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$(BAl_{12})Cs$: A cluster-assembled solid

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First-principles calculations on the geometry and stability of Al_nB_m clusters have been carried out to examine the effect of size, composition, and electronic-shell filling on their relative stability. It is shown that although Al and B are both trivalent, a BAl_{12} cluster is more stable than an Al_{13} by 3.4 eV. The enhanced stability is shown to arise due to the relaxation of surface strain in the Al cage when the central Al is replaced by a smaller B atom. Replacement of an additional Al by B to produce B_2Al_{11} results in deformation of the icosahedral BAl_{12} cage and reduces the stability. The possibility of forming crystals using BAl_{12} and Cs is examined via total-energy calculations. It is shown that a solid with icosahedral or cuboctahedral BAl_{12} and Cs and having the CsCl structure is metastable and could be synthesized. [S0163-1829(97)03124-X]

I. INTRODUCTION

An extensive body of work on atomic clusters indicates that they display a variety of novel electronic, magnetic, thermal, and chemical properties.[1] The properties vary strongly with size and/or composition. The possibility of producing clusters of a given size and composition[2] and with tailored properties provides hope that a new class of materials with clusters as building blocks[3] could be synthesized. The major difficulty in this process arises due to the fact that clusters are metastable and have a tendency to coalesce when assembled. This can be prevented in one of two ways—either by isolating these clusters in matrices or by coating them with surfactants. An alternative route is to find clusters that are so stable that the intracluster interaction is stronger than the intercluster interaction. Thus these clusters upon assembling will tend to keep their individual identity intact. Even though such a cluster-assembled material would be metastable against dissociation into their bulk phases, an energy barrier against such dissociation can make the synthesis possible. Solids made out of C_{60} clusters[4,5] are examples of such cluster-assembled materials.

In a recent paper, two of the present authors proposed[3] that it may be possible to synthesize a new class of cluster materials by assembling compound metallic clusters provided the clusters are designed to satisfy certain geometric and electronic-shell structures. Their arguments were based on the observation that the mass spectra of simple metal clusters generated in beams show pronounced peaks at ''magic numbers'' corresponding to closing of the electronic shells.[6] This can be understood within a simple picture in which the cluster is regarded as a jellium sphere with a uniform distribution of positive charge. The ''magic numbers'' correspond to the cases where the electrons fill the electronic shells of this super atom, i.e., clusters containing 2, 8, 18, 20, 40,... electrons. The electronic effects are particularly dominant at small sizes, whereas at larger sizes, the most stable clusters correspond to filled geometric shells[7] such as filled icosahedral shells. Khanna and Jena[8] proposed that if a metallic cluster could be designed in such a manner that it has a compact geometry as well as a filled electronic shell, it will be stable as well as chemically less active due to the filled electronic shell and hence may be a likely candidate for forming cluster solids. They proposed CAl_{12}, which has a compact icosahedral structure and 40 valence electrons, as a likely candidate. Indeed, the CAl_{12} cluster was found to be more stable than Al_{13} by 4.4 eV.

It is also interesting to note that the chemistry of the Al_{13} cluster resembles that of a halogen atom since its electron affinity of 3.7 eV is close to that of Cl. Motivated by this, Khanna and Jena[9] proposed forming a new class of solids analogous to the ionic solid KCl, but replacing Cl with Al_{13} as the new building block. To examine this possibility, Liu *et al.*[10] carried out *ab initio* total-energy calculations on a proposed $Al_{13}K$ solid assuming a CsCl structure shown in Fig. 1. They found that while the icosahedral structure for Al_{13} was preferred for large lattice spacings, reduction of the lattice spacing to minimize the energy led to a change in the geometry of Al_{13} to cuboctahedral in the minimum-energy structure. The resulting solid, although metastable, resembled fcc Al with K chains in which Al_{13} units in different cages formed metallic bonds.

In this paper we examine the possibility of designing a new solid. We propose BAl_{12} and Cs as the building blocks of the new solid. The choice of BAl_{12} is motivated by the fact that in an Al_{13} icosahedral cluster, the surface Al—Al

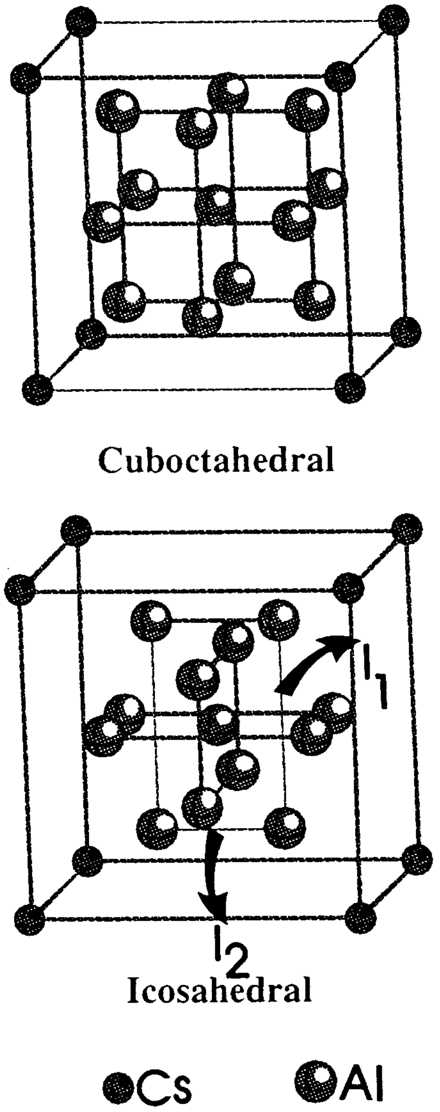

FIG. 1. Schematic picture of a prototype CsCl solid formed out of Al_{13} (cuboctahedral or icosahedral) and K atoms.

bonds are about 5% longer than the radial bonds. Replacing the central Al by a smaller B atom is expected to relax the surface strain and lead to a more stable BAl_{12} cluster. In addition the binding energy of the AlB dimer is 0.85 eV larger than that of Al_2. Thus BAl_{12} stands to gain more stability than Al_{13} from the electronic interaction as well. Since Al and B are both trivalent, we expect Al_{13} and BAl_{12} to have the same chemistry, i.e., they should resemble the chemistry of a halogen atom. In forming the solid made of K and Al_{13} units, we note that the K atom is much smaller in size than an Al_{13} cluster. In a crystal of KAl_{13}, the space is optimally filled and the Al_{13} clusters interact strongly. Thus we study a crystal containing BAl_{12} clusters and Cs atoms since Cs is much larger than K. The chemistry of the building blocks is, however, unchanged since BAl_{12} is expected to be electronegative and Cs is electropositive. The bonding between BAl_{12} and Cs is therefore expected to be ionic. We, indeed, show that a combination of these features leads to a $BAl_{12}Cs$ crystal in which the BAl_{12} may maintain their icosahedral structure because of a barrier even though cuboctahedral symmetry is energetically preferable by a small margin.

We first present a study of the electronic and geometric effects on the stability of individual clusters by studying 13-atom icosahedral B_xAl_y clusters containing one or two B atoms. Both B and Al are trivalent but differ in size. We show that BAl_{12} has a perfect icosahedral geometry and is 3.43 eV more bound than Al_{13}. The replacement of two Al by two B atoms, although it leaves the number of valence electrons unchanged, places at least one B in the outer shell. The icosahedron thus undergoes deformation and this leads to a reduced stability of B_2Al_{11} compared to BAl_{12} in agreement with the observed mass spectrum[11] of B_xAl_y clusters.

Having established the stability of the BAl_{12} cluster, we show that it has an electron affinity comparable to Al_{13} and resembles a halogen atom. To further support this observation, we present a calculation of a BAl_{12} K and show that the alkali-metal atom loses its charge to BAl_{12}. We then examine the possibility of forming a crystalline solid using BAl_{12} and alkali-metal atoms. In a recent paper[12] we had examined such a possibility for Al_{13} and K and assuming a CsCl structure. To further ensure that this is indeed the structure, in this work, we also present the corresponding results for the NaCl structure and show it to be far less stable than the CsCl structure. The Al_{13} clusters in a CsCl structure occupy central sites in cubes formed out of alkali-metal atoms. To minimize interaction between clusters, it is desirable to use larger alkali-metal ions. With this in mind we carry out electronic structure calculations on a (BAl_{12})Cs solid by assuming a CsCl structure and minimizing the total energy as a function of the lattice spacing. It will be shown that starting from large spacing, the energy of the solid with icosahedral-like BAl_{12} units goes through a minimum as the volume is decreased. Upon further compression, a second minimum corresponding to cuboctahedral BAl_{12} is obtained which is slightly more stable. The barrier height between the two minima is, however, significant, and it is possible that the material assembled by collecting individual BAl_{12} units and Cs will settle into either structure depending on the method of synthesis.

In Sec. II we describe our methods and results for B_xAl_y clusters. Section III contains details of the calculations and results on the solid phase. Section IV gives a summary of our findings.

II. ELECTRONIC STRUCTURE AND STABILITY OF B_xAl_y CLUSTERS

The electronic structure calculations on clusters were carried out using a linear combination of atomic orbitals molecular-orbital approach within the density-functional scheme.[12] The particular version we have used is based on a representation of molecular orbitals in terms of Gaussian functions centered at the atomic sites.[13] The Hamiltonian matrix elements are calculated by representing the charge density and the exchange-correlation potential in terms of auxiliary Gaussians centered at the atomic sites and in between atoms. To simplify the computations, the atomic cores have been replaced by norm conserving nonlocal pseudopotentials.[14] In this work we have used the form proposed by Bachelet, Hamann, and Schluter[14] along with the spin-polarized [local spin density approximation (LSDA)]

TABLE I. Geometrical parameters and binding energies of Al_{13}, BAl_{12}, BAl_{12}^-, and (BAl_{12}) K clusters.

Cluster	Radial distance of icosahedron (a_0)	Binding energy/atom (eV)
Al_{13}	5.06	2.82
BAl_{12}	4.76	3.09
BAl_{12}^-	4.81	3.36
$BAl_{12}K$	4.80	3.66

Ceperley-Alder form for exchange and correlation.[15] The computations involve first solving the Kohn-Sham equations[16] on a radial mesh of points for the isolated atoms. The numerical atomic orbitals are then fitted by Gaussians whose exponents are varied to optimize the fit. The Gaussian exponents serve to form the basis set. The molecular orbitals are the linear sum of Gaussians with coefficients determined by a self-consistent solution of the molecular Kohn-Sham equations. The details of the method are described in earlier papers.[13]

Before we present our results on bigger clusters, it is useful to look at the quality of our basis functions. For B, the basis function had $5s$ and $4p$ Gaussians. The calculated atomic ionization potential was 8.41 eV compared to the experimental value of 8.3 eV. For B_2 we calculate a bond length of $3.06a_0$ and a binding energy of 3.68 eV compared to the corresponding experimental values of $3.0a_0$ and 3.08 eV, respectively. For Al, the basis functions had $5s$ and $4p$ Gaussians. For Al_2 we obtain a triplet ground state with a bond length of $4.75a_0$ and a binding energy of 1.78 eV compared to experimental values of $4.84a_0$ and 1.93 eV, respectively. These comparisons show that the basis functions and the approach are reasonably accurate.

We begin with the BAl_{12} cluster. First we consider the effect of replacing an Al atom in Al_{13} by a B atom. The hetero atom can occupy a surface site or a central site depending on the energetics. We first calculated an AlB dimer. It has a binding energy of 2.63 eV compared to 1.78 of Al_2, indicating that BAl bonds are stronger. Further, the surface bonds in the Al_{13} icosahedron are 5% longer than the radial bonds. The B atom is smaller than an Al atom and if substituted at the central site, it can relax the surface stress. These considerations clearly suggest that the B atom will occupy the central site. We therefore optimized the geometry of an icosahedral cluster with a central B. The bond lengths and binding energy of BAl_{12} are given in Table I and compared with corresponding values of Al_{13}. As expected, the radial bonds are shorter and the binding is 3.4 eV higher than in Al_{13}. We believe that this is largely due to the relaxation of the surface bonds as well as due to enhanced bonding between Al and B. This enhanced stability is reflected in the mass spectrum. Nakajima *et al.*[11] have generated BAl_n clusters in beams and indeed find a magic peak at BAl_{12}.

While the new cluster is stabilized by the geometry, it has the same number of electrons (i.e., 39) as Al_{13}. As mentioned before, Al_{13} has a large electron affinity of 3.7 eV which can be understood within the simple jellium picture as arising due to a hole in the electronic shell closing at 40 electrons. Does BAl_{12} share this electronic feature with Al_{13}? To explore this possibility, we calculated the electron affinity by optimizing the geometry of the anionic cluster. The addition of an electron produces insignificant changes in the bond lengths but the cluster becomes significantly more stable (see Table I). BAl_{12} has an electron affinity of 3.6 eV which is close to that of Al_{13}. This shows that the substitution of B for the central Al in Al_{13} does not affect the chemistry and one should be able to form ionically bound molecules by combining BAl_{12} with alkali-metal atoms.

To investigate this possibility, we calculated the electronic structure and binding of a (BAl_{12}) K cluster. A K atom was brought towards a BAl_{12} cluster along the on top, bridge, and hollow directions. In each case, the radius of the icosahedral cluster was optimized to minimize the energy. The hollow site was found to be most stable. The icosahedral bond length and the binding energy per atom of (BAl_{12}) K are given in Table I. A Mulliken population analysis of the resulting charge indicates that the K atom loses its electron to BAl_{12}. The bonding is therefore primarily ionic. Assuming complete charge transfer and a uniform sphericity of charge around BAl_{12}, one can write the binding energy of K to the cluster as $-e^2/r$ where r is the distance of K from the center of the icosahedron. In our studies, the K atom is 9.037 a.u. from the center. This leads to an electrostatic energy of 3.01 eV. Our self-consistent calculation yields the binding energy of BAl_{12} with K to be 3.1 eV. This further illustrates that the K atom prefers the hollow site over other sites since at this configuration K can come closest to the center of the icosahedron.

We now consider another example that displays the interplay between geometry and electronic effects in clusters by studying clusters containing two B atoms, i.e., replacing an additional Al in BAl_{12} by B. The additional B must occupy a surface site and since it is smaller than Al, one expects a deformation of the icosahedral geometry. To calculate its structure, note that the cluster still has fivefold symmetry around the axis containing two B atoms. We optimized various bond lengths keeping the fivefold symmetry. The resulting geometry is shown in Fig. 2. Note that the icosahedral cluster undergoes significant geometrical distortions. The BAl surface bonds are $4.21a_0$ compared to Al—Al bonds of $4.83a_0-5.22a_0$. The cluster has an atomization energy of 3.28 eV per atom as compared to 3.09 eV/atom in BAl_{12}. This is puzzling since experiments on B_xAl_y clusters show that BAl_{12} is more abundant in the mass spectra than B_2Al_{11}. We believe that an analysis of the bonding may provide a clue. Note that whereas BAl_{12} is spherically symmetric, B_2Al_{11} has large distortions because the B atom in the outer shell is pushed inward and the central B is pushed upward to optimize the B—B bond which is stronger and shorter than B—Al or Al—Al bonds. This generates considerable strain in the outer layer as seen from Fig. 2, which shows that the B—Al bonds involving the surface B to surrounding Al are reduced to 4.2 a.u. compared to all other B—Al bond lengths of around 4.8 a.u. in B_2Al_{11} and in BAl_{12}. This is also reflected in the energetics. The energy difference

$$E(B_2Al_{11})+E(Al_{13})-2E(BAl_{12})$$

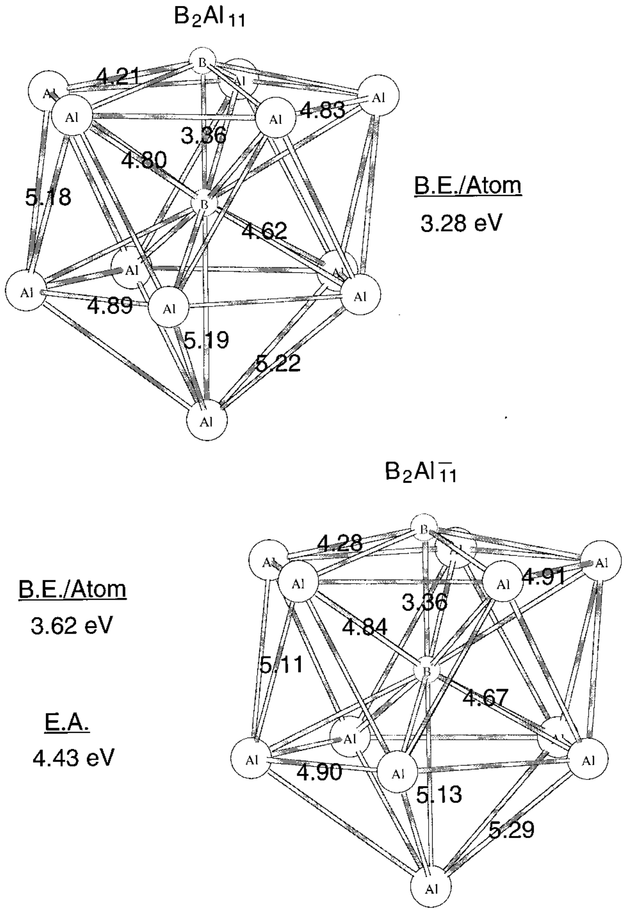

FIG. 2. The geometry of B_2Al_{11} and B_2Al_{11} clusters. The bond lengths are in are in atomic units.

is 1.1 eV, indicating that the reaction where a B_2Al_{11} and an Al_{13} combine to generate two BAl_{12} is energetically favorable. A calculation for the anionic cluster (B_2Al_{11}) leads to an electron affinity of 4.4 eV.

III. ELECTRONIC STRUCTURE OF BAl_{12} AND Cs ASSEMBLED CRYSTAL

In this section we investigate the possibility of forming a crystalline solid using BAl_{12} and alkali-metal atoms as the building blocks. Our electronic structure calculations are first principles and have been carried out within the density-functional approximation using a combination of the ultrasoft pseudopotentials[17] proposed by Vanderbilt with the preconditioned conjugate gradient algorithm.[18] We used neutral $5s^2 5p^6 6s^1$ as the reference state to construct the cesium potential (the shallow $5s$ and $5p$ core states are included to improve transferability). Nonlocal projectors are introduced for both s and p channels; the cutoff radii (r_c) for the s and p valence functions are $2.3a_0$ and $1.8a_0$, respectively. Each channel is matched to the all-electron wave function at two construction energies ($5s$ and $6s$ eigenvalues for the s channel and $6s$ and $5p$ eigenvalues for the p channel). For charge augmentation function, the cutoffs (r_{inner}) are chosen to be 0.8 ($l=0$), 1.0 ($l=1$), and 1.2 ($l=2$).

The B potential is generated from a neutral $2s^2 2p^1$ reference configuration. The cutoff radius (r_c) for both s and p wave functions is taken to be $1.7a_0$ with two construction energies at the s and p eigenvalues. The values for r_{inner} are 0.75 ($l=0$), 0.75 ($l=1$), and 0.80 a.u. ($l=2$). The details of the K and Al potentials have been published elsewhere.[10] All the pseudopotentials have been tested by calculating the corresponding bulk and/or dimer structures. In general they agree with experiments within a few percent.

In the solid-state calculation, the total-energy and force calculations are performed within the local-density approximation. The Ceperly-Alder form for the exchange-correlation potential[15] is used. The electronic solution is obtained via a preconditioned conjugate gradient minimization scheme, with all the bands updated simultaneously. The atomic positions are optimized via a Newtonian damping procedure. A plane-wave cutoff of 20 Ry is used and the Brillouin zone was sampled with 24 special k points in the cubic cell for the T_h group and 20 points for the O_h group. To account for the metallic nature, the one-electron Kohn-Sham eigenvalues are broadened with Gaussian functions with a width of 0.1 eV to determine the occupation numbers and the Fermi energy.

As mentioned before, because of the dissimilarity in size between the cluster and the alkali-metal atom, the solid is expected to favor a CsCl structure. But one has to worry about a change in geometry of the BAl_{12} clusters from icosahedral to fcc-like (from icosahedron to cuboctahedron) as the solid is formed. To allow this freedom, we arranged the Cs atoms in a cubic structure and placed the BAl_{12} clusters at the center of the Cs cubes in a manner as shown in Fig. 1. The latter were relaxed within a T_h point group using the two edges of the rectangle l_1 and l_2 as the characteristic lengths. Note that when $l_1=l_2$, the BAl_{12} cluster becomes cuboctahedral whereas $l_1=1.618l_2$ leads to an icosahedral cluster.

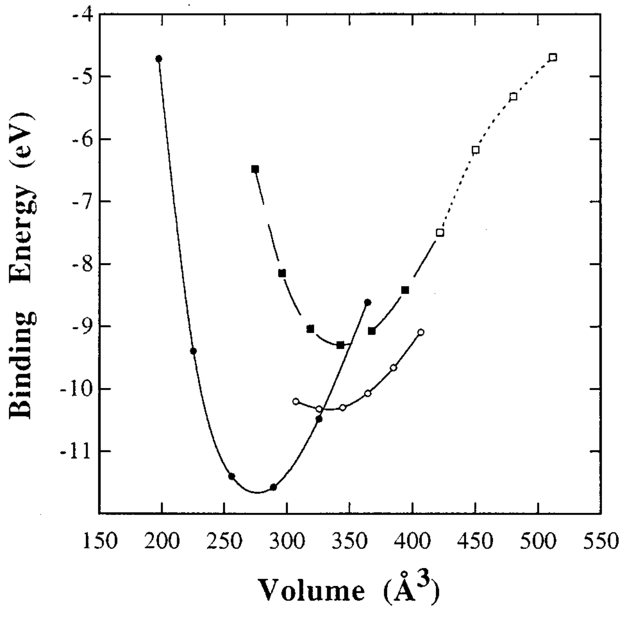

FIG. 3. Cohesive energy as a function of volume for $Al_{13}K$. The solid circles and hollow circles correspond to CsCl arrangement with cuboctatedral and icosahedral Al_{13} clusters, respectively. The squares are a NaCl arrangement with icosahedral Al_{13}.

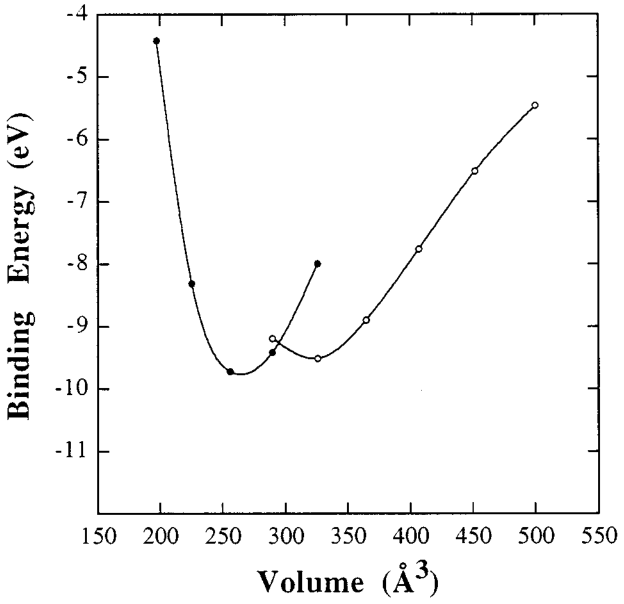

FIG. 4. Cohesive energy as a function of volume for $BAl_{12}Cs$ solid. The solid circles and hollow circles correspond to CsCl arrangement with cuboctatedral and icosahedral BAl_{12} clusters, respectively.

In a previous paper we had examined the stability of the ionic solid formed from Al_{13} and K. In Fig. 3 we show the energies of $Al_{13}K$ in the CsCl structure as a function of volume with an icosahedral-like (hollow circles) and a cuboctahedral (filled circles) central Al_{13}. We also show the energy of a possible NaCl structure (squares). One notices two things. First, as expected, the NaCl structure is far less stable than the CsCl structure. Second, while the solid favors icosahedral Al_{13} clusters at large volumes, the clusters change to the fcc form as one approaches the equilibrium configuration. The final solid thus resembles fcc Al. Can the enhanced stability of BAl_{12} force it to remain icosahedral?

Figure 4 shows the energy as a function of the volume for a CsCl structure composed of BAl_{12} and Cs. In each case, the energy was minimized by varying the l_1/l_2 ratio shown in Fig. 1. Starting at the large volume, as the volume is decreased, the crystal with icosahedral units goes through a minimum. The l_1/l_2 ratio changes from 1.68 to 1.69, 1.70, 1.66, 1.72, and 1.53 for the six points shown by hollow circles in Fig. 4. It had a value of 1.72 for the minimum-energy configuration. As mentioned before, the l_1/l_2 ratio is 1.618 for an icosahedral structure and 1.0 for the cuboctahedral structure. The minimum-energy structure in the graph of hollow circles is therefore primarily icosahedral. The energy rises as the volume is further reduced. A second minimum is found when the BAl_{12} cluster has cuboctahedral symmetry. This configuration is marginally more stable than the previous structure. However, unlike the case of Al_{13}, the minimum with icosahedral BAl_{12} units is separated from this more stable configuration by a barrier of about 0.3 eV. This indicates that it may be possible to form a cluster material with icosahedral subunits by assembling $BAl_{12}Cs$ clusters. To examine the electronic structure of the resulting solid, we calculated the electronic density of states. These are shown in Fig. 5 where the Fermi energy is chosen as the zero of energy. Note that there is an appreciable density of states at the Fermi energy, indicating that the solid is metallic.

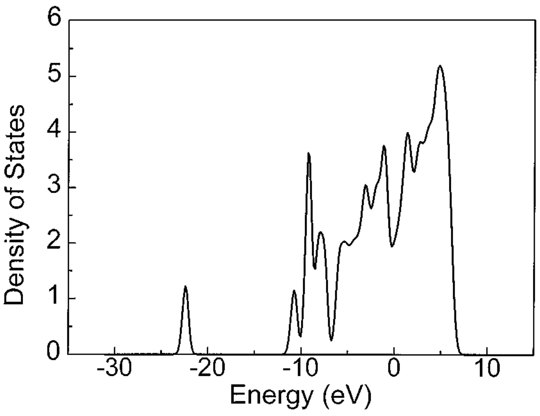

FIG. 5. The density of electronic states in the solid composed of icosahedral BAl_{12} units and Cs.

IV. SUMMARY

To summarize, we have shown how the size, geometry, and composition can be used to control the stability and electronic structure of clusters. An Al_{13} cluster is icosahedral, and the replacement of the central Al by another trivalent B atom enhances the stability largely due to relaxation of the surface strain. If another Al in BAl_{12} is replaced by B to form B_2Al_{11} the cluster undergoes significant geometrical distortions. All three clusters have high electron affinities, thus promising to be candidates to form ionically bound cluster compounds with alkali-metal atoms. For the case of Al_{13}, however, the clusters undergo a transition to cuboctahedral form as the $Al_{13}K$ solid is formed. A CsCl solid formed from Cs and BAl_{12} units has energy minima for both the icosahedral and cuboctahedral BAl_{12} clusters separated by an energy barrier of 0.3 eV.

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