

Assembling Crystals from Clusters

S. N. Khanna and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

(Received 14 April 1992)

It is shown that the stability of a cluster can be substantially enhanced by changing its size and/or composition so as to take advantage of the electronic shell filling as well as close atomic packing. The interaction between two such clusters is found to be weak and can form the basis for synthesizing a new class of cluster-assembled crystals with uncommon properties.

PACS numbers: 61.50.Cj, 36.40.+d, 68.65.+g

Atomic clusters have become one of the most exciting areas of research in the last decade not only because their study can bridge our understanding between molecular and condensed matter physics [1], but also because they can serve as a source of new materials with uncommon properties [2]. The electronic, optical, magnetic, and structural properties of clusters are size specific and the possibility that materials with desired properties can be custom made by changing the size and composition of cluster aggregates is limitless. However, there are some practical problems one encounters in synthesizing cluster materials. First, it is difficult to produce large quantities of clusters of specific size, although the recent development of cluster beam technology [3] is making that task easier. Second, clusters deposited on substrates or in matrices can interact with each other and coalesce to form larger clusters thus destroying the original properties. One way to minimize the cluster-cluster interaction is to passivate the cluster surface, but one must then wonder if the passivation can also alter the original cluster properties.

In this Letter we show that it is possible to select clusters in such a way that the cluster-cluster interaction can be very weak. These clusters, when soft landed on a noninteracting substrate, would not coalesce to form larger clusters. Thus, the individual properties of clusters can be retained. To choose weakly interacting clusters, one can consider two factors that characterize cluster stability: electronic structure and close atomic packing.

It was pointed out by Knight *et al.* [4] that metal clusters containing just enough electrons to close an electronic shell would exhibit marked stability. They showed that alkali-metal clusters containing 2,8,20,40,... valence electrons would be very stable since these electrons are just enough to close shells with *s,p,d,...* angular character. Since this discovery, many experiments [5] and calculations [6] have been done on heteroatomic as well as charged metal clusters to substantiate the importance of electronic shell filling on cluster stability. Small metal clusters, however, can gain energy by undergoing structural distortion and can have geometries that are not close packed. Large metal clusters, on the other hand, draw their stability from close atomic packing as has been seen from the icosahedric and cuboctahedric struc-

tures of large alkali-metal clusters [7]. It will, therefore, be ideal if the close atomic packing as well as the electronic shell closures can be simultaneously achieved to give a cluster-enhanced stability. It is expected that materials assembled from such clusters can retain the properties of individual clusters.

To illustrate this, we have studied the stability of Al_{13} , Al_{12}Si , Al_{12}C , and Mg_4 clusters as well as the energetics associated with cluster-cluster interaction. The total ground-state energies of Al_{13} , Al_{12}Si , and Al_{12}C , calculated self-consistently using the spin-polarized density functional theory and icosahedric symmetry clearly indicate that Al_{12}Si and Al_{12}C which have a closed electronic shell are more stable than Al_{13} . The Mg_4 cluster which also has a closed electronic shell and perfect tetrahedral symmetry is so stable that when two Mg_4 clusters are brought close to each other, the individual clusters retain their structural and electronic integrity. To our knowledge this is the first time cluster-cluster interactions have been studied from first principles in a realistic way [8] by allowing the individual atoms to change their spatial configuration as a function of intercluster distance.

We first concentrate on Al clusters. Al is a trivalent atom and it is impossible to choose a neutral Al cluster whose valence electrons can equal any of the magic numbers 2,8,20,40,... required for shell closing. However, Al clusters can be alloyed with impurity atoms so that the heteroatomic cluster can have the right number of electrons to close an electronic shell. For example, take Al_{13} : Recent studies [9-11] have revealed that Al_{13} prefers the icosahedric structure over the cuboctahedric one. It has 39 electrons—one short of closing the $2p$ shell. Al_{12}Si and Al_{12}C , on the other hand, contain 40 electrons and could derive additional stability not only from electron shell closing but also from icosahedric packing where the central Al atom is replaced by a Si or C atom.

To examine if this is indeed the case, we have calculated the total energies and ionization potentials of Al_{13} , Al_{12}Si , and Al_{12}C clusters confined to the icosahedric structure shown in Fig. 1(a). The calculations are done using the self-consistent field-linear combination of atomic orbitals-molecular orbital method (SCF-LCAO-MO). The atomic wave functions were obtained by solving the atomic Schrödinger equation numerically on a

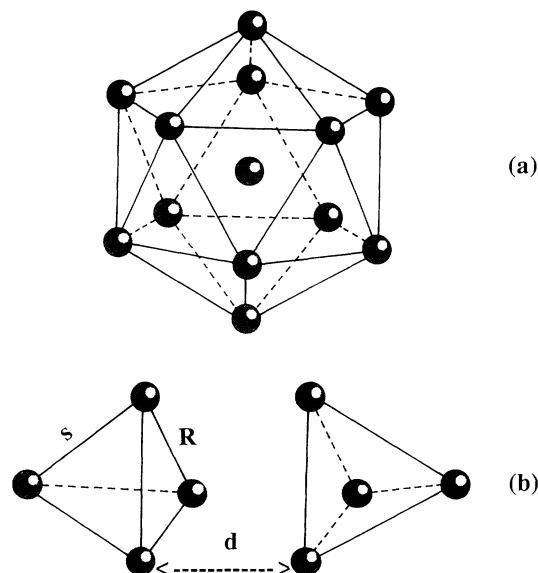


FIG. 1. Geometries of the Al_{13} , Al_{12}C , and Mg_4 clusters used in the present calculations.

mesh of points. The wave functions were fitted to a set of Gaussian basis sets using a nonlinear fit. The exchange-correlation contributions were treated within the local spin-density functional formalism. The details of the method have been described elsewhere [12]. In this work, we have used the form of the exchange-correlation potential proposed by Ceperley and Alder and parametrized by Perdew and Zunger [13]. The ionic cores were replaced by the norm-conserving nonlocal pseudopotentials proposed by Bachelet, Hamann, and Schlüter [14]. The basis functions for C, Al, and Si contained $(5s, 4p)$ functions while that of Mg contained $(4s, 2p)$ functions. These were tested for their completeness and ability to describe neutral and ionized atoms. The molecular calculations were carried out by solving the Kohn-Sham equations and the total energy was determined using the standard expression [12].

To gain confidence in our theoretical procedure we present in Table I the calculated values of the binding energy, bond length, and ionization potential of clusters and compare them with available experimental results. Note that for C, Si, Mg, Al, and Al_{13} , the calculated ionization potentials are in very good agreement with experiment. We are not aware of any reliable experimental value for the binding energy of the AlC dimer, but our results of 3.2 eV for the binding energy and 2.01 Å for the bond length are in very good agreement with the state-of-the-arts quantum chemical result [15] of 3.19 eV and 2.00 Å and the experimental bond length [16] of 1.95 Å. For the Al_{13} cluster, several studies [9–11] have been done using the density functional theory but with differing atomic basis. Our results of binding energy, nearest-neighbor distance, and ionization potential of Al_{13} icosahedric cluster [9–11] are not only consistent with the previous calculations but agree better with experiments [17] wherever available.

We next replaced the central atom in the Al_{13} icosahedron by a Si or C atom and recalculated the binding energy and the nearest-neighbor distance of Al_{12}Si and Al_{12}C by minimizing the total energy. Note that both Al_{12}Si and Al_{12}C contain forty valence electrons and can fill shells with $1s$, $1p$, $1d$, $2s$, $1f$, and $2p$ symmetry. According to the jellium shell model, this should represent a very stable cluster. Indeed, the binding energy of the Al_{12}Si cluster is 7.7 eV lower than that of Al_{13} . The binding energy of Al_{12}C , on the other hand, is only 1 eV lower than that of Al_{13} . This is due to the fact that C is a much smaller atom than Al and the AlC dimer distance is 1.95 Å while the Al_2 dimer distance is 2.56 Å. Thus in the global minimum geometry, the C atom is not likely to stay at the center of the icosahedron as required here. Consequently, the binding energy of Al_{12}C would increase. The size of Si, fortunately, is very close to that of Al and fits ideally. The large binding energy gain in Al_{13}Si over that in Al_{13} results not only from the close electronic shell but also from the enhanced binding energy of the AlSi dimer over that of the Al_2 dimer (see

TABLE I. Comparison between the calculated and experimental values of binding energy (BE), ionization potentials (IP), and bond lengths.

Atom or cluster	BE (eV)		IP (eV)		Bond length (Å)	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
C	11.75	11.26
Si	8.26	8.15
Mg	7.63	7.64
Al	5.99	5.99
Al_2	1.87	1.55	2.57	2.56
AlSi	2.31	2.60	2.38	2.41
AlC	3.2	...	9.03	...	2.01	1.95
Al_{13}	38.6	...	6.8	6.45	2.70	...
Al_{12}C	39.4	...	6.9	...	2.72	...
Al_{12}Si	46.3	...	6.5	...	2.75	...

Table I). It is interesting to note that the nearest-neighbor distance and the ionization potential of Al_{13} , Al_{12}Si , and Al_{12}C are rather similar.

In order to see if the interaction between two Al_{12}Si clusters is weaker than that between two Al_{13} clusters, one needs to calculate the total ground-state energy of each of the pair as a function of distance. This, indeed, is a very difficult task computationally if the total energies are to be calculated to the same rigor as done above and the geometries relaxed as clusters come together. We have, therefore, chosen a prototype system: two Mg_4 clusters with closed electronic shells. The Mg_4 cluster has eight valence electrons and represents a closed shell system like Al_{12}Si and Al_{12}C . The equilibrium structure of Mg_4 is a compact perfect tetrahedron. We have calculated the total energies of two Mg_4 clusters as a function of their intercluster distance d [see Fig. 1(b)]. For each distance d , the clusters were allowed 3 degrees of freedom — (i) rotation (Θ) about the axis joining the centers of mass, (ii) the length of the equilateral base triangle (r), and (iii) the length (s) between the apex atom and the base atoms. For each intercluster distance d , the three parameters r , s , and Θ were optimized. In Fig. 2(a), we plot the total energy per pair of atoms as a function of distance between two Mg_4 clusters. We compare this energy with the interaction energy between two Mg atoms since Mg has a closed electronic shell ($3s^2$) and Mg_2 is known to be a van der Waals system. Note that the energies between the two Mg_4 clusters are nearly the same as that between the two Mg atoms. The signature for this weak interaction is further evidenced from the little change one encounters in r and s as clusters come together; see Fig. 2(b). When the two clusters are brought to a distance of about 6 a.u., the clusters prefer to rotate abruptly as evidenced by a sharp rise in Θ , leaving the tetrahedral structure essentially intact [see Fig. 2(c)]. Thus, it is clear that two clusters that represent closed electronic shells would essentially remain in pristine form when deposited on a noninteracting substrate. Although calculations are not done for two Al_{12}Si clusters, we expect similar behavior as discussed above.

The question one then has to ask is the following: What would the electronic structure of a “supercrystal” assembled out of clusters be like and how would it differ from a crystal assembled out of atoms? It is known that the crystalline Mg is metallic even though a Mg atom has a closed electronic shell ($3s^2$) and Mg_2 is bound by a weak van der Waals force. Would a crystal assembled out of Mg_4 cluster units be metallic, even though two Mg_4 clusters are bound by a van der Waals force? In a similar vein, 8% Si impurities in Al are not likely to change Al from a metal to an insulator. Would a crystal assembled out of Al_{12}Si cluster units, which has similar Si concentration, be metallic? The answers to these questions ultimately have to come from experiment. This can only be achieved if one can invent a novel [18] way, simi-

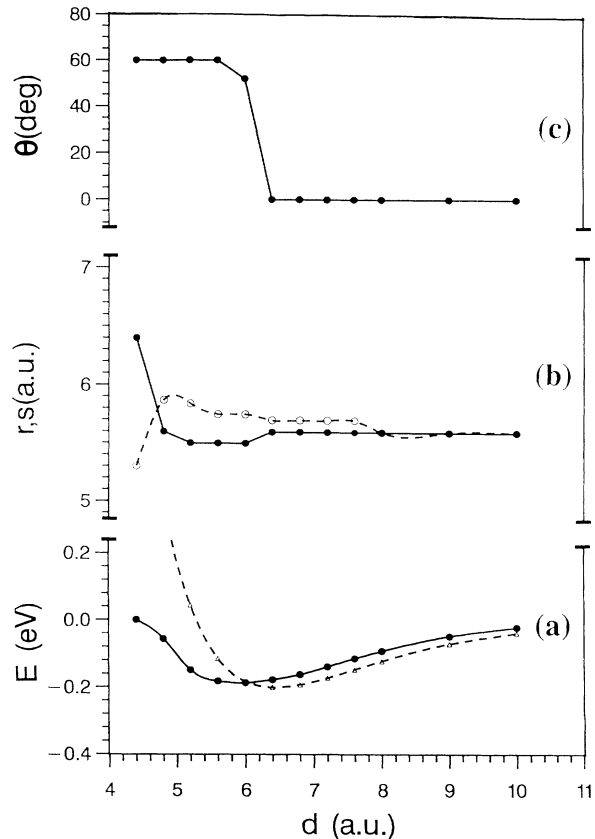


FIG. 2. (a) Spatial dependence of the binding energy per pair of Mg atoms in two interacting Mg_4 clusters (solid line) and a Mg dimer (dashed line). (b) Change in tetrahedral bond distances s (dashed line) and r (solid line) as a function of distance d between two Mg_4 clusters [see Fig. 1(b)]. (c) Angle Θ between the two triangular bases of the two Mg_4 clusters as a function of distance d .

lar to that for C_{60} , to mass produce clusters. Theorists, in the mean time, can still help in demonstrating how the electronic band structure of cluster-assembled crystals would differ from atom-assembled crystals. We are presently calculating the electronic band structure and cohesive energy of a fcc crystal composed of Al_{12}Si units to address this issue.

This work was supported in part by a grant from the U.S. Department of Energy (Grant No. DE-FG05-87ER45316). One of us (S.N.K.) is thankful to J. L. Martins and F. Reuse for help in computations.

- [1] *Physics and Chemistry of Small Clusters*, edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987).
- [2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature (London)* **318**, 162 (1985).
- [3] M. Abshagen, J. Kowalski, M. Meyberg, G. zu Putlitz, F. Trager, and J. Well, *Europhys. Lett.* **5**, 13 (1988); T. Takagi, in *Metal Clusters*, edited by F. Trager and G. zu

- Putlitz (Springer-Verlag, New York, 1986), p. 171.
- [4] W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, *Phys. Rev. Lett.* **52**, 2141 (1984).
- [5] R. E. Leuchtner, A. C. Harms, and A. W. Castleman, Jr., *J. Chem. Phys.* **91**, 2753 (1989); A. Nakajima, T. Kishi, T. Sugioka, and K. Kaya, *Chem. Phys. Lett.* **187**, 239 (1991).
- [6] See, for a review, B. K. Rao, S. N. Khanna, and P. Jena, *Phase Transitions* **24-26**, 35 (1990).
- [7] T. P. Martin, T. Bergmann, H. Gohlich, and T. Lange, *Chem. Phys. Lett.* **172**, 209 (1990).
- [8] S. Saito and S. Ohnishi, *Phys. Rev. Lett.* **59**, 190 (1987). These authors have considered the interaction between two Na_{19} jellium clusters.
- [9] H.-P. Cheng, R. S. Berry, and R. L. Whetten, *Phys. Rev. B* **43**, 10647 (1991).
- [10] M. R. Pederson, in *Proceedings of the International Symposium on the Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena, S. N. Khanna, and B. K. Rao (Kluwer Academic, Dordrecht, 1992).
- [11] J.-Y. Yi, D. J. Oh, and J. Bernholc, *Chem. Phys. Lett.* **174**, 461 (1990).
- [12] F. Reuse, S. N. Khanna, V. de Coulon, and J. Buttet, *Phys. Rev. B* **41**, 11743 (1990).
- [13] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [14] G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- [15] B. K. Rao and P. Jena, *Appl. Phys. Lett.* **57**, 2308 (1990).
- [16] V. I. Vedeneyev, L. V. Gurvich, V.N. Kondratyev, V. A. Madvedev, and Y. L. Frankevich, *Bond Energies, Ionisation Potentials, and Electron Affinities* (St. Martin's, New York, 1966), p. 31.
- [17] D. M. Cox, D. J. Trevor, R. L. Whetten, and A. Kaldor, *J. Phys. Chem.* **92**, 421 (1988).
- [18] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1990).

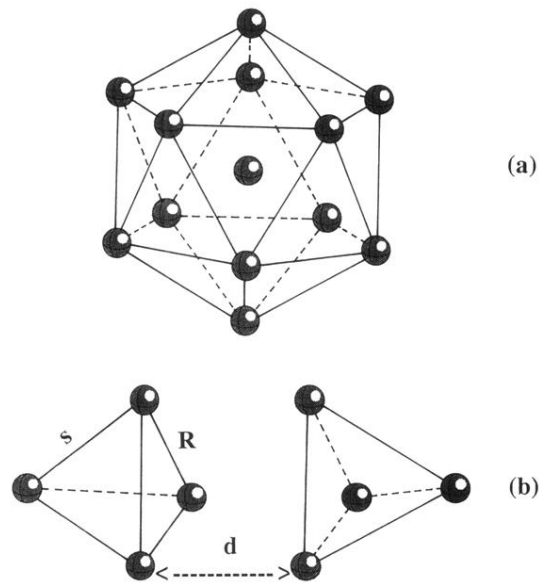


FIG. 1. Geometries of the Al_{13} , Al_{12}C , and Mg_4 clusters used in the present calculations.