

# Why is $\text{Al}_{11}\text{B}_2^-$ not a magic number in TOF-MS?

Jian Wan

Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario M3J 1P3, Canada  
and Department of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China

René Fournier<sup>a)</sup>

Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario M3J 1P3, Canada

(Received 20 May 2003; accepted 1 July 2003)

Bimetallic anionic and neutral clusters, consisting of group III elements ( $\text{Al}_{n-1}\text{B}_1$ ,  $\text{Al}_{n-2}\text{B}_2$ ,  $\text{Al}_{n-1}\text{In}_1$ , and  $\text{In}_{n-1}\text{Al}_1$ ,  $n = 11-14$ ), have been theoretically investigated by density functional theory at the B3LYP/6-31G\* (LanL2DZ for the In element) level. The calculated optimized equilibrium geometries and total energies of neutral and anionic clusters give a satisfactory interpretation of magic number clusters observed in time of flight mass spectra (TOF-MS). Our results show that  $\text{Al}_{11}\text{B}_2^-$  is the most stable among  $\text{Al}_{n-2}\text{B}_2^-$  ( $n = 11-14$ ) cluster anions and keeps an icosahedronlike structure, contrary to what had been suggested previously. Whether a magic number turns out in TOF-MS likely depends more on the stability of the neutral clusters than on the stability of the anions. The  $\text{Al}_{11}\text{B}_2$  neutral cluster is less stable than  $\text{Al}_{12}\text{B}_2$ , and this is why  $\text{Al}_{11}\text{B}_2^-$  does not appear as a magic number in TOF-MS. In addition, we found that icosahedral structures do not always hold for the magic cluster anions considered in the present study. © 2003 American Institute of Physics. [DOI: 10.1063/1.1603217]

## I. INTRODUCTION

Recently there has been renewed interest in searching for unusually stable (“magic”) metal clusters. The discovery of fullerenes<sup>1</sup> and metallocarbohedrenes<sup>2</sup> in molecular beams has prompted attempts to produce other magic clusters that might serve as building blocks for cluster-assembled materials. If such exotic materials could be formed, they might well exhibit unique electronic, magnetic, optical, mechanical, and/or catalytic properties. While several types of magic clusters have now been considered by theory, doped aluminum clusters<sup>3-11</sup> have been studied repeatedly and are especially promising candidates.

On the other hand, several studies have shown that bimetallic systems have certain characteristics that often make them better catalysts than pure metals.<sup>12-15</sup> For this reason, bimetallic nanoclusters are used in several commercial catalytic<sup>16</sup> and electrocatalytic<sup>17,18</sup> processes. The active components of dispersed metal catalysts are small clusters, and, therefore, cluster properties, not bulk properties, are responsible for the observed characteristics.<sup>19</sup> For these two reasons, understanding the electronic and dynamic properties of small bimetallic clusters, which constitute an intermediate between single atoms and condensed matter, and their relationship with observed macroscopic phenomena, has doubtless become one of the most important issues in cluster science.

In an experimental study<sup>3</sup> of the mass ion intensity distribution of  $\text{Al}_{n-1}\text{B}_1^-$  and  $\text{Al}_{n-2}\text{B}_2^-$  clusters, the intensity distribution of  $\text{Al}_{n-1}\text{B}_1^-$  was found to be almost the same as that of  $\text{Al}_n^-$  and “magic numbers” (i.e., unusually high peaks in the mass spectra) appear at  $n = 13$  (i.e.,  $\text{Al}_{12}\text{B}_1^-$ ) and  $n = 23$  clusters. However,  $\text{Al}_{11}\text{B}_2^-$  is not magic.

Nakajima *et al.*<sup>3</sup> attributed the anomalous properties of  $\text{Al}_{11}\text{B}_2^-$  to the fact that, under the icosahedral structure of  $\text{Al}_{13}^-$ , it is possible to substitute one smaller diameter B atom in the center of the cluster, but this structure can ill afford to substitute two Al atoms by the smaller B atoms.

From the point of view of the jellium electronic shells, the valence electrons of the boron atom could contribute to the formation of the closed shells (40 electrons) in both  $\text{Al}_{n-1}\text{B}_1^-$  and  $\text{Al}_{n-2}\text{B}_2^-$  clusters.  $\text{Al}_{11}\text{B}_2^-$  should be observed as a magic number as a consequence of the  $2p$  shell closing, but it is not.

In the present paper we focus on bimetallic anionic and neutral clusters consisting of group III elements (B,Al,In). We have calculated the equilibrium geometry and total energy of neutral and anionic  $\text{Al}_{n-1}\text{B}_1^-$ ,  $\text{Al}_{n-2}\text{B}_2^-$ ,  $\text{Al}_{n-1}\text{In}_1^-$ , and  $\text{In}_{n-1}\text{Al}_1^-$  ( $n = 11-14$ ) clusters using first principles theory. Our present theoretical results show that both  $\text{Al}_{12}\text{B}_1^-$  and  $\text{Al}_{12}\text{B}_1$  clusters are the most stable species among  $\text{Al}_{n-1}\text{B}_1^-$  and  $\text{Al}_{n-1}\text{B}_1$  clusters, respectively, supporting the criteria of magic clusters: electronic closed-shell and icosahedral geometry. Our results show that  $\text{Al}_{11}\text{B}_2^-$  is also the most stable among  $\text{Al}_{n-2}\text{B}_2^-$  cluster anions and that it keeps an icosahedronlike structure, which is in contradiction with the hypothesis made in Ref. 3. Whether a magic number shows up in TOF-MS is more likely dependent upon the stability of the corresponding neutral clusters. Because the  $\text{Al}_{11}\text{B}_2$  neutral cluster is less stable than  $\text{Al}_{12}\text{B}_2$ ,  $\text{Al}_{11}\text{B}_2^-$  does not appear as a magic number in TOF-MS (see Sec. III for details).

In Sec. II we provide a brief outline of our computational procedure. A discussion of our results and a summary are given in Secs. III and IV, respectively.

<sup>a)</sup>Electronic mail: renef@yorku.ca

## II. COMPUTATIONAL DETAILS

The geometry optimizations were performed by the density functional theory (DFT)<sup>20–27</sup> using the B3LYP<sup>24,25</sup> functional. A 6-31G\* basis set<sup>28</sup> was used for B and Al atoms, and a DZVP orbital basis set<sup>29</sup> for the In atom in the case of  $\text{Al}_{n-1}\text{In}_1$ . In the cases of  $\text{In}_{n-1}\text{Al}_1$ , an effective core potential (ECP) and LanL2DZ basis set<sup>30</sup> were used. It includes a double-zeta basis set and the relativistic effective core potential (RECP) determined from a relativistic calculation of an atom.

We did a thorough search for the lowest-energy structures using different initial configurations (with or without symmetry constraints) for each cluster. In cases with no symmetry constraint, possible Jahn–Teller distortions were taken into account. Vibrational frequencies were computed at the B3LYP/6-31G\* (DZVP/LanL2DZ) levels to characterize stationary points. All calculations were performed using the GAUSSIAN 98 program.<sup>31</sup>

For each cluster, the calculations were repeated for various spin multiplicities. The following results are based on the geometries and spin multiplicities corresponding to the lowest energies.

## III. RESULTS AND DISCUSSION

The optimized equilibrium geometries and total energies of anionic and neutral  $\text{Al}_{n-1}\text{B}_1^-$ ,  $\text{Al}_{n-2}\text{B}_2^-$ ,  $\text{Al}_{n-1}\text{In}_1^-$ , and  $\text{In}_{n-1}\text{Al}_1^-$  ( $n = 11–14$ ) clusters are shown in Figs. 1–4. The difference in the total energies between the ground states of the neutral and anionic clusters provides the adiabatic electron affinity (AEA).

In order to compare the relative stability of the clusters, we calculated energy gains ( $\Delta E$ ) corresponding to adding an “M” atom ( $M = \text{Al}$  or  $\text{In}$ ) to an  $\text{M}_{n-1}\text{X}_m$  cluster:

$$\Delta E_n = -[E(\text{M}_n\text{X}_m) - E(\text{M}_{n-1}\text{X}_m) - E(\text{M})],$$

$$\Delta E_n^- = -[E(\text{M}_n\text{X}_m^-) - E(\text{M}_{n-1}\text{X}_m^-) - E(\text{M})].$$

Here  $E$  is the total energy of the respective systems. A previous theoretical study<sup>32</sup> has shown that one of the factors contributing to the relative peak height in the mass spectra of clusters is the magnitude of this energy gain. Other properties that might correlate with peak height were also computed: AEAs, HOMO–LUMO gaps, and lowest vibrational frequencies of the clusters. These quantities are listed in Tables I–IV.

### A. $\text{Al}_{n-1}\text{B}_1^-$ clusters

The equilibrium geometries of  $\text{Al}_{n-1}\text{B}_1^-$  and  $\text{Al}_{n-1}\text{B}_1$  ( $n = 11–14$ ) clusters are illustrated in Fig. 1. Note that in all these clusters the B atom resides inside the  $\text{Al}_{n-1}$  cage, irrespective of their size and charge states. We did consider several other initial geometries in our search for the lowest equilibrium geometry of every cluster considered, for example, (i) the icosahedron with the B atom located on the surface; (ii) distorted icosahedra with symmetry point group  $D_{5d}$ ,  $C_{5v}$ ,  $C_{3v}$ , and  $C_{2v}$ ; and (iii) a few initial geometries completely different from the icosahedron. Similar searches were done for the other series of clusters considered. Both

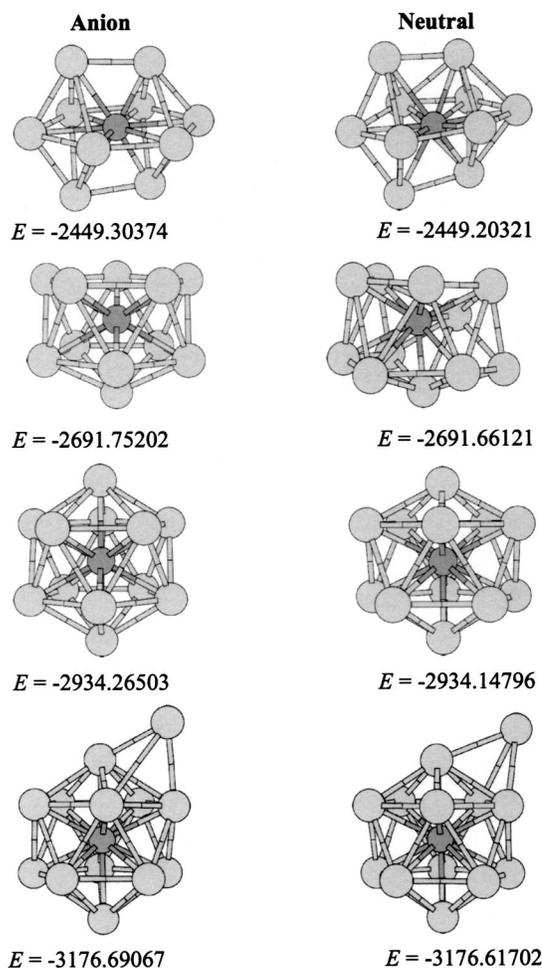


FIG. 1. Equilibrium geometries of anionic and neutral  $\text{Al}_{n-1}\text{B}_1$  clusters. The small dark shade circles are B atoms while the bigger and lighter shade circles are Al atoms. The total energies are in a.u.

$\text{Al}_{12}\text{B}_1^-$  and  $\text{Al}_{12}\text{B}_1$  clusters form a slightly distorted icosahedron. The  $\text{Al}_{11}\text{B}_1$  and  $\text{Al}_{13}\text{B}_1$  clusters both in anionic and neutral forms are related to the icosahedron structures: deleting one surface Al atom from the icosahedron cage gives  $\text{Al}_{11}\text{B}_1$ , and adding one more Al atom residing outside the icosahedron cage at a threefold coordinated site, similar with the case of the  $\text{Al}_{13}\text{K}_1$  cluster,<sup>33</sup> gives  $\text{Al}_{13}\text{B}_1$  (see Fig. 1). The  $\text{Al}_{10}\text{B}_1$  cluster both in anionic and neutral state is beyond the framework of the icosahedron, the B atom is located in the center of a distorted cube consisting of eight Al atoms, the other two Al atoms reside at the top and bottom of the cube. The geometry of a neutral  $\text{Al}_{10}\text{B}_1$  cluster is more distorted than that of its anionic partner.

From Table I, one can see that for the  $\text{Al}_{n-1}\text{B}_1$  clusters the energy gain,  $\Delta E_n$ , in going from  $\text{Al}_{10}\text{B}_1$  to  $\text{Al}_{11}\text{B}_1$  is 2.44 eV, while that in going from  $\text{Al}_{12}\text{B}_1$  to  $\text{Al}_{13}\text{B}_1$  is 2.74 eV. The energy gain in going from  $\text{Al}_{11}\text{B}_1$  to  $\text{Al}_{12}\text{B}_1$  is substantially higher, namely 3.23 eV. The energy gains of  $\text{Al}_{n-1}\text{B}_1^-$  clusters have similar trends to those of  $\text{Al}_{n-1}\text{B}_1$ . These energy gains suggest that  $\text{Al}_{12}\text{B}_1$  clusters should be more abundant than  $\text{Al}_{11}\text{B}_1$  and  $\text{Al}_{13}\text{B}_1$  in both neutral and anionic clusters. This is consistent with the electronic shell closure criterion<sup>34–36</sup> (40 valence electrons) of  $\text{Al}_{12}\text{B}_1^-$  and

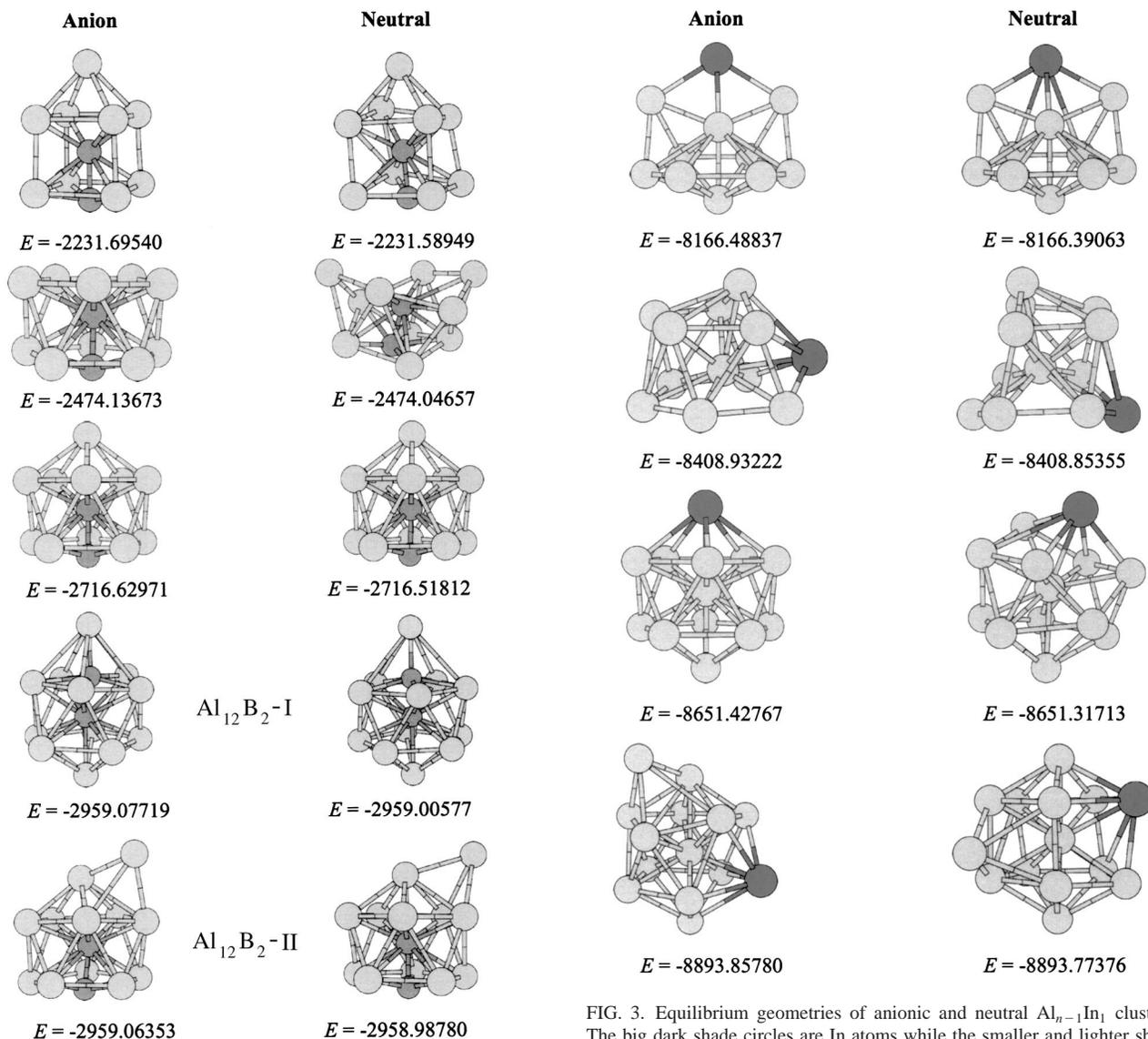


FIG. 2. Equilibrium geometries of anionic and neutral  $\text{Al}_{n-2}\text{B}_2$  clusters. The small dark shade circles are B atoms while the bigger and lighter shade circles are Al atoms. The total energies are in a.u.

the geometrical spherical shape (icosahedron) for both  $\text{Al}_{12}\text{B}_1$  and  $\text{Al}_{12}\text{B}_1^-$ . Thus, if  $\text{Al}_{n-1}\text{B}_1$  clusters are born neutral, the enhanced stability of  $\text{Al}_{12}\text{B}_1$  would result in producing more of the  $\text{Al}_{12}\text{B}_1^-$  clusters in TOF-MS. Note that all the calculated properties that we expect to correlate with the stability point to  $n=12$  as the most stable in both neutral and anionic forms (see the underlined numbers in Table I).

### B. $\text{Al}_{n-2}\text{B}_2^-$ clusters

The equilibrium geometries of  $\text{Al}_{n-2}\text{B}_2^-$  and  $\text{Al}_{n-2}\text{B}_2$  ( $n=11-14$ ) clusters are illustrated in Fig. 2. Note that these clusters have equilibrium geometries similar to those of  $\text{Al}_{n-1}\text{B}_1^-$  and  $\text{Al}_{n-1}\text{B}_1$  ( $n=11-13$ ) clusters with one Al atom replaced by one B atom. Two stable configurations of  $\text{Al}_{12}\text{B}_2^-$  and  $\text{Al}_{12}\text{B}_2$  clusters,  $\text{Al}_{12}\text{B}_2\text{-I}$  and  $\text{Al}_{12}\text{B}_2\text{-II}$ , were found. The  $\text{Al}_{12}\text{B}_2\text{-I}$  structure is a novel configuration in which one Al atom resides almost right on the top of the

FIG. 3. Equilibrium geometries of anionic and neutral  $\text{Al}_{n-1}\text{In}_1$  clusters. The big dark shade circles are In atoms while the smaller and lighter shade circles are Al atoms. The total energies are in a.u.

surface B atom. The anionic and neutral  $\text{Al}_{12}\text{B}_2\text{-II}$  clusters' structure are close to those of  $\text{Al}_{13}\text{B}_1$  and  $\text{Al}_{13}\text{B}_1^-$ . The total energies of  $\text{Al}_{12}\text{B}_2\text{-I}$  anionic and neutral clusters are lower than those of  $\text{Al}_{12}\text{B}_2\text{-II}$  anionic and neutral clusters, by 0.37 and 0.49 eV, respectively.

Nakajima *et al.*<sup>3</sup> speculated that the disappearance of the magic number  $\text{Al}_{11}\text{B}_2$  could be explained by the geometric structure. Namely, under the icosahedron structure, it is possible to substitute one smaller diameter atom in the center of the cluster, but this structure can ill afford to substitute two atoms. However, our present theoretical results show that  $\text{Al}_{11}\text{B}_2^-$  is the most stable among  $\text{Al}_{n-2}\text{B}_2^-$  ( $n=11-14$ ), and that it has an icosahedronlike structure. So the following question arises: Why does  $\text{Al}_{11}\text{B}_2^-$  not behave as a magic number like  $\text{Al}_{12}\text{B}_1^-$  in TOF-MS? One answer to the question could be found by the comparison of the energy gains ( $\Delta E_n$  in Table II) of the associated *neutral* clusters.

From Table II, one can see that for the  $\text{Al}_{n-2}\text{B}_2$  clusters the energy gain,  $\Delta E$ , in going from  $\text{Al}_9\text{B}_2$  to  $\text{Al}_{10}\text{B}_2$  is 2.42 eV while that in going from  $\text{Al}_{10}\text{B}_2$  to  $\text{Al}_{11}\text{B}_2$  is 2.81 eV. The

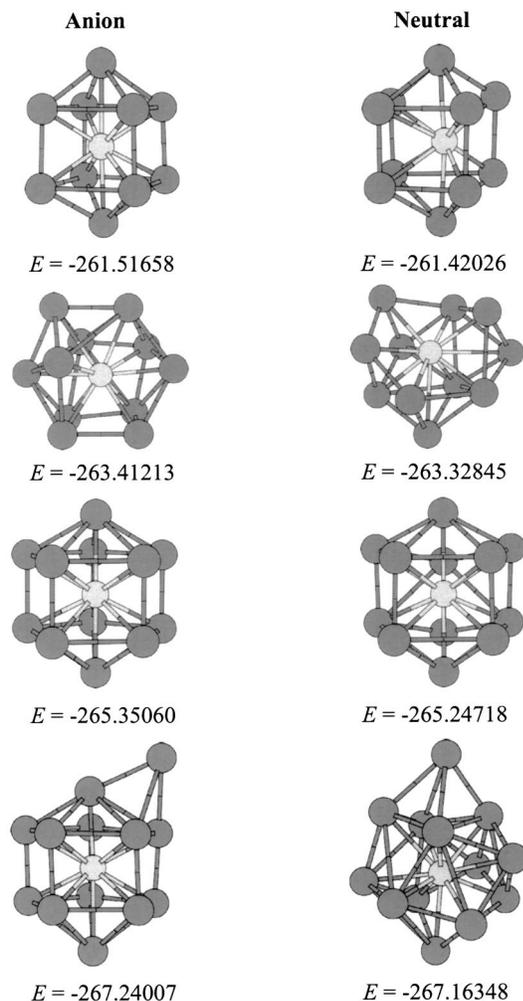


FIG. 4. Equilibrium geometries of anionic and neutral  $\text{In}_{n-1}\text{Al}_1$  clusters. The big dark shade circles are In atoms while the smaller and lighter shade circles are Al atoms. The total energies are in a.u.

energy gain in going from  $\text{Al}_{11}\text{B}_2$  to  $\text{Al}_{12}\text{B}_2\text{-I}$  is substantially higher, 3.25 eV. For the  $\text{Al}_{n-2}\text{B}_2^-$  clusters the energy gains have a different trend from those of  $\text{Al}_{n-2}\text{B}_2$ . The energy gain in going from  $\text{Al}_{10}\text{B}_2^-$  to  $\text{Al}_{11}\text{B}_2^-$  is 3.39 eV, which is substantially higher than others, which shows that  $\text{Al}_{11}\text{B}_2^-$  is still the most stable among  $\text{Al}_{n-2}\text{B}_2^-$  ( $n = 11-14$ ) cluster anions. Note that the lowest vibrational frequency ( $97 \text{ cm}^{-1}$ ),

TABLE I. Lowest vibrational frequencies, adiabatic electron affinities (AEA), HOMO–LUMO gaps, and energy gains ( $\Delta E_n$ ) in adding an Al atom to  $\text{Al}_{n-1}\text{B}_1$  clusters. The largest number in each column is underlined.

Cluster	Lowest freq. ( $\text{cm}^{-1}$ )		AEA (eV)	HOMO–LUMO gap		$\Delta E_n$ (eV)	
	Neut.	Anion		Neut. (eV)	Anion	Neut.	Anion
$\text{Al}_{10}\text{B}_1$	39	32	2.74	2.01( $\alpha$ ) 1.45( $\beta$ )	2.09		
$\text{Al}_{11}\text{B}_1$	42	19	2.47	1.30	1.81( $\alpha$ ) 1.13( $\beta$ )	2.44	2.18
$\text{Al}_{12}\text{B}_1$	<u>90</u>	<u>111</u>	<u>3.19</u>	<u>2.99(<math>\alpha</math>)</u> <u>1.32(<math>\beta</math>)</u>	<u>3.00</u>	<u>3.23</u>	<u>3.94</u>
$\text{Al}_{13}\text{B}_1$	65	34	2.00	2.19	1.46( $\alpha$ ) 2.04( $\beta$ )	2.74	1.56

TABLE II. Lowest vibrational frequencies, adiabatic electron affinities (AEA), HOMO–LUMO gaps, and energy gains ( $\Delta E_n$ ) in adding an Al atom to  $\text{Al}_{n-2}\text{B}_2$  clusters. The largest number in each column is underlined.

Cluster	Lowest freq. ( $\text{cm}^{-1}$ )		AEA (eV)	HOMO–LUMO gap		$\Delta E_n$ (eV)	
	Neut.	Anion		Neut. (eV)	Anion	Neut.	Anion
$\text{Al}_9\text{B}_2$	39	32	2.88	2.01( $\alpha$ ) 1.45( $\beta$ )	2.09		
$\text{Al}_{10}\text{B}_2$	<u>53</u>	20	2.45	1.72	2.04( $\alpha$ ) 1.16( $\beta$ )	2.42	1.99
$\text{Al}_{11}\text{B}_2$	52	<u>97</u>	<u>3.04</u>	<u>2.52(<math>\alpha</math>)</u> 1.12( $\beta$ )	<u>2.52</u>	2.81	<u>3.39</u>
$\text{Al}_{12}\text{B}_2\text{-I}$	25	21	1.94	<u>2.48</u>	1.40( $\alpha$ ) 2.35( $\beta$ )	<u>3.25</u>	2.16
$\text{Al}_{12}\text{B}_2\text{-II}$	63	41	2.88	2.01	1.54( $\alpha$ ) 1.89( $\beta$ )	2.76	1.78

adiabatic electronic affinity (3.04 eV), and HOMO–LUMO gap (2.52 eV) of  $\text{Al}_{11}\text{B}_2^-$  are properties that should correlate with stability and they are all the largest within the  $\text{Al}_{n-2}\text{B}_2^-$  ( $n = 11-14$ ) series. However, energy gains in Table II suggest that the neutral  $\text{Al}_{12}\text{B}_2$  clusters should be more abundant than  $\text{Al}_{10}\text{B}_2$  and  $\text{Al}_{11}\text{B}_2$  neutral clusters. Thus, the enhanced stability of  $\text{Al}_{12}\text{B}_2$  would result in more  $\text{Al}_{12}\text{B}_2^-$  clusters being observed than  $\text{Al}_{11}\text{B}_2^-$  in TOF-MS since there are more of the precursor  $\text{Al}_{12}\text{B}_2$  clusters to which an extra electron can get attached. This is probably the main reason why the mass peak of  $\text{Al}_{11}\text{B}_2^-$  never appears as a magic number.<sup>3</sup> This analysis is again evidence that the mass ion intensities of  $\text{Al}_n\text{B}_2^-$  anionic clusters might be tied to the abundance of the corresponding neutral clusters.<sup>32</sup>

### C. $\text{Al}_n\text{In}_1^-$ clusters

In Fig. 3, we present the equilibrium geometries of  $\text{Al}_{n-1}\text{In}_1$  and  $\text{Al}_{n-1}\text{In}_1^-$  ( $n = 11-14$ ) clusters. Note that in all these clusters the In atom resides outside the  $\text{Al}_{n-1}$  cage, irrespective of their size and charge states. Only the  $\text{Al}_{12}\text{In}_1^-$  cluster could form a slightly distorted icosahedron, albeit the In atom is not located in the center of the Al cage. The structure of the  $\text{Al}_{12}\text{In}_1$  neutral cluster is strongly distorted and very different from an icosahedron. For the neutral  $\text{Al}_{n-1}\text{In}_1$  clusters, the energy gain ( $\Delta E_n$ ) in going from  $\text{Al}_{10}\text{In}_1$  to  $\text{Al}_{11}\text{In}_1$  is 2.577 eV while that in going from  $\text{Al}_{11}\text{In}_1$  to  $\text{Al}_{12}\text{In}_1$  is 2.594 eV (see Table III). The energy

TABLE III. Lowest vibrational frequencies, adiabatic electron affinities (AEA), HOMO–LUMO gaps, and energy gains ( $\Delta E_n$ ) in adding an Al atom to  $\text{Al}_{n-1}\text{In}_1$  clusters. The largest number in each column is underlined.

Cluster	Lowest freq. ( $\text{cm}^{-1}$ )		AEA (eV)	HOMO–LUMO gap		$\Delta E_n$ (eV)	
	Neut.	Anion		Neut. (eV)	Anion	Neut.	Anion
$\text{Al}_{10}\text{In}_1$	<u>34</u>	27	2.66	1.97( $\alpha$ ) 1.37( $\beta$ )	1.94		
$\text{Al}_{11}\text{In}_1$	33	10	2.14	<u>1.87</u>	1.77( $\alpha$ ) 1.37( $\beta$ )	2.577	2.21
$\text{Al}_{12}\text{In}_1$	8	26	<u>3.01</u>	<u>2.16(<math>\alpha</math>)</u> <u>1.53(<math>\beta</math>)</u>	<u>2.37</u>	2.594	<u>3.31</u>
$\text{Al}_{13}\text{In}_1$	20	<u>31</u>	2.29	1.67	1.47( $\alpha$ ) 1.55( $\beta$ )	2.405	1.68

TABLE IV. Lowest vibrational frequencies, adiabatic electron affinities (AEA), HOMO–LUMO gaps, and energy gains ( $\Delta E_n$ ) in adding an Al atom to  $\text{In}_{n-1}\text{Al}_1$  clusters. The largest number in each column is underlined.

Cluster	Lowest freq. ( $\text{cm}^{-1}$ )		AEA (eV)	HOMO–LUMO gap		$\Delta E_n$ (eV)	
	Neut.	Anion		Neut. (eV)	Anion	Neut.	Anion
$\text{In}_{10}\text{Al}_1$	5	2	2.62	1.94( $\alpha$ ) 1.17( $\beta$ )	<u>1.91</u>		
$\text{In}_{11}\text{Al}_1$	<u>14</u> 1.13( $\beta$ )	7	2.28	1.48	1.46( $\alpha$ )	1.63	1.29
$\text{In}_{12}\text{Al}_1$	8	<u>17</u>	<u>2.81</u>	1.75( $\alpha$ )	1.77	<u>1.92</u>	<u>2.46</u>
$\text{In}_{13}\text{Al}_1$	10	9	2.08	<u>1.75</u>	1.41( $\alpha$ ) 1.36( $\beta$ )	1.85	1.12

gain in going from  $\text{Al}_{12}\text{In}_1$  to  $\text{Al}_{13}\text{In}_1$  is lower, 2.405 eV. However, for the anionic  $\text{Al}_{n-1}\text{In}_1^-$  clusters the energy gain in going from  $n=12$  to  $n=13$  is 3.31 eV, which is substantially higher than the others. This shows that  $\text{Al}_{12}\text{In}_1^-$  is still the most stable among  $\text{Al}_{n-1}\text{In}_1^-$  ( $n=11-14$ ) cluster anions due to its electronic shell closure.

For the  $\text{Al}_{n-1}\text{In}_1^-$  series, in going from  $n=12$  to  $n=13$ , we have simultaneously closing of the electronic shell (from 37 to 40 electrons), and the atomic shell ( $n$  from 12 to 13). It is not clear which of the two is the most important for the stability of the cluster.

#### D. $\text{In}_n\text{Al}_1^-$ clusters

In Fig. 4 we present the equilibrium geometries of  $\text{In}_{n-1}\text{Al}_1^-$  and  $\text{In}_{n-1}\text{Al}_1$  ( $n=11-14$ ) clusters. Note that in all these clusters the Al atom resides inside the  $\text{In}_n$  cage, irrespective of their size and charge states. However, the icosahedronlike conformation could not be found in either  $\text{In}_{12}\text{Al}_1^-$  or  $\text{In}_{12}\text{Al}_1$  clusters. Curiously,  $\text{In}_{12}\text{Al}_1$  adopts a  $D_{5h}$  symmetry structure that has formally five fewer pair interactions than the icosahedron. Generally, the configurations of neutral clusters are a little bit more distorted compared with those of their anionic partners.

For the neutral  $\text{In}_{n-1}\text{Al}_1$  clusters, the energy gain ( $\Delta E_n$ ; see Table IV) in going from the  $\text{In}_{10}\text{Al}_1$  to  $\text{In}_{11}\text{Al}_1$  is 1.63 eV while that in going from  $\text{Al}_{11}\text{In}_1$  to  $\text{In}_{12}\text{Al}_1$  is 1.92 eV. The energy gain in going from  $\text{In}_{12}\text{Al}_1$  to  $\text{In}_{13}\text{Al}_1$  is 1.85 eV, a little lower than the former. For the anionic  $\text{In}_n\text{Al}_1^-$  clusters, the energy gain in going from  $\text{In}_{11}\text{Al}_1^-$  to  $\text{In}_{12}\text{Al}_1^-$  is 2.46 eV, which is substantially higher than the others. This result shows that  $\text{In}_{12}\text{Al}_1^-$  is still the most stable among  $\text{In}_{n-1}\text{Al}_1^-$  ( $n=11-14$ ) cluster anions due to its electronic shell closure and approximate spherical shape (bicapped centered pentagonal prism, close to a  $D_{5h}$  symmetry point group). However, this conclusion is only tentative because the very low vibrational frequencies in Table IV suggest that we may well have missed the global minima for these clusters.

Finally, we briefly discuss the relation of an icosahedral structure with atomic radii. For a purely geometric reason (assuming atoms are rigid spheres), the ideal combination of atomic radii ( $R$ ) in a  $X_{12}Y$  icosahedral cluster is  $R_Y = 0.90R_X$  (assuming  $Y$  is in the center). The metallic radii of

B, Al, and In atoms are 0.98, 1.43, and 1.66 angstroms,<sup>37</sup> respectively. For  $\text{Al}_{12}\text{B}_1^-$ , we have  $R_B/R_{\text{Al}}=0.685$ , which is far from ideal, the B atom is too small. However, atoms have no fixed size, and there are reasons to believe that the B central atom is electron rich (it has a coordination of 12 versus only 6 for the peripheral atoms), and is therefore “bigger” than a typical B atom. In the case of  $\text{Al}_{12}\text{In}_1^-$ , we have  $R_{\text{In}}/R_{\text{Al}}=1.16$ : the In atom is much too big. This gives a simple rationale for why we could not find a local minimum for an icosahedron with the In atom in the center. Note that in the case of  $\text{Al}_{12}\text{Cu}_1^-$ , an icosahedron with a Cu atom (the radius is 1.28 angstrom)<sup>37</sup> located in the center has been found.<sup>32</sup> However, in the case of  $\text{In}_{12}\text{Al}_1^-$ , the ratio  $R_{\text{Al}}/R_{\text{In}}$  is 0.86, and yet we could not find a local minimum for an icosahedron with the Al atom in the center.

#### IV. CONCLUSIONS

Bimetallic anionic and neutral clusters,  $\text{Al}_{n-1}\text{B}_1$ ,  $\text{Al}_{n-2}\text{B}_2$ ,  $\text{Al}_{n-1}\text{In}_1$ , and  $\text{In}_{n-1}\text{Al}_1$ , ( $n=11-14$ ), have been theoretically investigated by density functional theory at the B3LYP/6-31G\* (LanL2DZ for Indium) level. The theoretical results and discussions clarify two important concepts associated with metal clusters. In a mass spectrum, it has been found that the charged metal clusters with certain numbers of atoms are more abundant than others and hence are called “magic numbers.” These magic numbers are related to the electronic shell and geometrical structures of charged and neutral clusters considered, but especially to those of the neutral clusters. However, the stability of small clusters is governed not only by the electronic shell closing but also by the geometric spherical shape. We see a rather strong correlation between the atom addition energy gain, HOMO–LUMO gap, electron affinity, and lowest harmonic vibrational frequency. We think that all of these calculated properties are useful indicators of stability.

#### ACKNOWLEDGMENT

This work was supported by a grant of the Natural Sciences and Engineering Research Council of Canada.

<sup>1</sup>H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl, and R. E. Smalley, *Nature* (London) **318**, 162 (1985).

<sup>2</sup>B. C. Guo, K. P. Kerns, and A. W. Castleman, Jr., *Science* **255**, 1411 (1992).

<sup>3</sup>A. Nakajima, T. Sugioka, T. Kishi, and K. Kaya, in *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena et al. (Kluwer Academic, Netherlands, 1992), Vol. 1, p. 99.

<sup>4</sup>S. N. Khanna and P. Jena, *Phys. Rev. Lett.* **69**, 1664 (1992).

<sup>5</sup>S. N. Khanna and P. Jena, *Phys. Rev. Lett.* **71**, 208 (1993).

<sup>6</sup>S. N. Khanna and P. Jena, *Chem. Phys. Lett.* **218**, 383 (1994).

<sup>7</sup>X. G. Gong and V. Kumar, *Phys. Rev. Lett.* **70**, 2078 (1993).

<sup>8</sup>M. Manninen, J. Mansikka-aho, S. N. Khanna, and P. Jena, *Solid State Commun.* **85**, 11 (1993).

<sup>9</sup>A. P. Seitsonen, M. J. Puska, M. Alatalo, R. M. Nieminen, V. Milman, and M. C. Payne, *Phys. Rev. Lett.* **219**, 479 (1994).

<sup>10</sup>S. N. Khanna and P. Jena, *Chem. Phys. Lett.* **219**, 479 (1994).

<sup>11</sup>S. N. Khanna and P. Jena, *Phys. Rev. B* **51**, 13705 (1995).

<sup>12</sup>J. H. Sinfelt, *Adv. Chem. Eng.* **5**, 37 (1964).

<sup>13</sup>J. H. Sinfelt, *Acc. Chem. Res.* **10**, 15 (1977).

<sup>14</sup>J. H. Sinfelt, *Bimetallic Catalysts, Discoveries, Concepts and Applications* (Wiley, New York, 1983).

<sup>15</sup>D. Bazin, C. Mottet, and G. Treglia, *Appl. Catal., A* **200**, 47 (2000).

<sup>16</sup>N. Toshima and T. Yonezawa, *New J. Chem.* **22**, 1179 (1998).

- <sup>17</sup>M. E. Tess, P. L. Hill, K. E. Torracca, M. E. Kerr, K. A. Abboud, and L. McElwee-White, *Inorg. Chem.* **39**, 3942 (2000).
- <sup>18</sup>H. Bonnemann, R. Brinkmann, P. Britz *et al.*, *J. New Mater. Electrochem. Syst.* **3**, 199 (2000).
- <sup>19</sup>K. Raghavachari and C. M. Rohlfing, *J. Phys. Chem.* **95**, 5768 (1991).
- <sup>20</sup>R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
- <sup>21</sup>S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- <sup>22</sup>A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- <sup>23</sup>C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>24</sup>A. D. Becke, *J. Chem. Phys.* **98**, 1372 (1993).
- <sup>25</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>26</sup>J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- <sup>27</sup>J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods* (Gaussian, Inc., Pittsburgh, PA, 1996).
- <sup>28</sup>G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.* **94**, 6081 (1991).
- <sup>29</sup>N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, *Can. J. Chem.* **70**, 560 (1992).
- <sup>30</sup>P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 270, 284, 299 (1985).
- <sup>31</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998).
- <sup>32</sup>(a) S. N. Khanna, C. Ashman, B. K. Rao, and P. Jena, *J. Chem. Phys.* **114**, 9792 (2001); (b) B. K. Rao, S. N. Khanna, and P. Jena, *ibid.* **115**, 778 (2001).
- <sup>33</sup>B. K. Rao, S. N. Khanna, and P. Jena, *Phys. Rev. B* **62**, 4666 (2000).
- <sup>34</sup>D. Bonatsos, C. Daskaloyannis, S. B. Drenska, N. Karoussos, N. Minkov, P. P. Raychev, and R. P. Roussev, *Phys. Rev. A* **62**, 013203 (2000).
- <sup>35</sup>C. Yannouleas and U. Landman, *Phys. Rev. Lett.* **78**, 1424 (1997), and references therein.
- <sup>36</sup>M. Brack, *Rev. Mod. Phys.* **65**, 677 (1993).
- <sup>37</sup>Periodic Table of the Elements, T. K. Varga and C. Bello, ISBN 1-55080-073-6, Papertech, Inc., 1998.