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Structure and binding of Lennard-Jones clusters: $13 \leqslant N \leqslant 147$

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An efficient lattice based search and optimization procedure has been developed and used with various assumed pair potentials to find minimal energy structures on an icosahedrally derived lattice. These were then taken as initial configurations and allowed to relax freely under the Lennard-Jones pair potential to the adjacent energy minimum. The initial configurations and relaxed energies of the most tightly bound structures found for each N are presented for the range $13 \leqslant N \leqslant 147$. While the energies obtained are rigorously only upper bounds to the absolute minimal energy of an N-atom Lennard-Jones cluster, they appear to be less than or equal to that of any other structures proposed previously. They are believed to be the most tightly bound structures of the multilayer icosahedral type, and to be reasonable candidates for the absolutely minimal energy structures in this size range. The most tightly bound configuration found was the truncated icosahedral structure at $N = 135$.

INTRODUCTION

In the study of microclusters, physical clusters—finite systems of atoms bound by van der Waals forces—play a special role. This results largely from the expectation that these weak forces will be simple and easier to model, but also in part from the existence of an easily produced physical realization of the system—rare gas microclusters. Without the tools provided by the assumption of translational invariance, however, modeling even these simple finite systems proves to be a tremendously complex problem. Undoubtedly the most straightforward and basic question one can ask about the system concerns the nature of its ground state. Yet even with the assumption of simple pairwise additive forces, the problem of rigorously identifying and characterizing the absolute minimum energy configuration appears to be insoluble, for all but the very smallest clusters. Nevertheless, it is still possible by a combination of physical reasoning and mathematical computation to learn quite a bit about the answer.

In the work to be described here, I will be concerned with the restricted problem of describing the ground state of a classical N-particle system interacting through the Lennard-Jones or "LJ" pair potential. The foundations of the problem have been clearly set out in the comprehensive review article by Hoare,[1] together with an extensive bibliography of previous work, and the reader will be assumed to be familiar with that article. The potential is given conventionally in reduced units

$$v_{\mathrm{LJ}}(r) = r^{-12} - 2r^{-6}, \tag{1}$$

where v_{LJ} is the potential in units of the well depth, and r is the interparticle distance in units of the distance at the potential minimum. The mathematical problem is then to find the absolute or global minimum of the potential energy hypersurface defined by

$$V_{\mathrm{LJ}}(r^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v_{\mathrm{LJ}}(|r_i - r_j|) \tag{2}$$

subject to the condition that the cluster does not translate or rotate, or more specifically, that $r_{1x} = r_{1y} = r_{1z} = r_{2y} = r_{2z} = r_{3z} = 0$.

The complexity of the problem lies in the fact that while it is always possible with a computer to allow a particular initial configuration to relax to the adjacent minimum of the potential energy surface, unless the starting configuration has been chosen to lie in the proper valley, or "catchment basin," the resulting configuration will not correspond to the absolute minimum. Hoare and McInnes[1,2] have shown that the number of local minima in the potential energy surface of a Lennard-Jones cluster becomes extremely large, however, even for quite small systems. For example, for a cluster size of $N = 13$ atoms there are already at least 988 such minima, and it is most likely that this number increases much faster than linearly with N. Clearly, it is not practical to perform an undirected search for all the local minima of the potential function in order to find the global minimum, except perhaps for the smallest cluster sizes. Instead one must resort to some form of a directed search procedure which incorporates in greater or lesser degree, physical intuition about the nature of the system in its stable states. Several such algorithms (sphere packing models, growth sequences, or aufbau schemes) have been proposed in the past, and have been reviewed in the article by Hoare cited above. The most extensive study of minimal energy structures to date is the work of Hoare and Pal.[3,4] They developed a rather general growth algorithm and used it to generate large numbers of stable structures, mostly in the range $N \leqslant 55$. These were compared to find the lowest energy structures, which in turn become candidates for the absolute minimal structures. Of particular interest here is their observation that while what they term the "icosahedral growth sequence" did not, in general, produce minimal structures, icosahedral subunits did appear regularly in relaxed configurations generated by other sequences. Icosahedral packings, which appear to play a sig-

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nificant role in the structure of small systems, were first suggested by Mackay.[5] These space filling but translationally noninvariant structures can be described[6] as 20 slightly flattened tetrahedrally shaped fcc units whose faces are (111) planes and which share a common vertex. The interatomic spacing in the 20 equilateral outer faces is about 5% larger than the spacing along the radial lines connecting the 12 vertices with the origin. The number of atoms in the sequence of closed shell icosahedral clusters is 13, 55, 147, 309, etc.

More recently, much new insight into the nature of cluster structure has been provided by molecular dynamic simulations,[7–10] most notably by the work of Farges and collaborators,[11–15] as well as by Monte Carlo techniques.[16–21] One of the most striking results of the simulation studies of Farges *et al.* is that the closed shell icosahedral structures ($N = 13,55$) appear with high probability as subunits of the local equilibrium configurations obtained on cooling clusters to zero temperature. The atoms which do not fit into the closed shell structures usually appear to be more or less randomly distributed over the surface, but near locations of high symmetry of the underlying icosahedral structure. In particular, they are located at the "pockets" or tetrahedrally bonded sites on the surface, at edge locations with two neighbors in the underlying layer, and at vertices with a single underlying neighbor. They refer to these structures as multilayer icosahedral, or "MIC" structures.

Just as important, the relatively recent ability to produce and study experimentally small isolated rare gas clusters in nozzle beams has also provided valuable guidance. In particular, the observation by electron diffraction techniques that the structure of small clusters has an icosahedral character,[12,15,22–24] and the discovery in mass spectrometric studies of intensity anomalies, or "magic numbers"[25–32] related to the relative stabilities of the underlying structures, are quite suggestive of an icosahedral symmetry. In addition, these experiments provide further impetus for the theoretical studies by supplying a physical system sufficiently similar to the model system that meaningful comparisons and predictions can be made.

In more detail, Farges *et al.*[11,12] have observed that the relaxed configurations obtained in their simulations for $N \leqslant 50$ contain a large number of interpenetrating icosahedra, and they have termed them polyicosahedral, or "PIC" structures. They have proposed[14] that the most tightly bound structures in this size range can be generated by the double icosahedral ("DIC") growth sequence, in which a 13 atom core is decorated with atoms in such a way as to produce the maximum number of interpenetrating double icosahedra. They[14] have also relaxed several icosahedral structures with incomplete second shells and found these to be more tightly bound than those of the DIC sequence for $35 \lesssim N \leqslant 55$. For clusters with $55 \leqslant N \leqslant 147$ they presume[13,15] that the third layer is completed in one of two surface arrangements. The first, termed "regular," consists of the partially filled sites of the third icosahedral shell, and the second, termed "twin," contains atoms in the three locations on each face in the twin positions with respect to the former. When complete, the twin arrangement contains 60 atoms in the outer layer and the regular, 92. They have relaxed several structures of each type and find the regular arrangement is energetically favored for $N \gtrsim 82$, and the twin for $N \lesssim 70$. Both arrangements have the same energy for $70 \lesssim N \lesssim 82$.

Based on intuition gained from their study of the mass spectra of very cold charged argon clusters, Harris *et al.*[29,30] independently arrived at what proves to be a similar model for *charged* cluster structure, but from a rather different set of hypotheses. In particular, they have assumed that the 13 atom charged core provides a rigid "substrate" with approximately icosahedral symmetry upon which the next shell of atoms is constructed. Assuming that the atoms in the next shell will reside at sites of high symmetry, where the force exerted by the core is purely radial, one can see that the core can support two mutually exclusive lattices. The first, consisting of face centered and vertex sites, is related to Farges *et al.*'s DIC structures, and the second, consisting of edge centered and vertex sites, is just the incomplete outer layer of an icosahedral structure. Rather than presuming how the atoms of the partially filled shell will arrange themselves on these lattices, as in previous work, it was assumed only that the minimal structure was the one that maximized the number of near neighbor bonds on a given lattice. A lattice based search and optimization algorithm was used to find the minimal structures in an unprejudiced way. Binding energy differences, which are related to the charged cluster mass spectrum, were taken to be proportional to the difference in the number of nearest neighbor bonds in an N cluster and an $(N-1)$ cluster. With this model they were able to explain the sequence of prominent peaks in the charged cluster mass spectrum for $N \leqslant 55$ as well as the magnitude of its intensity variations. Later[31] this model was extended to the third shell where it was called "icosahedrally derived shell structure" or the IDSS model.

It is my purpose in the present work to extend this lattice based search and optimization procedure to the neutral Lennard-Jones cluster problem, where it can be used to generate physically reasonable initial configurations. These can then be allowed to relax freely under the LJ potential to obtain the corresponding local minimum of the potential energy. The objective is to find which of all the MIC-type structures possible for a given N has the lowest energy. It is hoped that this model will lead to true global minima, but it must be emphasized rigorously that all that can be claimed is that it provides an upper bound on this quantity.

MODEL

It is apparent from the preceding observations that the closed shell icosahedral structures form particularly tightly bound units. Furthermore, it appears that the most tightly bound configurations of nonclosed shell clusters are those that contain the largest possible closed shell unit at their center with the remaining atoms distributed in a single layer on its surface. The core may be compressed a bit but does not appear to be radically deformed by the additional surface atoms. These atoms reside near either the tetrahedrally bonded sites on the faces of the icosahedral core, or the sites balanced on its edges with two underlying neighbors, or the

sites perched atop its vertices. The latter two categories are stable only when other neighboring sites in the layer are also occupied. Taken together, these sites approximate a lattice on the surface of an icosahedral core which when partially occupied forms what is called an MIC structure. The central hypothesis of this work is that all such MIC structures can be obtained by relaxing an initial configuration which lies on a perfectly *regular* lattice of sites built upon a *regular* icosahedral core. It is further assumed that there are no topological changes associated with this relaxation, or more precisely that, in the notation of Hoare,[1] the "adjacency matrix" is unchanged. The particular lattice which is used in the calculation consists simply of those sites forming a Mackay[5] icosahedron of unit diameter spheres at the center, together with the sites which correspond to the next completed icosahedral shell and those sites located on the faces at stacking fault locations relative to the first. The latter are located at a unit distance from each of the three corresponding neighbors on the central icosahedron. It will be noted that it is not always possible for adjacent sites to be occupied because of the overlap of the repulsive atomic cores, and thus the lattice cannot be fully occupied. Anticipating future results it will be helpful to define two sublattices, either of which *can* be fully occupied. The first of these, called the "IC" sublattice, consists of all those 42 (or in the third shell, 92) sites which will comprise the outer shell of the next complete Mackay icosahedron. The other, denoted the "FC" sublattice, consists of those tetrahedrally bonded face sites which lie at stacking fault locations relative to the first lattice, together with the vertex sites.[33] When full it contains 32 (or 72) atoms. One face of each of these sublattices is shown in Fig. 1. The set of all these sites together will be refered to as the combined, or "IF" lattice.

There is a significant problem which remains, however, and that is the following. Even though one knows (or assumes) that the most tightly bound states of a cluster will be MIC structures derivable from a regular lattice, there is still a tremendous uncertainty remaining about precisely which member of this class of structures will correspond to the ground state. For example, for a 34 atom cluster with an IC lattice structure there are $(42!)/(21!)^2 = 5.4\times 10^{11}$ possible configurations! Of course many are equivalent under the 120 symmetry operations of the lattice, but none the less it is still clearly impossible to test them all. Fortunately, it is possible to reduce the number of configurations to be tested to a manageable number of likely candidates by utilizing a lattice based search and optimization procedure similar to that described by Harris *et al.*[30,31] My initial qualitative expectation was that the minimal energy structure could be obtained by relaxing one of the lattice structures on the combined lattice which had the largest possible number of nearest neighbors. The lattice search and optimization procedure could then be used to identify all geometrically distinct isomers on the lattice which had this property. This idea proved to be somewhat too simplistic, however, since the various nearest neighbor pairs on the combined lattice are just too different to be treated as identical. Nonetheless, since there are assumed to be no significant topological changes associated with the relaxation process, it is still reasonable to expect that the optimal relaxed configuration will be derived from one of the set of configurations which are in *some* sense optimal on the lattice as well.

The general approach finally adopted is, for fixed N, to search for those configurations on the lattice or its separate sublattices which are minimal energy structures under various different pair interaction potentials. Usually there turn out to be several nonequivalent lattice isomers which have the same energy. The resulting "optimal" lattice structures provide a set of reasonable initial configurations which are then allowed to relax freely to the adjacent minimum under the LJ pair potential. It is expected (or more accurately, hoped!) that one of these will lie within the catchment basin corresponding to the global minimum of the LJ potential hypersurface. Since it is likely that the true minimal configurations will have in some general sense the largest possible number of nearest neighbors, the principal pair potential used in the lattice search is a radial square well potential which will be called the "NN" (nearest neighbor) potential:

$$\begin{aligned} V_{\mathrm{NN}}(r) &= +100; \quad r<0.8, \\ &= -1; \quad 0.8\leqslant r\leqslant 1.3,. \\ &= \ \ 0; \quad r>1.3 \end{aligned} \tag{3}$$

In addition, however, the full LJ potential [Eq. (1)] has been used, as well as several others.

The search and optimization procedure on the lattice will be described in detail below. Its principal advantages over simply choosing what appear to be reasonable initial configurations and allowing them to relax, are that it provides an unbiased and hopefully exhaustive method of identifying likely candidates for further relaxation. This is important, since as will be seen, the clusters which ultimately prove to be minimal after relaxation are often quite counterintuitive and do not follow a regular growth sequence, even for quite small clusters.

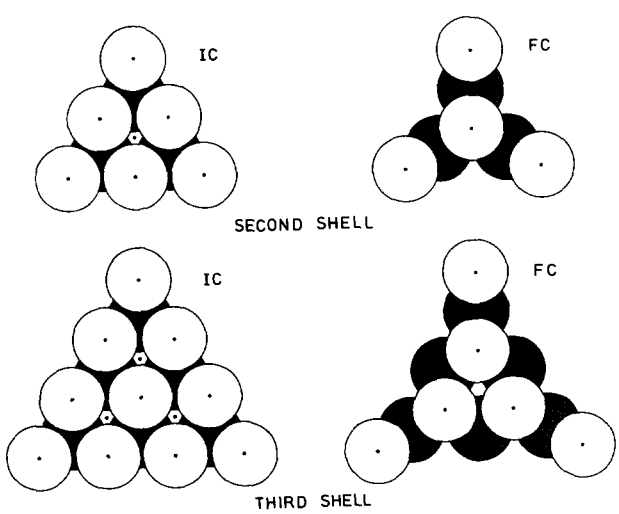

FIG. 1. Scale representation of the FC and IC sublattice sites (open circles) overlying a single face of the icosahedral substrate (shaded circles).

CALCULATION

The lattice based search and optimization routine which is central to the method operates in the following way. The physical problem is specified at the start by the interaction matrix $VP(I,J)$, the pair interaction between an atom on site I and one on site J. This is determined once the lattice coordinates and the pair interaction potential are chosen, and is stored as a lookup table. Each time an atom is added or removed from a site the program recalculates from VP the total potential V, and the energy change $DV(I)$ associated with adding or removing another atom at each site. From $DV(I)$ are obtained, in turn, lists of the most loosely bound filled sites and the most tightly binding vacant sites.

The search proceeds as follows: The N_c core sites are filled and then the remaining $(N - N_c)$ atoms are distributed at random over the N_s surface lattice sites. This defines an initial configuration CF, or list of filled sites. CF(I) is simply an N_s component vector whose elements are 1 if site I is occupied, and 0 if it is not. Next a particle is selected at random from the set of most loosely bound atoms and placed on a site chosen at random from the set of most tightly binding vacant sites. If this results in a decrease in V then the process is repeated. If not, then the previous configuration represents a "terminal state," i.e., a state from which one cannot reduce V by moving only one atom on the lattice at a time. If the corresponding value of V is less than or equal to the lowest V found on any previous trial, the configuration is recorded. If in addition it is strictly less, then all higher energy terminal states recorded previously are deleted. Another random initial configuration is then generated and the entire loop repeated. The process is continued, if necessary thousands of times, until at least 250 (often many more) terminal states corresponding to the minimal energy are found. Since this process can be implemented largely with integer arithmetic (mostly 1's and 0's) it is quite efficient with storage and CPU time.[34] It should be emphasized that while the true lattice minimum is by definition a terminal state, the converse is not true. Nonetheless the definition is quite restrictive, and the number of geometrically distinct terminal states on the lattice must be a relatively small number—certainly much less than the number of local minima of the freely relaxed cluster. Thus, the probability of finding the true minimal state from a random initial configuration is much greater.

Given the random nature of the search, it is clear that many of the configurations in this list will be equivalent under one of the 120 symmetry operations of the icosahedron. Consequently, the next step is to reduce this list to a set of geometrically distinct isomers, all of which lead to the same minimal lattice energy. In most cases there are only a few, and in many cases only one energetically equivalent isomer. For some values of N with the nearest neighbor potential, however, the number was as high as 43.

These geometrically distinct isomers, which in the case of the NN potential each have the same (maximum) number of nearest neighbors on the lattice, are now each allowed to relax freely under the Lennard-Jones potential. The method used for relaxation is a variant of the general class of gradient search methods called a "continued partan"[35] method. It consists of an alternation of one-dimensional energy minimizations along a direction determined by the N-dimensional gradient, with an "acceleration step"—a minimization along a direction obtained by connecting the results of the two previous gradient searches. This method is expected to be particularly efficient for minimizing along long narrow N-dimensional "valleys," and has the advantage of being quadratically convergent. The associated one-dimensional search procedure used is related to one developed by Powell.[36] It is also quadratically convergent and does not involve calculating derivatives. The final somewhat arbitrary part of the relaxation procedure is an algorithm to terminate the process. I have chosen to monitor the maximum force on any of the atoms in the cluster, and when this has fallen below a chosen value the relaxation is terminated. In practice this value is about 10^{-4} of the initial value, and at that point the potential V is changing by 10^{-5} reduced energy units per cycle or less. The resulting reduced energies represent upper bounds on the true local minimum, but they are believed to be accurate to better than 10^{-3} reduced energy units. This has been well confirmed in those cases in which the relaxation has run much longer. This relaxation algorithm appears to be reasonably efficient. The calculations were run on a mini computer,[34] and typically it took less than 15 min CPU time to relax an initial configuration. Highly symmetric configurations converged much faster. For example the 147 atom closed shell structure required less than 2 min CPU time. Occasionally an initial structure which was clearly going to be far from minimal, would not converge within the span of the author's patience. In these cases it was assumed that the structure was most likely collapsing into a topologically different one, and the relaxation was terminated.

It was not practical to relax all of the numerous isomers which were found with the NN interaction for some of the cluster sizes so the following process was adopted. First a limited relaxation was carried out in which all isomers were relaxed under the full LJ interaction with a radial scale change only, and their order of binding was recorded. Then, for every N for which there were ten or fewer isomers (which was most of them), all isomers were relaxed freely and compared. In no case was there a significant change in the order of binding from the restricted relaxation procedure. Thus it was assumed that the same would apply for the relatively few sizes with larger numbers of isomers, and for these only the lowest ten isomers were freely relaxed.

RESULTS

Second shell ($14 \leqslant N \leqslant 55$)

Since it was expected that the structures containing the largest number of nearest neighbors would be most tightly bound on relaxation, the initial lattice search was carried out with the NN interaction on the combined "IF" lattice. It was found that for $N \leqslant 45$ the minimal structures found were always on the pure FC sublattice. The various isomers were freely relaxed with the LJ potential for $N \leqslant 39$, and also for $N = 45$. The other FC structures found for $40 \leqslant N \leqslant 44$ did not relax within a reasonable time to a stable structure, which probably means they were collapsing into topological-

TABLE I. Relaxed binding energy $E_b(N)$ and energy differences $\Delta E_b(N) = E_b(N) - E_b(N-1)$ N. Right-hand columns indicate which lattice and search potential combination(s) generated the initial configuration.

Size N	Binding energy $E_b(N)$	Energy diff. $\Delta E_b(N)$	Initial config. found—x: not found—o FC NN	FC LJ	IC NN	IC LJ	IF NN	IF LJ
12	37.967[a]							
			Second shell					
13	44.327	6.360	x	x	x	x	x	x
14	47.845	3.518	x	·	·	o	x	x
15	52.323	4.478	x	·	·	o	x	x
16	56.816	4.493	x	·	·	o	x	x
17	61.318	4.502	x	·	·	o	x	o
18	66.531	5.213	x	·	·	o	x	x
19	72.660	6.129	x	·	·	o	x	o
20	77.177	4.517	x	·	·	o	x	o
21	81.685	4.508	x	·	·	o	x	o
22	86.810	5.125	x	·	·	o	x	o
23	92.844	6.034	x	·	·	o	x	o
24	97.349	4.505	x	·	·	o	x	o
25	102.373	5.024	x	·	·	o	x	o
26	108.316	5.943	x	·	·	o	x	o
27	112.874	4.558	x	·	o	o	x	o
28	117.822	4.948	x	·	o	o	x	o
29	123.587	5.765	x	·	o	o	x	o
30	128.287	4.700	x	·	o	o	x	o
31	133.586	5.299	o	·	x	x	o	x
32	139.636	6.050	o	·	x	x	o	x
33	144.843	5.207	o	·	x	x	o	x
34	150.045	5.202	o	·	x	x	o	x
35	155.757	5.712	o	·	x	x	o	x
36	161.825	6.068	o	·	x	x	o	x
37	167.034	5.209	o	·	x	o	o	o
38	173.134	6.100	o	·	x	x	o	x
39	180.033	6.899	o	·	x	x	o	x
40	185.250	5.217	·	·	x	x	·	x
41	190.536	5.286	·	·	x	x	·	x
42	196.278	5.742	·	·	x	x	·	x
43	202.365	6.087	·	·	x	x	·	x
44	207.689	5.324	·	·	x	x	·	x
45	213.785	6.096	o	·	x	x	o	x
46	220.680	6.895	·	·	x	x	·	x
47	226.012	5.332	·	·	x	x	·	x
48	232.200	6.188	·	·	x	x	·	x
49	239.092	6.892	·	·	x	x	·	x
50	244.550	5.458	·	·	x	o	·	o
51	251.254	6.704	·	·	x	x	·	x
52	258.230	6.976	·	·	x	x	·	x
53	265.203	6.973	·	·	x	x	·	x
54	272.209	7.006	·	·	x	x	·	x
55	279.248	7.039	·	·	x	x	·	x
			Third shell					
56	283.643	4.395	o	o	x	x	·	·
57	288.343	4.700	x	x	o	o	·	·
58	294.378	6.035	x	x	o	o	·	·
59	299.738	5.360	x	o	o	o	·	·
60	305.876	6.137	x	x	o	o	·	·
61	312.009	6.133	x	x	o	o	·	·
62	317.354	5.345	x	o	o	o	·	·
63	323.490	6.136	x	x	o	o	·	·
64	329.620	6.130	x	x	o	o	·	·
65	334.915	5.295	o	x	o	o	·	·
66	341.043	6.128	o	x	o	o	·	·
67	347.252	6.209	o	x	o	o	·	·
68	353.395	6.143	x	o	o	o	·	·
69	359.726	6.332	x	o	o	o	·	·
70	366.892	7.166	x	x	o	o	·	·
71	373.350	6.457	x	o	o	o	·	·

TABLE I (*continued*).

Size N	Binding energy $E_b(N)$	Energy diff. $\Delta E_b(N)$	Initial config. found—x: not found—o FC NN	FC LJ	IC NN	IC LJ	IF NN	IF LJ
72	378.524	5.174	x	o	o	o	·	·
73	384.789	6.265	x	o	o	o	·	·
74	390.909	6.119	x	o	o	o	·	·
75	396.037	5.129	o	x	o	o	·	·
76	402.177	6.139	o	x	o	o	·	·
77	408.463	6.287	o	o	x	x	·	·
78	414.681	6.217	o	o	x	x	·	·
79	421.811	7.140	o	x	o	o	·	·
80	428.084	6.273	x	o	o	o	·	·
81	434.344	6.260	x	o	o	o	·	·
82	440.550	6.207	o	o	x	x	·	·
83	446.924	6.374	o	o	x	x	·	·
84	452.657	5.733	o	o	x	x	·	·
85	459.056	6.399	o	x	o	o	·	·
86	465.385	6.329	o	o	x	x	·	·
87	472.098	6.714	o	o	x	x	·	·
88	478.935	6.837	o	o	x	x	·	·
89	486.054	7.119	o	o	x	x	·	·
90	492.434	6.380	o	o	x	x	·	·
91	498.811	6.377	o	o	x	x	·	·
92	505.185	6.374	o	o	x	x	·	·
93	510.878	5.692	o	o	x	x	·	·
94	517.264	6.386	o	o	x	x	·	·
95	523.640	6.376	o	o	x	x	·	·
96	529.879	6.239	o	o	x	x	·	·
97	536.681	6.802	o	o	x	x	·	·
98	543.547	6.865	o	o	x	x	·	·
99	550.667	7.120	o	o	x	x	·	·
100	557.040	6.373	o	o	x	x	·	·
101	563.411	6.372	o	o	x	x	·	·
102	569.278	5.867	o	o	x	x	·	·
103	575.659	6.381	o	o	x	x	·	·
104	582.038	6.380	o	o	x	x	·	·
105	588.267	6.228	o	o	x	x	·	·
106	595.061	6.795	o	o	x	x	·	·
107	601.912	6.851	o	o	x	x	·	·
108	609.033	7.121	o	o	x	x	·	·
109	615.411	6.378	o	o	x	x	·	·
110	621.788	6.377	o	o	x	x	·	·
111	628.068	6.280	o	o	x	x	·	·
112	634.875	6.806	o	o	x	x	·	·
113	641.700	6.826	o	o	x	x	·	·
114	648.833	7.133	o	o	x	x	·	·
115	655.636	6.803	o	o	x	x	·	·
116	662.809	7.174	o	o	x	x	·	·
117	668.283	5.473	o	o	x	x	·	·
118	674.770	6.487	o	o	x	x	·	·
119	681.419	6.650	o	o	x	x	·	·
120	687.022	5.603	o	o	x	x	·	·
121	693.820	6.798	o	o	x	x	·	·
122	700.939	7.120	o	o	x	x	·	·
123	707.802	6.863	o	o	x	x	·	·
124	714.921	7.119	o	o	x	x	·	·
125	721.303	6.382	o	o	x	x	·	·
126	727.350	6.047	o	o	x	x	·	·
127	734.480	7.130	o	o	x	x	·	·
128	741.332	6.853	·	·	x	x	·	·
129	748.461	7.129	·	·	x	x	·	·
130	755.271	6.811	·	·	x	x	·	·
131	762.442	7.171	·	·	x	x	·	·
132	768.042	5.600	·	·	x	o	·	·
133	775.023	6.981	·	·	o	x	·	·
134	781.989	6.966	·	·	x	o	·	·
135	790.278	8.290	·	·	o	x	·	·
136	797.453	7.175	·	·	o	x	·	·
137	804.632	7.178	·	·	o	x	·	·

TABLE I (*continued*).

Size N	Binding energy $E_b(N)$	Energy diff. $\Delta E_b(N)$	Initial config. found—x: not found—o FC NN	FC LJ	IC NN	IC LJ	IF NN	IF LJ
138	811.813	7.181	·	·	o	x	·	·
139	818.994	7.181	·	·	o	x	·	·
140	826.175	7.181	·	·	x	x	·	·
141	833.359	7.184	·	·	x	x	·	·
142	840.539	7.180	·	·	x	x	·	·
143	847.722	7.183	·	·	x	x	·	·
144	854.905	7.183	·	·	x	x	·	·
145	862.087	7.182	·	·	x	x	·	·
146	869.273	7.186	·	·	x	x	·	·
147	876.461	7.188	·	·	x	x	·	·
		Fourth shell						
148	(881.073)	(4.612)						
149	(886.693)	(5.620)						
150	(893.310)	(6.617)						

[a] Taken from Hoare and Pal (Ref. 3).

ly different structures. The filled FC sublattice at $N = 45$ relaxed to a stable, but what proved to be high energy structure. In the region $46 \leqslant N \leqslant 55$ the minimal structures were found to lie mostly on the pure IC sublattice. A few structures with the same number of nearest neighbors were found on mixed lattices, i.e., with an IC cap on one end and an FC cap on the other, but they always relaxed to quite high energy configurations.

The lattice search procedure on the nearly full IF lattice was relatively slow, because the randomly chosen initial configurations, in general, have a large degree of repulsive core overlap and thus a very large initial energy to be reduced. In addition, it never produced any energetically favorable configurations which were not pure IC or FC structures. Thus for more extended searches, attention was shifted to the pure IC sublattice. Searches were carried out on this lattice with the NN potential for $13 \leqslant N \leqslant 55$. On relaxation it was found that for $13 \leqslant N \leqslant 30$ the FC structures had produced the lowest energies, and beyond that, for $31 \leqslant N \leqslant 55$ the IC structures produced the lowest. As discussed above, no mixed lattice structures were ever minimal upon relaxation. The reason for the preference for FC structures when the shell is relatively empty, and for IC structures when it is relatively full, is easy to understand on a qualitative basis. The FC sites are more strongly bound to the core, but at the expense of a somewhat lower surface density than for the IC lattice. Thus, as the shell fills and intrashell interactions become more important, the favored structures shift to the IC lattice.

Another question concerns why the IC structures between $31 \leqslant N \leqslant 45$, which on relaxation are lower in energy than the corresponding FC structures, are not found by searching on the IF lattice with the NN potential. The answer appears to be that the NN interaction does not accurately reflect the relatively higher tension in the FC sublattice brought about by the larger average interparticle spacing, and thus overweighs the FC relative to the IC structures. One way to better account for the relative difference in bond length on the two lattices is to carry out the lattice search using the complete LJ potential from the start. Consequently, the next search was carried out on the IF lattice with the LJ potential. This search successfully picked up the IC structures for $N \geqslant 31$. Above this point, in all but two cases it was successful in finding the configuration which subsequently proved to be minimal under free relaxation. The reason for missing it in these two cases appears to be that the LJ potential somewhat underestimates the binding energy associated with vertex sites in the relaxed configuration.

The binding energy in reduced units, $E_b(N)$, of the most tightly bound structure found for a given N in the second shell is displayed in Table I. As discussed above, these energies are actually upper bounds, but are believed accurate to 10^{-3} in reduced units. The sequence of binding energy differences, $\Delta E_b(N)$, is also given. Finally, the lattice and search potential combinations which generated the corresponding initial configuration are also indicated. In Figs. 2 and 3 are shown schematic representations of the initial lattice configurations which led to the minimal structures on relaxation. It is expected that they are topologically equivalent to the relaxed structures derived from them. The figures represent schematically a view along a fivefold axis of an icosahedron. The edges of the icosahedron map onto straight lines and the sublattice sites are represented by small circles. The vertex at the "south pole" maps onto the circular ring on the border. Filled sites are represented by filled circles, and vacant sites by open circles. For clarity, filled sites are shown "on top" when the lattice is relatively empty, and vacancies when it is relatively full. The figures are labeled by the particular sublattice and the value of N.

Figure 6 shows the successive binding energy differences as a function of N for the second shell. This represents the minimum work required to remove an atom from an N-atom cluster in its lowest energy configuration, and displays most clearly the relative stabilities of the various configurations. The sequence of tightly bound FC configurations at $N = 19, 23, 26$, and 29 are equivalent to the "double icosahedral" structures discussed by Farges *et al.*[11,12] They are formed by placing a five membered ring surrounding a filled vertex site on a sequence of adjacent vertices on the FC sublattice. On relaxation these approximate a sequence of interpenetrating icosahedra. It must be emphasized, however, that the intermediate structures do not form a completely regular "growth sequence." For example, the minimal structure at $N = 18$ is not formed by adding an atom to the minimal structure at $N = 17$. This behavior is found frequently in our results, particularly in the third shell. The sequence of tightly bound IC structures at 49, 46, 43, (40), 39, 36, (33), and 32 form what Harris *et al.*[31] have called the "missing face"sequence. It is generated by sequentially removing the facets of an icosahedron—the next facet removed being the one with the fewest remaining occupants.[37] Again we note that the intermediate structures (e.g., 34/35:37/38:50/51) do not form a regular growth sequence. Those values of N which have been identified above as having "tightly bound" configurations share two other characteristics. First, in our lattice searches only one isomer was found for that cluster size, and second, the next larger cluster is particularly loosely bound.

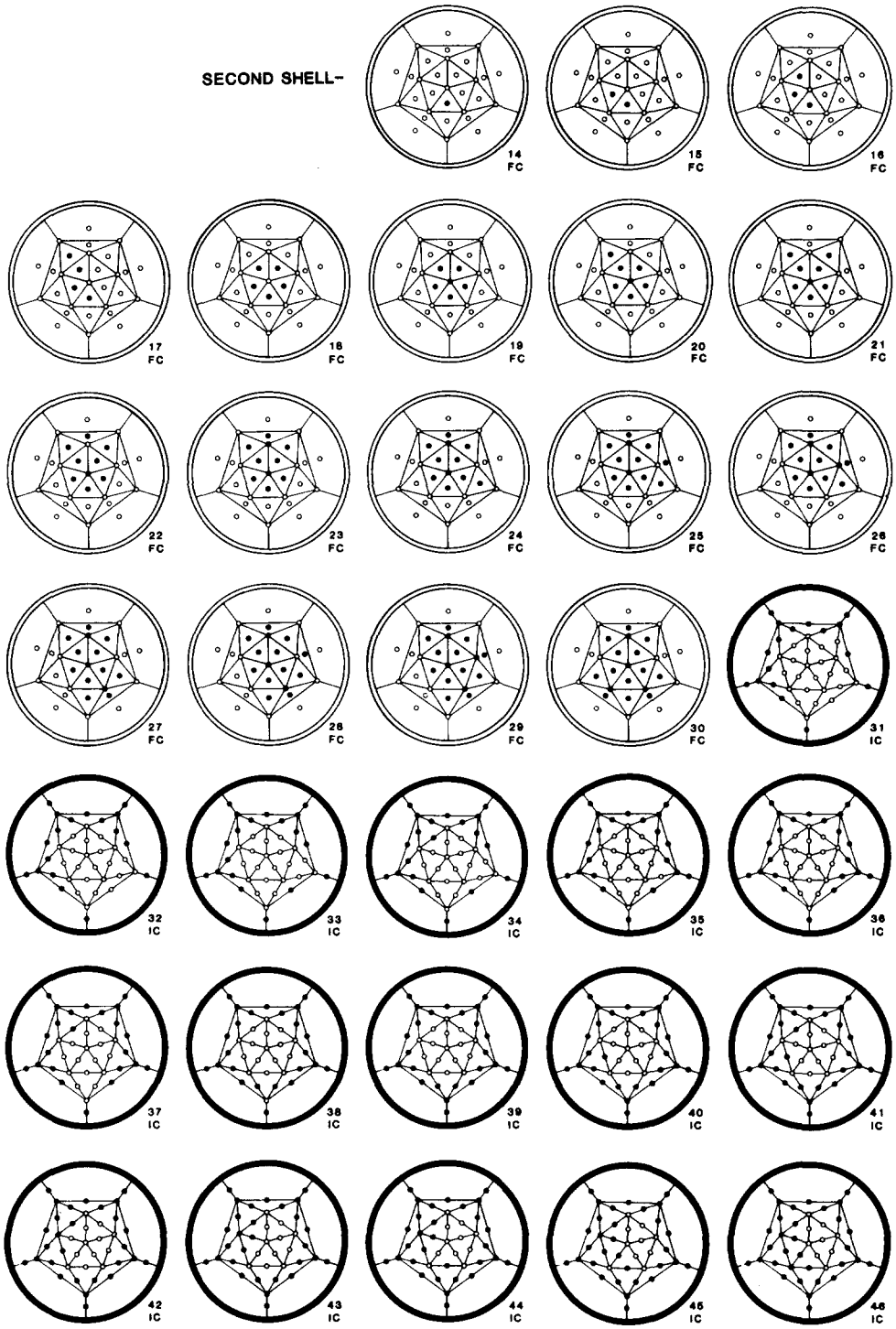

FIG. 2. Schematic representation of the initial configurations which lead to the minimal relaxed structures. $14 < N < 46$.

Third shell ($56 < N \leqslant 147$)

The search procedure was next extended to the third shell. Since the IF lattice had not produced any minimal structures which were not purely IC and FC, the search was restricted to the separate sublattices for reasons of efficiency. For each sublattice, complete searches were made with both the NN potential and the full LJ potential. As noted previously, the former appears somewhat to overestimate the binding of vertex sites in the relaxed configurations, and the latter somewhat to underestimate it. The minimal lattice isomers found by each procedure were then freely relaxed under the LJ potential to find the most tightly bound structure overall. The results for $E_b(N)$ and $\Delta E_b(N)$ for the minimal structures are also given in Table I, along with a list of which sublattices and search potentials generated the initial configurations which led to them. The initial configurations are represented schematically as before in Figs. 3, 4, and 5. Relaxed energy values for fourth shell structures with $N = 148$–150 are also given in the table. They are shown in

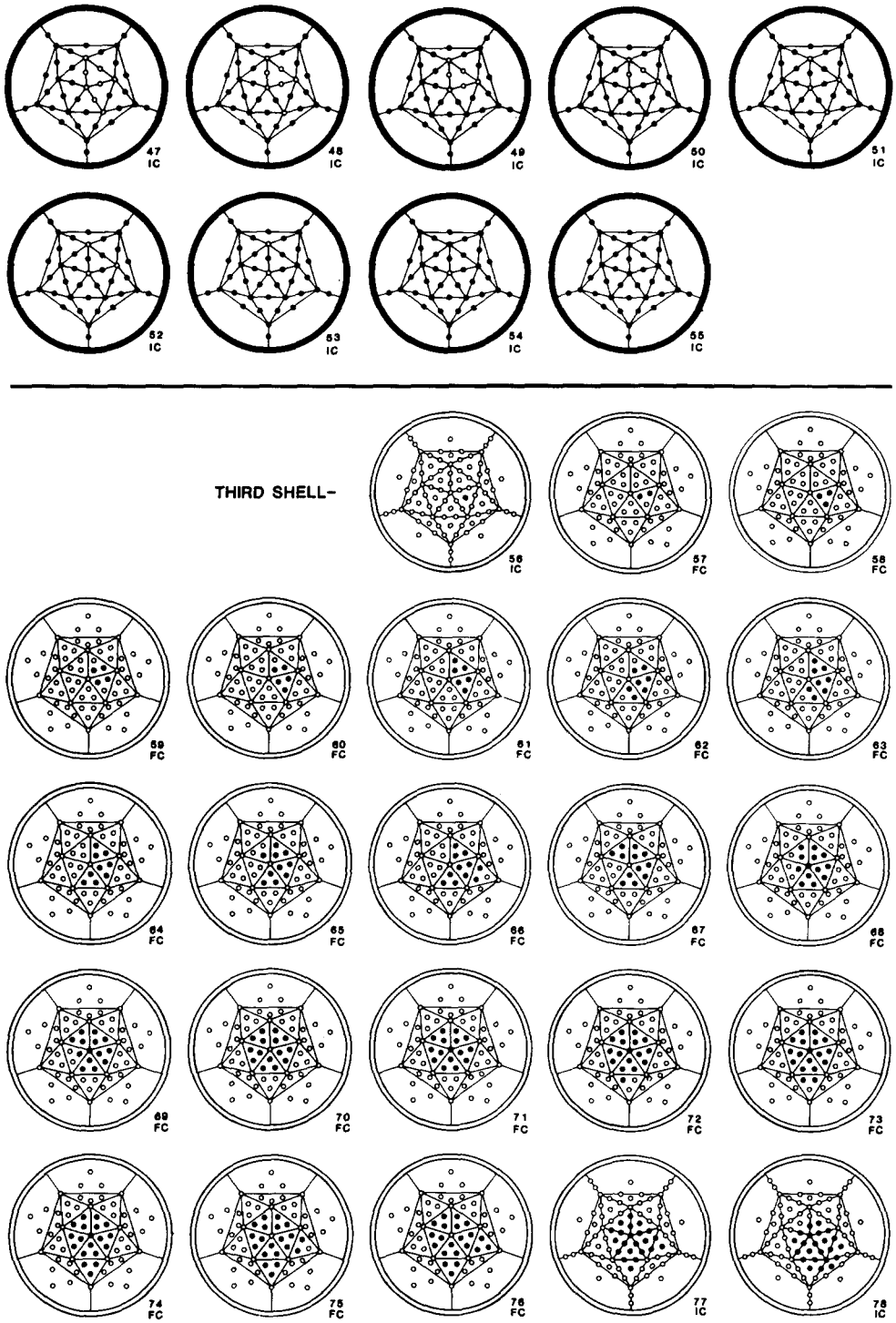

FIG. 3. Schematic representation of the initial configurations which lead to the minimal relaxed structures. $47 \leq N \leq 78$.

parentheses because the initial configurations did not result from a search procedure, but instead were arbitrarily taken from the triangle of sites on the fourth shell IC lattice which lie in the center of a face. They represent characteristic but possibly not precisely minimal energies. Successive binding energy differences for the third shell are shown in Fig. 7.

The most obvious result of the search for the third shell is that again, with the exception of the first atom in the shell, the FC structures are favored for smaller N and the IC structures for larger N. However, in this case the two lattices are competitive over a range of N between 77 and 85. Another very interesting result is that in contrast to the behavior in the second shell, the search with the LJ potential *did* succeed in generating configurations which were *not* found with the NN potential (and thus did not have the maximum number of nearest neighbors on the lattice), but which none the less proved to have the lowest energy on relaxation. The most significant example of this is on the IC lattice in the range

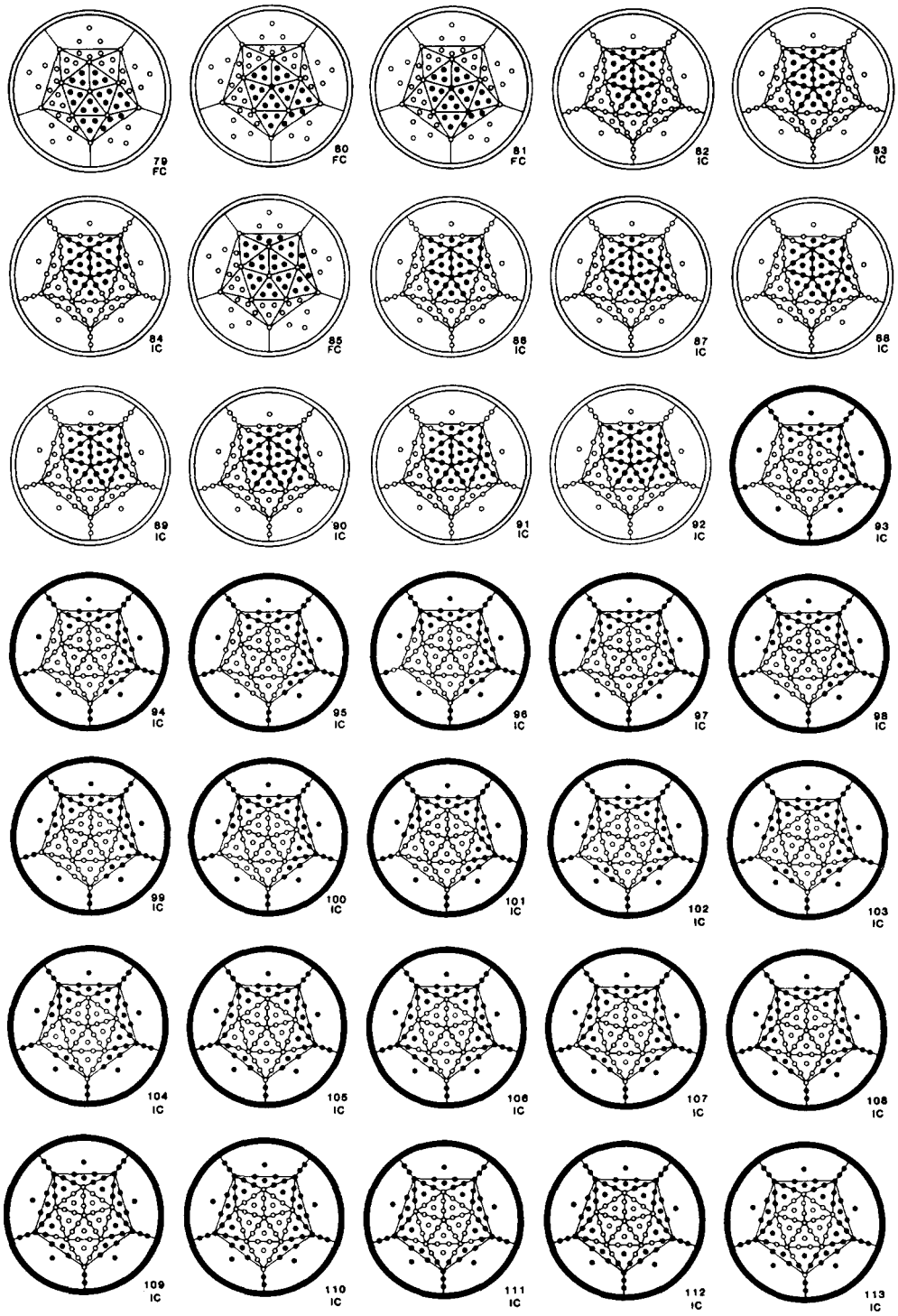

FIG. 4. Schematic representation of the initial configurations which lead to the minimal relaxed structures. $79 \leqslant N \leqslant 113$.

$135 \leqslant N \leqslant 139$. In particular, when $N = 137$ the nearest neighbor interaction is optimized by the configuration with one missing face, while the LJ interaction is optimized by the removal of 10 adjacent vertices. The latter proves most favorable on relaxation. In fact, the IC structure at $N = 135$ with all its vertices removed proves to be the most tightly bound structure of all—tighter even than the closed shell structure at 147! It is interesting to note that similar truncated icosahedral or "soccer ball shaped" structures have recently been proposed to describe the tightly bound C_{60} cluster,[38] and even as the building block for quasicrystals.[39] On the other hand, there are times when the NN generated structure is more tightly bound than the best LJ generated one, e.g., at $N = 134$, where the LJ structure contains 12 missing vertices, while the favored NN structure contains a missing face. This supports the idea that the NN interaction somewhat overestimates the binding that vertex sites will have in the relaxed lattice, while the LJ interaction somewhat underestimates it. Similar results are found on the FC lattice at smaller N, where the NN interaction favors struc-

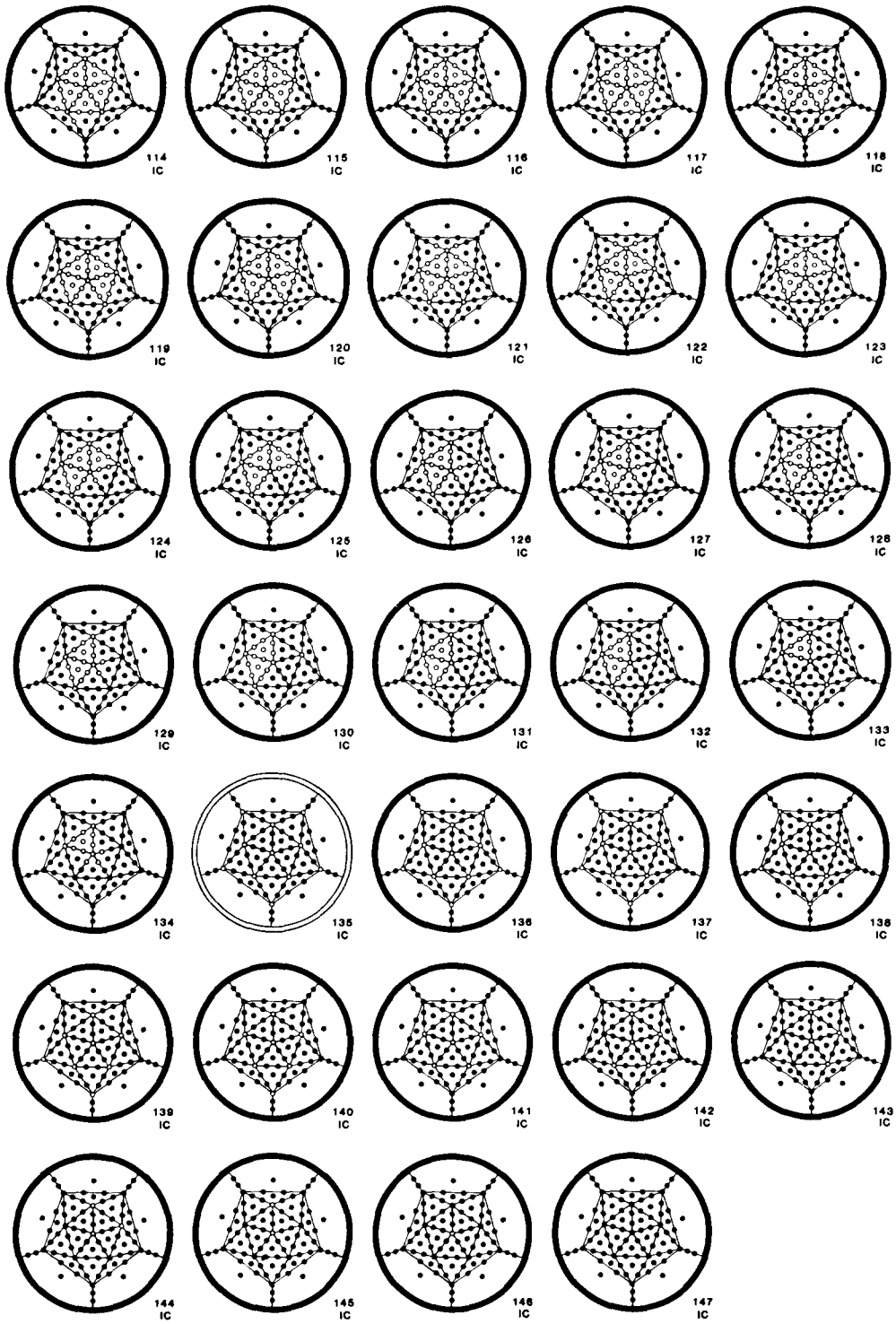

FIG. 5. Schematic representation of the initial configurations which lead to the minimal relaxed structures. $114 \leqslant N \leqslant 147$.

tures containing a five member ring surrounding a filled vertex site and the LJ interaction favors structures with filled triangles on the faces. The latter again often proves to be optimal on relaxation.

In the third shell there is not such a clear and obvious relationship between the binding energy differences and the structural regularities as was the case in the second shell, perhaps because the sequences are more complex. On the FC lattice the configurations in which adjacent faces are decorated with three atoms each (e.g., at 58, 61, 64, etc.) are all present in the minimal sequence up to $N = 85$ (10 faces) with the exception of 73 and 82. These are in conflict with the other dominant motif, the one and two capped structures at 71 and 81 which are the third shell analog of the double icosahedral structures at $N = 19$ and 23. On the IC lattice the dominant motif is again the missing face sequence, which

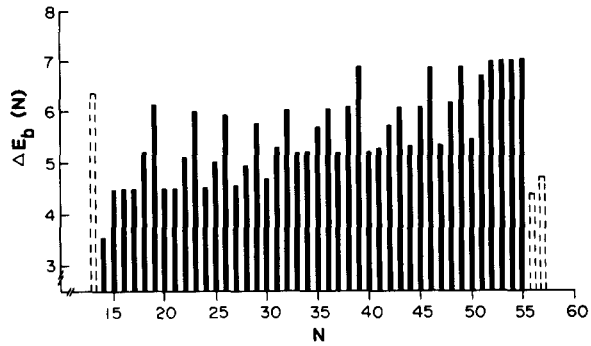

FIG. 6. Binding energy differences $\Delta E_b(N)$ vs N for the second shell.

is present in the sequence of minimal structures from 2 up to 13 missing faces at $N = 83$.[37] In the binding energy plot these structures correlate somewhat better with local minima at $N + 1$ than with local maxima at N. It must be emphasized again that while these structures are contained in the sequence of minimal structures, the latter is not a regular growth sequence. In the third shell it is, if anything, even less regular than before.

DISCUSSION

A natural question to ask at this point concerning the method is the following: Since each search potential has succeeded in generating minimal structures not found with the other, what assurance is there that a third search potential will not produce even more new minimal structures? In an attempt to answer this question I have tried several other physically reasonable search potentials for a more limited range of N values. In particular, I have searched in the range $134 \leqslant N \leqslant 143$ with two different truncated Lennard-Jones potentials, as well as with both full and truncated LJ potentials on a lattice scaled radially ($r \rightarrow 0.95r$) to approximate the relaxed dimensions, and finally with the LJ potential with an added central force. The latter was chosen to model the additional effect of a charge on the central atom of an argon cluster. In none of these cases were any new configurations discovered. While it is certainly possible to generate new configurations using exotic search potentials, it seems unlikely that they would lead to new minimal structures upon relaxation under the LJ potential. There appear to be two kinds of configurations corresponding to the relative weighting of the vertices in the search process. One is picked up by the NN potential and the other by the LJ potential. I am reasonably confident that no others exist, but that must remain only speculation.

The final point concerns the comparison of the minimal energies generated by this MIC derived search procedure and those found previously by other methods. There have been comparatively few accurate energy values published for other relaxed LJ cluster structures.[40] The most comprehensive list is that of Hoare and Pal.[3,4] Their results are identical to these for $N \leqslant 21$, with the exception of $N = 17$, where their configuration is somewhat less tightly bound (by 0.01 reduced energy units). Their structures are also identical at 25, 26, 29, and 55. The relaxed configuration at $N = 17$ has also been identified by Freeman and Doll,[19] and those at 17 and 24 by Willie.[21] This illustrates another feature that shows up clearly in these studies, namely that the energy differences between the minimal structure and other topologically quite different ones are often not very large, particularly if the structure lies in between the "tightly bound" cluster sizes. Thus, the energy relaxation must be quite complete in order to distinguish between them. As a simple example, consider the 17 atom cluster. The NN search on the FC lattice generates four isomers. They can be constructed from the 16 atom "V"-shaped structure shown in Fig. 2 by adding an atom either at the partially enclosed vertex site, or at one of the three nonequivalent adjacent face sites. The resulting lattice shapes may be roughly described as "Y"-shaped, "C"-shaped, and "Z"-shaped. The binding energies of the four corresponding relaxed configurations are 61.0945, 61.2968, 61.3071, and 61.3180. The next to last corresponds to the Hoare and Pal structure, and the last to the Freeman and Doll structure.

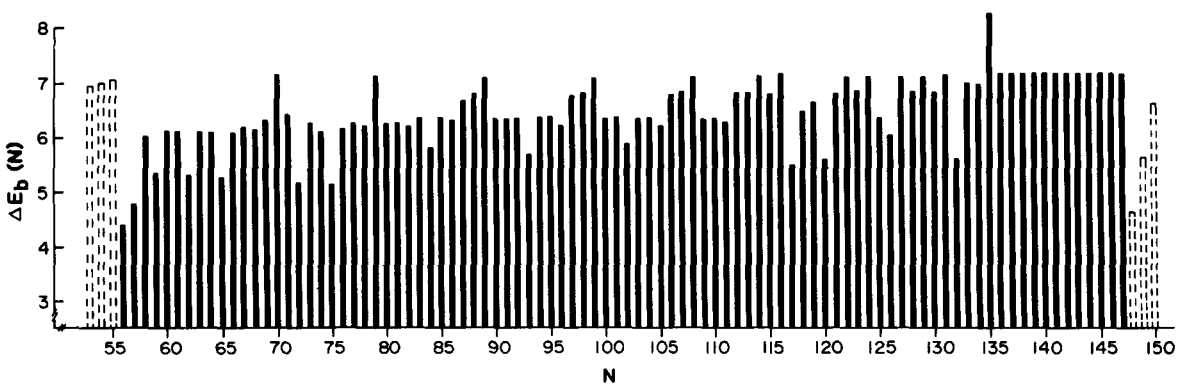

FIG. 7. Binding energy differences $\Delta E_b(N)$ vs N for the third shell.

The sequence of binding energies of MIC structures found by this search procedure equal or exceed those found for other structures in every case of which I am aware. In particular, to my knowledge, 124 of these configurations have not been described previously.[40] I am quite confident that the most tightly bound MIC structures have been found, and to the extent that the MIC structures represent the true ground state of Lennard-Jones clusters, that the N dependence of the ground state of the Lennard-Jones solid is well represented by this sequence. This assertion cannot be proved, but it could be disproved by a counter example. Rigorously, all that can be claimed is that these results provide a lower bound on the binding energy. Nevertheless, it is hoped that these results still will be of value as a sort of "benchmark" against which other proposed structures can be measured.

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[1]M. R. Hoare, Adv. Chem. Phys. **40**, 49 (1979).
[2]M. R. Hoare and M. McInnes, Faraday Discuss. Chem. Soc. **61**, 12 (1976); Adv. Phys. **32**, 791 (1983).
[3]M. R. Hoare and P. Pal, Adv. Phys. **20**, 161 (1971).
[4]M. R. Hoare and P. Pal, Adv. Phys. **24**, 645 (1975), see also Ref. 7.
[5]A. L. Mackay, Acta Crystallogr. **15**, 916 (1962).
[6]C. Y. Yang, J. Cryst. Growth **47**, 274 (1979).
[7]D. J. McGinty, J. Chem. Phys. **55**, 580 (1971); **58**, 4733 (1973).
[8]C. L. Briant and J. J. Burton, J. Chem. Phys. **63**, 2045 (1975).
[9]E. E. Polymeropoulos, S. Löffler, and J. Brickman, Z. Naturforsch. Teil A **40**, 516 (1985).
[10]J. M. Soler, J. J. Sáenz, N. García, and O. Echt, Chem. Phys. Lett. **109**, 71 (1984).
[11]J. Farges, M. F. deFeraudy, B. Raoult, and G. Torchet, J. Phys. (Paris) **38**, C2-47 (1977).
[12]J. Farges, M. F. deFeraudy, B. Raoult, and G. Torchet, J. Chem. Phys. **78**, 5067 (1983).
[13]J. Farges, M. F. deFeraudy, B. Raoult, and G. Torchet, *Dynamics on Surfaces*, edited by B. Pullman, J. Jortner, A. Nitzan, and B. Gerber (Reidel, Dordrecht, 1984), p. 425.
[14]J. Farges, M. F. deFeraudy, B. Raoult, and G. Torchet, Surf. Sci. **156**, 370 (1985).
[15]J. Farges, M. F. deFeraudy, B. Raoult, and G. Torchet, J. Chem. Phys. **84**, 3491 (1986).
[16]J. K. Lee, J. A. Barker, and F. F. Abraham, J. Chem. Phys. **58**, 3166 (1973).
[17]R. D. Etters and J. Kaelberer, Phys. Rev. A **11**, 1068 (1975).
[18]J. M. Soler and N. García, Phys. Rev. A **27**, 3307 (1983).
[19]D. L. Freeman and J. D. Doll, J. Chem. Phys. **82**, 462 (1985).
[20]D. L. Freeman and J. D. Doll, Adv. Chem. Phys. (to be published).
[21]L. T. Wille, Chem. Phys. Lett. **133**, 405 (1987).
[22]J. Farges, B. Raoult, and G. Torchet, J. Chem. Phys. **59**, 3454 (1973).
[23]S. S. Kim and G. D. Stein, J. Colloid Interface Sci. **87**, 180 (1982).
[24]J. W. Lee and G. D. Stein, Surf. Sci. **156**, 112 (1985); J. Phys. Chem. **91**, 2450 (1987).
[25]O. Echt, K. Sattler, and E. Recknagel, Phys. Rev. Lett. **47**, 1121 (1981).
[26]A. Ding and J. Hesslich, Chem. Phys. Lett. **94**, 54 (1983).
[27]P. W. Stephens and J. G. King, Phys. Rev. Lett. **51**, 1538 (1983).
[28]L. F. Friedman and R. J. Beuhler, J. Chem. Phys. **78**, 4669 (1983).
[29]I. A Harris, R. S. Kidwell, and J. A. Northby, in *Proceedings of the 17th International Conference on Low Temperature Physics*, edited by U. Eckern, A. Schmid, W. Weber, and H. Wühl (Elsevier, Amsterdam, 1984), p. 1393.
[30]I. A. Harris, R. S. Kidwell, and J. A. Northby, Phys. Rev. Lett. **53**, 2390 (1984).
[31]I. A. Harris, K. A. Norman, R. V. Mulkern, and J. A. Northby, Chem. Phys. Lett. **130**, 316 (1986).
[32]T. D. Märk, P. Scheier, K. Leiter, W. Ritter, K. Stephan, and A. Stamatovic, Int. J. Mass Spectrom. Ion Processes **74**, 281 (1986).
[33]The FC lattice is related to the DIC structures of Farges *et al.* in the second shell, and to their twin lattice but with vertices added in the third.
[34]All these calculations were performed on a Prime 850 minicomputer. A complete lattice search loop consumed 0.2 s CPU time.
[35]D. A. Pierre, *Optimization Theory With Applications* (Wiley, New York, 1969), p. 312.
[36]D. A. Pierre, Ref. 35, p. 277.
[37]In the case of the second shell, the structures with four and seven missing faces have only one atom more than the particularly tightly bound "missing cap" structures with five and eight missing faces, and do not show up in the sequence. They do for the next shell, however. In this case it should be noted that while the N sequence generated by this algorithm is unique (i.e., 137, 131, 125, 119, 116, 110, 104, 101, 95, 92, 86, 83, 77, 74, etc.), there is still a slight ambiguity in the precise configuration corresponding to 4, 7, and 13 missing faces.
[38]H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature **318**, 162 (1985).
[39]L. Pauling, Phys. Rev. Lett. **58**, 365 (1987).
[40]Farges *et al.* have identified many of the features of this MIC model but have focused their attention primarily on the geometrical configurations and not the precise energies. It is therefore difficult to make a detailed numerical comparison with their work.