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Energy and structure of copper clusters (n=70–150) studied by the Monte Carlo computer simulation*

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The structure and binding energy of copper clusters of the size range 70 to 150 were studied by using the embedded-atom method. The stability of the structure of the clusters was studied by calculating the average binding energy per atom, first difference energy and second difference energy of copper cluster. Most of the copper clusters of the size n=70–150 adopt an icosahedral structure. The results show that the trends are in agreement with theoretic prediction for copper clusters. The most stable structures for copper clusters are found at n=77, 90, 95, 131, 139.

Keywords: copper cluster, structure, energy
PACC: 3640, 3640B, 3120W

1. Introduction

The study of metal clusters has been a subject of intense research activities in recent years. This is due to their role as precursors of bulk material. The properties of clusters are different from bulk material. The study of structure of clusters is important to understand how the transition from atoms or molecules to the solid state may occur, and it may serve as an useful model for studying a chemisorption process on a solid surface. Metallic clusters are particularly interesting for their potential use in many processes like catalysis, nanotechnology and new electronic materials.[1−5] During the past twenty years, the structure and properties of copper clusters have been intensively studied from many aspects.

Copper clusters have been studied theoretically by various accurate quantum-mechanical, empirical methods and chemical approaches. Christensen *et al* [6] studied the structure of Cu_n (n=3–29) by simulated annealing. Delley *et al* [7] investigated the geometry, binding energy and electronic structure of Cu_n (n=2, 4, 13, 79) by using the self-consistent one-electron local-density theory. Erkoç and Shaltaf[5] investigated the structural stability and energy for copper clusters (n=3, ..., 55) within an empirical potential-energy function using Monte Carlo technique. Jug *et al* [8] used density function to study Cu_n, Cu_n^- and Cu_n^+ (n=2–10). Jaque and Toro-Labbé[9] studied nine neutral copper clusters by using the density function theory calculations with a hybrid combined with effective core potentials. Darby *et al* [10] studied copper clusters (n=10–56) within a many-body Gupta potential by using a genetic algorithm. Özçelik and Gürens[11] used a many-body embedded-atom model to investigate the melting behaviour of Cu_n(n=13, 14, 19, 55, 56) clusters. Kabir *et al* [4] used a tight-binding molecular dynamics with parameters fitted to first–principle calculations on the smaller clusters and with an environment correction to study Cu_n (n=3–55) clusters. Grigoryan *et al* [12] used the embedded-atom method (EAM) in the version of Daw, Baskes, and Foiles to determine the three most stable isomers of Cu_n clusters with n from 2 to 150. Wu *et al* [13] studied the melting and freezing processes of Cu_n (n=180, 256, 360, 408, 500, 628 and 736) nanoclusters by using the micro-canonical molecular dynamics simulation technique. Zhang *et al* [14] studied structural relaxation of a copper cluster containing 55 atoms at elevated temperatures by using molecular dynamics. Wang *et al* [15] calculated the equilibrium geometries and the atomization energies of Cu_n ($n \leq 9$) clusters using the B3LYP/LANL2DZ method. Gai and Li[16] corrected the parameters of EAM based on the experimental value of Cu_2 and found that corrected parameters were only fit for smaller copper clusters. In an earlier communication,[17] Zhang and Li

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studied Cu_n (n=2–70, 147, 500) clusters by using the EAM and the Monte Carlo method.

Copper clusters have also been studied experimentally. Knickelbein[18] measured ionization potentials of neutral copper clusters and found evidence of electronic shell structure. Spasov *et al* investigated cationic copper clusters by using the threshold collision-induced dissociation method.[19]

For the true copper cluster, many properties and cluster structure are difficult to measure directly. Hence, theoretical studies of clusters play an important role in cluster science. For large clusters with hundreds of atoms, *ab initio* electronic structure calculations are computationally expensive. This led to the utilization of empirical potentials for atomic interactions in the simulation of clusters. Up to date, a small number of studies use empirical many-body potentials for large copper clusters. In this study, an EAM[20−25] was utilized to investigate the energy and the structure of copper clusters (n=70–150) by Monte Carlo computer-simulation.

2. Computational details

The EAM was proposed by Daw and Baskes[20,21] and is based on the density-functional theory, as a means of calculating the ground-state properties of a realistic metal system. The main idea of EAM is to split the total energy of a metallic system of interest into two components. The embedding energy is obtained by considering each atom as an impurity embedded into a host provided by the rest of the atoms. The remaining part is written as a sum of pair potentials. Accordingly,

$$E_{\rm tot} = \sum_i F_i\left(\rho_{{\rm h},i}\right) + \frac{1}{2}\sum_{i,j}\phi_{ij}(R_{ij}), \tag{1}$$

$$\rho_{{\rm h},i} = \sum_{j(\neq i)} f_j(R_{ij}), \tag{2}$$

where $E_{\rm tot}$ is the total internal energy, $\rho_{{\rm h},i}$ is the electron density at atom i due to all the other atoms, f_j is the electron density of atom j as a function of the distance from its centre, R_{ij} is the separation distance between atoms i and j, $F_i(\rho_{{\rm h},i})$ is the energy to embed atom i in an electron density $\rho_{{\rm h},i}$, ϕ_{ij} is a two-body central potential between atom i and j. Thus the host electron density $\rho_{{\rm h},i}$ is assumed to be a linear superposition of contributions from individual atoms.

Johnson[22,23] has proposed an useful analytic model, simple analytic forms for the two-body potential $\phi(r)$, the electron density $f(r)$ and embedding function $F(\rho)$. The analytic forms are taken as

$$f(r) = f_{\rm e}\exp\left[-\beta\left[\frac{r}{r_0}-1\right]\right], \quad r \le r_{\rm c}, \tag{3}$$

$$\phi(r) = \phi_{\rm e}\exp\left[-\gamma\left[\frac{r}{r_0}-1\right]\right], \quad r \le r_{\rm c}, \tag{4}$$

$$F(\rho) = -E_{\rm c}\left[1-\frac{\alpha}{\beta}\ln\left[\frac{\rho}{\rho_{\rm e}}\right]\right]\left[\frac{\rho}{\rho_{\rm e}}\right]^{\alpha/\beta} - \Phi_{\rm e}\left[\frac{\rho}{\rho_{\rm e}}\right]^{\alpha/\beta}. \tag{5}$$

Where $r_{\rm c}$ is a cut off parameter, $\rho_{\rm e} = 12f_{\rm e}$ and $\Phi_{\rm e} = 6\phi_{\rm e}$. There are seven parameter included here: $E_{\rm c}$, $\phi_{\rm e}$, $r_{\rm c}$, r_0, α, β and γ. The values of those parameters used in this study are listed in Table 1.

Table 1. Parameters defined for copper cluster.[a]

parameter	$E_{\rm c}$	$\phi_{\rm e}$	$r_{\rm c}$	r_0	α	β	γ
value	3.54 eV	4.86 eV	0.5 nm	0.2556 nm	5.90	5.85	6.30

[a]Reference [25].

The Monte Carlo method was utilized to investigate the most stable structure and energy of copper clusters in this simulation. First, n copper atoms are randomly placed in a cubic cell (2 nm×2 nm×2 nm) as a starting structure. Second, n copper atoms are moved randomly one by one. For every atom moved once, we calculate the total energy of the n atoms system. If the new structure has a lower total energy than the old one, new structure is kept. If the new structure has a higher total energy than the old one, we accept the new structure by a probability of $p = \exp(-\Delta E/(kT))$, where T is temperature of the n atoms system. One Monte Carlo step is finished. Third, the temperature is decreased 10 K every 2000 Monte Carlo steps starting from 1500 K. With a total number of 10^6 Monte Carlo steps, the stable structure and energy of the Cu_n cluster was gained while the system was in equilibrium at 300 K.

Before we start with the computational simulation of large copper clusters ($n > 70$), we shall indicate the comparison (given in the Table 2) between the results of our previous computer-simulation for small Cu_n clusters ($n < 10$)[17] with other calculations and available experimental results. The results of our previous computer-simulation are in a good agreement with the experimental results, which allow us to continuously use EAM for computer-simulation of large copper clusters and to get good results.

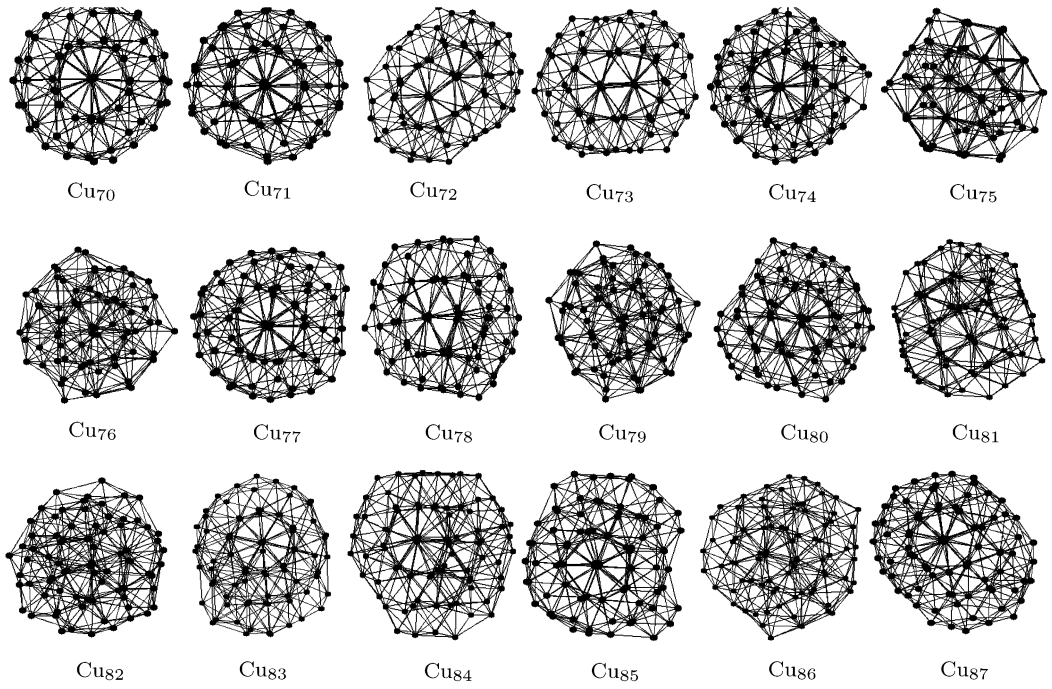
Table 2. Binding energy for Cu_n clusters ($n < 10$) obtained from EAM calculations as a comparison with tight-binding molecular dynamics calculation and the experimental values.

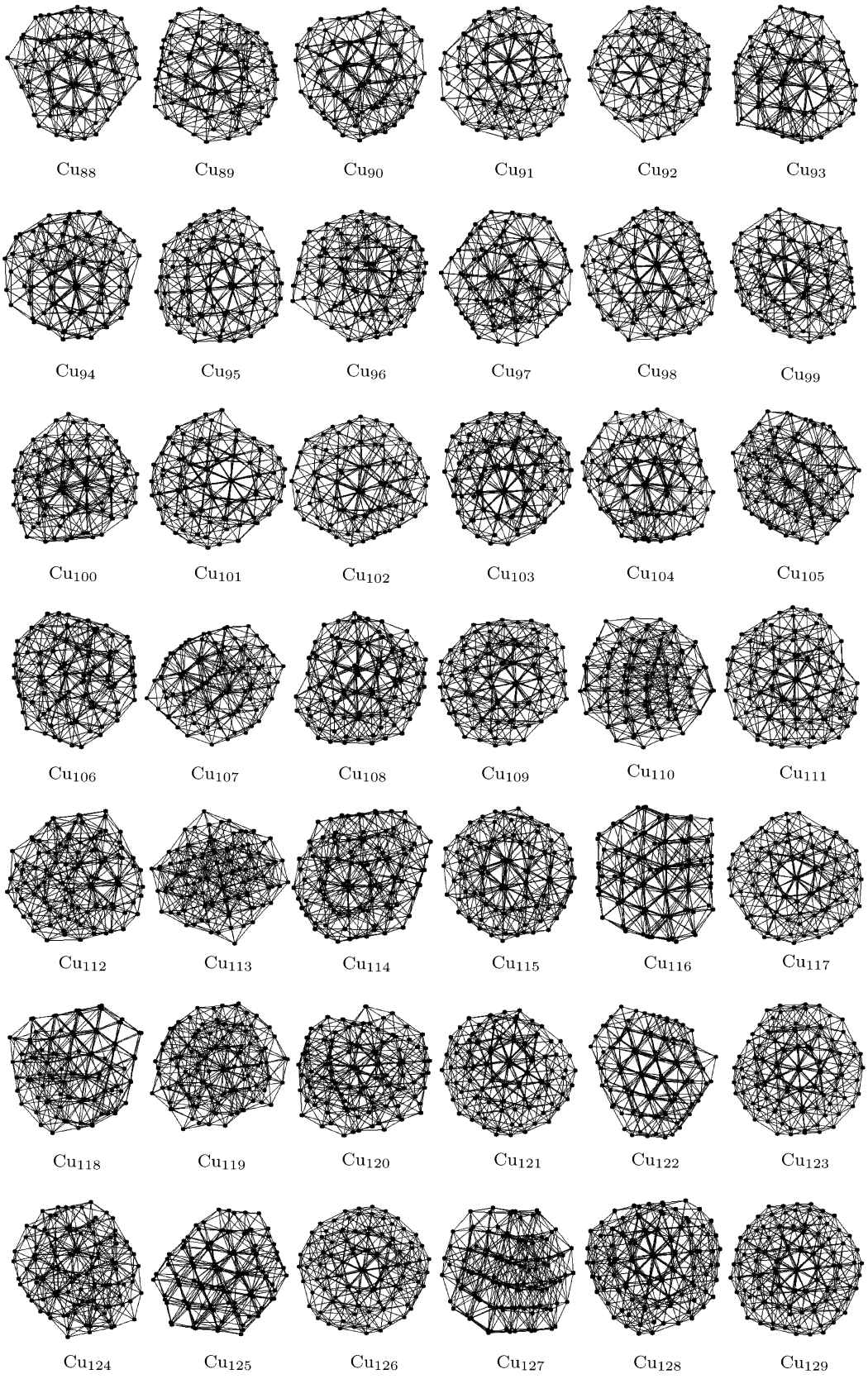
	binding energy (eV/atom)		
cluster	present[a]	theory[b]	experiment[c]
Cu_3	1.14	1.43, 1.32, 1.13	1.07±0.12
Cu_4	1.46	2.00, 1.73, 1.46	1.48±0.14
Cu_5	1.65	2.24, 2.03	1.56±0.15
Cu_6	1.84	2.54, 2.40, 1.98	1.73±0.18
Cu_7	1.94	2.63, 2.50, 2.30	1.86±0.22
Cu_8	2.02	2.87, 2.64, 2.57	2.00±0.23
Cu_9	2.10	2.87, 2.84, 2.60	

[a]Reference [17]; [b]Reference [4]; [c]Calculated by Kabir *et al.*[4]

3. Results and discussion

We have studied the most stable structure and energy of Cu_n (n=70–150) using the EAM model by Monte Carlo method. The most stable structures obtained by this method are shown in Fig.1. Most of the large clusters (n=70–150) have icosahedron-based geometries in this paper, the icosahedral growth continues for n=70–150 atoms. Exceptions to the icosahedral growth are found at n=112, 119, 130, 141, the structures for Cu_{112}, Cu_{119}, Cu_{130}, Cu_{141} are decahedronlike, fcc-like geometries. In theory, three-ply icosahedron should be formed for n=147, due to limited steps in the simulation, the structure of Cu_{147} is based on three-ply icosahedron, and some atoms are not in the proper position of three-ply icosahedron. The ground state of Cu_{148}, Cu_{149} and Cu_{150} are plus one, two and three atoms on the 147-atoms three-ply icosahedron.




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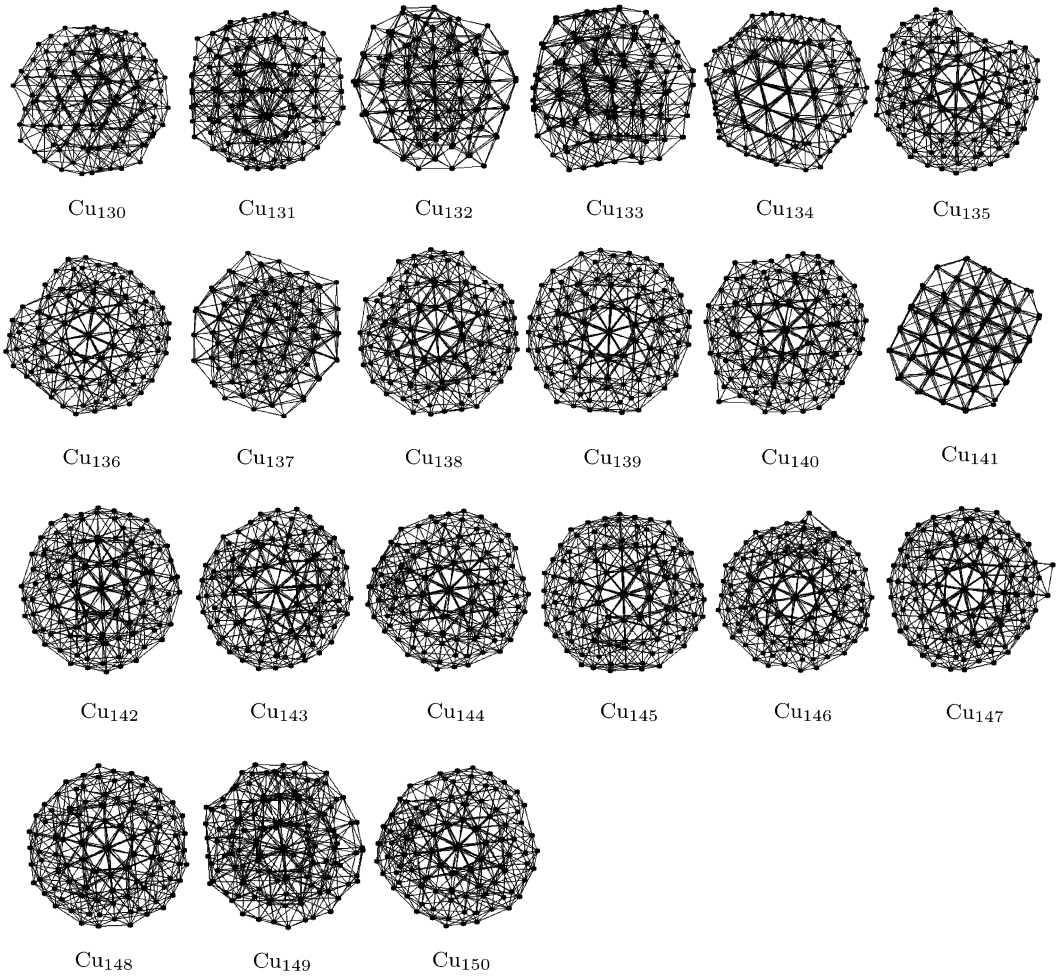


Fig.1. Most stable structures for copper clusters with n=71–150.

These results are in agreement with the prediction by Valkealahti and Manninen.[26] They have pointed out that icosahedral structures are energetically more favourable than the cuboctahedral structures for sizes up to $n \sim$2500. Reinhard *et al* [27] performed electron diffraction studies of copper clusters. They also pointed out that icosahedral structures occur at a size of $n < 2500$. Grigoryan *et al* [12] also pointed out that the copper cluster grows predominantly icosahedral, with islands of fcc, tetrahedral, and decahedral growth.

The relative stability of copper clusters can be studied by analysing their energies. We considered the average binding energy per atom BE_n, the first difference energy $\Delta_1 E_n$ and the second difference energy $\Delta_2 E_n$, where

$$\mathrm{BE}_n = E_n/n, \tag{6}$$

$$\Delta_1 E_n = E_n - E_{n-1}, \tag{7}$$

$$\Delta_2 E_n = E_{n+1} + E_{n-1} - 2E_n. \tag{8}$$

The average binding energy per atom BE_n as a function of the atom size n is shown in Fig.2, the first difference energy $\Delta_1 E_n$ as a function of the atom size n is shown in Fig.3 and the second difference energy $\Delta_2 E_n$ as a function of the atom size n is shown in Fig.4.

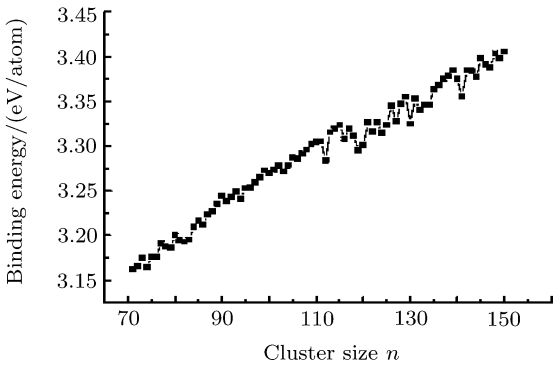


Fig.2. Average binging energy as a function of the copper cluster size n.

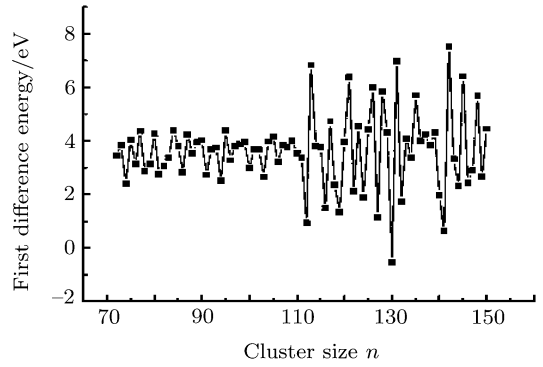


Fig.3. The first difference energy as a function of the copper cluster size n.

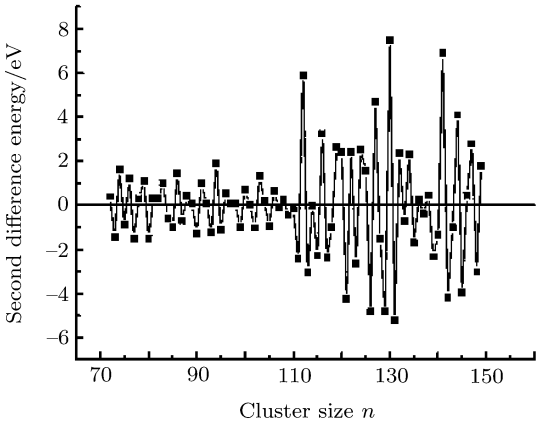


Fig.4. The second difference energy as a function of the copper cluster size n.

By increasing the cluster size n, the average binding energy per atom BE_n will approach the cohesive energy of bulk solid (3.5 eV/atom). The change of the structures also can be found in Fig.2. The binding energy per atom BE_n shows a sudden decrease at n=112, 119, 130, 141. The corresponding structures are based on decahedron.

The second difference energy $\Delta_2 E_n$ is the difference of the energy of two paths $Cu_{n+1} \rightarrow Cu_n$+Cu and $Cu_n \rightarrow Cu_{n-1}$+Cu. If $\Delta_2 E_n$ is negative, it means that the dissociation from Cu_{n+1} into Cu_n while leaving one atom free is more favourable than the dissociation of Cu_n into Cu_{n-1}, so $\Delta_2 E_n$ can be used as a measure of the stability of clusters with respect to their neighbours.

We found even–odd alternation of $\Delta_2 E_n$ as shown in Fig.4. This result is in agreement with previous studies by Kabier *et al.*[4] They studied the structure and stability of copper clusters (n=10–55) using tight-binding molecular dynamics and found an even–odd alternation of $\Delta_2 E_n$. They explained this in terms of electron pair HOMOs (the highest energy occupied molecular orbital) as:[4] Even clusters have an even number of electrons and HOMO is doubly occupied. The electron in a doubly occupied HOMO will feel a stronger effective core potential. The binding energy of the valence electron with an even cluster is larger than the one of an odd one. In experimental studies by Winter *et al*,[28] they found both jellium-like electronic behaviour and icosahedral structure in copper clusters. In our studies, the electronic effects cannot be found. The electronic effects dominate over the geometrical structure and consequently the above peaks cannot be observed.

In Fig.2, the clusters with a number of atoms n=73, 77, 80, 85, 90, 95, 110, 115, 131, 139 seem to be relatively more stable; in Fig.3, the clusters with a number of atoms n=77, 84, 90, 95, 99, 105, 109, 113, 117, 121, 126, 131, 135, 139, 142 seem to be relatively more stable; in Fig.4, the clusters with a number of atoms n=77, 85, 90, 95, 102, 111, 113, 117, 121, 131, 135, 139, 142 seem to be relatively more stable. The common numbers in these three groups are n=77, 90, 95, 131, 139. We may say that cluster structures with these size n=77, 90, 95, 131, 139 are the most stable copper clusters in this paper. In Ref.[12], the cluster sizes n=71, 75, 86, 92, 95, 101, 116, 119, 131, and 147 are identified as particularly stable clusters. Cluster sizes of n=95, 131 are commonly considered as the particularly stable clusters. The difference of the cluster size n for particularly stable clusters may be due to a different criterion used for identifying particularly stable clusters.

Although Grigoryan *et al* [12] studied copper clusters with $n \leq 150$ by using EAM. Comparing the method used by them and the results gained by them to our calculations, we find that there is some difference; the method used for structure optimization and the parameters of EAM are totally different, The Aufbau/Abbau[12] method was used by Grigoryan *et al* for searching the global minimum; we used the Monte Carlo method for searching the global minimum, and the starting structures which we used for optimization were random generated. The *Aufbau/Abbau* method works as follows: one atom is added to the Cu_n structure and one atom is removed from the Cu_{n+m} structure, where the Cu_n and the Cu_{n+m} structure are optimized with their lowest total energy starting from randomly generated structures; two series of structure size ranges n to $n+m$ are generated; the structures of the lowest energies are chosen and used as seeds for a new set of calcu-

lations. The results gained by those two methods are also different. The binding energy per atom obtained by us is 0.2 eV larger than that gained by Grigoryan *et al.* The average binding energy of 150-atoms clusters gained by us is 3.4 eV, the size which reaches the bulk energy is maybe 2,500 atoms. This result is in agreement with Ref.[27]; while the result gained by Grigoryan *et al* is less than 3.2 eV, and the size which reaches the bulk energy is maybe more than 10,000 atoms; Grigoryan *et al* found islands of fcc growth for Cu_{79}, tetrahedral growth for Cu_{91}–Cu_{95}, and decahedral growth for Cu_{75}–Cu_{78}, Cu_{81} and Cu_{101}–Cu_{103}. We found that icosahedral structures are energetically more favourable than the other structures for sizes up to $n \leq$150. Exceptions to the icosahedral growth are found at n=112, 119, 130, 141, the structures for Cu_{112}, Cu_{119}, Cu_{130}, Cu_{141} are decahedron, fcc-like geometries, and the binding energies of those cluster sizes suddenly decrease.

4. Conclusions

We have made a study of large copper clusters (n=70–150) using the EAM model by the Monte Carlo method. Binding energy, first difference energy and second difference energy were calculated in order to study the most stable structure of copper clusters. The following results were gained in this study. First, most of the copper cluster structures with the size n=70–150 are based on icosahedral structure, exceptions are found at n=112, 119, 130, 141. For those cluster sizes, a sudden decrease of the binding energy was observed. This result shows that icosahedral structures are energetically more favourable than the other structures at size $n \leq$150. Second, the most stable structures are found at n=77, 90, 95, 131, 139. We did not find a three-ply icosahedron for n=147 as expected due to limited steps in this calculation, the structure of Cu_{147} is based on three-ply icosahedron with some atoms which are not in the proper position.

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