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# $X_4Mg_3$ in $X_kMg_3$ (X = B, Al, Ga, In, Tl; k = 1-6) cluster series: Magic units for potential assembly

**Debesh R. Roy*[a], Esha V. Shah[a], Vipin Kumar[a,b], Kaptan Rajput[a] and Pankaj Kumar[a]**

[a]Materials and Biophysics Group, Department of Applied Physics, S. V. National Institute of Technology, Surat-395 007, Gujarat, India

[b]Computational Materials Science Laboratory, Department of Chemistry, University of Ulsan, Ulsan-44610, Republic of Korea

*E-mail:* drr@phy.svnit.ac.in

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A detail and comparative density functional investigation on the $X_kMg_3$ (X = B, Al, Ga, In and Tl; k = 1-6) cluster series is reported for identifying suitable cluster motifs for their future assembled materials with potential applications. Various structural and electronic properties are evaluated to identify magic clusters in the considered series and understanding their source of exceptional stability. HOMO-LUMO energy gap (HLG), ionization potential (IP), electron affinity (EA) and energy gain ($\Delta E_X$) in forming each cluster from their previous sizes are some electronic parameters as assessed in the present work. The results identifies $X_4Mg_3$ (X = B, Al, Ga, In and Tl) as the exceptional stable magic clusters in their respective series. To understand the source of exceptional stability, we have generated one electron orbital energy (OEOE) levels for $X_4$, $Mg_3$ and $X_4Mg_3$ clusters.

Keywords: Magic clusters, Jellium model, Density functional theory, Group III binary compounds.

## Introduction

Ever since the curiosity on understanding the origin of materials, researchers were dedicated to explore two primary approaches, viz. top down and bottom up[1,2]. The knowledge gained on the source of materials certainly help them in developing novel materials with useful applications[1–5]. The bottom up approach has gained significant attention over the top down since such method is free of defects or damages and advantageous in terms of control at the atomic level[1–5]. The atomic clusters are the aggregation of two to few hundreds of atoms whose property depends exclusively on the size, shape and charge state[3–5]. In the year of 1984, Knight *et al.*[6] have discovered a valence electron series as 2, 8, 18, 20, 34, 40, 58, 92 …. for atomic clusters from the experimental mass spectra of a series of sodium atom clusters $Na_x$ (x = 4-100). They have observed that $Na_x$ clusters with those particular total valence electrons shows exceptional stability with shell closure of cluster electronic shell ($1S^21P^61D^{10}2S^21F^{14}2P^6$ …. ), and termed them as 'magic clusters'[6]. The idea of magic valence shell is now extended from sodium cluster to various monoatomic and hetero-atomic clusters[4,5], now a days. Various magic clusters have been reported in their relevant series, e.g. $Al_{13}$, $Mg_4$, $Al_{13}K$ etc.[5,6]. Our research group has reported few magic clusters based on Jellium model[7] and aromaticity model[8] which includes $Si_4Mg_3$, $Ga_4Mg_3$, $In_4Mg_3$, $Tl_4Mg_3$, $Si_7Mg_3$, etc.[9–12]. The identified magic clusters are now explored as building units for developing useful cluster assembled materials both theoretically and experimentally[4,5,13,14]. Khanna and co-workers[4] performed joint experimental and theoretical investigations to develop cluster assembly of $As_7^{3-}$ magic unit from Zintle model[15] along this direction.

The purpose of the present work is to perform a comparative study on various group III – alkaline earth cluster series in the form of $X_kMg_3$ (X = B, Al, Ga, In and Tl; k = 1-6) and to identify exceptionally stable magic clusters. We have already reported couple of series in the recent past which includes $Ga_kMg_3$, $In_kMg_3$ and $Tl_kMg_3$ (k = 1-6)[10–12]. The electronic properties are evaluated through HOMO-LUMO energy gap (HLG), ionization potential (IP) and electron affinity (EA). To identify exceptional stable (magic) cluster in the considered series we have computed energy gain ($\Delta E_X$) in

forming each clusters. To understand the origin of the extraordinary stability of the identified magic clusters, one electron orbital energy (OEOE) level diagrams are generated for each magic cluster and their reactants.

## Theoretical methods

The gain in energy ($\Delta E_X$) in forming $X_kMg_3$ (X = B, Al, Ga, In and Tl; k = 1-6) clusters by adding a X atom to its previous size $X_{k-1}Mg_3$ is computed as follows:

$$\Delta E_X = E(X) + E(X_{k-1}Mg_3) - E(X_kMg_3) \quad (1)$$

where $E(X_kMg_3)$, $E(X_{k-1}Mg_3)$ and $E(X)$ are the total electronic energies of the $X_kMg_3$, $X_{k-1}Mg_3$ clusters and of the X atom, respectively.

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

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

## Computational details

The complete theoretical investigations are carried out using a very popular hybrid exchange-correlation functional within the density functional theory (DFT) framework[16–18]. A molecular orbital (MO) approach, using a linear combination of atomic orbitals (LCAO), is employed to probe the electronic structure of the considered clusters. The actual calculation is performed using the implementation in the GAUSSIAN 09[19] program. For exchange and correlation functional, we have utilized a very popular and reliable hybrid functional, B3LYP which has been introduced by A. D. Becke in 1993[20]. An all electron calculation with the 6-31+G[d,p] basis sets is employed[21] for all the clusters except for $In_kMg_3$ and $Tl_kMg_3$ series due to its limitation for In and Tl atoms in GAUSSIAN 09[19] code. For $In_kMg_3$ and $Tl_kMg_3$ clusters, we have used a popular pseudopotential based basis set LanL2dz[22] which includes a scalar relativistic effect. Large number of initial guesses for prediction of minimum energy cluster in each case are considered for the whole $X_kMg_3$ (X = B, Al, Ga, In and Tl; k = 1-6) series. Geometries of all the $X_kMg_3$ clusters are optimized without imposing any symmetry constrains, to allow full variational freedom. Further, harmonic vibrational frequency analyses are also carried out at the same respective levels 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 structures of optimized clusters are visualized and drawn with CHEMCRAFT[23] software.

## Results and discussion

Fig. 1 presents the minimum energy structures of $X_4Mg_3$ (X = B, Al, Ga, In and Tl) clusters along with their geometrical parameters and point groups. A tolerance limit of 0.1 Å is considered to assess the point groups of various structures. The minimum energy structures and their low-lying energy isomers for the other clusters in the series, viz. $X_kMg_3$ (X = B, Al, Ga, In and Tl; k = 1-3, 5, 6) are mostly reported in our past works[10–12]. Fig. 2 shows the profile of energy gain ($\Delta E_X$) in forming each clusters by adding one X (B, Al, Ga, In and Tl) atom to the previous $X_{k-1}Mg_3$ (k = 1-6) cluster. It may be noted that, for the entire group III compounds, the cluster with k = 4 shows the maximum energy gain in their respective series implying their exceptional stability. The stability of all these $X_4Mg_3$ is expected from the Jellium framework since the number of valence electrons of these systems is 18, which is a magic number with cluster electronic shell closure as $1S^21P^61D^{10}$. It also be noted that in general the amplitude of energy gain is maximum for $B_4Mg_3$ and it reduces as the size of X atom increases, viz. $\Delta E_B > \Delta E_{Al} > \Delta E_{Ga} > \Delta E_{In} > \Delta E_{Tl}$.

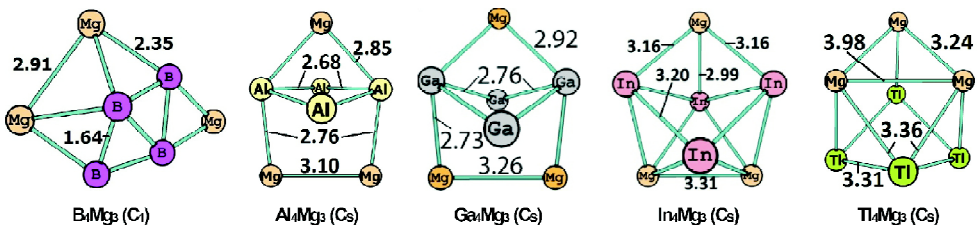


**Fig. 1.** Minimum energy structures and associated point group symmetries of $X_4Mg_3$ (X = B, Al, Ga, In and Tl) magic clusters.

**Table 1.** HOMO-LUMO energy gap (HLG), ionization potential (IP), electron affinity (EA) and energy gain ($\Delta E_X$) in adding a X atom to an previous $X_{k-1}Mg_3$ (k = 1-6) of the $X_kMg_3$ (k = 1-6) clusters

| X | k | HLG (eV) | IP (eV) | EA (eV) | $\Delta E_X$ (eV) |
|---|---|---|---|---|---|
| B | 1 | 2.30 | 4.62 | 2.32 | 2.48 |
| | 2 | 1.02 | 3.85 | 2.82 | 3.99 |
| | 3 | 1.76 | 4.46 | 2.70 | 4.61 |
| | 4 | 1.44 | 4.52 | 3.08 | 5.27 |
| | 5 | 2.18 | 4.76 | 2.58 | 4.31 |
| | 6 | 1.46 | 4.77 | 3.01 | 4.94 |
| Al | 1 | 3.18 | 5.39 | 2.21 | 1.41 |
| | 2 | 1.17 | 3.79 | 2.62 | 1.16 |
| | 3 | 1.38 | 4.13 | 2.75 | 2.15 |
| | 4 | 1.51 | 4.48 | 2.97 | 2.29 |
| | 5 | 1.47 | 4.30 | 2.84 | 1.34 |
| | 6 | 1.59 | 4.29 | 2.70 | 2.02 |
| Ga | 1 | 2.25 | 4.40 | 2.15 | 1.37 |
| | 2 | 1.24 | 3.85 | 2.62 | 1.09 |
| | 3 | 1.39 | 4.02 | 2.63 | 1.97 |
| | 4 | 1.53 | 4.42 | 2.89 | 2.17 |
| | 5 | 1.39 | 4.29 | 2.90 | 1.36 |
| | 6 | 1.45 | 4.06 | 2.61 | 1.32 |
| In | 1 | 2.20 | 4.36 | 2.16 | 1.15 |
| | 2 | 1.23 | 3.58 | 2.35 | 0.91 |
| | 3 | 0.85 | 3.71 | 2.86 | 0.82 |
| | 4 | 1.19 | 4.31 | 3.12 | 2.25 |
| | 5 | 1.95 | 4.34 | 2.39 | 1.82 |
| | 6 | 1.55 | 4.26 | 2.71 | 1.44 |
| Tl | 1 | 2.11 | 4.22 | 2.11 | 1.03 |
| | 2 | 0.86 | 3.27 | 2.41 | 0.82 |
| | 3 | 1.16 | 3.72 | 2.56 | 0.72 |
| | 4 | 1.17 | 3.79 | 2.62 | 2.04 |
| | 5 | 1.25 | 3.91 | 2.66 | 1.49 |
| | 6 | 1.29 | 3.88 | 2.60 | 1.24 |

Table 1 provides the HOMO-LUMO energy gap (HLG), ionization potential (IP), electron affinity (EA) and energy gain ($\Delta E_X$) of the $X_kMg_3$ (k = 1-6) clusters. The larger IP (~4 eV) values for all the considered clusters indicated their reasonable stability. Also, large electron affinities (ranging 2.62–3.12 eV) of the developed magic clusters ($X_4Mg_3$) implies their tendency to form assembly with the homologous units, and assembling certainly will stabilize the system more.

Although no such experimental work on $X_kMg_3$ clusters series is available, in order to check the reliability of the considered level of our calculations, we have compared the geometrical parameters for $X_2$ and $Mg_2$ dimmers to the available experimental values. Table 2 presents comparative results of the calculated bond lengths of X-X and Mg-Mg dimers with the available experimental results[24–27]. It may be noted that experimental [calculated] bond lengths for B-B (1.59 Å [1.65 Å]), Al-Al (2.56 Å [2.56 Å]), Ga-Ga (2.62 Å [2.56 Å]), In-In (- [3.51 Å]), Tl-Tl (3.70 Å [3.76 Å]) and Mg-Mg (3.89 Å [3.96 Å]) are in excellent agreement. Such close agreement with experimental values certainly justifies the choice of our exchange-correlation functional and basis sets.

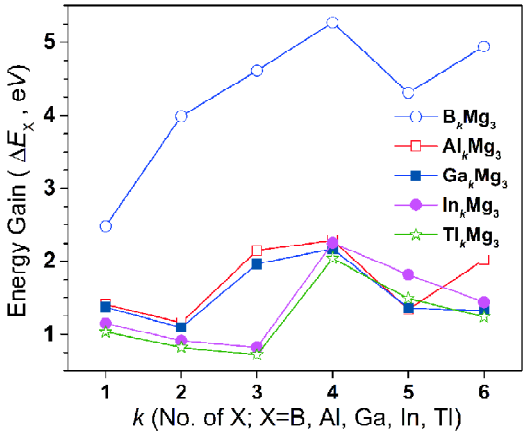


**Fig. 2.** Energy gain ($\Delta E_X$) of $X_kMg_3$ (X = B, Al, Ga, In and Tl; *k* = 1-6) clusters, in adding a X atom to a previous $X_{k-1}Mg_3$ cluster.

**Table 2.** Comparative results between available experimental bond lengths of $X_2$ and $Mg_2$ dimers and the same as calculated in present work

| Dimers (X-X) | Ref. | Methods | *r*(X-X) (Å) |
|---|---|---|---|
| B-B | Expt.[24] | Electron diffraction | 1.59 |
| | Present work | B3LYP | 1.65 |
| Al-Al | Expt.[24] | Electron diffraction | 2.56 |
| | Present work | B3LYP | 2.56 |
| Ga-Ga | Expt.[25] | Electron diffraction | 2.62 |
| | Present work | B3LYP | 2.56 |
| In-In | Expt. | – | – |
| | Present work | B3LYP | 3.51 |
| Tl-Tl | Expt.[26] | XRD | 3.70 |
| | Present work | B3LYP | 3.76 |
| Mg-Mg | Expt.[27] | Electron diffraction | 3.89 |
| | Present work | B3LYP | 3.96 |

To understanding of the source of exceptional stability in the $X_4Mg_3$ clusters, we have further explored the one electron orbital energy (OEOE) levels of those magic clusters along with their reactants, viz. $X_4$ and $Mg_3$. The minimum energy structures of most of the $X_4$ and $Mg_3$ clusters are reported elsewhere[10–12]. Fig. 3 represents the one-electron orbital energy (OEOE) levels for $X_4$, $Mg_3$ and $X_4Mg_3$ clusters. It may be noted from the OEOE 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 all the $X_4$ clusters, and their excellent hybridization, resulting exceptional stability in $X_4Mg_3$ cluster and therefore their high energy gain in the respective series.

The developed clusters are expected to serve as building units for relevant low density cluster assembled materials (CAM) in their possible form of 1D (e.g. $X_kMg_3$ nanowire), 2D (e.g. $X_kMg_3$ film) and 3D/bulk. The HLG of developed magic $X_4Mg_3$ clusters ranges between 1.17–1.53 eV indicates a possible semiconductor behavior in their assembled materials, with a key advantage of tunability of properties at the atomic scale. Such works are under progress in our laboratory[28].

It may be noted that electronic and/or other physicochemical properties of clusters are usually a preliminary indicator for their belongings in the metal-semiconductor-insulator (MIS) domain, as their assembled materials. However, our

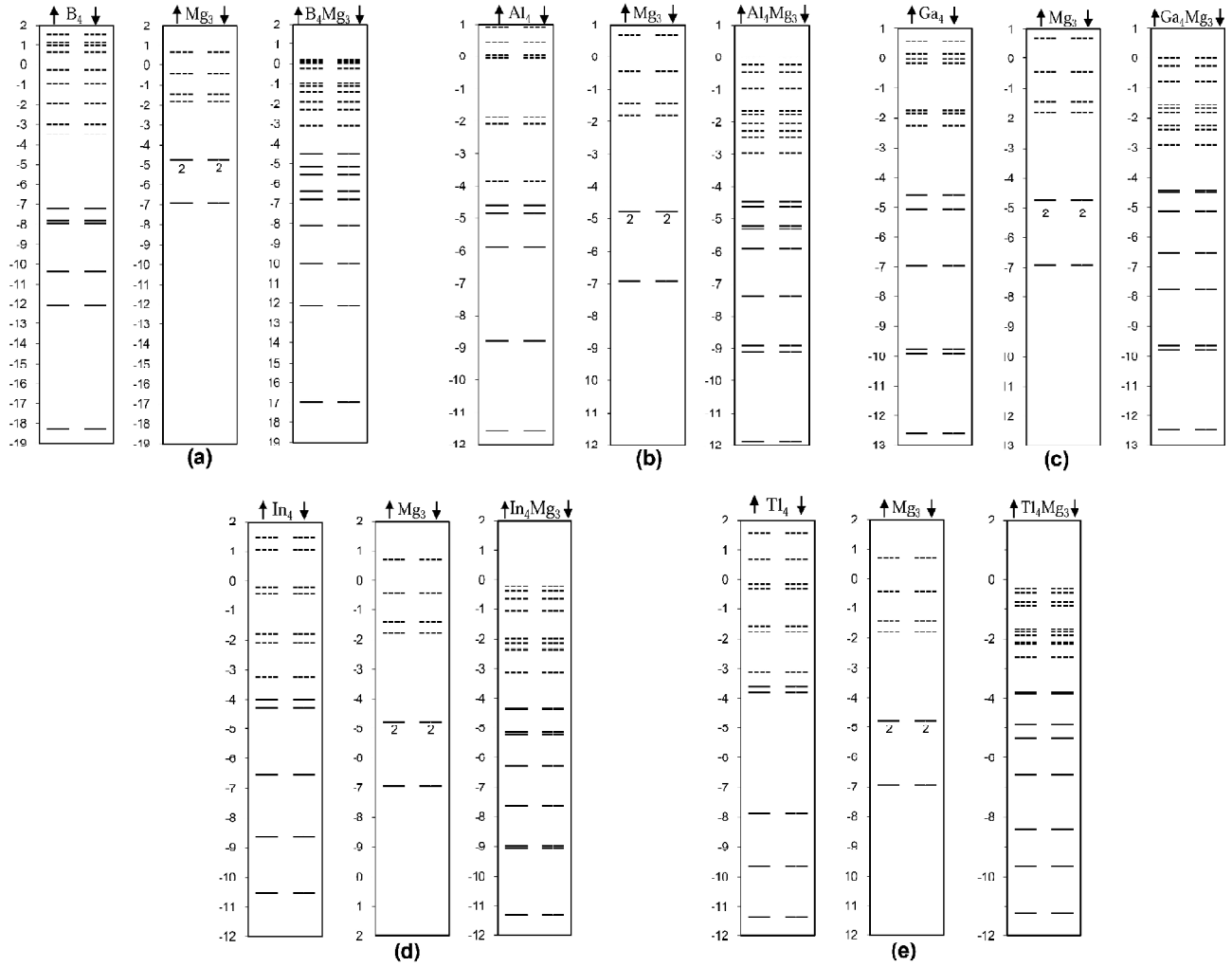


**Fig. 3.** One-electron energy levels (in eV) of $X_4$ (X = B, Al, Ga, In and Tl), $Mg_3$ and $X_4Mg_3$ clusters. The continuous and dotted lines represent occupied and unoccupied levels respectively. The degeneracy is marked next to each level. The arrows indicate the majority (up) and minority (down) spin states.

recent experience shows[28] that assembling of clusters in a material form reduces energy band gap in general. The nature of band gap in the developed materials (direct/indirect and narrow/moderate/wide) guides researchers for their further relevant applications accordingly, e.g. optical applications (direct band gap), thermoelectrical applications (indirect wide band gap) etc.

## Concluding remarks

In summary, a detail comparative study on the various group III magnesium clusters, viz. $X_kMg_3$ (X = B, Al, Ga, In and Tl; k = 1-6) is performed under density functional framework. It is observed that $X_4Mg_3$ (X = B, Al, Ga, In and Tl ) with 18 valence shell closure ($1S^21P^61D^{10}$) shows exceptional stability by identifying them as magic clusters in the respective series.

The energy gain ($\Delta E_X$) for $X_4Mg_3$ is found to be maximum implying the most stable magic cluster in the entire series. The larger ionization potential (~ 4 eV) for the considered clusters supports their stability in general. The HLG range for the identified magic clusters $X_4Mg_3$ ranges between 1.17–1.53 eV provides a preliminary idea for their possible semiconductor behavior in assembled materials. Also, higher electron affinity indicates that the developed magic clusters prefer to assemble with similar homologous units. The origin of the exceptional stability for $X_4Mg_3$ clusters is understood as the strong orbital hybridizations between their reactants $X_4$ and $Mg_3$.

The developed $X_4Mg_3$ building units may be utilized to develop 1D, 2D and bulk scale nanomaterials with industrial applications. Such efforts are now under progress in our laboratory.

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