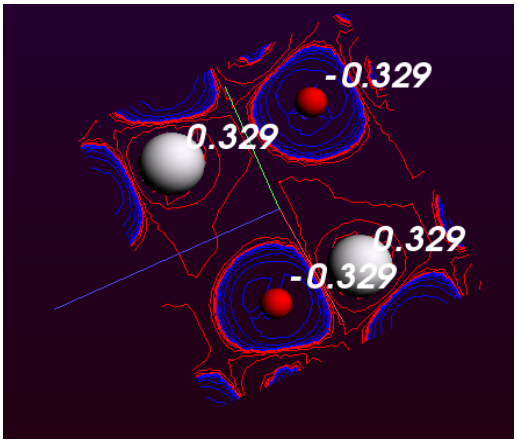

Fig.11:Amount of charge inZnO.

4. Conclusion:

In addition to the agreement between the experimental values and geometric confirmation [9-10], the underestimation of the ZnO band gap with standard LDA and GGA methods indicate that the function used is not suitable.However, they tell us about the characterand nature of the valence band (B.V) and the conduction band (B.C) and the charge transfers. In the case of ZnO, the valence band (B.V) come from 2p-orbital of Oxygen atoms and the conduction band (B.C) from 4s-orbital of Zinc atoms. The charge transfer is only partial.
The ADF Band offers also the possibility of doping, by insertion or substitution, with various proportions using the procedure of fragmentation.

Acknowledgment

This work was accomplished in the 'Laboratoire de critallographie - Université Constantine1-'Algeria and supported by the 'CNEPRU'.

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