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Citation: The Journal of Chemical Physics **141**, 054308 (2014); doi: 10.1063/1.4891867 View online: http://dx.doi.org/10.1063/1.4891867 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/141/5?ver=pdfcov Published by the AIP Publishing

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Scaling up the shape: A novel growth pattern of gallium clusters

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(Received 11 April 2014; accepted 21 July 2014; published online 6 August 2014)

Putative global minima for Ga_N^+ clusters with size "N" ranging from 49 to 70 are found by employing the Kohn-Sham formulation of the density functional theory, and their evolution is described and discussed in detail. We have discovered a unique growth pattern in these clusters, all of which are hollow core-shell structures. They evolve with size from one spherical core-shell to the next spherical core-shell structure mediated by prolate geometries, with an increase in overall diameter of the core, as well as the shell, without putting on new layers of atoms. We also present a complete picture of bonding in gallium clusters by critically analyzing the molecular orbitals, the electron localization function, and Bader charges. Bonding in these clusters is a mixture of metallic and covalent type that leans towards covalency, accompanied by marginal charge transfer from the surface to the core. Most molecular orbitals of Ga clusters are non-jellium type. Covalency of bonding is supported by a wide localization window of electron localization function, and joining of its basins along the bonds. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4891867]

I. INTRODUCTION

Over past few decades, considerable amount of scientific efforts have been invested in studying atomic clusters.^{1–11} All these efforts have provided us with many interesting and useful applications of clusters,¹⁻⁴ and satisfied some of our curiosity about them.^{11–14} At the same time it has also given rise to questions that are still unexplained. One such poorly understood aspect about them is the evolution of their various properties with size. Specifically, clusters with sizes less than 500 atoms exhibit pronounced, and irregular variation in their various different properties, 5-7 such as the ground state (GS) structure, melting temperature,^{9,10} electric¹⁵ and magnetic^{8,16} polarizability, HOMO-LUMO gap, and reactivity.¹⁷⁻¹⁹ Desirable as it may seem, there exist no ubiquitous rules that describe these variations. Among all the properties that vary with size, "geometry of the cluster" takes the center stage, since other properties like stability, melting temperature, reactivity can be explained based on the geometries of the GS of these clusters.^{7,11,12,20–22} The evolution of the GS geometries does not exhibit uniform traits even over different sizes of same element, let alone across homogeneous clusters of different elements. The same holds true for homogeneous metal clusters. By metal clusters, we mean clusters of elements that are "metals in their bulk form." Growth of homogeneous metal clusters is a mixture of a few common trends, accompanied by a considerable element specific variety. For instance, oscillations between ordered and disordered GS, and spherical to non-spherical GS, which is driven by competition between surface energy and binding energy, are common trends observed in growth of many metal clusters.^{14, 20, 22–27} In order to bring out the similarities and differences in the evolution of GS structures, it is instructive to compare the growth patterns of homogeneous metal clusters of various elements.

Sodium is a simple metal with only one electron in its valence orbital. Sodium clusters follow both the common trends noted above, since they exhibit oscillations in the shape parameter (spherical to nonspherical to spherical), and they follow the order-disorder-order pattern of formation.^{14,23,28} However, peculiar to their growth, going from one ordered structure to the other, they form localized centers with icosahedral order, forming interpenetrating icosahedra, that then give rise to a global order. Thus, the growth follows the pattern "global order \rightarrow local icosahedral order \rightarrow local nonicosahedral order \rightarrow global order." Notably, for larger sizes like Na_{147} , the last shell of atoms gets built up, keeping the shell structure formed till Na134 intact. The next element after sodium, with a single valence electron, is potassium. Potassium clusters are reported to follow different structural motifs for different ranges of sizes (between 13 and 80), with structures that are more like sodium clusters.²⁵ Their geometries are chiefly icosahedral, deltahedral, and polyicosahedral, and correlate well with electronic shell closing of the jellium model. Caesium lies below Na and K in group I of periodic table. However, in spite of belonging to the same group, the GS structures of caesium clusters are reported to be markedly different than those of either sodium or potassium, within size range 2–80.²⁶ They are more compact and endohedral or cage type structures mostly, and adopt more spherical shapes compared to sodium. Their larger size structures cannot be obtained simply by adding a new atom to lower size, unlike sodium. Also, in contrast to Na and K, most of the caesium clusters possess a net total magnetism. Their compact motifs are credited to higher polarizability, sd hybridization, and high spin multiplicities, which are due to delocalized electrons. Relative stabilities of certain sizes are explained using geometric packing and spin polarizations, rather than fitting it to jellium model. Moving horizontally, along the 3rd period of periodic table, next after Na, is

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element Mg, with 2 valence electrons. Mg clusters have been reported to follow the common trends of the oscillating shape variation, and the order-disorder transition.²⁴ However, peculiar to Mg, they follow growth in two directions simultaneously, and their growth is core centric, with cores of larger clusters being GS structures of lower sized clusters. Similarities between bulk Mg and its clusters exist for quite small sizes, and jellium model for Mg clusters needs modification before its shell completion orbitals can be matched with experimentally found magic numbers.²⁹ The next element in the 3rd period, aluminium, shows drastically different evolution of its clusters. Most of the aluminium anion clusters with N > 48 adopt face-centered-cubic (fcc) crystalline lattice fragments with distortions and defects, and adopt less compact structures.²² Aluminum clusters sustain this planar type growth pattern for quite large sizes, and spherical GS geometries are almost not present, at least till size 75 (with exception of 65-67). Gallium lies below aluminium (group IIIA) in periodic table, so one may expect that alike Na and K, their clusters might share more than a few common features in their evolution. This expectation is true to a large extent, for clusters of sizes $< 40.^{\overline{2}1,30,31}$ For sizes > 40, the evolution of their GS structures is drastically different. For instance, gallium clusters follow planar motif for their GS structures between size 31 and 38, but not after size 39 (instead, they form spherical core-shell structures),²⁰ whereas aluminium continues to have planar geometries in most cases, up to sizes 75.²²

Thus, we see that various homogeneous metal clusters grow in various different ways. While sodium forms icosahedral structures by addition of atoms to existing structures, and potassium clusters follow in closely, caesium clusters differ in their evolution, whose larger geometries cannot be obtained by simply adding atoms to smaller ones. Magnesium clusters follow two directional growth with smaller clusters being the cores of larger ones, but aluminium clusters prefer geometries that adopt fcc structure, alike its bulk counterpart. Although gallium and aluminium clusters show similar GS structure for small (<40) sizes, we demonstrate in this work that they follow entirely different growth paths for the larger sizes. In fact, the evolution pattern observed in these gallium clusters is unique in comparison to all other homogeneous metal clusters studied so far. We demonstrate that gallium clusters (49–70) grow from small sized (Ga_{46}^+) spherical core-shell geometry to the next spherical core-shell geometry (Ga_{66}^+) with an overall increase in core-shell diameters. From the above discussion, it is clear that finding GS structures of clusters for newer size ranges is an interesting and an essential task. It is expected to add to our wisdom about finite sized systems, their evolution, and provide insight into possible situations that could lead to their novel applications. For instance, gallium nanoclusters have earlier been shown to be a promising candidate as phase changing materials that could play a role as the future nanophotonic logical and memory devices.32

As much interesting as the GS evolution, another issue regarding gallium clusters which demands attention is its bonding. α -Ga is a very interesting case as far as its bonding and crystal structure is considered. Crystal structure of α -Ga consists of two main features, namely, the buckled planes of Ga atoms, and the short covalent bond that joins these buckled planes. Thus, each Ga atom in bulk possesses one short bond at 2.48 Å which is covalent in nature and connects the buckled planes. Six more nearest neighbors lie within the buckled plane that occur in three pairs at distances 2.69 Å, 2.73 Å, and 2.78 Å. This makes α -Ga's coordination number as seven. Its electronic structure shows a (pseudo)band gap at the Fermi level, which makes its bonding a mixture of metallic along (110) buckled plane, and covalent along direction almost perpendicular to it.33 As a consequence of mixed nature of bonding in bulk gallium, one may expect that bonding in gallium clusters will not be simple either. Indeed, it has been an issue of debate ever since Chacko et al. credited the high melting temperature of gallium clusters to the presence of covalent bonds.¹² More recently, bonding in gallium clusters is claimed to be metallic based on comparisons between clusters, bulk crystal (α -Ga),³¹ and the jellium model.³⁴

On a different note, comparison of GS structures found in this work with those of clusters of covalent non-metal silicon shows that their growth is closer to that of silicon, than with other metal clusters like Al. Clusters of metals like Al exhibit layer by layer growth of structures for medium and large sizes, whereas silicon clusters are reported to possess core-shell (endohedral) structures for its medium and large sizes.^{35–39} If fact, the trigonal tricapped prism (TTP) unit at the core of Ga_{46}^+ is a motif found in many silicon clusters.³⁸ Since bonding in a cluster influences the geometry of its GS, a similar trend in GS geometries could be expected due to similarities in their binding nature.

The motivation of this work is twofold. It aims at bringing out the unique growth pattern that gallium clusters follow in this size range, and presenting a complete picture of bonding in gallium clusters in order to highlight the fact that bonding, alike other physical quantities of small clusters, changes its nature with size of the clusters.⁴⁰ Growth pattern of gallium clusters in this size range is discussed here for the first time, which exhibits unique traits. Core-shell structures being central to the growth of these clusters evolve with size from one spherical core-shell to the next spherical core-shell structure with an increase in overall diameter of the core, as well as the shell, without putting on new layers of atoms. Inner core of Ga_{66}^+ has diameter 6.07 Å, comparable to that of the C_{60} Bucky ball. Growth between two spherical core-shell structures is mapped atom by atom. The initial single ad-atom becomes a cap, which finally forms the curved spherical outer surface of the larger clusters, that shows similarities with α -Ga. In the other part, we present results pertaining bonding in gallium clusters. Bonding in gallium clusters has been a debatable topic till now, since different parameters indicate different types of bonding. This dichotomy is resolved here by critically analyzing bonding in these clusters. The electron localization function (ELF), and a detailed and extensive analysis of the molecular orbitals (MOs) suggest that gallium clusters exhibit mixed type bonding that leans towards covalency. They follow jellium model only to a limited extent due to its atomic s-type valence electrons. We also present the Bader analysis, which brings out a new observation in clusters.

II. COMPUTATIONAL DETAILS

Born Oppenheimer molecular dynamics (BOMD) was carried out to explore the potential energy surface. Projector Augmented Wave (PAW)41,42 pseudopotential with Perdew-Burke–Ernzerhof (PBE)^{43,44} approximation for the exchangecorrelation and the generalized gradient approximation was used, as implemented in the plane wave basis code Vienna Ab initio Simulation Package (VASP).45-47 A cubic simulation box with 25 Å sides was found to be sufficient for convergence of total electronic energy below 10^{-4} eV, while the force convergence criterion was kept at 5×10^{-3} eV/Å. Finding the GS geometries of clusters is a formidable task at all scales. Systematic search methods like basin-hopping,⁴⁸ minima hopping,⁴⁹ genetic algorithm are practically less feasible within the framework of Density Functional Theory (DFT) for larger (greater than few tens of atoms) systems. Hence, we have followed a less systematic method for searching the GS. This method comprises of several cycles of slow heating, followed by unbiased sampling, atom plucking, and optimization of geometries. A flowchart depicting the procedure is presented in Fig. 1. As a first step, various different structural motifs were optimized for each size. The initial geometries were obtained from, (1) the Cambridge Cluster Database's classical potential repositories,⁵⁰ (2) reported GS structures of ab initio geometries of clusters like aluminium,^{27,51} (3) fragments from bulk structures of α -Ga, β -Ga, (4) fragments of large hcp, cuboctahedral, truncated octahedral structures. The lowest energy structure from these, for each size was either slow-heated or maintained at constant temperature, as well as atoms were plucked from them to obtain clusters of smaller size. A new set of structures was obtained by unbiased sampling of geometries from the slow heating/constant temperature run, along with those from



FIG. 1. Flowchart depicting iterative procedure followed in due course of finding the GS structures.

atom plucking. The procedure was repeated till no new structures with lower energy could be obtained in two successive cycles. Vibrational spectra of the concluded GS for all sizes were calculated to confirm that these GS geometries indeed belonged to the local energy minima, and were not a transition state. The set of lowest energy structures obtained after all these iterations of slow heating, atom plucking, and optimization exhibited a systematic evolution pattern, which was taken as the conformation to terminate our search.

Choice of temperatures for MD, during various steps of the procedures described above, is a critical issue. The atoms in a cluster must be supplied with enough kinetic energy so that they can hop from one potential well to the other, for better sampling of potential energy surface. However, supplying too much kinetic energy is bound to make the sampling of potential energy surface insufficiently small, and one may then miss the GS. This delicate balance of kinetic energy supply is achieved by heating the cluster at temperatures just less than the T_m . At this temperature, the atoms are mobile just enough so that isomerization has set in, but not too mobile so that the cluster is melted and the atoms move rigorously with high kinetic energy. It has been demonstrated that probability that the cluster visits the potential well corresponding to the GS is high below the melting temperature, and it diminishes drastically in the liquid-like region.⁵² Since experimental data regarding melting temperatures (T_m) of gallium clusters of these sizes (>49) are not available in literature, the clusters were heated slowly up to temperature just below melting temperature. Here, the melting temperature is decided by examining the generated MD trajectories using traditional parameters like root mean square bondlength fluctuations.

In this work, geometry optimization as well as the MD runs were performed at ab initio level of theory. The cumulative simulation time of MD for each size ranged between 670 ps and 1.1 ns, and a total of more than 5600 geometries were optimized during the search, of which, nearly 4500 were distinct isomers. Performing MD with ab initio methods avoids any bias that empirical/classical potentials might have towards certain shapes and/or coordination.53-56 This makes the geometries obtained here more vivid and unbiased, and in a way compensates for less number of optimizations compared to other search methods. The GS structure search was carried out for all the sizes exhaustively in the chosen size range, since searching for GS structures of intermittent sizes suffers from the disadvantage that it might miss on the correct GS and lead to erroneous one. Thus, all possibilities of missing the GS structure were reduced to a minimum, by performing all the procedures described above. As a result of the rationale developed and followed here, we started out with known structures and in due course were able to reach structures that were lower than the initial ones by a few eV. Thus, a complete ab initio treatment, novel combination of slow heating, atom plucking and unbiased sampling, BOMD of large simulation time, optimizing a large number of isomers for each size, and covering the continuous range of sizes, all make this search for GS structures vastly exhaustive and reliably conclusive.

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III. RESULTS AND DISCUSSION

A. GS structures

Fig. 2 shows GS structures of Ga_n^+ (n = 49–70) obtained in this work. (See the supplementary material for xyz coordinates of GS geometries.⁵⁷) Atoms that form the cap are colored green, the shell atoms white, and core of the cluster is colored red. The coloring schema is adopted to aid the eye in visualizing their structures. All clusters investigated here primarily have core-shell type structures as their GS, with no atom at their center of mass (COM), and can be divided into three classes broadly. The first class, where the GS structures are prolate with caps over the spherical core-shell structure of Ga_{46}^+ GS (Fig. 2(a)), the second where the structures are still prolate, but without any distinct cap, and the third class with geometries that have distinct spherical core-shells. Clusters become more prolate (elongated) with addition of each atom starting from size 49 up to 62. However, geometries only till size 59 are classified as belonging to the first class on account of distinct presence of cap of atoms over Ga⁺₄₆ GS (Fig. 2(a)). Geometries of sizes 60–62 belong to second class that consists of prolate geometries. These are the geometries for which the cap structure that was distinctly present in the



FIG. 2. GS geometries of gallium clusters within size range 49–70. Ga_{46}^+ GS (a) is taken from our previous work.²¹ Core atoms of the clusters are colored red, while those of the shell are colored white. Cap atoms are colored green. Convention of colors of atom is followed throughout the rest of the report, unless mentioned otherwise. Each structure is captioned with its size, charge, and its symmetry group. Symmetry group is " C_1 " whenever not mentioned. xyz coordinates of cationic geometries are provided in the supplementary material.⁵⁷

first class merges into the newly formed outer surface of the cluster. The third class arises with the change of overall shape of clusters to more or less spherical (size 63-70). Only a few sizes showed variation in the GS structures of neutral clusters, and are displayed in Fig. 2. The clusters transform from spherical shape (46) to spherical again (66), while assuming prolate geometries for the intermediate sizes. The diameter of the cluster, however, increases from ~ 8 Å to nearly 12 Å as the size increases from 46 to 66. The increase in diameter of the clusters is not on account of an added shell, but due to formation of larger inner as well as outer shell. Interestingly, the cores of these larger spherical clusters are hollow spheres of diameter ~6 Å which is comparable to that of the C_{60} Bucky ball. Further, this growth pattern is distinct from all the trends observed in metal clusters and resembles more to that of silicon clusters. Energetics of these clusters are presented in the supplementary material.⁵⁷

Analysis for isomers within 0.1 eV above the GS was performed for each size, and they were classified into different "families." Different families of isomers are characterized by either of the following changes, viz., (1) presence/absence of atom at its COM, (2) change in the number of atoms in cap/core/shell, and (3) change in its overall structure. Difference in energy between isomers belonging to different families is in general larger than those belonging to the same family. (See the supplementary material, for example.⁵⁷) Isomers that show minor rearrangement and/or reorientation of atom/s belong to the same family. (See the supplementary material, for example.⁵⁷) Owing to the same fact, nearly 25 different isomers of Ga_{66}^+ were found in a short interval of 0.1 eV. All of them possessed same number of core and shell atoms without any caps, and reflected minor changes in terms of coreshell orientation or rearrangement of certain atoms. Among all the cluster sizes studied in this work, a single exception was found for Ga_{67}^+ , which showed two different families of geometries, viz., (a) with hollow core, and another (b) with an atom at the COM of the cluster, as its GS. Ga_{67}^+ , thus, possesses a degenerate GS.

Gallium clusters, in this size range, are large enough so that the evolution of their GS geometries can be treated as the evolution of its different constituent parts, such as the cap, the shell, and the core atoms. Cap structures that appear for sizes 49-59 form an evolution pattern of their own. The cap consists of a linear chain of atoms for clusters of sizes 49-52, and become planar thereafter. Fig. 3 shows the evolution of caps with increasing size of the clusters from 54 to 59. White atoms shown in the figure are the extra atoms that get added to the initial 8 atom unit of size 54's cap. The two subfigures (atoms colored red, α -Ga) are fragments of the (110) buckled plane of the bulk α -Ga, shown from top (α -Ga top) and lateral perspective (α -Ga side). Direction [110] is perpendicular to the plane of paper in the " α -Ga top" view. " α -Ga side" view is obtained by rotating the top view by 90°. Initially, the size of cap increases from 1 add-atom for Ga_{48}^+ , to 2, 3, 4, 4, and 6 atoms for sizes 49-53, respectively (atoms colored green in Fig. 2). The figure shows that from size 54 onwards the cap grows progressively into a planar structure that resembles the atomic arrangement of the (110) buckled plane of bulk α -Ga (α -Ga top). However, these cap atoms are on the surface of



FIG. 3. Evolution of cap atoms: Cap of Ga_{54}^+ is the smallest cap that forms a 2-dimensional structure. Atoms that get added to the basic cap structure of 54 are colored white. Atoms in red are a fragment of bulk α -Ga. Figure α -Ga(side) is the lateral view of α -Ga(top). Similarly, 59(b), 62(b), and 63(b) are lateral views of 59(a), 62(a), and 63(a), respectively. Curved structure 63(a) is an extension of 57's cap, with golden atoms getting added to 57's cap. Similarly, 62(a)/(b) are an extension of 59(a)/(b) caps, respectively. 63(a) is the pentagonal symmetric and 62(a) the hexagonal symmetric unit.

the cluster and are not confined, like atoms in bulk α -Ga, thus resulting in to a curved surface (see Figs. 3, 59(b)) The curvature of cap structures is evident upon viewing it laterally (Fig. 3, 59(b)). This curved cap structure further forms the surface of the larger clusters, in form of two different structural units, the pentagonal and the hexagonal symmetric (see Fig. 3). The pentagonal symmetry type surface unit (Fig. 3, 63(a) and (b)) is an extension of the cap of 57, while the hexagonal type (Fig. 3, 62(a) and (b)) is an extension of 59's cap. Extra atoms are colored golden in the figure. Surfaces of larger clusters form out of an admixture of these two types of surface units. Distinct presence of the cap structures is absent from sizes 59 to 66, and the caps only reappear as 1, 2, 3, and 4 add-atoms for sizes 67–70 thereafter. Thus, we see that the caps are a distinct quintessential part of evolution of these clusters. They start out as single add-atoms, then grow into well-arranged cap surfaces that resemble the atoms in bulk, and further form structural units which become a part of the surface of larger clusters.

Presence of caps in clusters is best brought out by the distance from center of mass (DCOM) of atoms. Fig. 4 shows a graph of distance of each atom in a cluster from its cen-



FIG. 4. Distance from DCOM of clusters of representative sizes. 58 represents the class of geometries with distinct cap, signified by the set of largest values of DCOM. Similarly, graph 60 represents the class of elongated geometries without distinct cap, and spherical geometries without distinct caps are represented by graph 66. Graph 60 uses the top *x*-axis, while the other two use the bottom one.



FIG. 5. (a) Representative shell structures of three classes of clusters. All the shells are variants of two caps (hexagonal/pentagonal symmetric) of atoms joined together by rings of atoms in between. Sizes 60-62 have more number of rings, making the geometries elongated, whereas 63-70 shells are similar to those of 49-59, but are larger in diameter. (b) Cores of clusters in size range 49-70 also can be divided into three classes broadly. The first class, where the core consists of the TTP unit for sizes 49-59, the second class, in which two such units get stacked along one of its faces for GS of 60-62, and the third class of size 63-70, where the core takes an altogether different more compact motif, as shown.

ter of mass, for representative sizes plotted against the atom number. Graph 60 uses the top *x*-axis for atom number, while the other two use the bottom one. Size 58 graph is used to represent geometries with distinct caps, from size 49 to 59. The terminal set of 12 data points in graph 58 indicates the cap of 12 atoms, located farthest from the center of the base structure of core+shell (cluster less the cap atoms). Graph 60 represents the elongated geometries from 60 to 62 that do not have distinct cap of atoms, hence no distinct set of data points are visible at its end. Class of spherical geometries is represented by graph 66, which also does not show any terminal set of data points that indicate the cap.

The shell structures (atoms which are neither in the core nor in the cap) are an extension of the cap structures, as described above. Fig. 5(a) shows the representative shells of the clusters from size 49 to 70. The captions give the range of sizes of clusters for which these types of shells are present. The shells, as shown in the figure, appear mostly as two tent like caps, either pentagonal or hexagonal symmetric, held together by rings of atoms in between. These tent like caps are the same pentagonal/hexagonal structures that form out of caps (previously shown in Fig. 3). Elongated geometries (60–62) consist of more rings between the two caps. Shells for sizes 49–59, as well as 63–67 are spherical, but diameter of the later range is larger.

As mentioned before, not only do the caps of the clusters evolve with size, but also the cores of these clusters undergo rearrangements, and vary in size. The shape of internal atoms is dominated by the TTP structure till size 62. The TTP unit, either bare or modified, forms the motif for core of GS structures right from size 46 till size 62 (see Fig. 5(b)). The bare TTP unit is made up of 9 Ga atoms (for sizes 49-59). The number of atoms in the core initially decreases to 8 (truncated TTP) at size 57, and stays so till 59, but the motif of the core remains TTP. This decrease in number of core atoms between size 57 and 59 occurs, since an atom from the core is lost to the surface/shell, that gets covered more and more by increasing number of cap atoms. Single TTP unit based core is observed only till size 59, since the structures till size 59 are caps over the base Ga_{46}^+ GS structure, with minor modifications to the shell atoms. At size 60, two truncated TTP units join together, sharing a face of the trigonal prism, to form

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the elongated core of Ga_{60}^+ GS. Minor modifications occur to this two unit TTP core motif for sizes 61 and 62. However, size 63 onwards, allover shape of the cluster becomes more spherical, and keeping in line with this, the core assumes a more compact shape, which is a different motif than the TTP. The new motif is added with one atom for size 65, and two atoms for core of sizes 66-70. Size 66 onwards, the core remains the same, while addatoms form the new cap over the Ga_{66}^+ GS structure. Thus, we see that in this size range of gallium clusters, the core atoms also undergo constant rearrangement and grow in size as the cluster itself grows. As witnessed in the discussion of evolution of the cap and the core above, the growth of gallium clusters in this size range appears quite systematic and regular. Each atom that is added to the cluster takes its place precisely into the already well-defined cap structure, and makes way for the next. The cap growth is quite predictive when compared with the bulk gallium's structure. We note that an atom added to the cluster does not place itself isotropically, nor does it get influenced by the geometry's symmetry. On the contrary, it takes its place in the direction in which the cap has grown already, becoming a part of the same. This points to the fact that bonding in these clusters is direction dependent, and spherically symmetric models of charge density, like spherical jellium model, can only describe these clusters to a limited extent. On the contrary, covalent bonding, which is inherently directional, fits well in describing the observed evolution. Thus, any analysis that is performed to describe bonding, is expected to inevitably bring up the covalency of these clusters. In Sec. III B, we present a detailed investigation of the same.

B. Bonding

Bonding in gallium clusters has become an issue of debate lately. Chacko et al., in their work, performed the ELF analysis to conclude the presence of covalent bonds in gallium clusters.¹² Existence of large ELF isosurface basins at high ELF values around 0.65 provided sufficient evidence for the presence of covalent bonds in gallium clusters. Schebarchov et al., on the other hand, worked with small gallium cluster metalloids in which they found agreement with jellium molecular orbitals (MOs), which suggest the bonding in these metalloids to be metallic.³⁴ However, these results pertain to ligand protected small gallium clusters and not the free standing ones. In fact, MO analysis of free standing gallium clusters in the present work (discussed later) has yielded results that only partly agree with this jellium picture. In another work, Núñez et al. have compared gallium clusters with its bulk (α -Ga), based on which they propose that gallium clusters are metallically bonded.³¹ They have reported that coordination numbers of gallium clusters are higher than bulk α -Ga, typically close to those of metal clusters. However, coordination number and the conclusions from it depend largely upon the cutoff bondlength chosen. In general, drawing parallels between various physical properties of infinite solids, and their finite sized counterparts has its own limitations, in terms of interpretation of the property in question. For example, coordination number in bulk is calculated with a cutoff bondlength as the first minima in pair distribution function (3.3 Å for α -Ga). This value requires re-tuning when dealing with clusters. A smaller cutoff is more appropriate for finite sized systems. It is possible to choose an appropriate cutoff by investigating how charge distribution along the line joining two atoms in Ga dimer changes with their distance of separation. Charge density maxima will occur at atomic sites if two atoms are separated by distance 3.3 Å, and it appears along the bond only at 58% of maximum charge isosurface value. Hence, a more judicious choice for cutoff bondlength in finite system will involve such a testing to assure that it is not overestimated, treating atoms as individual entities while calculating coordination. Further, while buckling of atomic planes could be taken as a signature for covalency in bulk system, its absence in finite sized system cannot be treated as absence of covalency. As demonstrated earlier (Fig. 3), although these clusters exhibit similarities of structure with α -Ga, their surfaces become curved in order to minimize the surface energy, and do not show buckling. Hence, a direct comparison in exact details between structures of bulk and the clusters may lead to erroneous conclusions.

With two different views existing about bonding in gallium clusters, mainly because of different tools used for analyzing it, we revisit bonding in gallium. Next, we present a more detailed picture of bonding in gallium clusters with the help of an extensive analysis of the MOs, the ELF, and the Bader charges. The results of the analyses are arrived at by performing them on multiple sizes of the clusters, and hold good for gallium clusters in general.

1. Molecular orbitals

Analysis of the MOs of different representative clusters in the size range chosen was performed. Conclusions derived from analysis for each of those sizes were found to be qualitatively same, viz., (1) only initial few MOs of clusters follow the jellium model, (2) only atomic s orbitals contribute to the formation of jellium like MOs, (3) none of the p-complex MOs formed out of atomic p orbitals shows resemblance to jellium MOs. Presenting the data for all the clusters analyzed is bound to cause repetition, without any new insight. Hence, here we present the MO analysis of Ga_{66}^+ in detail, which represents the conclusions that hold good for of all other clusters in this size range. All occupied MOs and Ga_{66}^+ were analyzed in detail for their shapes, and their resemblance with MOs of the jellium model was checked. Detailed account of the findings for Ga⁺₆₆ is provided below. Since 2 out of 3 valence electrons of atomic Ga are s type, only the initial 66 MOs of Ga_{66}^+ , that form out of the 132 atomic s electrons, could be expected to show similarities with the jellium model. Atomic contribution to the MOs can be verified using the *lm* decomposition analysis. Graph of *lm* decomposition of the MOs (not shown here) shows that atomic s contribution to cluster MOs is high till 66th MO, and decreases thereafter. Atomic p contribution to MOs behaves complimentary to this, and is low till 66th, and increases thereafter. Unlike Al, sp hybridization was not observed for any size in this range.

TABLE I. Analysis of number of basins and number of atoms in each basin at ELF = 0.65 for three clusters chosen. A "c" in the parentheses indicates that the atoms belong to the core of the cluster.

N _{atoms} in a basin	Ga_{46}^+				Ga^+_{60}	Ga ⁺ ₆₆							
	1	8	30	1	4	39	1	2	4	7	8	10	16
No. of basins	7+1(c)	1(c)	1	9	3(c)	1	17	2	1	1	1	1	1(c)

Ga⁺₆₆ possesses a total of 99 occupied MOs, of which, initial 66 are formed out of the atomic s orbitals, which are the ones that can be expected to form jellium like MOs. All the MOs of Ga⁺₆₆ were inspected at 1/6th their maximum isosurface value to arrive at the following conclusions. First 66 jellium orbitals, arranged in increasing order of their energies are:⁵⁸ 1S, 1P, 1D, 2S, 1F, 2P, 1G, 2D, 3S, 1H, 2F, 3P, 1I. Of these, only 1S, 1P, 2S, and 2P can be unambiguously mapped with those of the Ga_{66}^+ MOs. Of the remaining MOs, 1D (4) out of 5), 1F (3 out of 7), 1G (5 out of 9), 2D (4 out of 5), 1H (6 out of 11), and 2F (4 out of 7) can be partially mapped in terms of their shapes, and their occurrence in the order of increasing energies. Among the first 66, MO 3S, expected to occur after 2D is absent altogether, along with MO 3P, and all the MOs occurring thereafter. Thus, taking them all in account, only 34 out of the total 99 occupied MOs of Ga₆₆⁺ map onto those of jellium model's MOs. The reason for the observed deviation of most of the MOs composed of atomic s electrons from jellium model could be explained on the basis of anomalous spatial contraction of 4p as well as 4s atomic orbitals due to partial screening of nucleus by 3*d* electrons.^{59,60} All MOs after the initial 66 (i.e., after 1*I*) in Ga_{66}^+ form the p complex and follow the symmetry of the cluster, exhibiting no resemblance with any higher jellium MOs. To shed more light on bonding in these clusters, next we analyze the ELF.

2. ELF analysis

The electron localization function has been used for quite some time now, to classify bonding in various situations.^{61,62} The ELF ranges in value between 0 and 1. ELF value of 1 signifies complete localization, while ELF=0.5 implies delocalized homogeneous electron gas. Maxima of ELF are called the attractors, and points that can be connected to the attractors by maximum gradient path form the (ELF) basins. A perfectly localized (covalent) system is characterized by valence attractors (ELF basins) at the center of the bond between two atoms at ELF values close to 1. Metallic bonding, on the other hand, is defined by a narrow localization window of ELF. Localization window is defined as the range of ELF values over which the valence attractors appear, and merge into a single ELF basin. Width of this window for a typical metal like aluminium is as small as 0.04.⁶³

For Ga⁴₄₆, 46 different attractors appear at ELF=0.8, stay separated till ELF=0.76, and they all merge into a single basin at ELF=0.56. The localization window, thus, has a width of 0.24, which is clearly much wider than what is expected in a typical metallically bonded system. Localization window has almost the same value for other clusters of gallium as well. A testimony to the fact that bonding in gallium clusters is not entirely metallic. Also, we observe that the attractors that initially grow around atomic sites join together along bonds, a characteristic of the covalent ELF.

Although these clusters have almost same localization window, subtle differences in the way different parts of each clusters bind are brought out by ELF basin analysis, which can be used to infer about the melting behaviour of clusters. A detailed analysis of basin connectivity was carried out for three different clusters, Ga_{46}^+ , Ga_{60}^+ , and Ga_{66}^+ , representative of the spherical core-shell, prolate core-shell, and spherical core-shell geometry classes, respectively, at ELF values 0.70, 0.68, 0.65, and 0.60. Table I shows the analysis for ELF = 0.65, which brings out the differences in bonding of the three clusters. Note that Ga_{46}^+ has 9 core atoms, Ga_{60}^+ has 12, and Ga_{66}^+ has 16 core atoms. We see from the table, that 89% core atoms of Ga_{46}^+ , and 100% of Ga_{66}^+ form the single largest basin, whereas only 25% core atoms form the largest basin in Ga_{60}^+ . This signifies that cores of Ga_{46}^+ and Ga_{66}^+ are better connected than the Ga_{60}^+ core. We have shown in our previous work²¹ that strongly connected cores give rise to delayed isomerization, which in turn leads to a high melting temperature for that cluster. Thus, it can be expected that Ga_{66}^+ , alike Ga_{46}^+ , will melt at a relatively higher temperature than Ga_{60}^+ .

3. Bader charge analysis

In addition to the MO and ELF analysis, Bader charge analysis was performed on the GS of all the sizes of gallium clusters considered here. The analysis emphasized the fact that simple quantity like charge homogeneity, observed in infinite bulk solids, gets modified due to the finite extent of the clusters. Bader charge analysis uses a 2D surface on which the charge density is a minimum perpendicular to the surface.⁶⁴ Typically in molecular systems, the charge density reaches a minimum between atoms and this is a natural place to separate atoms from each other. The charge enclosed within the Bader volume is a good approximation to the total electronic charge of an atom. We use this analysis to quantify atomic charges in the clusters. Bader analysis is performed on these geometries without any charge on them (neutral clusters). Neutral clusters are used for the charge analysis in order to assure that the effects as shown by Bader analysis are not an implication of added/subtracted charge on the cluster.

Initially, we map the atoms in the GS structures onto 2D plane, using their respective distances from a given $axis^{21}$ (not from origin), and color the resulting data points according to the magnitude of Bader charge they possess. Fig. 6 shows the resulting graphs of this analysis for representative sizes about either *x*, *y*, or *z* axis suitably. Bader charge analysis shows an accumulation of -ve charge towards the core of the gallium clusters, and of +ve charge on the surface. The Ga⁰₆₆ core,



FIG. 6. Excess Bader charge on each atom mapped onto the 2-D plane using their distance from axes. –ve charge gathers at the center, and +ve on the surface. Sizes of the clusters are mentioned at the top right corner of each frame, superscripted with a "0." Superscript "0" signifies that charge neutral clusters are used for Bader charge analysis.

consisting of 16 atoms, has an accumulative charge of 50 $|e^-|$, while the surface (50 atoms) has cumulative charge as 148, a deficit of 2 electronic charge between core and the shell. The observed charge transfer is consistent for all the GS structures, and is geometry dependent.

IV. CONCLUSIONS

In this work, putative GS structures for previously unknown sizes Ga_{49}^+ - Ga_{70}^+ are found within the framework of Kohn-Sham DFT. There are two main aspects of the work, (i) the growth pattern of gallium clusters in this size range, which diverges drastically from all known growth patterns of metal clusters and resembles that of silicon clusters, and (ii) critical analysis of bonding in these clusters to present a definitive picture of the same. The growth pattern observed here can be aptly described as "scaling up the shape," since clusters evolve from smaller core-shell structure to a larger core-shell structure with size. Initially, ad-atoms form into caps, and then evolve into structures that eventually merge into the outer surface. Bonding in these clusters is a mixture of metallic and covalent, exhibiting nearness to covalency, in contrast to the one observed in α -Ga which is more metallic with a stint of covalency. The clusters exhibit covalent bonding characteristics of a wide ELF localization window and ELF localization along the bonds. Except first few, rest of the MOs do not fit into the jellium model. It will be of great interest to examine if this behaviour of expanding to larger shells instead of building additional new shells continues after size 70. With GS structures predicted for new extended range of Ga clusters, it would indeed be interesting to measure various properties experimentally.

ACKNOWLEDGMENTS

The authors thank Professor D. G. Kanhere for his valuable suggestions and fruitful discussions, and Anju Susan for her useful inputs. The authors are grateful to the CDAC, and CSIR-4PI for availing the computational facility, and thank CSIR (CSC-0129) for funding this research partially. V.K. thanks the DST (GOI-555A) for partial financial help.

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