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Structural, electronic, and Fermi surface evolution in zinc oxide under high pressure

M. ZEMZEMI[a], S. ALAYA[a,b]
[a]*Laboratoire de Physique des Matériaux et des Nanomatériaux Appliquée à l'Environnement, Université de Gabès, Faculté des Sciences de Gabès, Cité Erriadh Manara Zrig, Gabès, 6072, Tunisia*
[b]*King Faisal University, College of Science, Physics Department 31982 Hofuf, Saudi Arabia*

The first principles calculations by using the plane-wave pseudopotential method in the scheme of Density Functional Theory were performed for polymo*Keywords:* rphs of ZnO: wurtzite and rocksalt structures. The present paper aims at understanding the reconstructive phase from the four-coordinate wurtzite to the six-coordinate rocksalt crystalline structures. The relation between mechanism phase transition and electronic properties has been revised. A new level of understanding to this mechanism of phase transition is presented. The evolution of the Fermi surface under pressure is evaluated and discussed.

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1. Introduction

Metal oxides play a very important role in many areas of chemistry, physics, and materials science. The metal elements can form a large diversity of oxide compounds. ZnO can be considered as an old semiconductor which has been attracting researchers' attention for a long time now because of its potential applications in many such scientific and industrial areas as piezoelectric transducers, optical waveguides, acousto-optic media, conductive gas sensors, transparent conductive electrodes, varistors, etc [1]. Recently, zinc oxide (ZnO) has attracted much attention within the scientific community as a future material in its different states: bulk, film and nanowire [2]. The non-toxicity and natural abundance of its components make ZnO an ideal candidate for many industrial manufacturing processes including paints, cosmetics, pharmaceuticals, batteries, electrical equipments, etc [3]. ZnO is a material of the family of transparent conductive oxides (TCO). With a wide bandgap of 3.4 eV and a large exciton binding energy of 60 meV, ZnO, like GaN, can be a potential candidate for blue and ultra-violet optical devices [4].

Metal oxides present a very big number of polymorphs. Stability and mechanism of phase transition represent an active field of investigation to discover a new stable phase or improve an existent one [5]. In ambient conditions, ZnO stabilizes in the wurtzite (B4) structure. ZnO can also crystallize in the zinc-blende (B3) cubic structure, NaCl-like rocksalt (B1) structure and CsCl structure (B2). Two stable and important phases are B4 (wurtzite) and B1 (cubic NaCl). Under high pressure (Pt ~ 9.5 GPa), the B4 phase transforms into a cubic NaCl structure (B1 phase). This phase transition has been studied both theoretically and experimentally. There are experimental measurements showing that ZnO transforms from the B4 phase to B1 phase under high pressure and confirm the value of transition pressure Pt ~ 9.5 GPa [6][7]. The transition Phase in ZnO structure has been the subject of several theoretical studies in recent years [8]. Phase transformations involve changes of the atom positions. This action caused a change in the structural, electronic and mechanical properties. For example, the gap in the passage B4 to B1 in the case of the ZnO passes from direct to indirect.

This paper presents a study of the structural and electronic properties of ZnO in wurtzite and rocksalt structures in the framework of DFT based on the local density approximation (LDA) and the plane wave (PW) method. A relation has been established between the electronic structure and the mechanism of the transition phase in the ZnO. The paper is organized as follows: the details of the calculations were outlined in Section 2; section 3 is devoted to the results and discussions, including the structure, electronic, relation between atoms displacement and properties, and more information about the nature of the Fermi surface deformation under pressure; the main conclusions are summarized in Section 4.

2. Computational details

Theoretical calculations were performed in the framework of the Density Functional Theory (DFT) [9][10] using pseudopotentials and a plane wave basis implemented in the ABINIT package [11]. ABINIT is available under a free software licence, it allows to compute a large set of properties useful for solid state studies [12]. The valence electron wave functions were expanded in plane waves with the kinetic energy cutoff, E_{cut}, of 50 Hartree. The pseudopotentials were generated with the $3d^{10}4s^2$, and $2s^22p^4$ atomic configurations of zinc and oxygen, respectively. Norm-conserving pseudopotentials [13] of Troullier-Martins (TM) scheme [14] generated from the Fritz-Haber-Institute package [15] are used. The exchange-correlation terms were described with the local density approximation (LDA) of Ceperly and Adler [15] by the parameterization of Perdew and Zunger [17]. For the Brillouin zone sampling, a 8x8x8 kpoint distributed on a shifted Monkhorst-Pack grid was used [18]. The numerical results given below correspond to the zero-temperature results. A judicious choice of Ecut value and kpoint number is very important because if we increase this number the CPU time and memory space follow this augmentation. The Fermi surfaces have been drawn by Xcrysden [19].

3. Results and discussion

3.1. Structure properties under pressure

At ambient pressure and temperature, ZnO crystallizes in the wurtzite (B4) structure. This is a hexagonal lattice belonging to the space group $P6_3mc$ and is characterized by two interconnected sublattices of Zn^{2+} and O^{2-} in such a way that each Zn ion is surrounded by a tetrahedra of O ions, and vice-versa. This tetrahedral coordination gives rise to a polar symmetry along the hexagonal axis. This polarity is responsible for a number of ZnO properties including its piezoelectricity and spontaneous polarization. It is also a key factor in crystal growth. Wurtzite structure is characterized by three parameters including the lattice constant a, the c/a ratio, and the internal parameter u [20]. Under high pressure (~10 GPa), wurtzite ZnO transforms into a cubic NaCl structure (B1) [21]. The space group symmetry of the rocksalt type of structure is Fm-3m, which is six fold coordinated.

First, we calculate the total energy of the previous wurtzite structure as a function of the unit cell volume, then for a given unit cell volume, the unit cell shape (c/a ratio) and unit cell geometry (internal parameter u) are optimized. Second, the same work is repeated for ZnO in the cubic structure. The total calculated energy is fitted with Murnaghan equation of state (EOS) [22]. The expression of the EOS equation is:

$$E(V) = E_o - \frac{B_o V_o}{B' - 1} + \frac{B_o V}{B'}\left[\frac{(V_o/V)^{B'}}{B' - 1} + 1\right]$$

where E_o and V_o are the total energy and volume per ZnO formula unit at zero pressure. The total energies calculated as a function of the unit cell volumes E(V) for the two structures are shown in Fig. 1. The equilibrium lattice parameters, bulk modulus, and its pressure derivative are obtained by fitting the calculated E(V) data. Our calculated lattice parameters, bulk modulus B_o and its pressure derivative $B' = dB_o/dP$ together with other theoretical and experimental values are listed in Table 1. Comparing our results with the previous experimental and other theoretical data, we find that our results are in excellent agreement with them.

Table 1. Calculated and experimental lattice parameters, bulk modulus, and pressure derivative of the bulk modulus for the previous wurtzite rocksalt structures of ZnO.

Structure	a(Å)	c(Å)	Bo(GPa)	B’	Reference
Wurtzite	3.192	5.190	158.613	4.484	This study
	3.238	5.232	154	4.3	Other cal.[24]
	3.25	5.207	142.6	3.6	Exp.[25]
Rocksalt	4.226		202.961	4.526	This study
	4.272		198	4.6	Other cal.[24]
	4.275		194	4.8	Exp.[26]

In good agreement with this work and other calculations and experimental results, we show in Fig. 1 that the wurtzite phase is lower in energy than the rocksalt phase. Again, we note that a reduction of about 17.6 % in cell volume between the B4 and B1 phases. We also note an increase in the bulk modulus during the B4 to B1 transition. The increase of this large bulk modulus in the rocksalt structure can be explained by the increase of the oxygen coordination from four to six in the wurtzite to rocksalt transition phase. The variation of the bulk modulus is a precursor of the appearance of a new phase transition. In a hydrostatic pressure, the bulk modulus is associated with the volume strain

$$e_v = (e_{11} + e_{22} + e_{33})/\sqrt{3}$$

which plays the role of the order parameter of the phase change [23]. The strain components e_{ii} express the relative variations of the lattice constants.

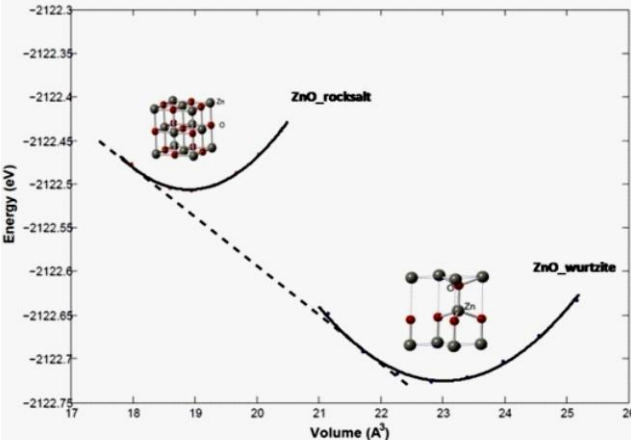

Fig. 1. Total energies as a function of the unit cell volumes for the previous wurtzite and rocksalt structures of ZnO.

3.2. Electronic properties

The band structure of a material determines several of its characteristics, in particular the electronic and optical properties. Density Functional Theory (DFT) is a powerful method to calculate, with a good agreement, the electronic properties. In particular, the band shape is typically well-reproduced by DFT. But there are also systematic errors in DFT bands when compared to experiment results. The band gap energy is underestimated in DFT calculations [27]. The solution to this problem is to judiciously choose the exchange-correlation term. Several theoretical approaches have been employed to calculate the band structure of ZnO in the different polymorphs. Experimental data have been published regarding the band structure of this material [28]. The energy band structures of the wurtzite and rocksalt ZnO at zero pressure are compared in fig. 2 along the high symmetry directions in the first Brillouin zone. The Fermi level (EF) is chosen to locate at 0 eV and coincides with the top of the valence band. The valence band maximum is found to be 0 eV at L point for rocksalt and Γ point for wurtzite structure, while the minimum conduction bands are of the order of 1.1 eV and 0.8 eV at Γ point for the rocksalt and wurtzite structures, respectively. Consequently, the rocksalt structure of ZnO has an indirect band energy gap, in contrast to the direct band energy gap for the wurtzite ZnO. The value of the energy gap for the wurtzite structure is smaller than the experimental data 3.4 eV [2]. This is a confirmation that the theoretical band gaps are underestimated within LDA in comparison with the experimental values.

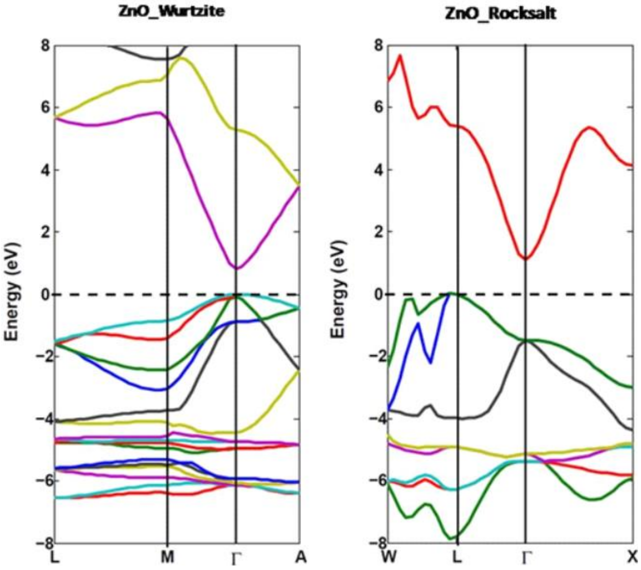

Fig. 2. Calculated band structure of wurtzite and rocksalt ZnO at zero pressure.

The properties of crystals are governed by the electrons of the highest occupied states at the Fermi level and determined by Fermi surfaces, the Fermi energy contours in momentum space [29]. Topological regulation of the Fermi surface has been an important issue in synthesizing functional materials but this topology is very complex in the most cases. An analysis based on the evolution of the Fermi surface might also provide a new perspective to understand the experimentally observed high superconduction transition temperature. We choose to illustrate the Fermi surface of ZnO under pressure (see fig. 3). The increasing pressure generates a structural phase transition and a drastic change in the Fermi surface changes of lattice constant. These differences in Fermi surface topology are mainly due to changes in inter-atomic distances and bonding angles in ZnO. Comparing the Fermi surface of ZnO in the wurtzite and rocksalt structure at 9 GPa, the flat piece of Fermi surface of wurtzite structure is bigger and flatter than rocksalt structure, which proves that rocksalt is less stable.

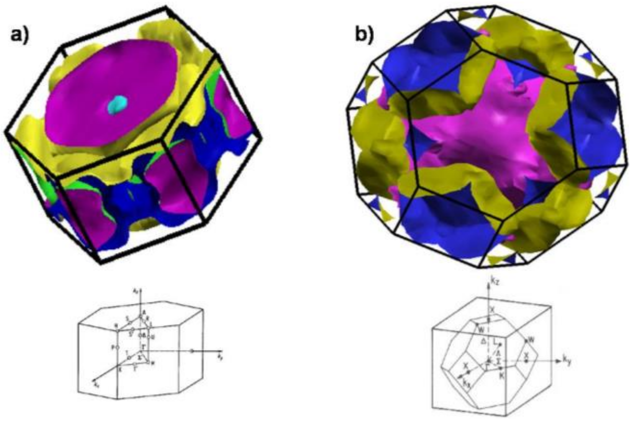

Fig. 3. Fermi surface of ZnO in the wurtzite structure (a) and under pressure in the rocksalt structure (b).

3.4. Phase transition mechanism

Zinc oxide is one of the optically transparent oxides which, doped, exhibits type-n conducting properties. ZnO is also expected to become a p-type transparent conductor under particular conditions. Although fascinating properties of such unusual material may lead to a vast area of novel applications, there are several problems which remain to be solved. Studying phase transitions of ZnO will help us to theoretically understand and, in some cases, even theoretically predict these properties. The atoms in the wurtzite structure of ZnO rearrange into the rocksalt structure once placed under extreme high pressure. In this work, we describe qualitatively how the atoms move during this transition phase. Wurtzite and rocksalt conventional cell units of ZnO contain four and eight atoms, respectively. The transition phase appears to be initiated by O atom displacements within the ZnO_4 structural pyramidal unit leading to an octahedral arrangement of the atoms (see Fig. 4). This atomic rearrangement is accompanied by a special bonding mechanism attributed to changes in nearest-neighbor bond lengths as they affect overlaps and bandwidths and to changes in symmetry as they affect p-d hybridization and interaction between the anion p states and the cation d states [28][30]. Also, the anion-cation interaction causes an increase in the interatomic Coulomb interaction to favor an ionicity over the covalent nature.

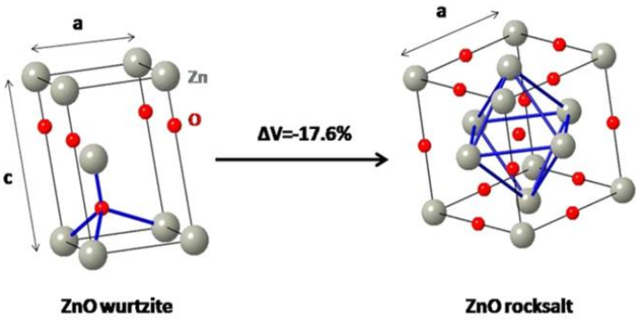

Fig. 4. Wurtzite and rocksalt conventional unit cell.

The wurtzite to rocksalt phase change is a reconstructive phase transformation and involves large atomic displacements. A large study is required for the determination of possible transition paths in phase transitions with no group-subgroup relation between their phases. It is assumed that the transformation involves an intermediate state described by a common subgroup of the symmetry groups. The possible mappings between possible structures are restricted by symmetry constraints following from the occupied atomic orbits, and tolerances for lattice strains and atomic displacements [31]. The wurtzite-rocksalt phase transition is observed in other semiconductors like SiC, GaN, AlN and CdSe at lower transition pressure compared to that of ZnO [32].

Therefore, the system can transform from one phase to another by passing through various closely related paths during the transition. This transition is accompanied by structural, electronic and thermodynamic changes. There is an intimate relation between atomic displacement and thermodynamic properties. The pressure at which a phase transition occurs can be deduced from the common tangent between wurtzite and rocksalt energy-volume curve (see Fig. 1). This method is not very accurate. However, for pressure induced phase transitions, it is more suitable to consider the Gibbs free energy. In thermodynamics, at constant temperature and pressure, the state of a system is determined by the Gibbs free energy

$$G = E + PV - TS = H - TS$$

Where respectively E and H note the internal energy and the enthalpy; T and S are the temperature and the entropy; and P and V represent pressure and volume. We are considering only the zero temperature limit in our calculation, Gibbs free energy becomes equal to the enthalpy

$$H = E + PV$$

The fit of the curves H *vs*. P has been performed by using this equation

$$G(p) = H(p) = E_o + \frac{B_o V_o}{B' - 1}\left[\left[1 + \frac{B'}{B_o}p\right]^{(B'-1)/B'} - 1\right]$$

where E_o and V_o are the energy and volume at equilibrium conditions, B_o and B' are the values of the bulk modulus and its pressure derivative at P=0. This equation of state depends on a few parameters and covering a wide range of pressures [23]. This approach relies on some knowledge or intuition of reasonable candidates crystal structures [33]. It depends on the nature of the interatomic interactions and thus provides insight into the nature of the solid-state. At the same time it determines the values of fundamental thermodynamic parameters [34]. Generally the results are in good agreement with experiments. The minimum enthalpy state is the thermodynamic condition of stability at zero temperature and at constant pressure. In fig. 5 we show also the pressure function of volume given by the expression

$$P(V) = \frac{B_o}{B'}\left[(V_o/V)^{B'} - 1\right]$$

The equilibrium pressure is determined by the intersection of the two Gibbs free energy isotherms (see Fig. 5). At Pt = 9.15 GPa, the rocksalt and wurtzite enthalpy minima become equal, meaning that the two phases can be in equilibrium with each other. This is equivalent to the common tangent construction and defines the equilibrium transition pressure Pt = 9.15 GPa.

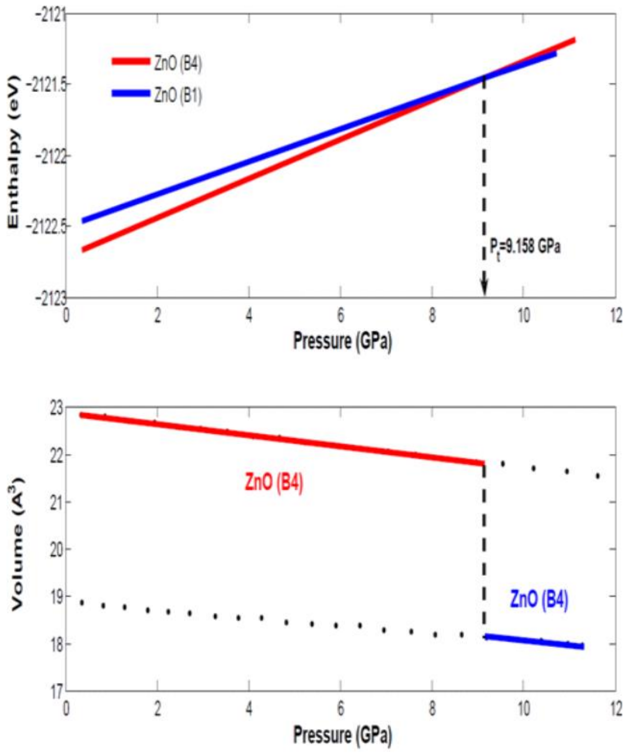

Fig. 5. Enthalpy versus pressure of the wurtzite (red) and rocksalt (blue) phases of ZnO. Calculated equations of state and transition pressure wurtzite to rocksalt structure.

4. Conclusion

First principles have been used to calculate the structural, electronic and thermodynamic properties of wurtzite and rocksalt phases of ZnO. This work has focused on the relation between phase transition, band gap, Fermi surface and atomic displacement. The structural properties including equilibrium lattice constants, bulk modulus and pressure derivative are in good agreement with other theoretical and experimental results. The value of transition pressure of the wurtzite to rocksalt phase is calculated in very good agreement with literature results.

References

[1] N. H. Nickel, E. Terukov (eds.), Zinc Oxide – A Material for Micro- and Optoelectronic Applications. Springer, Netherlands, 2005.
[2] C. Jagadish, S. Pearton (eds.), Zinc Oxide Bulk, Thin Films and Nanostructures. Elsevier, Amsterdam, 2007.
[3] D. C. Look, Mat. Sc. and Eng. B, **80,** 383 (2001).
[4] H. Morkoç, Ü. Özgür, Zinc Oxide: materials preparation, properties, and devices, WILEY, Berlin, 2008.
[5] F. J. Manjón, D. Errandonea, Phys. Status Solidi B, **246,** 9 (2009).
[6] S. -C. Yu, I. L. Spain, E. F. Skelton, Solid State Commun., **25,** 49 (1978).
[7] F. Decremps, J. Z. zhang, B. S. Li, R. C. Liebermann, Phys. Rev. B, **63,** 224105 (2001).
[8] B. Amrani, I. Chiboub, S. Hiadsi, T. Benmessabih, N. Hamdadou, Solid State Commun., **137**, 395 (2006).
[9] P. Hohenberg, W. Kohn, Phys. Rev., **136**, 864 (1964).
[10] W. Kohn, L. J. Sham, Phys. Rev., **140**, 1133 (1965).
[11] X. Gonze et al., Comput. Mater. Sci., **25,** 478 (2002). See also http://www.abinit.org.
[12] X. Gonze et al., Comput. Phys. Commun., **180,** 2582 (2009).
[13] W. C. Topp, J. J. Hopfield, Phys. Rev. B, **7**, 1295 (1973).
[14] N. Troullier, J. L. Martins, Phys. Rev. B, **43** 1993 (1991).
[15] M. Fuchs, M. Scheffler, Comput. Phys. Commun., **119,** 67 (1999).
[16] D. M. Ceperley, B. J. Alder, Phys. Rev. Lett., **45,** 566 (1980).
[17] J. P. Perdew, A. Zunger, Phys. Rev. B, **23,** 5048 (1981).
[18] H. J. Monkhorst, J. D. Pack, Phys. Rev. B, **13,** 5188 (1976).
[19] A. Kokalj, Comp. Mater. Sci. Vol. **28,** 155 (2003). Code available from http://www.xcrysden.org/
[20] W. B. Pearson, Handbook of Lattice Spacings and Structures of Metals and Alloys. Pergamon Press, Belfast, 1958.
[21] C. H. Bates, W. B. White, R. Roy, Science, **137**, 993 (1962).
[22] F. D. Murnaghan, Proc. Nat. Acad. Sci., **30,** 244 (1944).
[23] M. Hebbache, M. Zemzemi, Phys. Rev. B, **70,** 224107 (2004).
[24] F. Decremps, F. Datchi, A. M. Saitta, A. Polian, Phys. Rev. B, **68,** 104101 (2003).
[25] S. Desgreniers, Phys. Rev. B, **58,** 14102 (1998).
[26] J. M. Recio, M. A. Blanco, V. Luana, R. Pandey, L. Gerward, J. S. Olsen, Phys. Rev. B, **58,** 8949 (1998).
[27] M. S. Hybertsen, S. G. Louie, Phys. Rev. Lett., **55,** 1418 (1985).
[28] U. Ozgur et al., J. Appl. Phys., **98,** 041301 (2005).
[29] W. A. Harisson, Elementary Electronic Structure, Singapore, World Scientific, 1999.
[30] G.. C. Zhou, L. Z. Suna, J. B. Wanga, X. L. Zhong, Y. C. Zhou, Physica B: C, **403,** 2832 (2008).
[31] C. Capillas, J. M. Perez-Mato, M. I. Aroyo, J. Phys: C, **19,** 275203 (2007).
[32] K. Sarasamak, A. J. Kulkarni, M. Zhou, S. Limpijumnong, Phys. Rev. B, **77,** 024104 (2008).
[33] Orson L. Anderson, Equations of state of solids for geophysics and ceramic science, Oxford University Press, 1995.
[34] P. Vinet, J. H. Rose, J. Ferrante, J. R. Smith, J. Phys. : Condens. Matter **1**, 1941 (1989).

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[*] Corresponding author: mzemzemi@gmail.com