

## Cobalt doped rings and cages of ZnO clusters: Motifs for magnetic cluster-assembled materials

A.C. Reber<sup>a,\*</sup>, S.N. Khanna<sup>a</sup>, J.S. Hunjan<sup>b</sup>, M.R. Beltrán<sup>b</sup>

<sup>a</sup> *Physics Department, Virginia Commonwealth University, Richmond, VA 23284-2000, USA*

<sup>b</sup> *Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de Mexico, A.P. 70-360, C.P. 04510, México D.F., Mexico*

Received 19 June 2006; in final form 10 July 2006

Available online 21 July 2006

### Abstract

First principles electronic structure studies on pure and doped  $Zn_nO_n$  clusters have been carried out to identify elementary motifs with potential for cluster materials. In pure clusters  $Zn_{12}O_{12}$  cages are shown to be particularly stable. When doped with a single Co or Fe atom, the doped units carry a magnetic moment of  $3.0 \mu_B$  and  $4.0 \mu_B$ , respectively. Doping of  $Zn_{12}O_{12}$  with two Co sites leads to ferromagnetically coupled Co moments due to direct exchange interaction. It is proposed that the assemblies of such multiple doped units may lead to semiconductors with larger doping than attainable in bulk or films.

© 2006 Elsevier B.V. All rights reserved.

One of the significant developments in the field of clusters and nanoscale materials is the possibility of synthesizing nanoscale materials where individual stable clusters serve as the elementary building blocks [1–6]. As the properties of clusters can be controlled by changing size and composition, such a synthesis may offer the potential to design materials with desirable traits. The first step towards such a goal is to identify designer clusters that are interesting and yet so stable as to maintain their identity and individual characteristics upon assembly. The discovery of fullerenes and the eventual synthesis of fullerene materials [7] with novel properties is just one example of such a possibility. Extending the fullerene experience to metal and semiconductor systems is therefore an important undertaking. Indeed, over the past few years, several stable metal clusters with novel properties have been identified and it has recently been possible [8] to synthesize materials based on metallic cluster units. The purpose of this Letter is to extend this experience to magnetic semiconductors with two objectives: (1) To identify semiconductor motifs that are particularly stable and amenable to cluster material

synthesis. (2) To show that doping of these units with transition metal atoms results in magnetic units that might lead to a new class of doped magnetic semiconductors. The cluster approach overcomes naturally the limitations of doping levels encountered in synthesis of such materials by doping bulk semiconductors.

Dilute magnetic semiconductors (DMS) have recently attracted considerable attention [9–11]. While the initial interest of DMS focused on doped GaN, recent interest has shifted to ZnO as it is easier to synthesize ZnO single crystals [12]. Bulk ZnO has a wurtzite structure and is a wide band gap semiconductor [12] with a direct band gap of around 3.3 eV. It is found [13–18] that when the bulk material or films are doped with transition metal impurities, they substitute at the Zn sites and the resulting material exhibits magnetic order. In fact, recent experiments on (110) oriented ZnO films [18] show that the films containing 5 at.% Sc, Ti, V, Fe, Co, and Ni are all ferromagnetic but the magnetic moment is highest for Co with a value of  $2.6 \mu_B$  per atom. As recent work shows [19], the magnetic properties are sensitive to the preparation method and the level of doping. Further, the magnetization is highly anisotropic [14] and varies by almost a factor of three with the orientation of the applied field. While the

\* Corresponding author.

E-mail address: [acreber@vcu.edu](mailto:acreber@vcu.edu) (A.C. Reber).

findings of magnetism in bulk and in films are exciting, the observation of complex magnetic order and the limitation in the amount of doping do present problems.

In this Letter, we focus on pure ZnO clusters and ZnO doped with Co to examine the possibility of a bottom up approach where the nanoscale material is synthesized using size selected stable clusters as the building blocks. Our approach involves three steps: (1) To identify which  $Zn_nO_n$  motifs are stable, resistant towards fragmentation, and relatively inert to serve as building blocks? (2) To explore which elements can dope these clusters and lead to highly magnetic species? (3) Examine the magnetic character of motifs doped with multiple Co atoms to examine the location of Co sites and their coupling in a single motif? We first demonstrate that unlike bulk compact arrangement, the geometrical arrangements in the pure clusters evolve from single rings to pillars to hollow cages. A  $Zn_3O_3$  ring, a  $Zn_9O_9$  pillar/cage, and a  $Zn_{12}O_{12}$  cage are shown to be particularly stable. The excitement in these structures stems from our observation that when doped with transition elements, the resulting entities substitutes at the Zn site and are magnetic. Guided by these observations, we primarily focus on Co doping and show that the magnetic moments per doped site can be considerably higher than attainable in the bulk. In clusters with multiply doped Co atoms, the magnetic coupling depends on the location of Co sites. For cases where the Co sites are near neighbor and interact directly, the magnetic coupling is ferromagnetic. On the other hand, when Co sites are separated, the ferro and antiferromagnetic states are degenerate, similar to the recently reported magnetic order in Co-doped ZnO nanoparticles [19]. Recent work has shown that similar doping results in antiferromagnetic coupling in Manganese [20]. What is exciting is that in small sizes, the ease of structural rearrangements indeed favors structures with enhanced Co–Co interaction, which in turn stabilize the ferromagnetic state. This coupled with the fact that the bottom up approach allows multiple doping of Co atoms, suggests that it may lead to new family of magnetic semiconductors. We also examine doping with a single Fe site that is found to carry a spin moment of  $4.0 \mu_B$  per atom, higher than currently attainable in bulk films.

The theoretical calculations are carried out within a density functional formalism [21] that incorporates exchange and correlation effects within the generalized gradient approximation of Perdew et al. [22]. Gaussian basis sets are employed to construct atomic wave function while the cluster wave function is formed from a linear combination of atomic orbitals. The calculations were carried out using the Naval Research Laboratory Molecular Orbital Library set of codes developed by Pederson and co-workers [23–25]. For the calculations, we used a 6s, 5p and 3d basis set for the O atoms and 7s, 5p and 4d basis for transition metal atoms [25]. In each case, the basis set was supplemented by a diffuse Gaussian. We also carried out supplementary calculations using DE DEMON software [26] with the quadruple zeta valence polarized basis sets [27].

To establish the accuracy of our calculations, we first compare our results on a ZnO molecule with available studies. We find a bond length of  $1.71 \text{ \AA}$  and a binding energy of  $1.97 \text{ eV}$ . The previous studies [28] also report a bond length of  $1.71 \text{ \AA}$ . As to the binding energy, the available experimental data indicates that it is less than  $2.8 \text{ eV}$ .

Fig. 1 shows the ground state geometries of  $Zn_nO_n$  clusters for  $n = 2–16$ , and 21. Note that the ground states for  $Zn_nO_n$  containing 2–7 are all open ring structures. This is particularly interesting in view of the fact that bulk ZnO has a compact wurtzite structure. Beyond  $n = 7$ , the basic rings begin to assemble to form extended structures. The ground state of  $Zn_8O_8$  is a tower built out of two  $Zn_4O_4$  units. Starting at  $n = 9$ , the tower begin to develop cage like features built from  $Zn_2O_2$  and  $Zn_3O_3$  rings. The structure of  $Zn_{12}O_{12}$  is a stable cage containing 4 and 6 atom rings. The single cages continue to grow for  $n = 13, 14, 15$ , and 16 and the ground state of  $Zn_{21}O_{21}$  is a double cage built out of two  $Zn_{12}O_{12}$  cages sharing a common  $Zn_3O_3$  ring. Our results on the geometries of smaller clusters also agree with previous theoretical studies [29–31].

To understand the evolutions in geometries and to identify the particularly stable species, we now focus on the progression in the energetics. We calculated the atomization energy (A.E.) indicating the energy required to break a  $(ZnO)_n$  cluster into  $n$  Zn and  $n$  O atoms and the removal energy (R.E.) that represents the energy required to remove a ZnO unit from the cluster, which is an indicative of the stability. The A.E. was calculated using the equation

$$\text{A.E.} = nE(\text{Zn}) + nE(\text{O}) - E(\text{Zn}_n\text{O}_n) \quad (1)$$

while R.E. was calculated using the equation

$$\text{R.E.} = E(\text{Zn}_{n-1}\text{O}_{n-1}) + E(\text{ZnO}) - E(\text{Zn}_n\text{O}_n) \quad (2)$$

In addition, we calculated the vertical and adiabatic ionization potentials, adiabatic electron affinities, and the HOMO–LUMO gap that are all electronic signatures to the stability and reactivity.

Fig. 1 shows the A.E. while Fig. 2 shows the variation of the R.E. as a function of size. From A.E. in Fig. 1, one can calculate the A.E. per formulae unit ZnO, and one finds that it increases monotonically with size. However, the amount of increase changes with size. There is a significant gain in energy in going from  $n = 2$  to 3 while the energy gain in going from  $n = 3$  to 4 is less indicating that  $Zn_3O_3$  is a very stable species. The next stable clusters are  $Zn_8O_8$  and  $Zn_9O_9$  that are marked by a column and distorted column structure. Among cage species,  $Zn_{12}O_{12}$  and  $Zn_{15}O_{15}$  are particularly stable. While R.E. represents stability towards addition of individual formulae unit, one can also assess the stability by examining the minimum energy required to break a cluster into two fragments. To this end, we examined the fragmentation pathways for each cluster by calculating the minimum fragmentation energy (F.E.)

$$\text{F.E.} = E(\text{Zn}_{n-m}\text{O}_{n-m}) + E(\text{Zn}_m\text{O}_m) - E(\text{Zn}_n\text{O}_n) \quad (3)$$

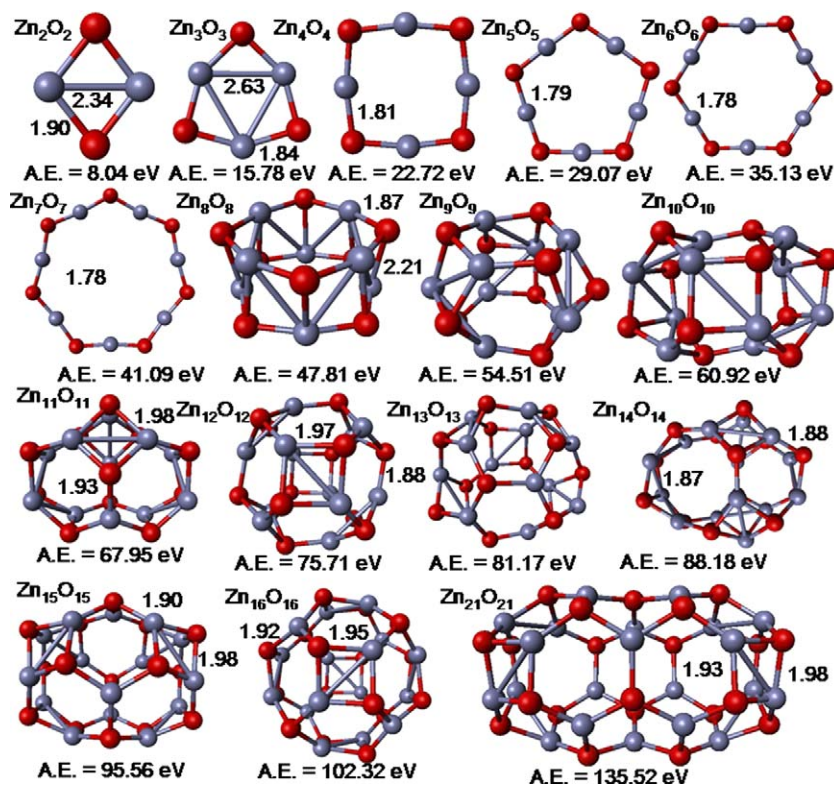


Fig. 1. Calculated ground state geometries for  $Zn_nO_n$  where  $n = 2-16, 21$ . The total atomization energy in eV and selected bond lengths in Angstroms are listed.

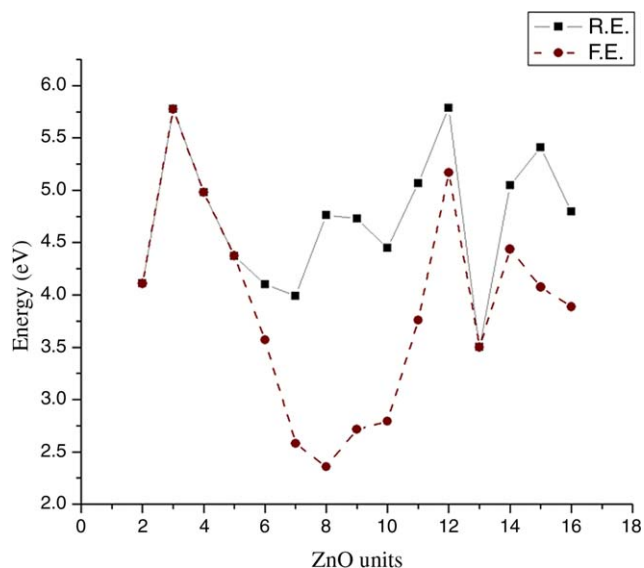


Fig. 2. The ZnO removal energy (R.E.) (Eq. (2)) and fragmentation energy (F.E.) (Eq. (3)) as a function of cluster size.

required to break a cluster of size  $n$  into fragments of size  $n - m$  and  $m$ . The results are shown by the red line in Fig. 2.  $Zn_3O_3$  and  $Zn_{12}O_{12}$  emerge as stable species in this analysis as well. We also found that  $Zn_3O_3$  and  $Zn_{12}O_{12}$  had high ionization potentials of 9.02 and 7.95 eV, respectively, and a large HOMO–LUMO gap of 2.74 and 2.49, respectively. The stability through R.E. and F.E. coupled

with high HOMO–LUMO gaps are signatures that these units may be potential building blocks for forming cluster materials.

Having identified the stable units, we now examined the possibility of magnetic building blocks. To this end, we examined the effect of adding a Co atom to stable motifs. The additional atom can occupy an exterior site or substitute for a Zn site. In the later case, the replaced Zn atom can remain bound to the cluster or dissociate away. The energetics of the three possibilities are shown in Fig. 3 where we show the atomization energies of the pure  $Zn_3O_3$ , a  $Zn_3O_3$  with a Co located at an external site, a  $ZnZn_2CoO_3$  cluster with a Co substituting for a Zn site and the displaced Zn occupying the outside site, and that of a  $Zn_2CoO_3$  cluster. Note that the Zn atom is weakly bound to the cluster relative to the displaced structure. This is consistent with findings in the bulk and on films where Co is known to substitute at the Zn sites. Note that the substitution does induce structural changes i.e. the replacement introduce a change in bond length from 1.84 Å to 1.79 Å. For bulk systems, the lattice distortions are energetically unfavorable and this may limit the amount of doping. In clusters, on the other hand, the ease of structural rearrangements does not preclude multiple Co substitutions. What is interesting is that the Co site has a spin moment of  $3.0 \mu_B$ . This is higher than the moment per Co of  $2.6 \mu_B$  found for Co impurities in bulk. Next, one wonder about the coupling between the spin moments as multiple Co atoms are substituted. To

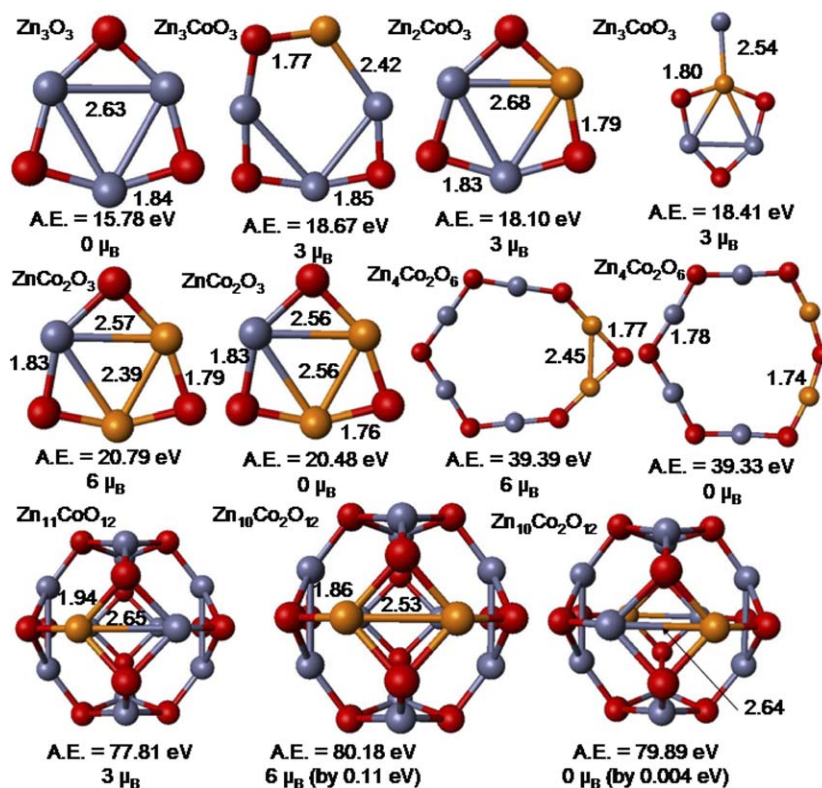


Fig. 3. Calculated energies and magnetic moments of selected Cobalt doped clusters. The total atomization energy in eV and selected bond lengths in Angstrom are listed.

answer this, we first replaced two Zn sites in  $Zn_3O_3$  by Co atoms and Fig. 3 shows the relative stability of the ferromagnetic and antiferromagnetic arrangements. One notes that the ferromagnetic arrangement is more stable. As the two Co atoms in a  $ZnCo_2O_3$  cluster are close to each other, one might wonder if the Co sites also cluster in larger sizes, and favor ferromagnetic coupling. This can be answered by taking a larger cluster and in Fig. 3 we show the ground state of a  $Zn_4Co_2O_6$  ring where the Co are again adjacent and are ferromagnetically coupled! Note that the distance between the two substituted Zn sites is reduced upon the insertion of Co atoms to 2.45 Å again suggesting a direct Co–Co coupling.

Does the behavior in rings extend to cages? To this end, we replaced one and two Zn atoms in  $Zn_{12}O_{12}$  cage by Co atoms at various locations. The ground states are shown in Fig. 3 and the Co sites again have a moment of 3.0  $\mu_B$  each. Again note that in the ground state, the Co sites are near to each other with a Co–Co separation of 2.53 Å as opposed to 2.70 Å between the original Zn atoms. A higher energy structure with Co atoms occupying sites farther from each other, shown in Fig. 3, had nearly degenerate ferromagnetic and antiferromagnetic states. These results suggest that Co–Co coupling stabilizes the ferromagnetic state. To further ascertain that Co–Co interactions are needed to stabilize a ferromagnetic state, we took a dual approach. First, through a Mulliken population charge analysis and visual inspection of each molecular orbital, we identified

the molecular orbitals that have appreciable contributions from both Co atoms. As we will show, these orbitals belong to the majority spin state. Secondly we examined the charge density in these orbitals to examine if there is a bond between the two Co sites that would indicate a direct coupling. Fig. 4a shows the one electron levels in  $Co_2Zn_{10}O_{12}$ . The highlighted (orange) orbitals were found to have appreciable charge density on both Co atoms and hence, could signify either direct Co–Co interaction or Co–Co interaction mediated through the host. Note that these orbitals belong to majority spin and hence play the vital role in stabilizing the ferromagnetic order. To demonstrate that there is direct bonding between Co-sites in the ferromagnetic state, Fig. 4b shows the electronic charge density in a representative orbital showing charge along the Co–Co bond. An alternate approach to identify chemical bonds between a pair of atoms is to look for critical points in charge density [32]. Consequently, we analyzed the total charge density to look for maxima in the charge density [32]. We found a critical point along the Co–Co bond. In combination with our earlier results on rings, all this indicates that the direct coupling between Co sites stabilizes the ferromagnetic state and hence may be the first step towards generating DMS. It is important to note that such clustering is favored by the overall energetics, and involves shortening of the original Zn–Zn bond. The last question that remains to be answered is whether the magnetic moment can be further enhanced by substituting another metal.

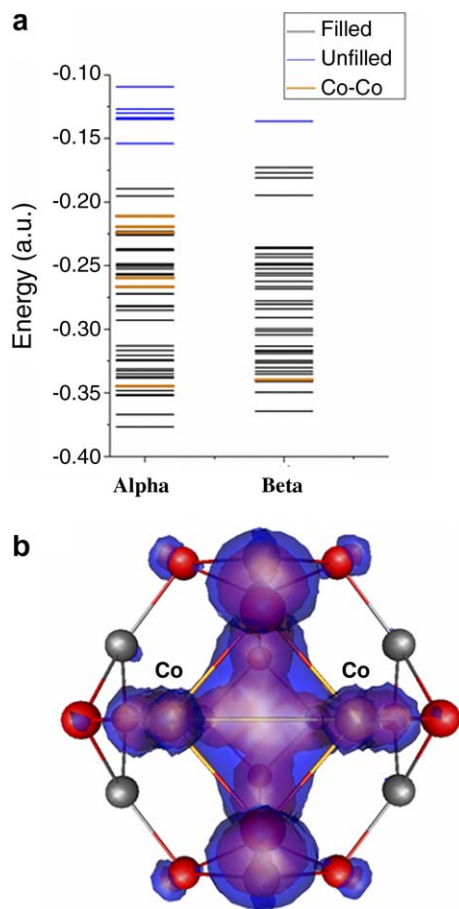


Fig. 4. (a) One electron energy levels for  $\text{Zn}_{10}\text{Co}_2\text{O}_{12}$ . The light levels indicate levels that have appreciable contribution from both Co sites. (b) The charge density coming from a light (orange) orbital. Note the pile up of charge between Co-sites indicative of direct Co–Co bonding in  $\text{Zn}_{10}\text{Co}_2\text{O}_{12}$  cluster.

To this end, we suited the magnetic moment of  $\text{FeZn}_{11}\text{O}_{12}$  cluster with Fe substituting at the Zn sites. The resulting ground state structure is magnetic with a moment of  $4.0 \mu_B$ .

To conclude, we have demonstrated that the structural motifs in small  $(\text{ZnO})_n$  clusters evolve from single rings to towers to spherical cages. These progressions are not specific to ZnO but seem to underline other metal-oxide systems. For example, the earlier work by Castleman and co-workers had speculated tower arrangements in  $\text{Mn}_n\text{O}_n$  clusters [33]. Similarly, one of the authors of this Letter had recently suggested the possibility of rings and towers in  $\text{Fe}_n\text{O}_n$  [34] and fully saturated rings in some of the  $\text{Cr}_n\text{O}_{3n}$  clusters [35]. What is truly exciting is that some of the new stable structural motifs exhibit ferromagnetic order when doped with transition metals like Co and Fe. For multiple doping, structures with coupled transition metal atoms are energetically more stable and the direct coupling between the transition metal impurities favors the ferromagnetic state offering a dual benefit. Finally, we would like to add that while the current studies offer the first step towards nano-cluster assemblies, the next step is to put such clusters together to create such materials. We

are currently working towards such an objective and these will be reported later.

### Acknowledgements

ACR and SNK acknowledge support from the Department of Energy Grant DE-FGO2-96ER45579. MRB acknowledges support from IN1150306, and CONACYT 40393-F.

### References

- [1] S.N. Khanna, P. Jena, *Phys. Rev. Lett.* 69 (1992) 1664.
- [2] D.E. Bergeron, A.W. Castleman Jr., T. Morisato, S.N. Khanna, *Science* 304 (2004) 84.
- [3] D.E. Bergeron, P.J. Roach, A.W. Castleman Jr., N.O. Jones, S.N. Khanna, *Science* 307 (2005) 231.
- [4] J. Zhao, R.-H. Xie, *Phys. Rev. B* 68 (2003) 035401.
- [5] W. Zheng, J.M. Nilles, D. Radisic, K.H. Bowen, *J. Chem. Phys.* 122 (2005) 071101.
- [6] T. Baruah, M.R. Pederson, R.J. Zope, M.R. Beltran, *Chem. Phys. Lett.* 387 (2004) 476.
- [7] W. Kratschmer, L.D. Lamb, F. Fostiropoulos, D.R. Huffman, *Nature* 347 (1990) 354.
- [8] A.W. Castleman Jr., S.N. Khanna, A. Sen, A.C. Reber, in press.
- [9] H. Ohno, *Science* 281 (1998) 951.
- [10] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* 287 (2000) 1019.
- [11] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, K. Ohtani, *Nature (London)* 408 (2000) 944.
- [12] U. Ozgur, A. Teke, C. Liu, S.-J. Cho, H. Morkoc, H.O. Everitt, *J. Appl. Phys.* 98 (2005) 041301.
- [13] M.H.F. Sluiter, Y. Kawazoe, P. Sharma, A. Inoue, A.R. Raju, C. Rout, U.V. Waghmare, *Phys. Rev. Lett.* 94 (2005) 187204.
- [14] K. Sato, H. Katayama-Yoshida, *J. Phys. E* 10 (2001) 251.
- [15] P. Sharma, A. Gupta, K.V. Rao, F.J. Owens, R. Sharma, R. Ahuja, J.M.O. Guillen, B. Johansson, G.A. Gehring, *Nat. Mater.* 2 (2003) 673.
- [16] K. Ueda, H. Tabata, T. Kawai, *Appl. Phys. Lett.* 79 (2001).
- [17] J.H. Park, M.G. Kim, H.M. Jang, S. Ryu, Y.M. Kim, *Appl. Phys. Lett.* 84 (2004) 1338.
- [18] M. Venkatesan, C.B. Fitzgerald, J.G. Lunney, J.M.D. Coey, *Phys. Rev. Lett.* 93 (2004) 177206.
- [19] B. Martinez, F. Sandiumenge, L. Balcells, F. Fontcuberta, F. Sibiude, C. Monty, *J. Appl. Phys.* 97 (2005) 10D311.
- [20] H. Liu, S. Wang, G. Zhou, J. Wu, W. Duan, *J. Chem. Phys.* 124 (2006) 174705.
- [21] W. Kohn, L.J. Sham, *Phys. Rev.* 140 (1965) A1133.
- [22] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [23] M.R. Pederson, K.A. Jackson, *Phys. Rev. B* 41 (1990) 7453.
- [24] K. Jackson, M.R. Pederson, *Phys. Rev. B* 42 (1990) 3276.
- [25] D. Porezag, M.R. Pederson, *Phys. Rev. A* 60 (1999) 2840.
- [26] A.M. Köster et al., DEMON2K, NRC, Canada, 2003.
- [27] F. Weigend, F. Furche, R. Ahlrichs, *J. Chem. Phys.* 119 (24) (2003) 12753.
- [28] G.L. Gutsev, B.K. Rao, P. Jena, *J. Phys. Chem. A* 104 (2000) 5374.
- [29] J.M. Matxain, J.E. Fowler, J.M. Ugalde, *Phys. Rev. B* 62 (2000) 053201.
- [30] J.M. Matxain, J.M. Mercero, J.E. Fowler, J.M. Ugalde, *JACS* 125 (2003) 9494.
- [31] Y. Ohta, T. Haga, Y. Abe, *Jpn. J. Appl. Phys.* 36 (1997) L1040.
- [32] G. Merino, A. Vela, T. Heine, *Chem. Rev.* 105 (2005) 3812.
- [33] P.J. Ziemann, A.W. Castleman Jr., *Phys. Rev. B* 46 (1992) 13480.
- [34] N.O. Jones, B.V. Reddy, F. Rasouli, S.N. Khanna, et al., *Phys. Rev. B* 72 (2005) 165411.
- [35] D.E. Bergeron, A.W. Castleman Jr., N.O. Jones, S.N. Khanna, *Nano Lett.* 4 (2004) 261.