

Atomic Clusters: A Unique Building Motif for Future Smart Nanomaterials

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Abstract—The fundamental issue in understanding the origin and growth mechanism of nanomaterials, from a fundamental unit is a big challenging problem to the scientists. Recently, an immense attention is generated to the researchers for prediction of exceptionally stable atomic cluster units as the building units for future smart materials. The present study is a systematic investigation on the stability and electronic properties of a series of bimetallic (semiconductor-alkaline earth) clusters, viz., B_xMg_3 ($x=1-5$) is performed, in search for exceptional and/ or unusual stable motifs. A very popular hybrid exchange-correlation functional, B3LYP along with a higher basis set, viz., 6-31+G[d,p] is employed for this purpose under the density functional formalism. The magic stability among the concerned clusters is explained using the jellium model. It is evident from the present study that the magic stability of B_4Mg_3 cluster arises due to the jellium shell closure.

Keywords—Atomic Clusters, Density Functional Theory, Jellium Model, Magic Clusters, Smart Nanomaterials.

I. INTRODUCTION

RECENTLY, atomic and molecular clusters are found to be potential candidates for designing novel nanomaterials [1]-[6], as a consequence of the discovery of fullerene [7]. The most exciting fact is that atomic clusters of sub-nano or nano-scale dimensions exhibits drastic change in the physicochemical properties with respect to their bulk counterpart, due to the effect of quantum confinement [8]. This important behavior of nano-scale materials is found to be very useful in various kinds of applications to the mankind over the last two decades [1]-[4]. Various theoretical and experimental effort have been tendered on designing, synthesis, characterization and application for either carbon based nanomaterials or its inorganic analogues with different conformations, e.g., wires, rods, cones, quantum dots, tubes, graphene or any customized crystal shapes [9]-[12].

It is noticed that the cluster materials are metastable in many cases and have a tendency to coalesce. To overcome such situation, the main focus of the researchers is offered on the search of clusters with unusual or exceptional stability and/or useful physicochemical properties. The jellium is a quantum mechanical model of interacting electrons within an infinite volume of space and neutralized with an artificially assumed uniformly distributed background positive charge [13]. The jellium is usually treated within the density functional theory (DFT) [14]-[16], since at zeroth temperature the properties of a jellium depend solely on electron density (ρ) [13]. W. D. Knight et al. [17] have observed a series of

magic numbers (size of the clusters) for the free sodium clusters as 2, 8, 18, 20, 34, 40, ... etc. from their experimental mass spectra. Based on the jellium model, they explained the stability of those magic clusters considering the energy levels of valence electrons for such a charge distribution as $1S^21P^61D^{10}2S^21F^{14}2P^6...$, which implies the shell closure for those magic clusters. The concept of magic valence series is now extended beyond alkali metal clusters towards various other all-metal or heteroatomic clusters, e.g., Al_{13}^- , Mg_4 , $Al_{13}K$, Si_4Mg_3 etc. [18]-[20] The exceptional stable cluster motifs may have potency for utilizing as the building blocks for designing novel cluster assembled materials [3], [21]. The cluster assembled materials are solids, where atomic clusters serve as the fundamental units with tunable properties at such scale.

Recently, it has also been reported that, the combinations of group III(A) and V(A), II(A) and VI(A), III(A)-semiconducting elements and alkali/alkaline-earth metals etc. to form bimetallic clusters/alloys often exhibit useful properties and applications [1]-[4], [21]. In this line, no attempt has been taken so far for alkaline-earth metal and boron bimetallic clusters. The purpose of the present work is a detail study on the geometries, electronic properties and search for any unusual and/or exceptional stable cluster building motifs from a series of bimetallic (semiconductor – alkaline earth) clusters, B_xMg_3 ($x=1-5$). The structure and stability of these clusters is monitored with a sincere effort, considering various physicochemical properties, e.g., energy gain in adding a B atom (ΔE_B) to the previous sizes, energy gap between the highest occupied and lowest unoccupied molecular orbitals (HLG), ionization potential (IP), chemical hardness (η), one-electron energy levels (OEL) etc., and explained under jellium framework.

II. THEORETICAL METHODS

The energy gain (ΔE_B) in forming B_xMg_3 clusters by adding a boron atom to the previous $B_{x-1}Mg_3$ ($x=1-5$) size is giving as,

$$\Delta E_B = E(B) + E(B_{x-1}Mg_3) - E(B_xMg_3) \quad (1)$$

where $E(B_xMg_3)$, $E(B_{x-1}Mg_3)$ and $E(B)$ are the total energies of the B_xMg_3 , $B_{x-1}Mg_3$ clusters and of the B atom, respectively.

Using Koopmans' finite difference approximation [16], ionization potential (IP) and electron affinity (EA) can be expressed in terms of the highest occupied (ϵ_{HOMO}) and the lowest unoccupied (ϵ_{LUMO}) molecular orbital energies as,

$$IP \approx -\epsilon_{HOMO} ; EA \approx -\epsilon_{LUMO} \quad (2)$$

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To account for the stability of a molecule, Pearson [22] has introduced an important parameter, viz., ‘chemical hardness’. For an N -electron system, the second derivative of energy with respect to N , keeping external potential $v(\vec{r})$ fixed, is considered to be a measure of the chemical hardness [22]:

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} \quad (3)$$

The hardness can be expressed in terms of ϵ_{HOMO} and ϵ_{LUMO} as [16]:

$$\eta \approx \frac{IP - EA}{2} \approx \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2} \quad (4)$$

III. COMPUTATIONAL DETAILS

The theoretical investigations are carried out using a very reliable gradient corrected approach within the density functional theory (DFT) framework [14]-[16]. A molecular orbital approach, using a linear combination of atomic orbitals, is applied to probe the electronic structure. The actual calculation is performed using the implementation in the GAUSSIAN 09 [23] program. For exchange and correlation functional, we have used a very popular and reliable hybrid functional, B3LYP which has been introduced by A. D. Becke in 1993 [24]. An all electron calculation with the 6-31+G[d, p] basis sets is employed [25] for calculations. A large number of initial guesses in every possible way is considered for each of the B_xMg_3 ($x=1-5$) clusters to predict their ground state structures. Geometries of all the B_xMg_3 ($x=1-5$) clusters are optimized without imposing any symmetry constraints, to allow full variational freedom. Further, harmonic vibrational frequency analyses are also performed at the same level of theory to confirm the lowest energy state of those structures on the potential energy surface (PES). The zero number of imaginary frequencies (NIMAG=0) for all the lowest energy structures confirms that they are the minima on the PES. The geometries of optimized clusters are drawn with CHEMCRAFT [26] visualization software.

IV. RESULTS AND DISCUSSION

The ground state structures of B_xMg_3 ($x=1-5$) clusters along with the geometrical parameters and point groups is represented in Fig. 1. The point group of various structures is considered within the tolerance limit of 0.1 Å. Fig. 2 provides the profile of energy gain (ΔE_B) in forming each clusters by adding one boron atom to an existing $B_{x-1}Mg_3$ ($x=1-5$) cluster. It can be noticed that, B_4Mg_3 cluster have very high energy gain (>5 eV) compared to its neighboring clusters, implying its exceptional stability in the considered series. The stability of B_4Mg_3 is expected from the jellium framework since the number of valence electrons of the system is 18, which is a magic number with cluster electronic shell closure as $1S^21P^61D^{10}$. Table I provides the energy gain (ΔE_{Ga}), HOMO-LUMO energy gap (HLG), ionization potential (IP), electron

affinity (EA) and chemical hardness (η) of the B_xMg_3 ($x=1-5$) clusters. The maximum values of ΔE_B (5.27 eV) for B_4Mg_3 cluster justifies itself as the most stable motif in the series. The stability of the B_4Mg_3 cluster is further confirmed by its large IP (4.52 eV) value in the series.

Although no such experimental work on B_xMg_3 clusters series is available, in order to check the reliability of the considered level of calculations in the present work, we have compared the geometrical parameters for B_2 and Mg_2 dimmers to the available experimental and other reported theoretical values. Table II presents comparative results of the calculated bond lengths of B-B and Mg-Mg dimmers with the available experimental and other theoretical results [27]-[30]. It may be noted that calculated B-B and Mg-Mg distance using the present method as 1.65 Å (1.59 Å, expt. [30]) and 3.93 Å (3.89 Å, expt. [30]) are in excellent agreement with the experimental values, compared to the other theoretical results reported in past [27]-[29]. Therefore, the method that is considered in the present work is expected to provide us reliable predictions.

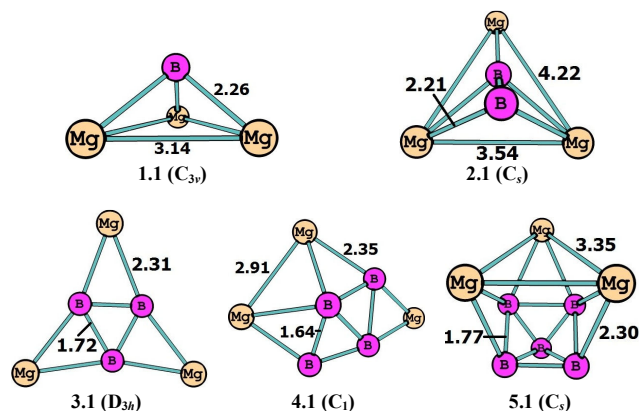


Fig. 1 Ground state structures and associated point groups of B_xMg_3 ($x=1-5$) clusters. Isomer $x.n$ ($x=1-5$) represents the clusters with x boron atoms in its lowest energy state ($n=1$)

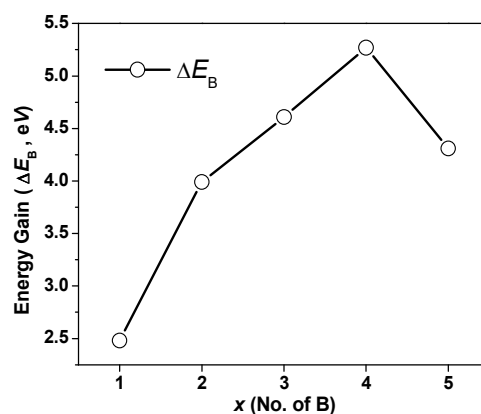


Fig. 2 Energy gain (ΔE_B) of B_xMg_3 clusters, in adding a boron atom to an existing $B_{x-1}Mg_3$ ($x=1-5$) cluster

TABLE I
ENERGY GAIN IN ADDING A B ATOM (ΔE_B) TO AN EXISTING $B_{x-1}Mg_3$ ($x=1-5$), HOMO-LUMO ENERGY GAP (HLG), IONIZATION POTENTIAL (IP), ELECTRON AFFINITY (EA) AND CHEMICAL HARDNESS (η) OF THE B_xMg_3 ($x=1-5$) CLUSTERS

x	ΔE_B (eV)	HLG (eV)	IP (eV)	EA (eV)	η (eV)
1	2.48	2.30	4.62	2.32	1.15
2	3.99	1.02	3.85	2.82	0.51
3	4.61	1.76	4.46	2.70	0.88
4	5.27	1.44	4.52	3.08	0.72
5	4.31	2.18	4.76	2.58	1.09

The understanding of the source of exceptional stability of the B_4Mg_3 cluster is explored further. The ground state geometries of B_4 and Mg_3 clusters are provided in Fig. 3. Fig. 4 represents the one-electron energy levels (OEL) for B_4 , Mg_3 and B_4Mg_3 clusters. It may be noted from the OEL diagrams that the occupied energy levels of the six valence electrons of Mg_3 belongs to the range of occupied energy levels of the twelve valence electrons of the B_4 cluster, and their excellent hybridization, resulting exceptional stability in B_4Mg_3 cluster and therefore its energy gain is found to be exceptionally high in the series.

TABLE II
COMPARATIVE RESULTS OF THE CALCULATED BOND LENGTHS (IN Å) OF B_2 AND Mg_2 DIMMERS IN THE PRESENT WORK, WITH THE EXPERIMENTAL AND OTHER THEORETICAL REPORTED VALUES

Reference	Methods	r(B-B)	r(Mg-Mg)
I. Boustani [27]	HF-SCF	1.69	
A. F. Jalbout [28]	MP2		4.39
Lyalin et al. [29]	B3PW91		3.61
Experimental [30]	Electron diffraction	1.59	3.89
Present work	B3LYP	1.65	3.93

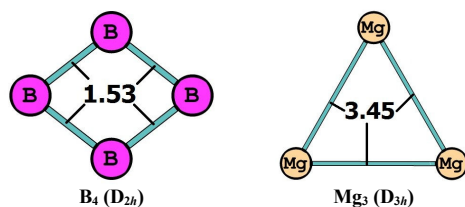


Fig. 3 Ground state structures and associated point groups of B_4 and Mg_3 clusters

In summary, B_4Mg_3 cluster is identified as a new magic cluster in the family of bimetallic magic clusters [18]-[20]. The origin of unusual stability of this cluster unit is explained by jellium shell closure with 18 valence electrons ($1S^21P^61D^{10}$). The maximum ΔE_B value along with significant HLG (1.44 eV), IP (4.52 eV), η (0.72 eV) and EA (3.08 eV) of B_4Mg_3 provides a strong support to be recognized it as a magic cluster and therefore obeying magic valence electronic shell of the jellium model. The possibility for utilizing B_4Mg_3 cluster as a potential building block for future cluster assembled materials by linking them with suitable inorganic/organic linkers is under progress in our laboratory.

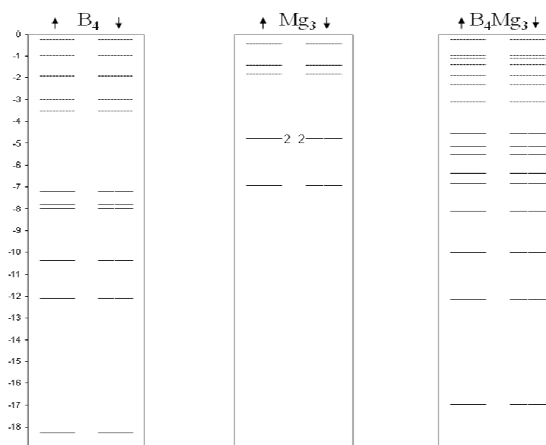


Fig. 4 One-electron energy levels (in eV) of B_4 , Mg_3 and B_4Mg_3 clusters. The continuous and dotted lines represent occupied and unoccupied levels respectively. The degeneracy is marked next to each level. The arrows indicate the majority (up) and minority (down) spin state

V. CONCLUSIONS

A detail theoretical study is performed in search of the exceptional stable or magic clusters in the B_xMg_3 ($x=1-5$) series. B_4Mg_3 shows magic stability with the effect of jellium shell closure. The significant energy gain, HOMO-LUMO energy gap (HLG), ionization potential, chemical hardness and electron affinity explains the origin of the extraordinary stability of B_4Mg_3 motif and implies its suitability to be considered as a building motif for novel inorganic nanomaterials. In addition, HLG value for B_4Mg_3 as 1.44 eV implies an initial classification for its suitability to design novel semiconductor materials.

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