Ab initio density functional investigation of $\text{B}_{24}$ cluster: Rings, Tubes, Planes, and Cages

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We investigate the equilibrium geometries and the systematics of bonding in various isomers of a 24-atom boron cluster using Born-Oppenheimer molecular dynamics within the framework of density functional theory. The isomers studied are the rings, the convex and the quasiplanar structures, the tubes and, the closed structures. A staggered double-ring is found to be the most stable structure amongst the isomers studied. Our calculations reveal that a 24-atom boron cluster does form closed 3-d structures. All isomers show staggered arrangement of nearest neighbor atoms. Such a staggering facilitates $sp^2$ hybridization in boron cluster. A polarization of bonds between the peripheral atoms in the ring and the planar isomers is also seen. Finally, we discuss the fusion of two boron icosahedra. We find that the fusion occurs when the distance between the two icosahedra is less than a critical distance of about 6.5a.u.

I. INTRODUCTION

Atomic clusters are of great interest due to their novel properties which can serve as building blocks for self-assembled material in order to realize miniaturized nanodevices. Due to increasing technological importance of nanoscale devices, the investigation of the structural, and the related physical and chemical properties of clusters, especially boron, carbon, silicon-based systems, is becoming an expanding research area.

The discovery of $\text{C}_{60}$ carbon buckminsterfullerene molecule\(^1\) and its unique electronic properties has triggered an explosive growth of research in the field of cluster physics. Superconducting and magnetic fullerides\(^2\), atoms trapped inside the fullerene cage, chemically bonded fullerene complexes have generated much excitement. Since then, much attention has been focused to fabricate small caged clusters of various elements like C, Si, and B. However, small clusters of silicon and carbon ($n<15$) do not form stable cage structures. One of the ways of stabilizing these cages is by trapping a foreign atom at the center of the cage. Recent work by Kumar \textit{et al} demonstrated the feasibility of metal-encapsulation of fullerene-like caged clusters of Si\(^4\).

On the similar grounds it would be interesting to look at boron cages, since boron and boron-rich compounds exhibit some of the most interesting chemistry of all elements in the periodic table\(^5\). Atomic boron is the first light element of group III with one $p$- valence electron\(^3\). It is semiconducting in its bulk phase with low density, very high melting point, and hardness close to that of diamond. Due to $sp^2$ hybridization of the valence electron, large coordination number, and short covalent radius, boron prefers to form strong directional bond with various elements.

Boron clusters have been investigated mainly via computer simulation although some experimental results are available. La Placa \textit{et al} proposed existence of $\text{B}_{36}\text{N}_{24}$ cluster with the same structure as that of the fullerene $\text{C}_{60}$\(^6\). However, the only heteroatomic species that were observed in the experiment were BN and B$_2$N. In contrast, an earlier experiment had detected the existence of $\text{B}_n\text{N}_m^+$ for various combination of $n$ and $m$ for $n = 2 - 17$\(^7\). Other abundant distribution and fragments of clusters of group III were also found\(^8\). Rao and Jena carried out a comprehensive theoretical study of the equilibrium geometries, vertical ionization potentials, and the fragmentation patterns of $\text{B}_2$-$\text{B}_6$ clusters in neutral and singly charged states, as well as the stability of boron-rich clusters, $\text{B}_nX$; $n=1,5,12;X=\text{Be, C}\(^9\)$. They show that the electronic bonding in boron clusters is similar to that in boron-rich solids and is characterized by a three-center bond. In spite of being trivalent element having three centered bonds, a $\text{B}_{20}$ dodecahedron composed of pentagonal faces with each atom being three-fold coordinated, does not exhibit unusual stability\(^9\). Ab initio investigations of small boron clusters by Boustani reveal that most of the stable structures are composed of two fundamental units: hexagonal or pentagonal pyramids\(^10\). Hayami has investigated the encapsulation of impurity atoms, from H to Ne, in $\text{B}_{12}$\(^11\) icosahedron. He found that H and Li are most likely to get trapped and stabilize the cage. He also found that the highest occupied molecular orbital(HOMO)-lowest unoccupied molecular orbital(LUMO) gap is largest for C.
Boron exists in various crystalline and amorphous forms of which \( \alpha - \), \( \beta - \) rhombohedral (\( \alpha - \)rh and \( \beta - \)rh) and \( \alpha - \) tetragonal (\( \alpha - \)tet) are well known phases\(^5\). The \( \alpha - \)rh boron solids are composed of unit cells containing \( B_{12} \) icosahedra. The \( \alpha - \)rh boron, also called low temperature or red boron, have high level of crystal purity. The \( B_{12} \) icosahedra in this form are slightly distorted which are weakly bound to each other by three-center bonds situated in alternating parallel planes. This leads to weak thermal stability and therefore \( \alpha - \)rh boron on annealing at a temperature of about 1200°C transforms into \( \beta - \)rh. In contrast, a hypothetical \( \alpha - \)rh boron quasicrystal contains two elemental unit cells: a prolate and an oblate, stacked in a quasi-periodic manner\(^{12,13}\). The prolate unit cell in the quasicrystal is slightly distorted which transforms into oblate unit cell to form the quasicrystal. Formation of such icosahedral quasicrystal is also seen in Al-Mn alloy\(^{14}\). An interesting question concerns the transformation of the distorted prolate unit cells into oblate unit cell. Takeda \( et \ al \) found that the mechanism of this transition as an inter-penetrating process of the two \( B_{12} \) icosahedra lying along the short body diagonal in a prolate cell in the quasicrystal\(^{15}\). Boustan and coworkers investigated the fusion of those two \( B_{12} \) icosahedra lying along the short body diagonal\(^{16}\). Their calculations reveal that a stable drum-like boron cluster can be formed without removing any atoms within the two approaching icosahedra as suggested by Takeda \( et \ al \). They have considered various configurations of two \( B_{12} \) icosahedra connected to each other in different orientation. The optimization and search for local minima was performed with certain symmetry restrictions. The relative stability of these geometries were not compared with the other possible isomers of the 24-atom boron cluster. This is especially important since the geometry most stable isomer of \( B_{24} \) could be completely different from the drum-like structure and could be much lower in energy.

In the present work, we address some of these questions concerning fusion of two boron icosahedra and the \( B_{24} \) cluster. It is known that the number of isomers on an energy surfaces increases exponentially with the size of the cluster. Since, \( B_{24} \) is a medium size cluster, it has a large number of isomers. An interesting aspect of medium size boron cluster is the competition between quasiplanar, tubular and closed structures\(^{17}\). The strains in the bonds due to the curvature in the closed structures favors the quasiplanar structure, whereas, the dangling bonds in quasiplanar and convex structures favors the tube and cage isomers. We discuss the energetics, stability and bonding properties in certain representative isomers of the 24-atom boron cluster, followed by the discussion on the process of fusion of two \( B_{12} \) icosahedra. Previous reports as well as our investigation reveals that such the fusion results into a closed structure. Although, this structure is stable, it need not be the lowest energy isomer. In order to understand the relative stability of this fused structure, and hence the stability of the quasicrystal, we have investigated the various representative low-lying structure of the 24-atom boron cluster.

In section-II, we describe the numerical method used followed by a discussion of the results in section-III.

### II. THEORETICAL DETAILS

We employ Born-Oppenheimer molecular dynamics (BOMD) based on \textit{Kohn-Sham} (KS) formulation of density functional theory using \textit{exchange-correlation potential for LDA and the Perdew-Wang} potential for GGA has been used. The \textit{VASP} package. The Ceperley-Alder exchange-correlation potential within the local density approximation (LDA) and the generalized gradient approximation (GGA) using the VASP package. The Ceperley-Alder exchange-correlation potential for LDA and the Perdew-Wang potential for GGA has been used. The geometries were optimized using the conjugate gradient and the steepest descent method\(^{18}\). The size of the simulation cell was varied according to the structure studied.

| Isomer                  | Simulation Cell (Å) |
|-------------------------|---------------------|
| Ring 1x24               | 18x18x8             |
| Ring 1x24               | 17x17x11            |
| Tube 3x8                | 14x14x13            |
| Tube 4x6                | 15x15x16            |
| Quasiplanar and Convex  | 15x15x10            |
| Cages                   | 13x13x15            |

The structures were considered to be converged when the forces on each ion was less than 0.01eV/Å with a convergence in the total energy of about \( 10^{-4} \sim 10^{-6} \) eV.

The fusion of two icosahedra was carried out using the inhouse package. Norm-conserving pseudopotential of Bachelet \( et \ al \) in Kleinman and Bylander form with s-part treated as non-local was employed. The exchange-correlation potential of Ceperley-Alder, was used. A cubic supercell of length 40a.u. with an energy cutoff of 21.0 rydberg provided sufficient convergence in the total energy. During the dynamics, the norm of each of the states defined as, \( | h\psi_i - \epsilon_i \psi_i |^2 \) (where \( \epsilon_i \) being the KS-eigenvalue corresponding to the KS-eigenstate \( \psi_i \) ) was maintained at \( 10^{-7} \sim 10^{-9} \) a.u. The final structures were considered to be converged when the forces on all atoms were less than \( 10^{-4} \) to \( 10^{-3} \) a.u.
The nature of the bonding has been investigated using the electron localization function (ELF) along with the charge density. Such ELF have been found to be useful for elucidating the bonding characteristics of a variety of system, especially in conjunction with the charge density. For a single determinantal wavefunction built from KS orbitals $\psi_i$, the ELF is defined as

$$\chi_{ELF} = \left[ 1 + \frac{D}{D_h} \right]^{-1}$$

where

$$D = \frac{1}{2} \sum_i |\nabla \phi_i|^2 - \frac{1}{8} \frac{|
abla \rho|^2}{\rho}$$

$$D_h = \frac{3}{10} \left( 3\pi^2 \right)^{5/3} \rho^{5/3}$$

with $\rho = \rho(r)$ the valence-electron density. A value of $\chi_{ELF}$ nearly 1 represents a perfect localization of the valence electron density.

### III. RESULTS AND DISCUSSION

The present investigation can be separated into two groups. First, we present results for various isomers of a 24-atom boron cluster which can be classified into: (i) the rings, (ii) the tubes, (iii) the convex and the quasiplanar structures and, (iv) the closed structure isomers of $B_{24}$. Since $B_{24}$ has a large number of isomers, we restrict our study to a certain isomers of the above representative classes. First, we discuss the geometry and the bonding in these isomers computed by GGA, followed by the energetics and stability of these isomers. Finally, we discuss the fusion of two boron icosahedra.

#### A. Isomers of $B_{24}$

1. **Rings**

In this section, we present the results for two rings, viz. a monocyclic-ring and a double-ring. In fig.1, we show, the optimized geometry, the isovalued surfaces of the electron localization function, and the total charge density for the HOMO and the LUMO states for the monocyclic-ring. It turns out that this structure is the least stable, and makes an interesting contrast with the most stable structure, viz., the double-ring.

The monocyclic-ring has a diameter of 11.81Å. In spite of being the least stable isomer, the ELF plot, in fig.1b, shows a localized $p_x - p_x \sigma$ bond. It is interesting to examine the behavior of the HOMO state. The HOMO state in the monocyclic ring is doubly degenerate. In fig.1c, we show the charge density for the one of the HOMO state. As a result, an effective delocalisation of the $\pi$ bond similar to that in benzene is seen. The difference in the HOMO states of benzene and $B_{24}$ is that in benzene the $\pi$ bonds is perpendicular to the plane of the carbon ring, whereas in $B_{24}$, the HOMO is formed by the in-plane $p_y - p_y$ orbitals. During the formation of benzene molecule, each carbon atom promotes an electron from the 2$s^2$ state into the empty 2$p_z$ orbital, whereas in boron, an electron from the 2$s^2$ state is promoted to the empty 2$p_y$ orbital. Thus, the reason for formation of in-plane $\pi$ bond in $B_{24}$ is the absence of $p_z$ electron. The LUMO state of $B_{24}$, on the other hand, is out of the ring-plane $p_z - p_z$ (fig.1d).

In fig.2, we show, the optimized geometry, the isovalued surfaces of the electron localization function, and the total charge density for the HOMO and LUMO states for a double-ring. The double ring of diameter of 6.22Å, is composed two ring of 12-atoms each, 1.45Å apart, arranged in a staggered configuration. Each ring is rotated by an angle of $\pi/12$ with respect to the other ring in order to form the staggered configuration. It is known that boron, boron-rich compounds and boron clusters exhibit $sp^2$ hybridization. Such a staggered double-ring formation, facilitates such an hybridization, thereby making it the most stable structure.
The ELF plot (fig.2b) shows a polarized $\sigma$ bond between the atoms in the same ring, the polarization caused by the atoms in the neighboring ring. This is a signature of three-centered boron bond which is a precursor to the bonding in solid state boron. The total charge density (not shown) is also localized in the region between the two rings. The charge-density for the HOMO (fig.2c) and the LUMO (fig.2d) represents a strongly localized $\pi$-bond between two atoms. While the HOMO state is a $\pi$ bond between an atom of each ring, the LUMO state shows a lateral $p-p$ overlap between the atoms of both the rings. Similar to the monocyclic ring, the HOMO state in this case is also doubly degenerate, giving rise to an effective delocalization.

It is instructive to analyze the total $p$-character in the orbitals as a function of orbital number. In fig.3a and 3b, we show such a plot for the monocyclic and the double-ring, respectively. The character in the orbitals is calculated by projecting the orbitals onto spherical harmonics centered at each ionic sites within a sphere of a specified radius around each ion. The radius of the sphere is usually taken to be half of the distance of the ion from the nearest ion. It can be noted that a monotonic decrease in the amount of $s$-character in a monocyclic-ring is seen, whereas, it is oscillatory for the double-ring in the central occupied orbitals. A substantial amount of $p$-character in the lower occupied states in the double-ring is seen. This indicates a higher degree of $sp^2$-hybridization. For both the structures, a double degeneracy is seen in most of the occupied states. These states represents resonant structures.

2. Tubes

We discuss three tubes composed of: (a) three planar rings of eight atoms, (b) four planar rings of six atoms, and (c) four rings, each ring consisting of six atoms arranged in a staggered configuration.

In fig.4, we show, the optimized geometry of the tubular drum shaped boron cluster along with the HOMO state, and the ELF. This structure is composed of three rings of eight boron atoms each, with the height of the drum alternating between 2.92\,Å and 3.01\,Å. The surface of the drum is made up of an elongated rhombus with the atoms in the central rings coming closer to each other, thereby pushing apart the atoms on the outer rings. This structure has a distorted $D_{4h}$ symmetry. Energetically, this structure is nearly degenerate to the double ring. It has a very small HOMO-LUMO gap (0.3eV as compared to 1.28eV in the double-ring), due to Jahn-Teller distortions. The HOMO state is doubly degenerate, which on distortion gives rise to this small gap. The isovalued plot of the HOMO (fig.4b), shows a bond between an atom of the outermost rings with the two nearest atoms in the central ring along the bonding region, unlike the ring isomers where a $\pi$ bond is formed. The peculiar alternating height is due to the characteristic bonding in this structure. The ELF (fig.4c), shows a strong localized bond between the central atoms of the rhombus. The bonds amongst the outer-ring atoms are similar to that of the double-ring, i.e. polarized by the atoms in the central ring.

A four-ring tube with six boron atoms each, is shown in fig.5a. This tube with a small diameter of about 3.0Å is the initial structure. On geometry optimization, the open tubular structure distorts thereby closing both the ends. The optimized geometry is shown in fig.5b. It is seen that the alternate atoms in the outermost rings on either side, approach the center of the ring closing the ends. This structure can also be viewed as a distorted cage, as shown in fig.7b, without the icosahedral closing. It is interesting to note that, despite of $sp^2$-hybridization, there is a possibility of getting a 3-d closed structure.

We have also carried out a geometry optimization of a $B_{24}$-$D_{3d}$ open structure. The geometry of this structure is depicted in fig.5c. This structure too undergoes a similar structural transformation into a close $D_{3d}$ boron cage (fig.7b), due to higher bond strains and a large curvature at the open ends. This result is contradictory to that reported by Boustani and coworkers\textsuperscript{16}. According to them, the stability of the closed tubular form $B_{24}$-$D_{3d}$ increases when the closed tubular ends rearrange to form an additional ring of 6-atoms, as found within an open tubular structure of $B_{24}$-$D_{6d}$. This difference is mainly due to the differences in the theoretical approaches. We have done unrestricted geometry optimization, whereas, they have imposed certain symmetry restriction for the minimization. Moreover, we have used density functional method within plane-wave pseudopotential and GGA approximations, whereas, Boustani\textit{ et al} have done an all electron calculations using Hartree-Fock and local spin density functional theory.

3. Quasiplanar and Convex Structures

We present the results for a couple of open structures viz. the quasiplanar and the convex stable isomers of $B_{24}$. According to the \textit{Aufbau principle} proposed by Boustani\textsuperscript{10}, we construct a quasiplanar and a convex structure from the basic unit of a hexagonal pyramid $B_7$. Upon optimization, we find that the LDA computed geometry of the quasiplanar structure is nearly planar. The quasi-planarity comes from the GGA calculations. The GGA-optimized geometry of the quasiplanar structure is shown in fig.6a. Some atoms are raised above the plane while some atoms are
The total charge density is the sum of all the projection over all ionic sites. Interestingly, the density computed by GGA. The that of the convex structure. In fig.6e, we show, the plot of the HOMO state for the convex structure at 1/6th of its maximum value. The HOMO state is delocalized within the plane along the bonding region. An excess electron cloud outside the cluster is also seen. This behavior in the HOMO state of the quasiplanar structure can be contrasted with that of the convex structure. In fig.6c, we show, the plot of the HOMO state for the convex structure at 1/6th of the maximum value. It is clear from this plot that the HOMO state is more localized. It represents a π bond between atoms of the outermost layer, the π bond being formed on the two sides of the plane of the structure.

In fig.6c and 6f, we plot, the ELF for these two structures, respectively. The nature of the ELF in both the structures is nearly similar. A polarization of the bond between the peripheral atoms is seen in both the cases. A higher degree of polarization in the quasiplanar structure is seen. Moreover, a 3-centered bond is seen in interior atoms in the quasiplanar structure.

4. Closed Structures

In this class we have studied three structures. The geometry of these structures are shown in fig.7a(i), 7b(i) and fig.7c(i). We will refer these closed structures as cage-I, cage-II and cage-III respectively. It is seen that upon formation of closed structure the stability of the boron isomers decreases as compared to that of the most stable isomer. Cage-I (7a(i)) represents two interacting B\textsubscript{12}. It has D\textsubscript{5h} symmetry. These two icosahedra, on fusion, transforms into a closed tubular form viz. cage-II, shown in fig.7b(i). The fusion process will be discussed later. This structure has the symmetry D\textsubscript{3d}. In case of cage-II, it is seen that the atoms moves towards the fusion region, thereby decreasing the bond strains in the icosahedral units. This structure is the most stable cage isomer of B\textsubscript{24}. Cage-III shows a different behavior than the other two structures. The first two cages show an icosahedral unit, whereas, cage-III can be visualized as double ring of eight atoms, placed side by side. Each side of this ring is capped by 4 atoms which forms a quinched roof or bend rhombus-like structure. This cage turns out to be the least stable closed isomer of B\textsubscript{24}.

The bonding in the cage-I and II is similar to that of the B\textsubscript{12} icosahedra except at the fusion region. In fig.7a(ii), fig.7b(ii), fig.7c(ii), we plot the ELF for cage-I through cage-III. It can be seen that in case of cage-I and cage-II, the ELF shows a high localization of the charge in the fusion region of the two icosahedra. A slight delocalization at the tube ends, as compared to the central fusion region, is seen. This shows an affinity of the boron icosahedra to get bonded to each other. On the other hand, the ELF for the cage-III, depicted in fig.7c, shows a three-centered bond between an atom of the quinched roof and two atoms from the octagonal ring. It is interesting to note that such bonding is seen in solid state boron\textsuperscript{5}. Thus, in spite of a three-centered bond, the boron clusters does not show enhanced stability.

5. Energetics and Stability

The energetics and the stability of isomers of B\textsubscript{24} can be explained via the binding energy, content of p-character in the total density, and the HOMO-LUMO gap. In fig.8a, we plot, the the binding energy per atom for all the isomers studied, computed by LDA and GGA. The binding energy is calculated as $E_b = E_{\text{atom}} - E_{B_{24}}/24$. The trend in the binding energy by both methods is remarkably similar. The GGA gives lower binding energy for all isomers, the shift being nearly identical. The double-ring is the most stable isomer. With the exception of the monocylic-ring and the cage-III, all the isomers are nearly degenerate to the double-ring. The stability of the isomers can be associated to the amount of p-character in the total charge density. In fig.8c, we plot, the content of p-character in the total charge density computed by GGA. The p-character is calculated by the method discussed above. The amount of p-character in the total charge density is the sum of all the projection over all the ionic sites. Interestingly, the p-character plot, nearly follows a similar trend to the binding energy. The least stable structure, viz. the monocylic-ring, has the least p-character in the total charge density. Thus, the binding energy is largely influenced by the amount of p-character contained in the total charge density. It can be noted that due to similar structure, the convex and quasiplanar structures have nearly same binding energy, and the amount of p-character in the total density. The lower binding energy of the monocylic-ring is not only a result of lower content of p-character but also the coordination number. The coordination number for the monocylic-ring is 2, whereas, it is 4 for the double-ring. Among the closed structure studied, cage-II, is the most stable structure, due to larger content of p-character. In fig.8d, we plot, the minimum interatomic distances for various isomers. An increase in the interatomic distances in the double-ring is seen over the
monocyclic-ring. This is due to increases the coordination number in the double-ring. The strains in the bonds also influences the interatomic distances. In the cage-I and cage-III, due to larger bond strains, the boron atoms moves away from each other, leading to a larger bond distance. As a result their binding energies is lowered.

The HOMO-LUMO gap shows a different behavior. In fig.8b, we plot, the HOMO-LUMO gap for these isomers, computed by LDA and GGA. Unlike the the binding energy, both methods gives nearly same value for the gap, with the exceptions of the double-ring and the isomer shown in fig.5b, where the gap is lowered as expected, and the cage-III, where the gap is increased. The increase in the gap for the cage-III is due to the degenerate HOMO state. Moreover, a wide variation in the gap for various isomers is seen. The drum-shaped isomer (fig.4a), in spite of being nearly degenerate to the most stable structure, the double-ring, exhibits a very small gap due to Jahn-Teller distortion. A similar behavior is also seen for cage-III. The quasiplanar and the convex isomer exhibits nearly same HOMO-LUMO gap.

B. Fusion of Two Boron Icosahedra

As mentioned earlier, an unit cell of α-rh boron hypothetical quasicrystal consists of a prolate unit cell and an oblate unit cell, stacked in a quasi-periodic manner. The prolate unit cell is slightly distorted which transforms into oblate unit cell. The mechanism of this transformation has been studied by Takeda et al. and Boustani et al. Takeda et al. suggests that in order to undergo this transformation, the two icosahedra lying along the short body diagonal in the prolate unit cell should inter-penetrate. Their model also suggests the removal of three interfacing atoms. On the other hand, Boustani et al. has shown that there is no need of removing any such atoms. Their investigation reveals that a much stable closed tubular structure is formed upon fusion of the two icosahedra. To get a better inside of the fusion process, as the two icosahedra approaches towards each other, we simulate the process by the following method. Two icosahedra were kept at various distances starting from 5.0a.u. to 8.5a.u., and a linear search for an equivalent local minima was carried out. This distance is defined as the distance between the icosahedral centers. It is assumed that the composite B_{12}-B_{12} will take the structures corresponding to these local minima as they approach towards each other. Local geometry minimization was carried out for nine different distances in the above mentioned range. The corresponding total energies, in hartrees, of the equilibrium structures as a function of the distances are plotted in fig.9a. This plot shows a barrier of 5.31eV at a critical distance of 6.5a.u., which the icosahedra has to cross in order to get fused. The composite structure of the two icosahedra sees a local minima just before the barrier. The structure corresponding to this minima is shown in fig.7a(i). It can be seen that the icosahedra are bonded to each other by three bonds. Each black atom of the left icosahedra is bonded to the nearest white atom of the right icosahedra. As the icosahedra moves further towards each other, these six atoms forms a staggered ring-like structure. Such staggering, as discussed earlier, facilitates sp^2 hybridization, thereby increasing the stability. At the barrier, an intermediate structure during the transition is seen. The geometry of this structure is depicted in fig.9b. Due to strained staggered ring, this structure is unstable. As the icosahedra moves further towards each other, the strains in the ring is reduced finally giving a closed D_{3d} structure, shown in fig.7b(i). A slight rearrangement is seen during the formation of this closed tubular structure. The atoms moves towards the fusion region, consequently reducing the strains in the icosahedral units. This structure is the most stable cage isomer of B_{24} cluster. It is also nearly degenerate to the most stable isomer i.e. the double ring. This structure (cage-II) is about 1.91eV lower than the structure corresponding to the local minima (cage-I) just before the barrier. Thus, the effective barrier as seen by the fused structure is about 7.22eV. As a result, the oblate unit cell becomes much more stable than the prolate unit cell. Hence, the transformation of the prolate unit cell to oblate unit cell enhances the stability of the quasicrystal significantly.

IV. CONCLUSION

In the present work, we have reported the geometries and the systematics of bonding in various isomers of a 24-atom boron cluster and the fusion of two boron icosahedra using BOMD method within the framework of density functional theory. We find that the monocyclic-ring is the least stable structure. A staggered double-ring formation facilitates the sp^2 hybridization, thereby making it the most stable structure. Our calculations reveal that a 24-atom boron cluster does form a closed 3-d structures. The bonding analysis shows that a polarization of the bonds between the peripheral atoms is seen in the ring and the planar isomers. The binding energy of all isomers is largely influenced by the amount of p-character in the total charge density. An interesting observation common to all structures is the staggered arrangement of nearest neighbor atoms. In the rings, the staggering obtained by rotating the alternate rings, while in the open structures it is obtained by moving the atoms out of the plane as well as within the plane.
The fusion occurs when the distance between the two icosahedra is less than a critical distance of about 6.5\text{a.u.} In order to get fused, the icosahedra has to then cross a barrier of 5.31\text{eV}. Such fusion enhances the stability of the quasicrystal significantly.

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List of figures

1 (a) The optimized geometry of the monocyclic-ring of 24-boron atoms. (b) The isovalued surface of the ELF at the value 0.75. (c) The isovalued charge density surface of the HOMO state at the value 0.0059\(\text{electron/Å}^3\), (d) The isovalued charge density surface of the LUMO state at the value 0.0052\(\text{electron/Å}^3\).

2 (a) The optimized geometry of the double-ring of 24-boron atoms. (b) The isovalued surface of the ELF at the value 0.75. (c) The isovalued charge density surface of the HOMO state of the double-ring at the value 0.0075\(\text{electron/Å}^3\). (d) The isovalued charge density surface of the LUMO state of the double-ring at the value 0.0091\(\text{electron/Å}^3\).

3 The amount of \(s\) (continuous line) and \(p\)-character (dotted line), in arbitrary units, in various occupied states and the LUMO state as a function of orbital number for, (a) the monocyclic-ring and, (b) the double-ring.

4 (a) The optimized geometry of the drum shaped boron \(\text{B}_{24}\) cluster composed of three rings of eight boron atoms each. (b) The isovalued charge density surface of the HOMO state at the value 0.0036\(\text{electron/Å}^3\). (c) The isovalued surface of the ELF at the value 0.75.

5 (a) The initial geometry of the four-ring tube, each ring formed by 6-boron atoms. (b) The optimized structure. (c) The open tube with \(D_{3d}\) symmetry composed of 4-rings of staggered \(\text{B}_6\).

6 (a) The optimized geometry of the quasiplanar structure. The black circles represents atoms below the plane while the white circles represents atoms above the plane, giving the quasiplanar nature. (b) The isovalued charge density surface of the HOMO state of the quasiplanar structure at the value 0.0017\(\text{electron/Å}^3\). This value is 1/10\(^{th}\) of the maximum. (c) The isovalued surface of the ELF at the value 0.75. (d) The optimized geometry of the convex structure. The black circles represents atoms above the plane giving the convex nature. Remaining atoms are nearly planar. (e) The isovalued charge density surface of the HOMO state of the convex structure at the value 0.0031\(\text{electron/Å}^3\). This value is 1/6\(^{th}\) of the maximum. (f) The isovalued surface of the ELF at the value 0.75.

7 The geometries of closed structures: a(i) Cage-I representing two icosahedra interacting by three bond, each bond formed by atoms represented by black and white dots. a(ii) ELF plots for Cage-I at the value 0.75, b(i) Cage-II, the resultant structure of the fusion of two \(\text{B}_{12}\) icosahedra. A staggered-ring of six atoms (3 white and 3 black) is seen. b(ii) ELF plots for Cage-II at the value 0.75, c(i) Cage-III, composed of two rings of eight atoms each placed side by side, and capped by four atoms on both sides. The four atoms forms a quinted roof-like structure. c(ii) ELF plots for Cage-III at the value 0.75.

8 (a) Binding energy in eV per atom of the various \(\text{B}_{24}\) isomer computed by LDA and GGA. The dotted line represents the LDA binding energy while the continuous line represents the GGA binding energy. (b) The amount of \(p\)-character in the total density for various isomers computed by GGA. (c) The minimum interatomic distances in various isomers computed by GGA. (d) HOMO-LUMO gap, in eV, of the various \(\text{B}_{24}\) isomer computed by LDA and GGA. The dotted line represents the LDA gap while the continuous line represents the GGA gap.

9 (a) The total energy (in hartrees) of the clusters composed of two \(\text{B}_{12}\) icosahedra as they approach towards each other as a function of the inter-icosahedral distance. The arrows marked with (I) and (II) corresponds to the cage-I and cage-II, respectively, while the arrow marked with (T) corresponds to the transition structure (cage-T) depicted in fig.9b. (d) Cage-T, the intermediate structure between cage-I (fig.7a(i)) and cage-II (fig.7b(i)), representing the transition state during the fusion of two icosahedra. It shows an intermediate stage of formation of completely relaxed staggered-ring of six atoms (3 white and 3 black).

FIG. 1.

FIG. 2.

FIG. 3.
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