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The Bonding Nature of Icosahedral Clusters of the Group III Elements

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The bonding nature of icosahedral clusters of the group III elements was investigated to obtain the relation between properties of the clusters and their aggregates, i.e., icosahedral boron-rich solids and icosahedral aluminum-based quasicrystals. By means of a molecular orbital method of the bonding nature was evaluated whether it is metallic or covalent type. It is found that the 12-atom icosahedra (B_{12} and Al_{12}) and the 13-atom icosahedra (B_{13} and Al_{13}) show covalent and metallic-type bonding, respectively. Solid state properties of a cluster solid of the group III elements are considered to be profoundly related to the question whether the central icosahedral position is occupied or not. © 1997 Academic Press

INTRODUCTION

Elemental boron and many of boron-rich compounds including boron icosahedra, B_{12}, are semiconducting materials. It may be appropriate to consider that the semiconducting property is caused by the B_{12} cluster due to its role as a common structural element. In the aluminum-based icosahedral quasicrystal (QC), the atomic structure is also made by aluminum-based icosahedra. QC were discovered in 1984 (1) and are a new type of solid phase distinguished from crystalline and amorphous phases, because they have no translational symmetry but a fivefold rotational symmetry, which is forbidden in a crystal. There are two types of QC distinguishable by atomic occupation at the center of constituent icosahedral clusters. One is constructed from 13-atom icosahedra, Al_{13} (e.g., Al–Mn–Zn), and the other is composed of 12-atom icosahedra, Al_{12} (e.g., Al–Pd–Re). While the former have the metallic-like properties, the latter are characterized by a peculiar electric feature as well as their symmetries: (a) High-quality QC have extremely high values of resistivity which reach those of doped semiconductors and (b) the temperature coefficient is always negative in all QC systems (2, 3). Consequently, QC constructed from Al_{12} show semiconductor-like properties though all the constituent atoms are metals.

Both boron- and aluminum-based compounds show semiconductor-like properties when the icosahedron comprises 12 atoms, while aluminum-based compounds composed of 13-atom icosahedra have metallic properties. The packing fractions of 12- and 13-atom icosahedra are 0.726 and 0.604, respectively. The high value (0.726) is reminiscent of the close-packed structure (0.740) observed in normal metals; the low value (0.604), which is lower than that of body-centered cubic (0.698), may indicate that there is a tendency to approach a typical covalent bonding system (diamond structure, 0.340). In group III elements, therefore, atomic occupation at the center of an icosahedron seems profoundly to be related to the bonding nature of the icosahedron and the properties of the solid.

In this paper we present the results of molecular orbital (MO) calculations aimed to obtain the bonding nature of the icosahedral clusters in the group III elements.

METHOD

We used the semi-empirical MO method (6) for all calculations, in which the following approximations are employed:

1. neglect of diatomic overlap integrals,
2. neglect of three- and four-center two-electron integrals,
3. parametrization of the other two-electron and two-center one-electron integrals and the core–core repulsion.

We used the PM3 hamiltonian for core–core repulsion in all calculations except for the system including the boron atom. If a system contains boron atoms we chose the MNDO hamiltonian, because no parameters are available for boron in PM3. The MNDO and PM3 differ in the values of parameters and the method of approximation of the core–core repulsive force.

Our calculations can be divided into two parts. One is a geometry optimization of a cluster by total energy calcuations, and the other is a successive search for stationary point of an atom added to a cluster. Besides clusters of group III elements, clusters composed of group II elements, Be and Mg, are also included in our consideration to compare the bonding nature with group III elements. Atomic arrangement of a cluster is constrained to I_h symmetry for group III elements and to D_{3h} symmetry for group II elements (for D_{3h} symmetry, the bond angles are fixed to that of

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a close-packed structure). The latter is the same symmetry as that of the coordination polyhedron of hcp-type structure, which is the most common structure for group II elements. We discuss both 13- and 12-atom clusters for each symmetry. In a search for a stable location of an added atom, hydrogen, lithium, and the same kind of atom as the cluster are used for an external atom. The initial position of the external atom is chosen symmetrically with respect to the vertex, face, and edge center of the cluster (Figs. 1 and 2). Only one variable is optimized in the search: the distance between an added atom and the center of a cluster. This is because no significant stabilization energy is gained when an added atom is fully optimized.

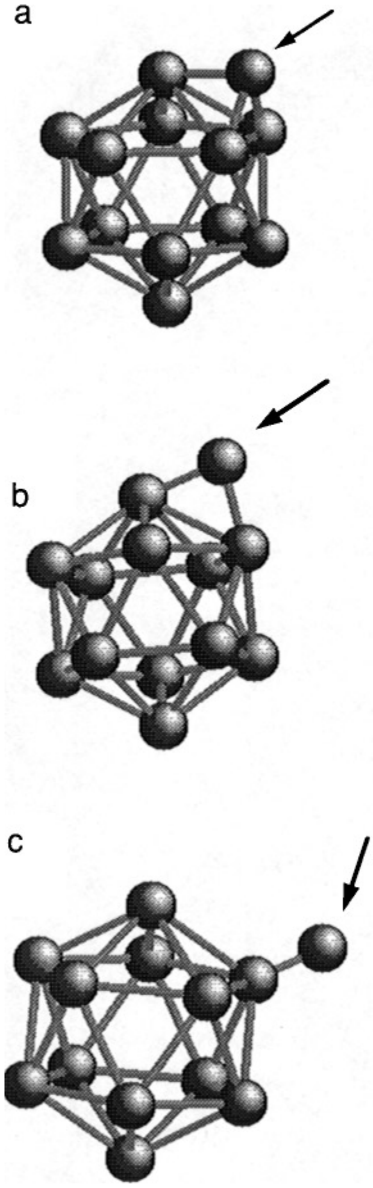

FIG. 1. Additional positions of an external atom added to icosahedral cluster. Arrows point to an additional atom. (a) face, (b) edge, (c) vertex.

RESULTS AND DISCUSSION

Cohesive energies of clusters obtainable from total energy and equilibrium cluster radii are shown in Table 1. In Table 1, the results for the clusters surrounded will 12 hydrogen atoms are also shown. The clusters are forced to bind by covalent bonds because each hydrogen atom occupies a vertex of the icosahedron and binds with a constituent atom of the cluster by a covalent bond. When the cluster is constrained to covalent bonds and an atom is embedded at the center, no gain of cohesive energy is obtained for a boron cluster, but not for the aluminum cluster. A system composed of covalent bonds cannot gain cohesive energy by increasing a value of packing fraction, whereas a metallic system can do so, because satisfaction of the specific bonding direction is significant to gain cohesive energy for a covalent system. Thus only a boron cluster makes a covalent bond on equilibrium geometry, if a cluster consists of 12 atoms. This fact is seen in the results for stationary position of an additional atom (in Table 2). The tendency to have directional binding is clearly seen for a 12-atom boron cluster, but a 13-atom boron cluster has a small variety for an additional position. The other clusters seem to prefer nondirectional bonding.

The interatomic distance for aluminum atoms in the icosahedral aluminium QC (about 2.5 Å) is shorter than that of fcc-type aluminum (2.86 Å). We carried out the same calculations for contracted clusters with the fact in mind.

TABLE 1
Cohesive Energy and Cluster Size

(a) I_h

	E (eV)		r_{cluster} (Å)	$d_{\mathrm{cluster–H}}$ (Å)
B_{12}	50.3	(4.19)	1.71	—
$B@B_{12}$	52.2	(4.01)	1.84	—
$B_{12}H_{12}$	94.1		1.75	1.17
$B@B_{12}H_{12}$	94.0		1.83	1.16
Al_{12}	9.74	(0.812)	2.43	—
$Al@Al_{12}$	12.7	(0.974)	2.46	—
$Al_{12}H_{12}$	26.9		2.41	1.63
$Al@Al_{12}H_{12}$	29.9		2.46	1.66

(b) D_{3h}

	E (eV)		r_{cluster} (Å)
Be_{12}	15.5	(0.455)	2.03
$Be@Be_{12}$	20.3	(1.56)	2.14
Mg_{12}	12.4	(1.03)	2.49
$Mg@Mg_{12}$	14.4	(1.11)	2.49

Note. The mark @ shows inclusion of an atom into the center of the cluster. The values in parentheses are cohesive energy per one atom.

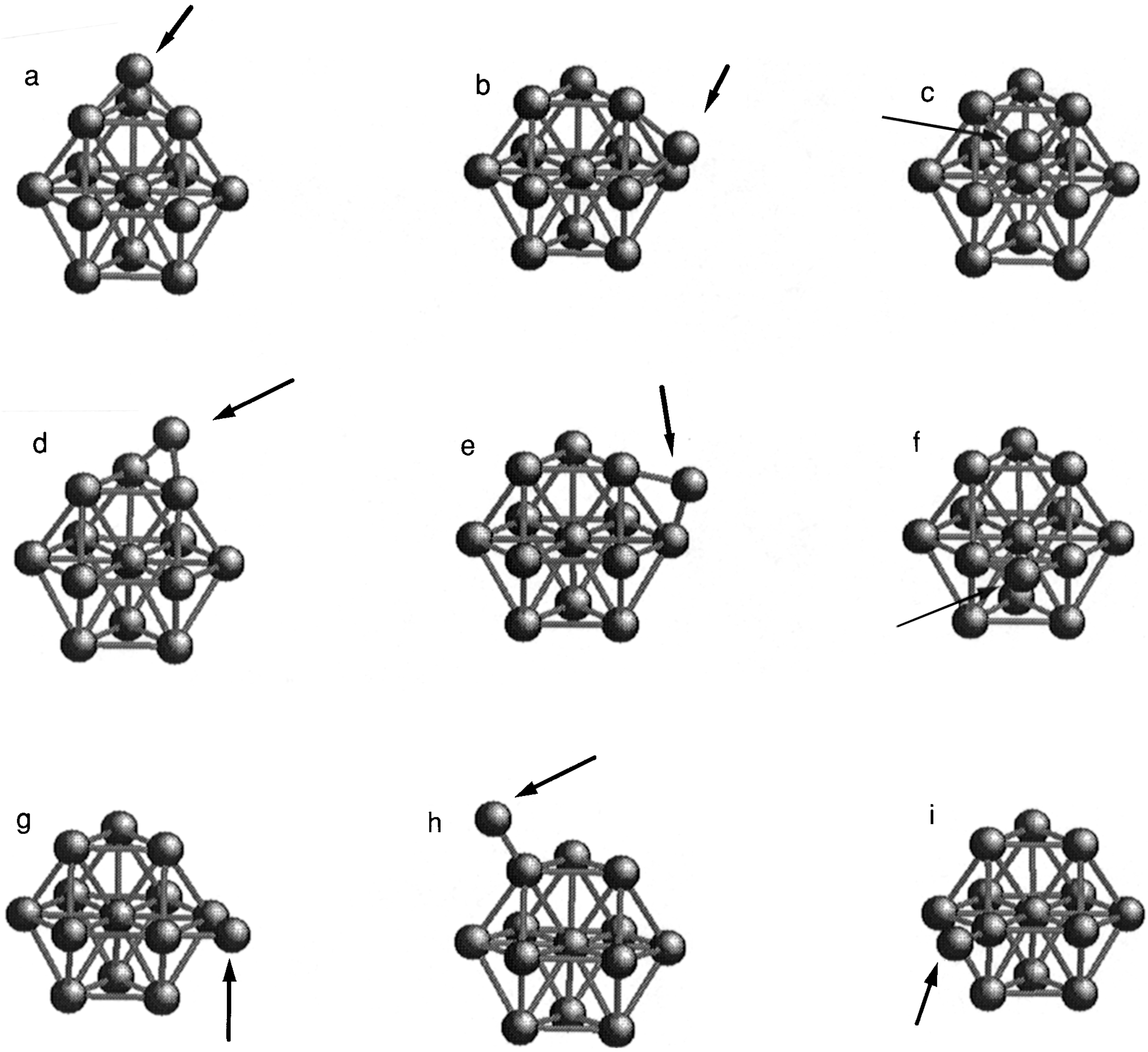

FIG. 2. Additional positions of an external atom added to cluster with D_{3h} symmetry. Arrows point to an additional atom. (a) face-1, (b) face-2, (c) face-3, (d) edge-1, (e) edge-2, (f) edge-3, (g) edge-4, (h) vertex-1, (i) vertex-2.

Hatakeyama shows by an *ab initio* method that an icosahedron of aluminum is stable rather than the fcc-type structure, when the interatomic distance is shorter than about 2.5 Å (7). We shortened the cluster radii about 10% in consideration for Hatakeyama's calculations (2.5 Å is about 90% of the interatomic distance of fcc-type aluminum, 2.86 Å). Only the most stable positions of an additional atom are presented in Table 3 for the contracted clusters. The characteristic feature is that the position of an external atom for aluminum clusters changes from face to vertex as a result of the cluster contraction, whereas the other clusters are independent of the contraction.

Although some deviation is presented, we can summarize all the calculations: (A) In the clusters of group III elements, atomic occupation of the center of a cluster changes the bonding nature from covalent to metallic type, though a mechanism to shorten the interatomic distance is necessary for aluminum clusters (in QC, the transition metal atom may act as a role of the mechanism). This implies that the bonding nature can be changed from covalent to metallic by

TABLE 2
Cohesive Energies of the Clusters with an Additional Atom (in eV)

(a) I_h boron cluster

		B_{12}			B_{13}	
	H	Li	B	H	Li	B
face	51.7	54.0	55.2	55.4	*57.6*	*58.2*
edge	52.3	54.1	*56.0*	*55.8*	*57.6*	58.1
vertex	*54.9*	*54.2*	55.8	*55.8*	57.3	58.0

(b) I_h aluminum cluster

		Al_{12}			Al_{13}	
	H	Li	Al	H	Li	Al
face	*12.6*	*13.1*	*15.1*	*15.6*	16.4	*18.1*
edge	12.1	13.0	10.3	15.2	*16.5*	13.6
vertex	10.8	12.8	9.99	14.2	16.2	13.0

(c) D_{3h} beryllium cluster

		Be_{12}			Be_{13}	
	H	Li	Be	H	Li	Be
face-1	17.5	17.2	17.2	22.9	22.9	22.2
face-2	17.9	17.0	17.1	22.8	22.8	22.1
face-3	17.8	*17.8*	*17.5*	22.9	*23.2*	*22.5*
edge-1	*18.4*	17.1	17.2	23.0	22.4	22.0
edge-2	18.0	17.1	16.8	*23.2*	22.4	22.0
edge-3	17.9	16.8	16.5	23.0	22.6	21.6
edge-4	18.3	17.0	17.2	23.1	22.7	22.2
vertex-1	18.3	16.5	15.9	23.0	21.4	20.7
vertex-2	18.2	16.7	16.0	23.1	21.5	20.5

(d) D_{3h} magnesium cluster

		Mg_{12}			Mg_{13}	
	H	Li	Mg	H	Li	Mg
face-1	14.3	13.3	13.7	16.2		15.6
face-2	*14.4*	13.3	13.6	*16.4*	15.4	15.6
face-3	14.2	*13.4*	*13.9*	16.3		*15.9*
edge-1	14.0		13.0	16.3	15.2	15.4
edge-2	14.1		13.2	16.2	*15.5*	15.1
edge-3	14.3	13.2	13.2	*16.4*	15.4	15.4
edge-4	14.2	13.2	13.1	16.2	15.1	15.2
vertex-1	13.5	13.2	12.4	15.7		14.6
vertex-2	13.6	13.2	12.3	15.7	*15.5*	14.5

Note. Blanks mean calculations did not converge. The respective lowest energy are italic.

TABLE 3
Stationary Position of Additional Atoms

(a) I_h boron cluser

		B_{12}			B_{13}	
Cluster shape	H	Li	B	H	Li	B
equilibrium	vertex	vertex	edge	edge/vertex	edge/face	face
contracted	vertex	vertex	vertex	vertex	vertex	face

(b) I_h aluminum cluster

		Al_{12}			Al_{13}	
Cluster shape	H	Li	Al	H	Li	Al
equilibrium	face	face	face	face	edge	face
contracted	vertex	vertex	vertex	face	edge	face

(c) D_{3h} Be cluster

		Be_{12}			Be_{13}	
Cluster shape	H	Li	Be	H	Li	Be
equilibrium	edge	face	face	edge	face	face
contracted	vertex	face	face	edge/vertex	face	face

(d) D_{3h} Mg cluster

		Mg_{12}			Mg_{13}	
Cluster shape	H	Li	Mg	H	Li	Mg
equilibrium	face	face	face	face/edge	edge/vertex	face
contracted	face	face/vertex	face	face	face	face

varying the packing fraction. (B) clusters of group II elements bind by metallic bond regardless of the presence of an atom at the center. Thus (A) is considered as the property attributing to group III elements.

When clusters are aggregated to form a solid, the solid is bound by intercluster bonds so that there is a great relation between bonding of the cluster and that of the solid. Thus properties of a solid formed by clusters of group III elements could be changed by varying the packing fraction. Doping to interstitial sites among clusters is realized in that in β-boron (8). In QC, the presence of two categories which are classified by the temperature dependence of resistivity correspond in a one to one relationship to whether an atom occupies the center of the icosahedral aluminum cluster or not.

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