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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

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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 (ΔE_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 applications¹⁻⁵. 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 level¹⁻⁵. The atomic clusters are the aggregation of two to few hundreds of atoms whose property depends exclusively on the size, shape and charge state³⁻⁵. 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 model⁷ and aromaticity model⁸ 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-workers⁴ performed joint experimental and theoretical investigations to develop cluster assembly of As_7^{3-} magic unit from Zintl model¹⁵ 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 (ΔE_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 (ΔE_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 Koopmans¹⁶, 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) framework¹⁶⁻¹⁸. 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 09¹⁹ 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 1993²⁰. An all electron calculation with the 6-31+G[d,p] basis sets is employed²¹ 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 09¹⁹ code. For In_kMg_3 and Tl_kMg_3 clusters, we have used a popular pseudopotential based basis

set LanL2dz²² 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 constraints, 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 CHEMCRAFT²³ 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 works¹⁰⁻¹². Fig. 2 shows the profile of energy gain (ΔE_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. $\Delta E_B > \Delta E_{Al} > \Delta E_{Ga} > \Delta E_{In} > \Delta E_{Tl}$.

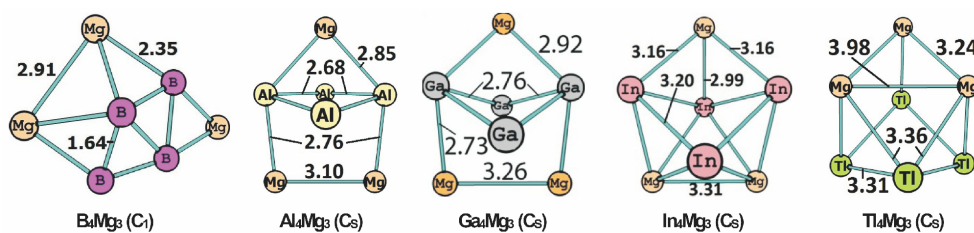


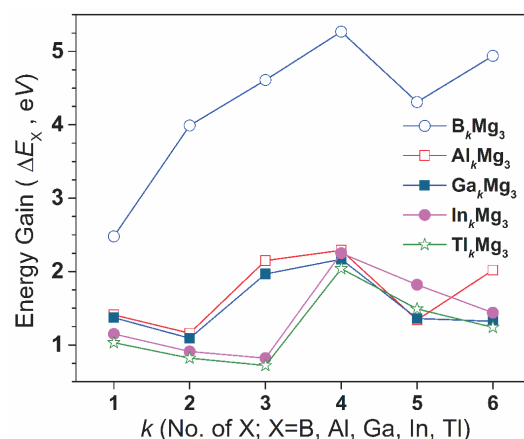
Fig. 1. Minimum energy structures and associated point group symmetries of X_4Mg_3 ($X = B, Al, Ga, In$ and Tl) magic clusters.

Table 1. HOMO-LUMO energy gap (HLG), ionization potential (IP), electron affinity (EA) and energy gain (ΔE_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)	ΔE_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 (ΔE_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


Fig. 2. Energy gain (ΔE_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.

considered level of our calculations, we have compared the geometrical parameters for X_2 and Mg_2 dimers 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.

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 laboratory²⁸.

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

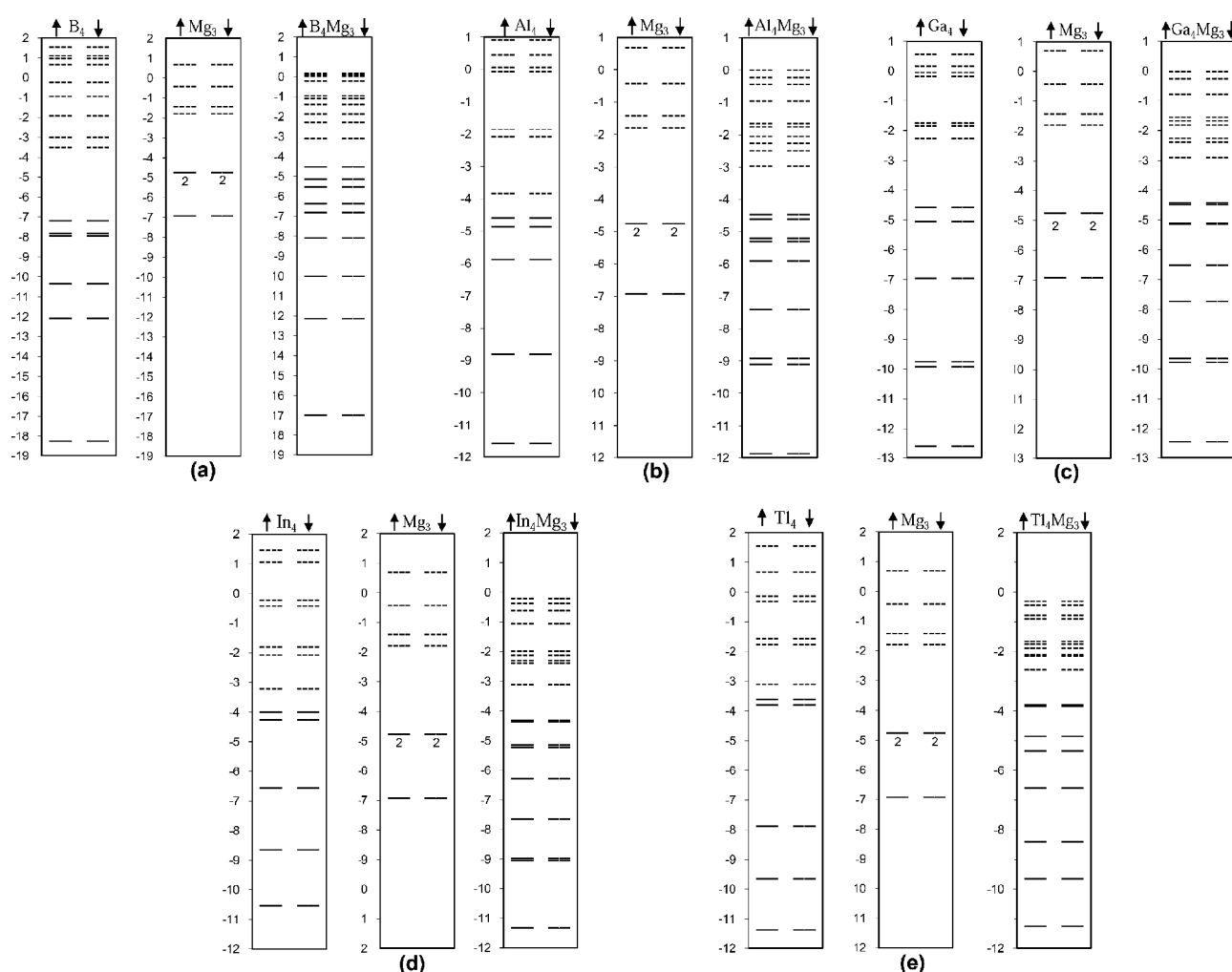


Fig. 3. One-electron energy levels (in eV) of X_4 ($X = B, Al, Ga, In$ and Tl), Mg_3 and X_4Mg_3 clusters. The continuous and dotted lines represent occupied and unoccupied levels respectively. The degeneracy is marked next to each level. The arrows indicate the majority (up) and minority (down) spin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

recent experience shows²⁸ 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 (ΔE_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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