

## Rings, towers, cages of ZnO

A.C. Reber<sup>1</sup>, S.N. Khanna<sup>1</sup>, J.S. Hunjan<sup>2</sup>, and M.R. Beltran<sup>2,a</sup>

<sup>1</sup> Physics Department, Virginia Commonwealth University, Richmond, Va. 23284-2000, USA

<sup>2</sup> Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México A.P. 70-360, C.P. 04510, México

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**Abstract.** Theoretical electronic structure studies on  $(\text{ZnO})_n$  ( $n = 2-18, 21$ ) have been carried out to show that the transition from an elementary ZnO molecule to the bulk wurtzite ZnO proceeds via hollow rings, towers, and cages. Our first principles electronic structure calculations carried out within a gradient corrected density functional framework show that small  $\text{Zn}_n\text{O}_n$  ( $n = 2-7$ ) clusters form single, highly stable rings.  $\text{Zn}_3\text{O}_3$  and the symmetric cage  $\text{Zn}_{12}\text{O}_{12}$  are shown to be particularly stable clusters. Among larger clusters, the most stable are oblong cages,  $\text{Zn}_{15}\text{O}_{15}$ ,  $\text{Zn}_{18}\text{O}_{18}$ , and  $\text{Zn}_{21}\text{O}_{21}$ , which are reminiscent of nanotubes.

**PACS.** 31.15.Ar Ab initio calculations – 31.15.Ew Density-functional theory – 36.40.Qv Stability and fragmentation of clusters – 36.40.Cg Electronic and magnetic properties of clusters

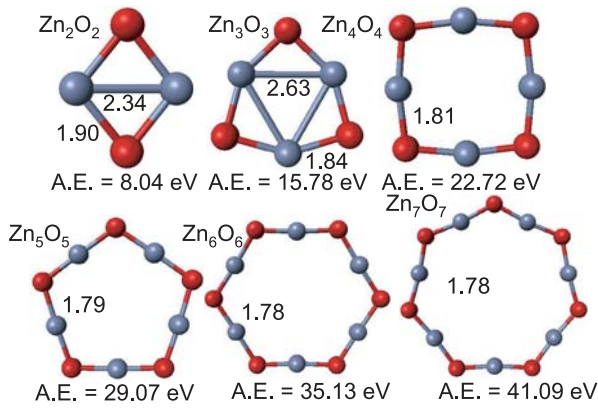
The recent discovery of one-dimensional nano-structures [1,2] in semiconducting oxides has created considerable excitement. By controlling the experimental conditions, it is now possible to form nanobelts [3], nanorods [4], nanosprings [5] and a variety of other one dimensional structures [6] of varying sizes. The interest in these systems is largely by the fact that the quantum confinement and the new topologies lead to novel behaviors. For example, the nanobelts [3] and nanosprings [4] are found to exhibit interesting piezoelectric behavior. The exciton binding energy is found to be substantially enhanced and many of these oxides can be doped with transition metal impurities to form magnetic semiconductors [7–10]. One of the materials that have drawn considerable interest is ZnO. The bulk has a wurtzite structure and is a wide band gap semiconductor. Are there different families of structures with novel properties that can be formed at smaller sizes?

The purpose of this paper is to take a bottom up approach where we consider the evolution of the structures as individual formula units (ZnO) are brought together. As previous calculations by Matxain et al. [11,12], Behrman [13], we also found that at the molecular sizes, the formula units first assemble to form hollow rings. We show that starting around  $\text{Zn}_8\text{O}_8$ , the single hollow rings begin to transform to hollow drums. An analysis of the energy binding shows that the intra-ring interactions are stronger than inter-ring bonding. As the size increases, the drums ultimately take the form of cages and oblong

cages reminiscent of nanotubes. The physical properties are shown to change discontinuously with size and many of the structures exhibit large band gaps and ionization potentials. Matxain et al. [11,12], Behrman [13] have previously reported studies on  $\text{Zn}_i\text{O}_i$  clusters containing up to 15 units. Reporting ground state geometries and their isomers. We on the other hand, focus on the evolution of bonding and physical properties with size. The geometries for our smallest cluster,  $n = 1-9$  reproduce fairly closely to those found earlier by Matxain et al. [11,12], but we found different structures where  $n = 10, 13$ , and 14. In an earlier work [10], the present authors have emphasized magnetic doping in on ZnO clusters, while the present work focuses on geometric evolution and electronic properties, and includes additional larger clusters. As we show, it is by going to larger sizes that one can truly understand the role of intra and inter-ring interactions and their effect on physical properties.

The theoretical calculations are carried out within a density functional formalism [14] that incorporates exchange and correlation effects within the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof [15]. In particular, the Gaussian basis sets are employed to construct atomic wave function while the cluster wave function is formed from a linear combination of atomic orbitals. All calculations were performed using the NRLMOL software [16–18]. Supplemental calculations were performed using the deMon code of Koester [19–22] et al. In each case, the basis set was supplemented by a diffuse Gaussian. For details, the reader is referred to original papers [16–22]. A Fair search of a total 200 initial

<sup>a</sup> e-mail: mbeltran@servidor.unam.mx



**Fig. 1.** (Color online) The structure and atomization energy of  $Zn_nO_n$   $n = 2-7$ .

geometrical configurations in the Potential Energy Surface (PES) has been performed in order to prevent being trapped in local minima in the PES.

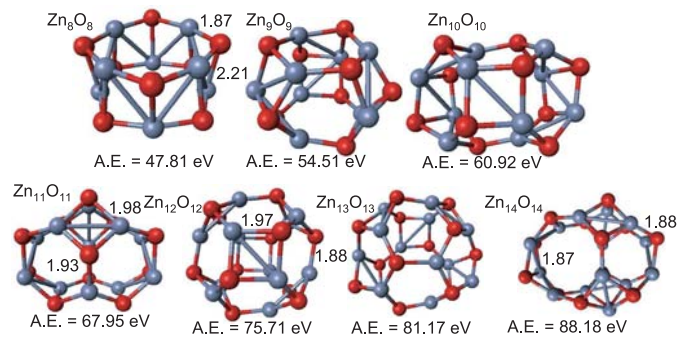
To establish the accuracy of our calculations, we first present results on a single ZnO molecule on which the experimental data exists. We find a bond length of 1.71 Å and a binding energy of 1.97 eV. The previous studies [23] also report a bond length of 1.71–1.75 Å. As to the binding energy, the available experimental data indicates that it is less than 2.8 eV. However, there are no precise estimates of the binding energy.

Figure 1 shows the ground state geometries of  $Zn_nO_n$  clusters for  $n = 2-7$ . Also given are the atomization energies (A.E.) per monomer (ZnO) calculated using

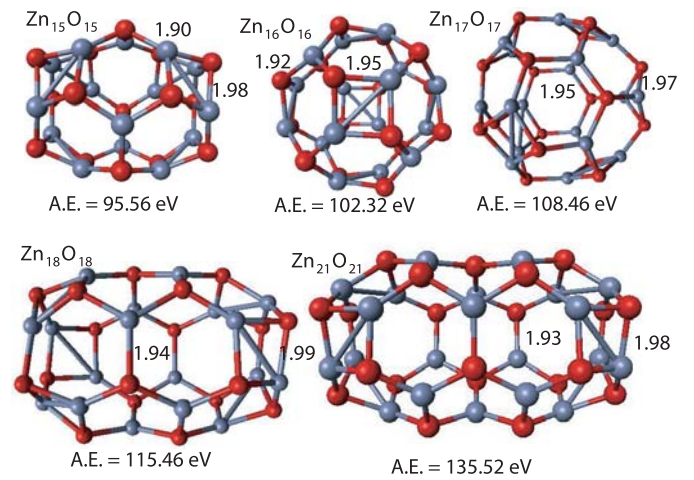
$$A.E. = nE(Zn) + mE(O) - E(Zn_nO_m) \quad (1)$$

representing the energy required to break the cluster into individual Zn and O atoms and dividing by  $n$ . In equation (1),  $E(Zn_nO_m)$  is the total energy of the cluster, and  $E(Zn)$  and  $E(O)$  are the ground state energies of the Zn and O atoms. Note that the ground states for  $Zn_nO_n$ ,  $n = 2-7$ , are open ring structures. This is particularly interesting in view of the fact that bulk ZnO has a compact Wurtzite structure. The A.E. increases monotonically with size but the maximum increase is in going from 2 to 3 indicating a particular stability of  $Zn_3O_3$ .

The formation of stable rings raises interesting questions. As  $n$  increases, do the rings continue to grow or do the basic rings begin to assemble to form extended structures? In the later case, do they form planar structures or towers? How strong are the interactions between the rings in these extended structures and do the rings maintain their identity? In Figures 2 and 3 we show the ground state structures and the A.E. for  $(ZnO)_n$  clusters containing 8–18 and 21 units. Note that unlike the smaller motifs, these structures can be looked upon as towers or cages. The ground state of  $(ZnO)_8$  is a tower composed of two  $Zn_4O_4$  units while  $(ZnO)_9$  is a cage composed of 2 and 3 unit rings. The ground state of  $Zn_{10}O_{10}$  is a distorted cages made of 4,6 and one 8 membered rings.



**Fig. 2.** (Color online) The structure and atomization energy of  $Zn_nO_n$   $n = 8-14$ .



**Fig. 3.** (Color online) The structure and atomization energy of  $Zn_nO_n$   $n = 15-18, 21$ .

$Zn_{11}O_{11}$  is another distorted cage.  $Zn_{12}O_{12}$  is a highly stable truncated octahedron.  $Zn_{13}O_{13}$  and  $Zn_{14}O_{14}$  are distorted cages made primarily out of 4 and six membered rings with one and two eight membered ring respectively. While in the above we have reported the ground state geometries, are there bigger rings and towers that form meta-stable species.

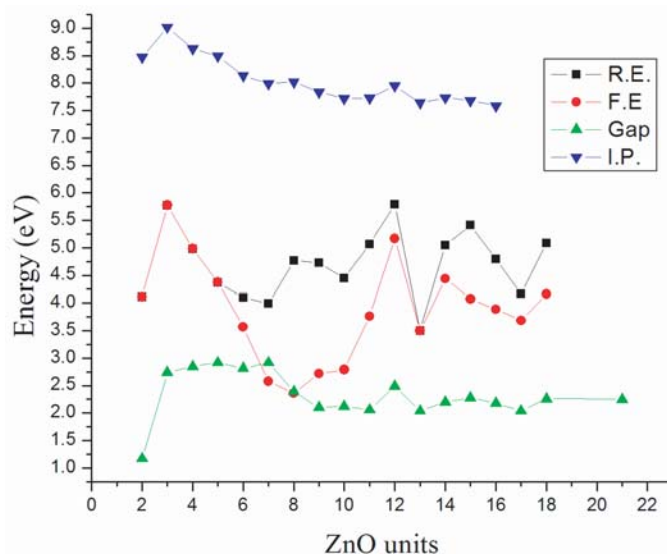
Figure 3 shows the  $Zn_nO_n$  clusters where  $n = 15-18$ , and 21. The  $n = 15, 18$ , and 21 clusters are tubular cages made entirely of 4 and 6 membered rings.  $Zn_{16}O_{16}$  is a truncated cuboctahedron and  $Zn_{17}O_{17}$  is a distorted cage.

We now consider the stability of the clusters. Figure 4 shows the R.E. (removal energy), fragmentation energy (F.E.) HOMO-LUMO gap, and ionization potential (I.P.). The R.E. was calculated using the equation

$$R.E. = E(Zn_{n-1}O_{n-1}) + E(ZnO) - E(Zn_nO_n). \quad (2)$$

While the F.E. was calculated by, examining all the fragmentation pathways for each cluster by calculating the minimum fragmentation energy

$$F.E. = E(Zn_{n-m}O_{n-m}) + E(Zn_mO_m) - E(Zn_nO_n) \quad (3)$$



**Fig. 4.** (Color online) The removal energy (R.E.), fragmentation energy (F.E.), HOMO-LUMO gap, and adiabatic ionization potential (I.P.) of the  $Zn_nO_n$  clusters.

required to break a cluster of size  $n$  into fragments of size  $n - m$  and  $m$ .

Note that at small sizes the R.E. and F.E. peak at  $Zn_3O_3$ , indicating the stability of the recurring  $Zn_3O_3$  motif. The next peak occurs at  $Zn_8O_8$  and is due to the formation of 10 additional Zn-O bonds in the progression from the  $Zn_7O_7$  ring to the  $Zn_8O_8$  stacked rings, and the 6 and 4 membered ring structure of  $Zn_9O_9$ . A small drop in R.E. follows at  $Zn_{10}O_{10}$  where an 8 membered ring is added. The second largest peak in R.E. and F.E. is at  $Zn_{12}O_{12}$  which indicates that this cluster is especially stable and a prospective candidate for cluster assembly. Note that  $Zn_3O_3$  is a particularly stable species.  $Zn_{12}O_{12}$  is composed of 8  $Zn_3O_3$  rings joined by 6  $Zn_2O_2$  squares and presents a cuboctahedral structure. Its stability can therefore be linked to the preponderance of  $Zn_3O_3$  rings. In addition it is a highly symmetric structure thereby reducing any strain. It is also interesting to point out that the ground state geometry of a 24 unit species composed of 12 +2 and 12 -2 charges is also a truncated cuboctahedron [24]. In this regard, the Mulliken charge analysis indicates a charge of +0.75 and -0.75 and it is possible that charge plays a role in stabilizing the structure.

The electronic properties of ZnO clusters exhibit interesting progressions, as shown in Figure 4. The planar structure ( $n = 2-7$ ) have generally larger HOMO-LUMO gaps partly due to the low coordination of Zn and O sites. Interestingly, the HOMO-LUMO gap shows a peak at  $n = 12$  indicating the electronic stability of the cuboctahedral cage. Of further note, there are increases in both the band gap and R.E. at in the 12, 15, 18, 21 series. The relative stability of these clusters may hint at the observed nanowires. While it is expected that the solid phase wires have a different structure than these clusters,

observed directionality in these clusters may be related to the nucleation of similarly shaped ZnO crystals.

To conclude, we have confirmed that while bulk ZnO has a compact wurtzite structure, the ground state geometries of small  $Zn_nO_n$  clusters for  $n = 2-7$  are rings. In particular,  $Zn_3O_3$  is shown to be a very stable species. Starting from  $Zn_8O_8$ , the highly stable rings grow by assembling the rings to form towers. We would like to point out that the progressions outlined here are not specific to zinc oxide. For example, Castleman [25] and co-workers had speculated the possibility of a tower structure for  $Mn_{12}O_{12}$  based on their fragmentation studies of  $Mn_nO_n$  clusters. Similarly, one of the authors of this paper had recently suggested the possibility [26] of rings in  $Fe_nO_n$  and fully saturated rings in some of the  $Cr_nO_{3n}$  clusters [27]. Further, we would like to extend the connection between the stability of 15, 18, and 21 hollow tubes and their relationship with nanowires. It is our hope that the present investigations would stimulate more coordinated effort in the search of rings and towers and cages in oxides of other materials. We are currently carrying out more detailed studies of the electronic, magnetic, and chemical properties of these new families.

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