

Polytetrahedral Clusters

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By studying the structures of clusters bound by a model potential that favors polytetrahedral order, we find a previously unknown series of “magic numbers” (i.e., sizes of special stability) whose polytetrahedral structures are characterized by disclination networks that are analogous to hydrocarbons.

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Polytetrahedral order [1,2] has become an increasingly important concept in condensed-matter physics. Such polytetrahedral structures, for which the whole of space can be naturally divided up into tetrahedra with atoms at their vertices, are the basis of crystalline Frank-Kasper phases [3,4], and have been invoked in order to understand the structure of quasicrystals [5–7] and atomic liquids and glasses [1,8,9]. However, little is known about the consequences of polytetrahedral order for the structure of clusters and nanoparticles. This situation contrasts with close-packing schemes, which give rise to fascinating cluster structures, such as Mackay icosahedra [10], Marks decahedra [11], and Leary tetrahedra [12].

However, recent experiments indicate that small cobalt clusters can have polytetrahedral order [13], although only limited information about their detailed structure could be obtained. Furthermore, there is an increasing interest in mixed metal clusters [14,15], and polytetrahedral structures would be expected for those alloys that exhibit Frank-Kasper or quasicrystalline phases in bulk.

The distinctive features of polytetrahedral packings stem from the inability of regular tetrahedra to fill all space. When five regular tetrahedra are packed around a common edge there is a small angular deficit of 7.4° , whose closure requires a small distortion of the tetrahedra. If this method of packing is extended to larger collections of tetrahedra, local icosahedral coordination results, but the strain that needs to be introduced to close all the gaps grows very rapidly. Therefore, in order to form an extended polytetrahedral structure, sites where six tetrahedra share a common edge need to be introduced—a negative disclination line is said to run along this common edge. Even though the local distortion required to remove the overlap that occurs when packing six regular tetrahedra is larger, the overall strain is reduced.

Polytetrahedral packings can therefore be described by a network of disclination lines threading an icosahedrally coordinated medium. In Frank-Kasper crystals this disclination network is ordered and periodic, whereas it has been suggested that atomic liquids and glasses are characterized by disordered entangled disclination networks [1,8].

Many very small clusters naturally form polytetrahedral clusters. The 13-atom icosahedron (20 slightly distorted tetrahedra sharing a vertex) is an extremely common struc-

ture for rare gases [16], as well as metal [17] and molecular [18] clusters, and is generally favored over a close-packed structure because of its lower surface energy. However, structures that continue this polytetrahedral packing soon become disfavored for most materials because the associated strain cannot be accommodated. The largest polytetrahedral clusters have been obtained for a model system where the width of the potential allows the system to tolerate ordered polytetrahedral structures up to $N \approx 70$ [19].

A model system that exhibits polytetrahedral clusters and enables us to make structural predictions about such clusters would therefore be of great interest. Here we seek to address this issue by studying clusters interacting with a potential of the Dzugutov form [20]:

$$V(r) = A(r^{-m} - B) \exp\left(\frac{c}{r-a}\right) \Theta(a-r) + B \exp\left(\frac{d}{r-b}\right) \Theta(b-r), \quad (1)$$

where $\Theta(x)$, the Heaviside step function, is 0 for $x < 0$ and 1 otherwise. The total potential energy of a cluster is then $E = \sum_{i < j} V(r_{ij})$, where r_{ij} is the distance between atoms i and j . This potential was designed to encourage polytetrahedral and local icosahedral order in supercooled liquids through the introduction of a local maximum in the potential near $\sqrt{2}$ times the equilibrium pair distance (Fig. 1) that disfavors close-packed structures [21]. This maximum also resembles the first of the Friedel oscillations that can occur for metal potentials. The potential provides a good model for metallic glasses [21,22], and interestingly, under certain conditions a dodecagonal quasicrystal can be generated [23].

For the original parametrization of the Dzugutov potential, clusters form noncompact polytetrahedral structures composed of needles, rings, and three-dimensional networks of interpenetrating and face-sharing icosahedra [24]. Thus the original potential cannot provide a realistic model of the compact polytetrahedral clusters formed for cobalt or that might occur for metallic alloys. Noncompact structures occur because the relatively narrow potential well (Fig. 1) does not allow the system to accommodate the strain associated with compact polytetrahedral clusters. Therefore, we chose a new parametrization of the Dzugutov potential that both increases the width of

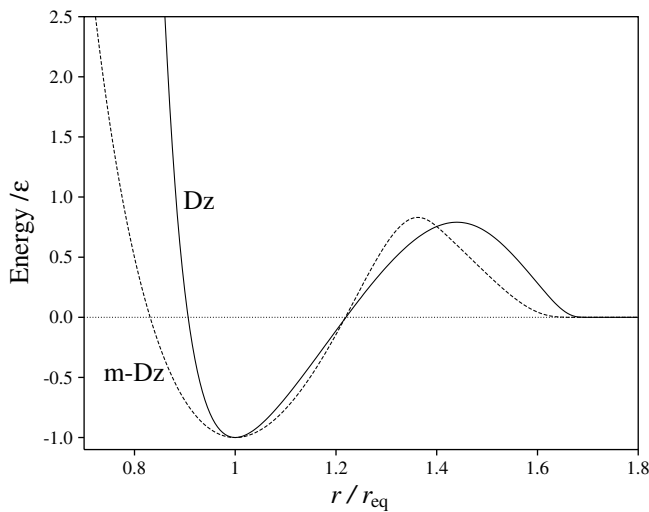


FIG. 1. Comparison of the Dzugutov potential in its original (Dz) and modified (m-Dz) form.

the minimum (mainly through softening the repulsive core) and reduces the width of the potential maximum. As envisaged, this new potential gives rise to compact polytetrahedral clusters. The parameters in our modified potential have the values

$$\begin{aligned} A = 3.00 & \quad B = 2.109 & \quad a = 1.65 & \quad b = 1.94 \\ c = 0.52 & \quad d = 0.55 & \quad m = 4. \end{aligned} \quad (2)$$

The pair potential has a maximum at $r_{\max} = 1.36r_{\text{eq}}$ of height 0.83ϵ , where r_{eq} and ϵ are the equilibrium pair separation and well depth, respectively.

To find the global minima of clusters interacting with this potential we used the basin-hopping algorithm [25,26]. For each size up to $N = 100$ we performed five runs of 100 000 steps starting from a random configuration. We also performed short runs starting from configurations generated by adding or removing the appropriate number of atoms from some of the lowest-energy minima for sizes one, two, or three atoms above or below the current size. These latter seeded runs were repeated until no new putative global minima were found and were particularly important because the roughness of the energy landscape [24] makes optimization from a random starting point particularly difficult. Indeed, above $N = 100$ no runs from

a random starting point found the global minima, so in this size range we used a different approach. Using the structural principles obtained from the particularly stable structures for clusters with less than 100 atoms, we were able to construct a series of candidate geometries for particularly stable sizes in the range $N = 100$ –250. These structures then served as the initial seed configurations for a series of short basin-hopping runs for the intervening sizes. Again seeded runs using the lowest-energy minima of nearby sizes were repeated until no further improvements were obtained for any size.

The energies of the resulting putative global minima are depicted in Fig. 2 in a manner that emphasizes particularly stable minima or “magic numbers.” At small sizes the magic numbers ($N = 13, 19, 23, 26, 29$) are those expected for polytetrahedral growth upon the 13-atom icosahedron and are similar to those seen for Lennard-Jones clusters [27] and their experimental analog, argon clusters [28]. The next magic number corresponds to the disklike 38-atom cluster that was previously found for clusters interacting with the original Dzugutov potential; this structure has a single disclination line running along its axis and is a fragment of the Z phase, one of the Frank-Kasper phases [24]. Then, for the rest of the size range we consider, there is a series of roughly equally spaced minima in Fig. 2 that correspond to a new sequence of magic numbers.

Some of the structures of these new clusters are depicted in the right-hand column of Fig. 3. Each cluster consists of a disclinated central structure that is surrounded by an overlayer in which an atom is added to each face and above each vertex that is not at the end of a disclination line. This is the same overlayer as for the initial polytetrahedral growth on the 13-atom icosahedron, and in that context has been called the anti-Mackay [19] or face-capping [27] overlayer. This overlayer does not extend the disclinations of the central cluster, thus giving rise to characteristic six-fold pits where the disclinations exit onto the surface of the resultant cluster (Fig. 3).

At the center of the 57-atom cluster is a 17-atom structure in which the central atom is the node for four disclinations in a tetrahedral arrangement. This coordination shell (often denoted as Z16) is commonly found in the

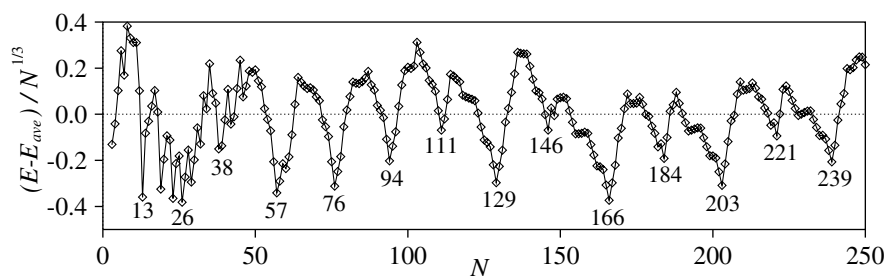


FIG. 2. Energies of the lowest-energy minima as a function of size relative to E_{ave} , where E_{ave} is a four parameter fit to these energies. $E_{\text{ave}} = -3.040N + 2.023N^{2/3} + 1.949N^{1/3} + 0.545$.

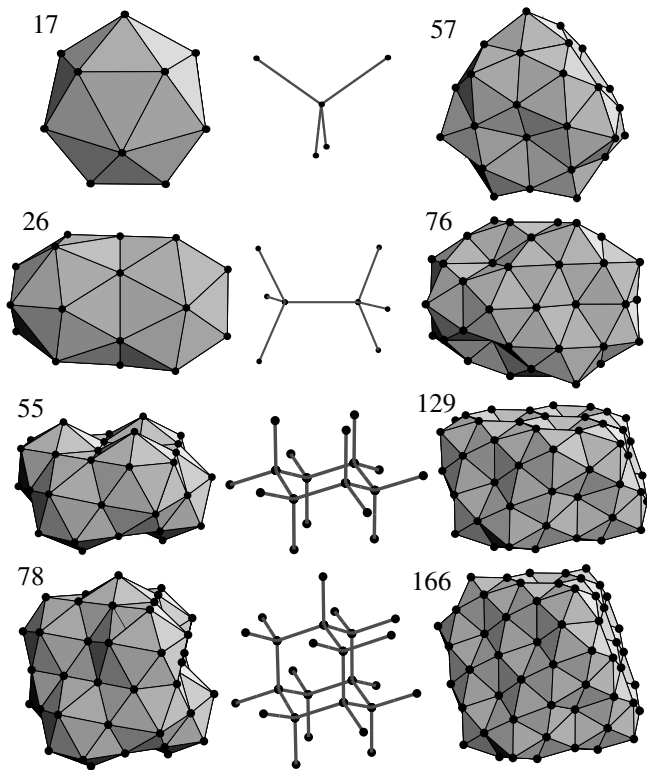


FIG. 3. Structures of some of the magic number clusters. On the right is the complete structure, in the middle the corresponding disclination network, and on the left the structure that is at the center of the cluster. All three have the same orientation.

Frank-Kasper phases [4]. Furthermore, the atoms of all the central clusters either have this or an icosahedral coordination shell, thus giving rise to a tetrahedrally coordinated disclination network (Fig. 4). There are two bulk Frank-Kasper phases that involve such networks, the C14 and C15 phases. In the C15 phase the disclination network has the structure of the diamond lattice and in the C14 phase the wurtzite structure. All the cluster centers can be considered to be fragments of these two Frank-Kasper phases, except the center of the 221-atom cluster which involves a mixture of the two phases.

The easiest way to understand the progression of structures is to note the correspondence between the disclination networks and hydrocarbon structures (Fig. 4). The disclination network of the 57-atom cluster is analogous to methane. Next comes a series corresponding to the linear alkanes, ethane (76), propane (94), and *n*-butane (112), and the branched alkane, isobutane (111). At this point it becomes favorable to form more compact structures analogous to cycloalkanes, e.g., the chair form of cyclohexane (129) and methyl-cyclohexane (146). Above this size structures analogous to cage hydrocarbons [29] are favorable, such as bicyclo[2.2.2]octane (148), adamantane (166), iceane (184), diamantane (203), and triamantane (239). It is noticeable that the most stable of these latter magic numbers correspond to the polyman-
tanes (or diamondoids), where the central structures are

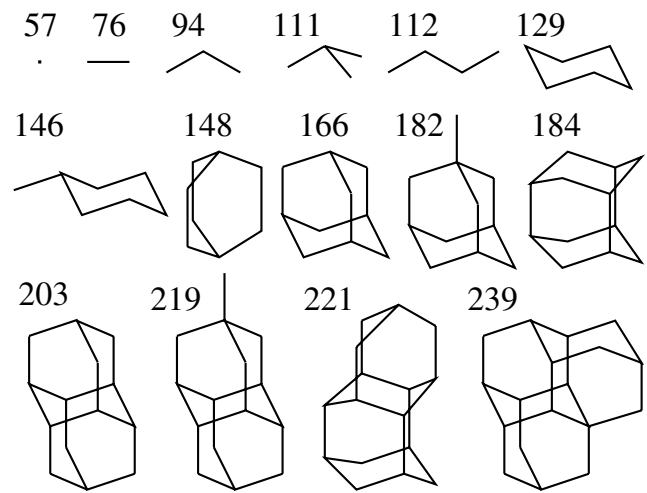


FIG. 4. Schematic representations of the disclination networks for the particularly stable clusters. The terminal disclination lines have been omitted for clarity. The networks, thus drawn, are analogous to the carbon backbones of a series of hydrocarbons.

fragments of the C15 phase. C14 and mixed disclination networks are competitive only in between these sizes when they are competing with structures analogous to methyl-polyman-
tanes.

The analogy to the hydrocarbons also allows ready prediction of the structure of larger clusters. For example, it is well known that the next polyman-
tane, tetramantane has three isomers [29]. However, as for the original parametrization of the Dzugutov potential [30], the body-centered-cubic (bcc) lattice is lowest in energy for bulk. A comparison of E_{ave} to a similar function fitted to a series of bcc rhombic dodecahedra indicates that bcc clusters are lowest in energy beyond $N \approx 1400$.

Experiments can usually probe only cluster structure indirectly and so comparisons with calculations from candidate geometries are required for structural identification. Therefore, to enable the potential identification of the structures described here, all are accessible from the Cambridge Cluster Database [31]. Furthermore, as the series of magic numbers does not coincide with any previously known [17], there is also the potential for identification through mass spectral abundances. One should note that if for the experimental material it is favorable to cap the six-fold pits on the cluster surface the magic numbers would then occur at $N = 61, 82, 102, 121, 141, 161, 182, 202, 223, 243, \text{ and } 261$.

Calculations for an example cluster, the 166-atom adamantane analog, are consistent with the experimental results for cobalt clusters [13]. The calculated scattering function reproduces many of the features observed in the x-ray data, and the structure has perpendicular planes of atoms that can account for the square arrays of lattice fringes seen in the electron microscopy images. However, this agreement may result more from the polytetrahedral order than the actual detailed structure of our clusters [13].

It is remarkable that many of the unusual cluster structures that have been predicted by theory have been subsequently observed experimentally. For example, the Mackay icosahedron [10], first suggested in 1962, has since been seen for a wide variety of systems over a large size range [17,32]. Furthermore, the small truncated octahedron at $N = 38$ and Marks decahedron at $N = 75$, whose stability was first identified in calculations on model clusters [33], have since been identified for Ni_{38} [34], Au_{38} [35], and Au_{75} [36]. Most recently the Leary tetrahedron, a surprise global minimum for a 98-atom Lennard-Jones cluster [12], has since been found for $(\text{C}_{60})_{98}$ [37]. Therefore, it would be no surprise if the polytetrahedral structures that we have described here were likewise to be positively identified experimentally.

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