New Lowest Energy Sequence of Marks' Decahedral Lennard-Jones Clusters Containing up to 10 000 Atoms

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A method for constructing Marks' decahedral lattice for the studies of Lennard-Jones cluster structures is proposed. With the proposed method, clusters with Marks' decahedral structure are studied up to the size 10 000. By comparing the energies of these Marks' decahedral structures, the growth sequences with different structural characteristics, denoted by the term "family", are investigated. It is found that the structures with lowest energies are not always attributed to the even families; odd families also provide the structures with lowest energies. Therefore, a new lowest energy sequence is proposed.

1. Introduction

In the research of atomic or molecular clusters, the geometric structure with the lowest energy and the dependence of structure on cluster size are significant issues. In theoretical studies, optimization methods often succeed in obtaining the optimal structures and the corresponding energies of the small size clusters. But for the large size clusters, it is too complicated to be optimized with current computational conditions, because the number of local minima grows exponentially with the cluster size. Whereas if we start with the structures constructed by the modeling method, the energetic study will become easier. The results of the modeling method are often used to assess the relative energetic merits of various structural motifs and their dependence on cluster size. Such investigations have been employed in a variety of cluster systems including rare gas clusters,[1−3] nickel clusters,[4] iron clusters,[5] gold clusters,[6] calcium and strontium clusters,[7] aluminum clusters[8] C60 molecular clusters,[9] and so forth.

The famous structural motifs of clusters include icosahedron, truncated octahedron, face centered cubic (fcc), and Marks' decahedron. Marks' decahedron is an important structural motif, because the particles shaped as a decahedron have often been observed by microscopy in a wide size range in metal deposits of gold, silver, nickel, palladium, and platinum.[1,10] Motivated by the experimental results, a modified Wulff construction is introduced by Marks to model the Marks' decahedron.[10,11] The reentrant faces at the twin boundaries of the decahedron decrease its surface energy and make it a competitive structural motif in the medium cluster size range.

The Lennard-Jones (LJ) potential provides a reasonable description of the interaction of rare gas atoms. The optimal structures of the LJ clusters have been extensively studied.[12−14] For smaller size LJ clusters, the optimal sequence of Marks' decahedra is often considered as the sequence of 75, 192, and 389. Around these numbers, the decahedral configuration may become the favorable motif by competing with the icosahedral structure. For instance, the optimal motif of LJ75−77 is Marks' decahedron, and the 76-, 77-atom clusters are based on the 75-atom decahedron.[15,16] The structures and energies of rare gas clusters in the range 500−6000 atoms with LJ potential have been studied by Raoult et al.[1] using a relaxation method.[17] They found that a growth sequence of Marks' decahedra with lowest energy is 686, 1103, 1228, 1840, 2622, 3594, and 4776.[1]

Cleveland et al[4] used the term "family" (see section 2 for a detailed explanation) to define a series of Marks' decahedra in their study of nickel clusters. According to the structural characteristics, families 1, 3, 5, ... and 2, 4, 6, ... are categorized. In their work, the structures of families 2, 4, 6, and 8 with different notching degrees were studied. It was found that the decahedral structures with lowest energy tend to have square (100) faces. These structures belong to families 2, 4, and 6 with notching degrees 1, 2, and 3, respectively. Furthermore, if the above-mentioned sequence of 75, 192, 389, and 686, 1103, 1228, 1840, 2622, 3594, 4776 is described by "family", it can be found that their structures should belong to families 2 and 4, respectively.

Whereas recent optimization results show that the optimal structures of LJ102−104[16] and LJ236−238[18] are also the clusters with Marks' decahedral motif, they belong to family 1 of Marks' decahedron. This fact intrigued us about the question of what roles families 1, 3, and 5 play in the lowest energy sequence.

In this study, a geometric construction method for modeling Marks' decahedra is developed by adopting the term "family". Besides, the formulas for predicting the size of complete Marks' decahedra are also provided. The lattice construction method is proved to be reliable in modeling Marks' decahedra. With the modeling method, six decahedral families with three notching degrees of LJ clusters in the range from 75 to 10 000 atoms are investigated systematically. By analyzing the energies of different sequences, it is found that the energies of families 1, 3, and 5 are very close to those of their neighboring families 2, 4, and 6, respectively. In the range, some clusters in the sequence of family 3 with notching degree 2 and the sequence of family 5 with notching degree 3 are even lower in energy than the corresponding sequences of families 4 and 6. Therefore, a new lowest energy sequence of completed LJ Marks' decahedra is proposed as 75, 192, 389, 686, 1103, 1389, 2046, 2622, 3594, 4776, 5507, 7074, and 8906. Furthermore, the

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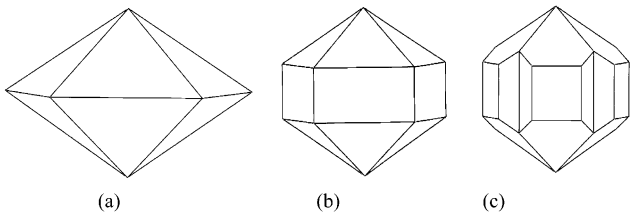

Figure 1. Structural schemes of classic decahedron (a), Ino's decahedron (b), and Marks' decahedron (c).

sequences of two modified Marks' decahedral models are also studied, and the new lowest energy sequence of the modified decahedra is obtained.

2. Method

2.1. Structural Characteristic of Marks' Decahedra and Definition of the Family. Figure 1 illustrates the structural transformation from classic decahedron to Marks' decahedron. First, Ino's decahedron is derived from the classic decahedron by truncating a decahedron to generate five (100) faces.[19] Then, the modified Wulff construction[11] introduces 10 additional faces that are the reentrant surface (111) at the five twin boundaries. This configuration is called Marks' decahedron.[10]

The parameters used to define a Marks' decahedron are shown in Figure 2a. The parameters m, n, and p denote the number of atoms on an edge joining a (100) face and a caping (111) face, on the vertical edge of the (100) face, and on an edge joining the two kinds of (111) face, respectively. Another parameter s represents the depth of notching, with $s = p - 1$. The notations are the same as that used by Cleveland et al.[4] and Raoult et al.[1] The parameters m and n are also used to define Ino's decahedron, and the clusters with the same $m - n$ value belong to a "family".[4] Since any Marks' decahedron can be derived from a completed Ino's decahedron by notching, the family number of Marks' decahedron is the same as that of Ino's decahedron, from which the Marks' decahedron is made, or deduced by the expression $m - n + 2s$. For example, the decahedron shown in Figure 2 with parameters $m = 3$, $n = 4$, and $s = 1$ belongs to family 1. In the definition of "family", "$m - n$" is a measure of the "squareness" of the (100) face of an Ino's decahedron. Generally, the family numbers of Marks' decahedra are positive, and the Marks' decahedra generated from Ino's decahedra with $m < n$ are not considered because they are energetically less favorable.

2.2. Lattice Construction Method. An atom cluster with a complete Ino's decahedral motif can be decomposed into a series of atomic layers. For example, the complete Ino's decahedron of the Marks' decahedron in Figure 2a can be decomposed into five kinds of layers, L_k ($k = 0$, ..., 4), as shown in Figure 2b. The layout of each layer in the complete Ino's decahedron can be represented by Figure 2c. If k is used to indicate a kind of layer, there will be $k + 1$ atoms on one edge of the maximal pentagon of the layer k. For Ino's decahedron, the number of atoms, N_k, on the layer k can be calculated by

$$N_k = N_{k-2} + 5k, \quad \text{with} \quad N_0 = 1 \quad \text{and} \quad N_1 = 5 \qquad (1)$$

Marks' decahedron can be created by removing some atoms from the layers of Ino' decahedron. Taking the Marks' decahedron in Figure 2a as an example, it can be created by removing the five atoms on the vertex of the pentagon, which are represented as the hollow circles in Figure 2b L_4, and then putting each layer together according to the layout in Figure 2c. In this example, the notching degree is 1, and only 26 atoms represented by solid circles will remain in the L_4 layer.

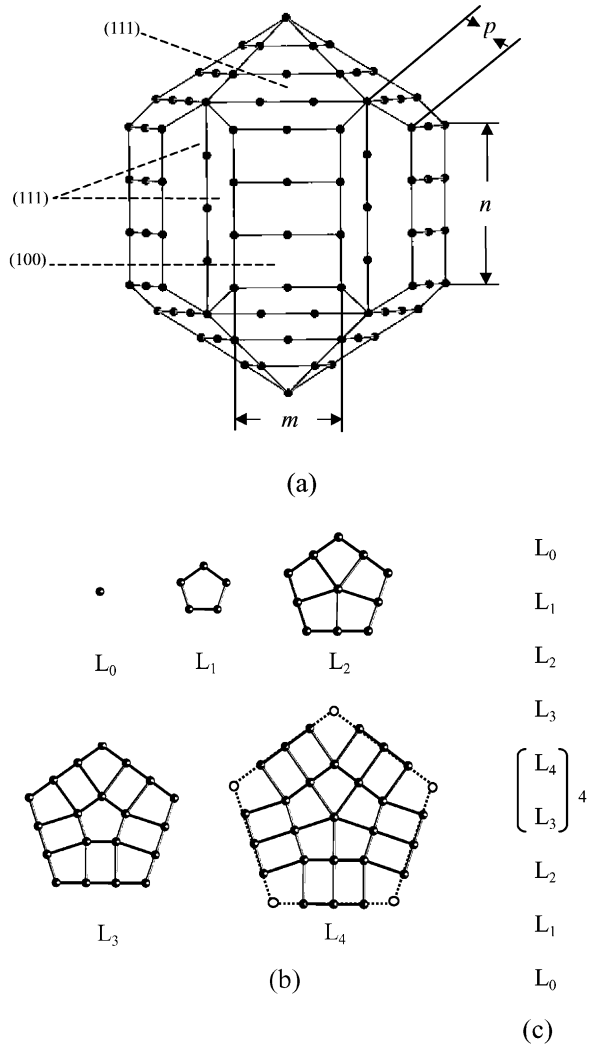

Figure 2. Configuration of Marks' decahedron: (a) an example of Marks' decahedron with $m = 3$, $n = 4$, $p = 2$, and $s = 1$; (b) structure of different layers in the Marks' decahedron; (c) layout of Marks' decahedron layers.

From above analysis, the Marks' decahedral growth sequences with notching degrees $s = 1$, 2, and 3, represented as M^1_{dec}, M^2_{dec}, and M^3_{dec}, can be computed by eqs 2, 3, and 4, respectively.

$$M^1_{dec} = 2(N_0 + N_1 + ... + N_{w-2}) + (n + 1)N_{w-1} + n(N_w - 5) \qquad (2)$$

$$M^2_{dec} = 2(N_0 + N_1 + ... + N_{w-2}) + (n + 1)(N_{w-1} - 5) + n(N_w - 15) \qquad (3)$$

$$M^3_{dec} = 2(N_0 + N_1 + ... + N_{w-3}) + 2(N_{w-2} - 5) + (n + 1)(N_{w-1} - 15) + n(N_w - 30) \qquad (4)$$

where $w = m + 2(s - 1) + 1$, representing the layer having the maximal pentagon. For the Marks' decahedral cluster in Figure 2 with parameters $m = 3$, $n = 4$, and $s = 1$, w is 4, and the cluster size is 238.

Therefore, in our method to construct a Marks' decahedron, the lattices of Ino's decahedral layers from L_0 to L_w are constructed first. For each layer, the total atom number is defined

by N_k, and the lattice is constructed according to the corresponding configuration as shown in Figure 2b. The position of each atom is defined by the Cartesian coordinates (x, y, z). For the atoms on layer k, the values of x and y are calculated according to the configuration, and z values are set to zero. The distance between two nearest atoms on the side of a pentagon is taken from the optimal Marks' decahedron structure of LJ75.

After the lattice of each Ino' decahedral layer is constructed, the notching procedure is performed. For $s = 1$, the five atoms on the vertex of the maximal pentagon are removed from the layer L_w of the Ino's decahedron. For $s = 2$ and $s = 3$, the number of the removed atoms will be 15 atoms from L_w and 5 atoms from L_{w-1}, and 30 atoms from L_w, 15 atoms from L_{w-1}, and 5 atoms from L_{w-2}, respectively. After notching, the lattices for the layers of Marks' decahedron can be obtained.

To form Marks' decahedron, the lattices of layers L_0 to L_w are arranged in the following order: L_0, L_1, L_2, ..., L_{w-2}, L_{w-1}, $(L_w, L_{w-1})_n$, L_{w-2}, ..., L_2, L_1, L_0. If n is odd, the center layer in Marks' decahedron is L_w; otherwise, the center layer is L_{w-1}. The third variable z of atom coordinates on the center layer is set to zero. Then the Marks' decahedral lattice is formed with other layers placed according to the order, and the distance between two neighboring layers is the same as that of the optimal Marks' decahedron structure of LJ75. To obtain the optimal lattice with lowest energy, a limited memory BFGS (L-BFGS) method[20,21] is applied to optimize the lattice with LJ potential. The optimized structure and energy are adopted for the analysis of the lowest energy sequences of the Marks' decahedra.

3. Results and Discussion

For LJ clusters with size from 75 to 10 000, the Marks' decahedra of six families, for example, families 1 to 6 with $s = 1$, 2, and 3, are investigated systematically with the lattice construction method. An abbreviation is used to denote a Marks' decahedral growth sequence in the following discussion. For example, F1S1 represents the sequence of family 1 with notching degree 1.

3.1. Validation of the Lattice Construction Method. With the lattice construction method, the energies of all the investigated clusters are reported in Table 1. At first, the structures and energies of the LJ75, LJ101, LJ192, and LJ238 are compared with those obtained in refs 16 and 18. Results show that the structures and energies are all correctly obtained. Furthermore, the energies of the growth sequences of families 2, 4, and 6 are compared with those reported by Raoult et al.[1] It is found that all these values are very consistent. By the two comparisons, we should have confidence that the lattice construction method proposed in this study is reliable.

3.2. Energetic Comparison of the Marks' Decahedral Families 2, 4, 6 and 1, 3, 5. The Marks' decahedral configurations with square (100) faces, that is, $m = n$, always attract more interest. The results presented by Raoult et al.[1] showed that the structures with lowest energy belong to the sequences of F2S1 and F4S2 in the range of 500 to 6000 atoms among the sequences they studied, including F2S1, F4S2, and F6S3. In the study of nickel clusters, it was found that the decahedra with lowest energies often tend to have square (100) faces.[4] These structures belong to the families 2, 4, 6, and 8 with notching degrees 1, 2, 3, and 4, respectively. The viewpoint of the optimal Marks' decahedra having square (100) faces is also adopted in other studies about the lowest decahedral sequence,[2,3] whereas the structural features of the sequences F1S1, F3S2, and F5S3 in which $m = n - 1$ are very close to those of the sequences F2S1, F4S2, and F6S3. To answer the question what roles the families 1, 3, and 5 play in the lowest energy sequence of the Marks' decahedra, the energetic growth properties of the neighboring families (families 1 and 2, 3 and 4, 5 and 6) are investigated.

The energies of the three pairs of sequences F1S1 and F2S1, F3S2 and F4S2, F5S3 and F6S3 are studied, and the comparison is given in Figure 3. The energies of clusters are plotted as $(E - E_{oct})/N^{2/3}$ versus N, where E is the energy of a Marks' decahedron and E_{oct} is the four-term least-squares fit to the binding energies of fcc cuboctahedra.[22] In the figure, the line lying lower corresponds to the sequence with lower energy.

It is clear that the line of F2S1 (line with circles) always lies lower than that of F1S1 (line with squares), which indicates that the sequence of F2S1 is more favored in energy. This is consistent with the previous studies.[1,4] As for the two lines of F3S2 (line with up-triangle) and F4S2 (line with down-triangle), the energies of F3S2 are lower than those of F4S2 in the range 268−2046. It can be found that they are quite close from 2046 to 3594. But from the enlarged graph surrounded by the dashed rectangle, it can be clearly seen that the energies of F4S2 become lower than that of F3S2 when the size is larger than 2622. Furthermore, the line of F5S3 always lies below the line of F6S3 when the cluster size is larger than 550. But as the cluster size increase, the two lines of F5S3 and F6S3 get closer.

Therefore, the energy of Marks' decahedral family 2, 4, or 6 with a square (100) faces is not always lower than that of its neighboring family. In some cases, the energy of the family 1, 3, or 5 may be even lower and is favorable in the lowest energy sequence of Marks' decahedron. In conclusion, the Marks' decahedra with nonsquare (100) faces, for example, $m = n - 1$, also can be the optimal sequence.

3.3. Lowest Energy Sequence of Marks' Decahedra. Since the family 8 with notching degree 4 is not the optimal sequence when the cluster size is lower than 13 000,[2] the sequences of families 1−6 with different notching degrees 1−3 are studied to determine the lowest energy sequence when the cluster size is lower than 10 000. The energies of all the Marks' decahedral clusters are shown in Table 1. The lowest energy sequence can be obtained by careful comparison of the six lines (sequences) in Figure 3, which are the sequences with comparatively lower energy in Table 1.

It is found that the energetically most stable sequence is the sequence of F2S1 in the range 75−1103. For larger sizes, the stable decahedra belong to the sequences with $s = 2$, in which F3S2 and F4S2 are the favorable sequences. The energies of the sequences with $s = 3$ exhibit a trend to getting nearer to the lowest energy sequences of notching degree 2 gradually as the cluster size increases, and F5S3 becomes the favorable sequence when the cluster size is greater than 6000. This result is in agreement with the finding that the number of the energetically optimal family and the notching degree will increase with cluster size.[1,4]

Upon the basis of the above analysis, the lowest energy sequence of Marks' decahedra in the range 75−10 000 can be obtained. The new sequence is 75 (F2S1), 192 (F2S1), 389 (F2S1), 686 (F2S1), 1103 (F2S1), 1389 (F3S2), 2046 (F3S2), 2622 (F4S2), 3594 (F4S2), 4776 (F4S2), 5507 (F5S3), 7074 (F5S3), and 8906 (F5S3).

3.4. Lowest Energy Sequence of Modified Marks' Decahedra. Two modifications have been introduced by Raoult et al. to improve the decahedral model in energy. One has 20 additional (110) faces that are created by removing edge atoms situated between (111) faces and (111) reentrant faces from the

TABLE 1. Energies of Marks' Decahedral Sequence of Families 1−6 of LJ Clusters

	family 1				family 2				family 3			
s	*N*	*m*	*n*	*E*	*N*	*m*	*n*	*E*	*N*	*m*	*n*	*E*
1	101	2	3	−563.329 326	75	2	2	−397.492 331	146	3	2	−857.459 571
1	238	3	4	−1 494.438 248	192	3	3	−1 175.697 144	318	4	3	−2 057.555 951
1	460	4	5	−3 086.800 861	389	4	4	−2 572.069 663	585	5	4	−4 005.081 292
1	787	5	6	−5 512.492 436	686	5	5	−4 758.735 581	967	6	5	−6 872.048 310
1	1239	6	7	−8 943.623 851	1103	6	6	−7 907.812 915	1484	7	6	−10 830.541 963
1	1836	7	8	−13 552.311 658	1660	7	7	−12 191.419 126	2156	8	7	−16 052.666 375
1	2598	8	9	−19 510.672 969	2377	8	8	−17 781.671 209	3003	9	8	−22 710.532 180
1	3545	9	10	−26 990.824 598	3274	9	9	−24 850.685 752	4045	10	9	−30 976.252 622
1	4697	10	11	−36 164.882 991	4371	10	10	−33 570.579 027	5302	11	10	−41 021.942 092
1	6074	11	12	−47 204.964 844	5688	11	11	−44 113.467 079	6794	12	11	−53 019.714 844
1	7696	12	13	−60 283.183 594	7245	12	12	−56 651.464 844	8541	13	12	−67 141.687 500
1	9583	13	14	−75 571.656 250	9062	13	13	−71 356.687 500				
2	173	1	4	−1 015.192 799	142	1	3	−817.090 767	111	1	2	−619.144 890
2	380	2	5	−2 482.142 298	324	2	4	−2 089.194 411	268	2	3	−1 696.364 163
2	692	3	6	−4 784.814 917	606	3	5	−4 153.100 800	520	3	4	−3 521.458 561
2	1129	4	7	−8 093.382 154	1008	4	6	−7 179.709 717	887	4	5	−6 266.075 964
2	1711	5	8	−12 579.606 922	1550	5	7	−11 340.904 269	1389	5	6	−10 102.217 553
2	2458	6	9	−18 415.517 411	2252	6	8	−16 808.740 994	2046	6	7	−15 201.964 966
2	3390	7	10	−25 773.207 633	3134	7	9	−23 755.321 962	2878	7	8	−21 737.425 930
2	4527	8	11	−34 824.790 161	4216	8	10	−32 352.762 467	3905	8	9	−29 880.716 848
2	5889	9	12	−45 742.382 505	5518	9	11	−42 773.181 182	5147	9	10	−39 803.956 502
2	7496	10	13	−58 698.101 562	7060	10	12	−55 188.695 312	6624	10	11	−51 679.265 625
2	9368	11	14	−73 864.070 312	8862	11	13	−69 771.429 688	8356	11	12	−65 678.757 812
3	522	1	6	−3 450.806 732	461	1	5	−3 026.014 476	400	1	4	−2 601.253 796
3	934	2	7	−6 545.101 475	838	2	6	−5 839.502 698	742	2	5	−5 133.932 376
3	1491	3	8	−10 821.548 914	1355	3	7	−9 791.158 109	1219	3	6	−8 760.785 028
3	2213	4	9	−16 448.607 054	2032	4	8	−15 050.209 913	1851	4	7	−13 651.819 719
3	3120	5	10	−23 597.680 755	2889	5	9	−21 788.200 762	2658	5	8	−19 978.718 465
3	4232	6	11	−32 440.683 859	3946	6	10	−30 177.079 250	3660	6	9	−27 913.464 812
3	5569	7	12	−43 149.671 136	5223	7	11	−40 388.909 544	4877	7	10	−37 628.132 135
3	7151	8	13	−55 896.746 094	6740	8	12	−52 595.796 875	6329	8	11	−49 294.828 125
3	8998	9	14	−70 854.023 438	8517	9	13	−66 969.859 375	8036	9	12	−63 085.667 969

	family 4				family 5				family 6			
s	*N*	*m*	*n*	*E*	*N*	*m*	*n*	*E*	*N*	*m*	*N*	*E*
1	100	3	1	−541.779 337	176	4	1	−1 033.662 625	282	5	1	−1 751.777 172
1	247	4	2	−1 543.793 139	383	5	2	−2 499.399 084	559	6	2	−3 767.271 381
1	484	5	3	−3 251.733 699	695	6	3	−4 801.206 923	956	7	3	−6 748.985 752
1	831	6	4	−5 836.424 540	1132	7	4	−8 109.100 898	1493	8	4	−10 866.127 908
1	1308	7	5	−9 469.728 024	1714	8	5	−12 594.786 403	2190	9	5	−16 290.244 448
1	1935	8	6	−14 323.683 374	2461	9	6	−18 430.253 575	3067	10	6	−23 193.275 213
1	2732	9	7	−20 570.376 440	3393	10	7	−25 787.568 220	4144	11	7	−31 747.265 160
1	3719	10	8	−28 381.909 268	4530	11	8	−34 838.822 787	5441	12	8	−42 124.296 576
1	4916	11	9	−37 930.390 622	5892	12	9	−45 756.120 955	6978	13	9	−54 496.468 750
1	6343	12	10	−49 387.933 594	7499	13	10	−58 711.570 312	8775	14	10	−69 035.882 812
1	8020	13	11	−62 926.648 438	9371	14	11	−73 877.289 062				
1	9967	14	12	−78 718.648 438								
2	80	1	1	−421.902 497	156	2	1	−913.108 099	262	3	1	−1 631.051 754
2	212	2	2	−1 303.898 256	348	3	2	−2 259.159 774	524	4	2	−3 526.898 175
2	434	3	3	−2 890.008 069	645	4	3	−4 439.291 033	906	5	3	−6 386.966 520
2	766	4	4	−5 352.544 304	1067	5	4	−7 625.086 017	1428	6	4	−10 382.018 767
2	1228	5	5	−8 863.581 589	1634	6	5	−11 988.520 278	2110	7	5	−15 683.882 561
2	1840	6	6	−13 595.208 267	2366	7	6	−17 701.659 559	2972	8	6	−22 464.580 850
2	2622	7	7	−19 719.529 154	3283	8	7	−24 936.599 212	4034	9	7	−30 896.191 341
2	3594	8	8	−27 408.657 251	4405	9	8	−33 865.446 334	5316	10	8	−41 150.811 986
2	4776	9	9	−36 834.708 877	5752	10	9	−44 660.313 164	6838	11	9	−53 400.550 781
2	6188	10	10	−48 169.800 781	7344	11	10	−57 493.312 500	8620	12	10	−67 817.515 625
2	7850	11	11	−61 586.050 781	9201	12	11	−72 536.562 500				
2	9782	12	12	−77 255.578 125								
3	339	1	3	−2 176.562 617	278	1	2	−1 752.057 240	217	1	1	−1 328.300 693
3	646	2	4	−4 428.421 920	550	2	3	−3 723.051 432	454	2	2	−3 018.077 269
3	1083	3	5	−7 730.450 736	947	3	4	−6 700.205 669	811	3	3	−5 670.180 009
3	1670	4	6	−12 253.449 252	1489	4	5	−10 855.129 796	1308	4	4	−9 456.935 088
3	2427	5	7	−18 169.240 698	2196	5	6	−16 359.786 410	1965	5	5	−14 550.399 934
3	3374	6	8	−25 649.843 251	3088	6	7	−23 386.225 433	2802	6	6	−21 122.638 547
3	4531	7	9	−34 867.338 795	4185	7	8	−32 106.535 018	3839	7	7	−29 345.737 278
3	5918	8	10	−45 993.835 090	5507	8	9	−42 692.822 528	5096	8	8	−39 391.798 786
3	7555	9	11	−59 201.449 219	7074	9	10	−55 317.203 125	6593	9	9	−51 432.933 594
3	9462	10	12	−74 662.304 688	8906	10	11	−70 151.796 875	8350	10	10	−65 641.265 625

completed Marks' decahedra, and it is termed as PTK.[1] The other one is PTK without two vertex atoms. In the following discussion, M1 and M2 are used to represent the two models. An example of the completed Marks' decahedron of LJ686 and its M1 and M2 configurations is shown in Figure 4.

Twenty additional (110) faces make the Marks' decahedron more rounded. It has been reported that the energy of the decahedron decreases after the modification.[1−3] Therefore, the M1 model is implemented on the six completed Marks' decahedral sequences F1S1, F2S1, F3S2, F4S2, F5S3, and F6S3

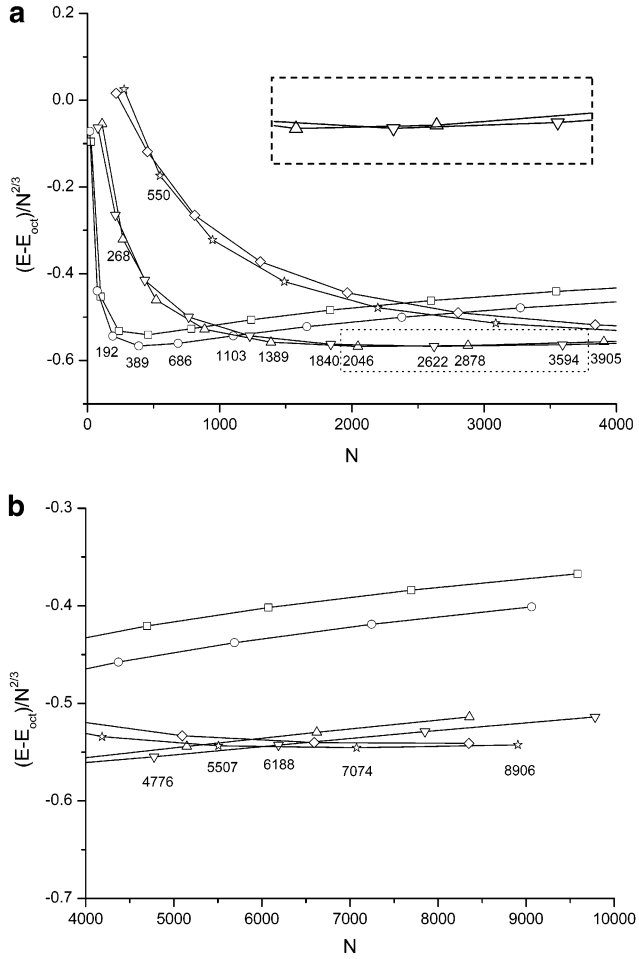

Figure 3. Energetic comparison of the Marks' decahedral sequences: (a) $N = 75-4000$; (b) $N = 4000-10000$. F1S1, F3S2, and F5S3 are plotted with □, △, and ☆, while F2S1, F4S2, and F6S3 are plotted with ○, ▽, and ◇, respectively, and connected with solid lines. N is the number of atoms, E is the energy of the cluster, and E_{oct} is the fitting energy of cuboctahedra.

in the study. To create the 20 (110) faces, 30, 50, and 70 atoms are removed from the completed Marks' decahedra with $s = 1$, 2, and 3, respectively. The energies of these clusters are given in Figure 5. It is obvious that the energies of M1 sequences are lower than those of Marks' decahedra, but the modification only reduces the energies of the clusters with relatively larger size. For example, the energy of the M1 (F2S1) sequence is lower than that of its father sequence (the corresponding Marks' decahedral sequence) when the cluster size is greater than 656. Whereas the energy of the M1 sequence for smaller size is higher. From Figure 5, the lowest energy sequence of M1 can be obtained as 656 (F2S1), 1073 (F2S1), 1790 (F4S2), 1996 (F3S2), 2572 (F4S2), 3544 (F4S2), 4726 (F4S2), 5437 (F5S3), 7004 (F5S3), and 8836 (F5S3).

Generally, M1 is adopted as the optimal decahedral model in studying the energy of decahedra,[2,3] and further improvement of M2 is considered less important in the decahedral sequence because there are only two vertex atoms removed from M1.[1] The energy of every atom in the completed Marks' decahedron LJ 686 is calculated, and the result is given in Figure 6. It is shown that there is an energy gap from atom 389 to atom 390. It is clear that the atoms before 389 are the inner atoms of LJ686 with energy lower than $-7.0\ \epsilon$, and the atoms after 390 are the surface atoms with energy greater than $-7.0\ \epsilon$. In Figure 6, the atoms that should be removed in generating the M1 and M2 models are surrounded by the dashed circle and the dashed

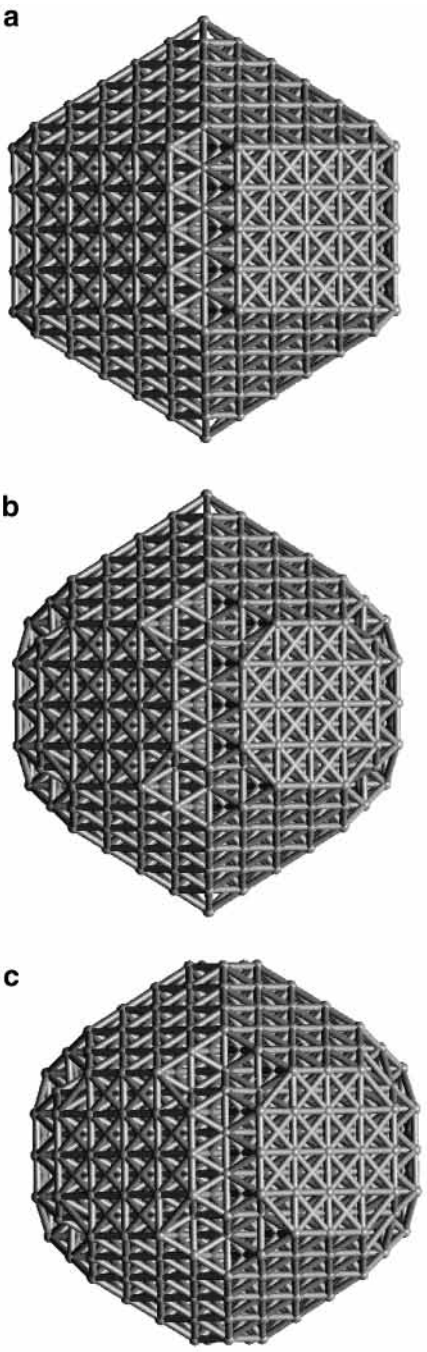

Figure 4. Structures of the completed Marks' decahedron (LJ686) (a); M1, the decahedron with an additional 20 (110) faces (LJ656) (b); and M2, the M1 decahedron without vertex atoms (LJ654) (c).

rectangle, respectively. As it is shown in the enlarged graph surrounded by the dashed rectangle, the two vertex atoms have the highest energy in the cluster, and the 30 atoms surrounded by the dashed circle are lower in energy. Therefore, the sequences of M2 should be lower than those of M1 by removing the two atoms with the highest energy. The sequences of F2S1, F3S2, F4S2, and F5S3 (the optimal sequences when $N < 10\,000$) in the M2 configuration are compared with those of M1 (see Figure 7). It is clear that the energies of the M2 sequences are lower than those of M1, and this improvement is always effective in the range up to 10 000. Consequently, the M2 sequence, a PTK model without vertex atoms, is the most favorable decahedral sequence. Compared with the sequence 654, 1071, 1628, 1790, 2572, 3544, and 4726 reported in Raoult's work,[1] the lowest energy decahedral sequence when

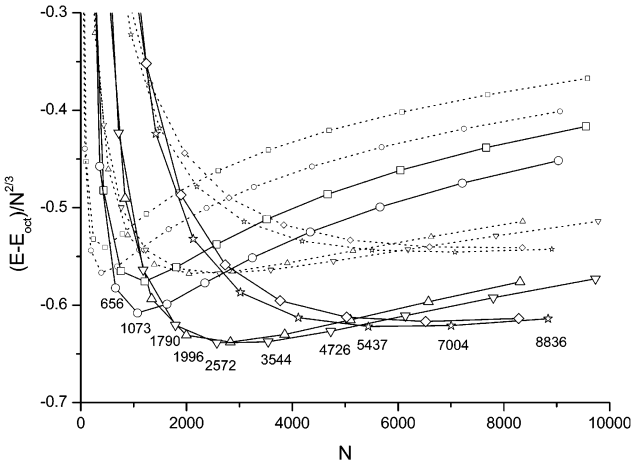

Figure 5. Energetic comparison of the M1 decahedral sequences (larger symbols connected with solid lines) and the completed Marks' decahedral sequences (smaller symbols connected with dashed lines). Each symbol indicates a sequence of a Marks' decahedral family with a certain notching degree, and all symbols are the same as those in Figure 3.

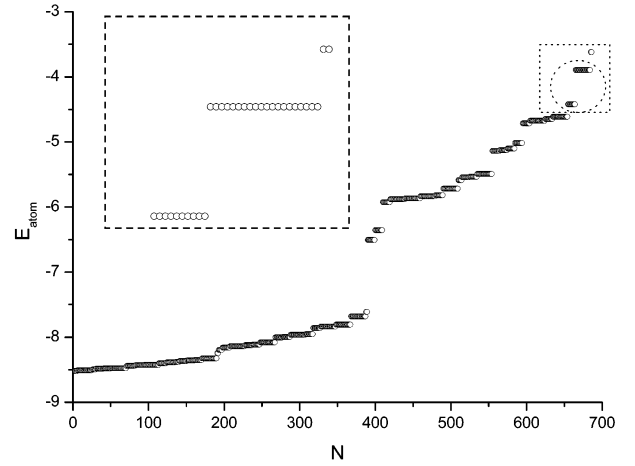

Figure 6. Energy of each atom in the decahedral cluster of LJ686.

cluster size is lower than 10 000 is 654 (F2S1), 1071 (F2S1), 1788 (F4S2), 1994 (F3S2), 2570 (F4S2), 3542 (F4S2), 4724 (F4S2), 5435 (F5S3), 7002 (F5S3), and 8834 (F5S3).

4. Conclusion

A method for constructing a Marks' decahedral lattice is developed, and it is proved to be reliable by practical construction of various Marks' decahedral models. The lattice construction method is applied to investigate the lowest energy sequence of Marks' decahedra in LJ clusters with $N < 10\,000$. By comparing the energies of the sequences of odd families and even families, it is found that the energies of decahedral sequences with $m = n - 1$ are even lower in some range than those of the sequences with square (100) faces. Consequently, a new lowest energy sequence of Marks' decahedra is proposed. Besides, the sequences of the two modified decahedral models having 20 additional (110) faces with and without vertex atoms are also investigated, and the PTK model without vertex atoms is proved to be the optimal configuration in the lowest energy decahedral sequence. The new lowest energy growth sequences

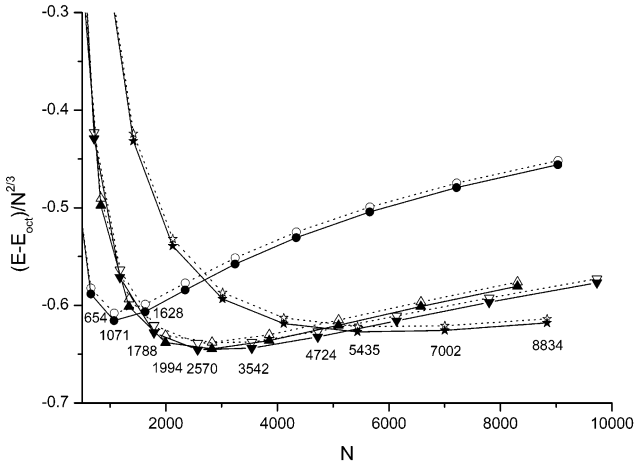

Figure 7. Energetic comparison of the M1 decahedral sequences (hollow symbols connected with dashed lines) and the M2 decahedral sequences (filled symbols connected with solid lines).

may be helpful in theoretic studies of LJ clusters, but they still need further proof of experimental or optimization results.

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