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Structures and Energetics of Cu_{21}-Cu_{71} Clusters: A Molecular Dynamics Study

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ABSTRACT

Using Molecular Dynamics and thermal quenching simulations the stable geometrical structures and energies of Cu_n (n=21-71) clusters are identified. The interaction between the cluster atoms is modeled by an Embedded-Atom Potential Surface, Voter and Chen's version. The stable geometrical structures and energies are obtained from 500 phase space coordinates generated along high-energy trajectories. The internal energy (about T=2500 K) is above the melting temperature of the Cu_n clusters. The thermal quenching technique is employed to remove slowly the internal kinetic energy of the clusters. Because of this slow minimization process the locally stable isomers are separated from those meta-stable ones.

Key Words: Cu clusters, Cluster Structures, Molecular Dynamics, Computer Simulations.

1. INTRODUCTION

Geometrical structures and energetics of the clusters are important factors for determining their chemical and physical properties. Therefore, the structure and dynamics of small clusters, in particular transition metal clusters, have been attracted much attention theoretically [1-16] and experimentally [17-20] in the last decade. Theoretical calculations can complement such experimental investigations using ab initio methods and/or sufficiently accurate interaction potentials in dynamical simulations to investigate the structure, dynamics, and reactivity of clusters as a function of cluster size. A new scientific filed so-called "nano-science" has been formed by these activities. Small copper clusters with up to 5 atoms [1] and 10 atoms [2] were studied by using density functional theory. Decay pathways and dissociation energies of Cu^+ ($2\leq n \leq 25$) cluster were studied experimentally [19]. Structures and stability of up to 56 atoms of the copper were employed by Darby et al.[21] using the many body Gupta potential. In Ref. [14], original version of the Embedded Atom Model (EAM) developed by Foiles et al. [16] for fcc metals was employed in their Molecular Dynamics (MD) study. In Ref. [14] however, Voter and Chen's version of the EAM potential was used to study structures and binding energies of the lowest energy isomers, and melting behavior of the Cu_n, (n=2-23) clusters. We have also used Voter and Chen's version of the EAM (see for details Ref.[22]) in our work. Our focus is on obtaining the number of stable isomers, average bond lengths, and magic sizes of the Cu_n, (n=21-71) in addition to the lowest energy structures and energetics of the clusters. In Section 2 the detail of computational procedure is given. The results and their analyses are discussed in Section 3, and we conclude with a brief summary.

2. THE POTENTIAL AND COMPUTATIONAL PROCEDURE

Because of the fitting procedure mentioned above, we have incorporated the EAM [4] in our studies since such fitting may increase the validity of this potential in the finite size range. The stable geometrical structures of the Cu_n, n=21-71, clusters are identified using MD and thermal quenching (TQ) simulations. The clusters are prepared initially with zero total linear and angular moment. After that their internal energies are increased to about T = 2500K. These energies are much higher than the "melting" temperatures of the Cu_n clusters. Along the high-energy trajectories in phase space 500

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independent set of phase space coordinates are selected. Hamilton's equations of motion were solved for all the atoms in the cluster using Hamming's modified 4th order predictor-corrector algorithm with a step-size of $1x10^{-15}$ s. For each set of the phase space coordinates the TQ technique is used to remove the internal kinetic energies of the clusters (the internal kinetic energy of a cluster is set to zero at every 50 simulation steps, and the process continues until the energy is completely removed). Because of this slow minimization process, clusters cannot stay at the meta-stable locations of the potential energy surface (PES), and finally, they will be trapped at the bottom of the PES "wells". Thus, the locally stable isomers are separated from meta-stable ones.

3. RESULTS AND DISCUSSION

The geometries of the most stable isomers of Cun (n = 21-71) clusters, average bond lengths of their stable isomers and energetics, average interaction energy per atom of these clusters are obtained. The minimum energy geometries and energetics of the most stable copper clusters are given in Figures 1 and 2. As seen the Cu55 has a structure of shell form (I_h) [21]. The Cu56 is simply formed by capping one of the faces of this icosahedral structure.

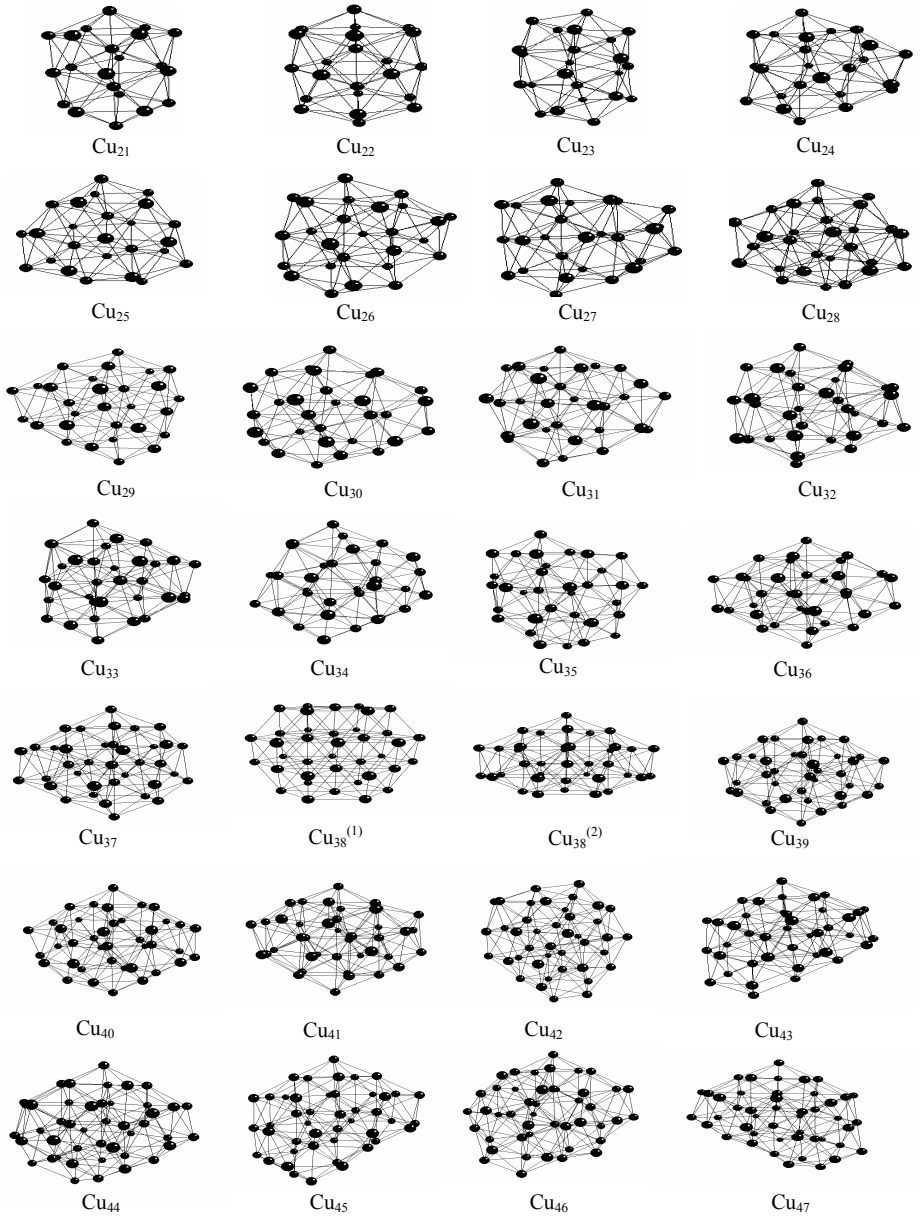

Figure 1. The Minimum energy geometries of the most stable copper clusters n=21-47.

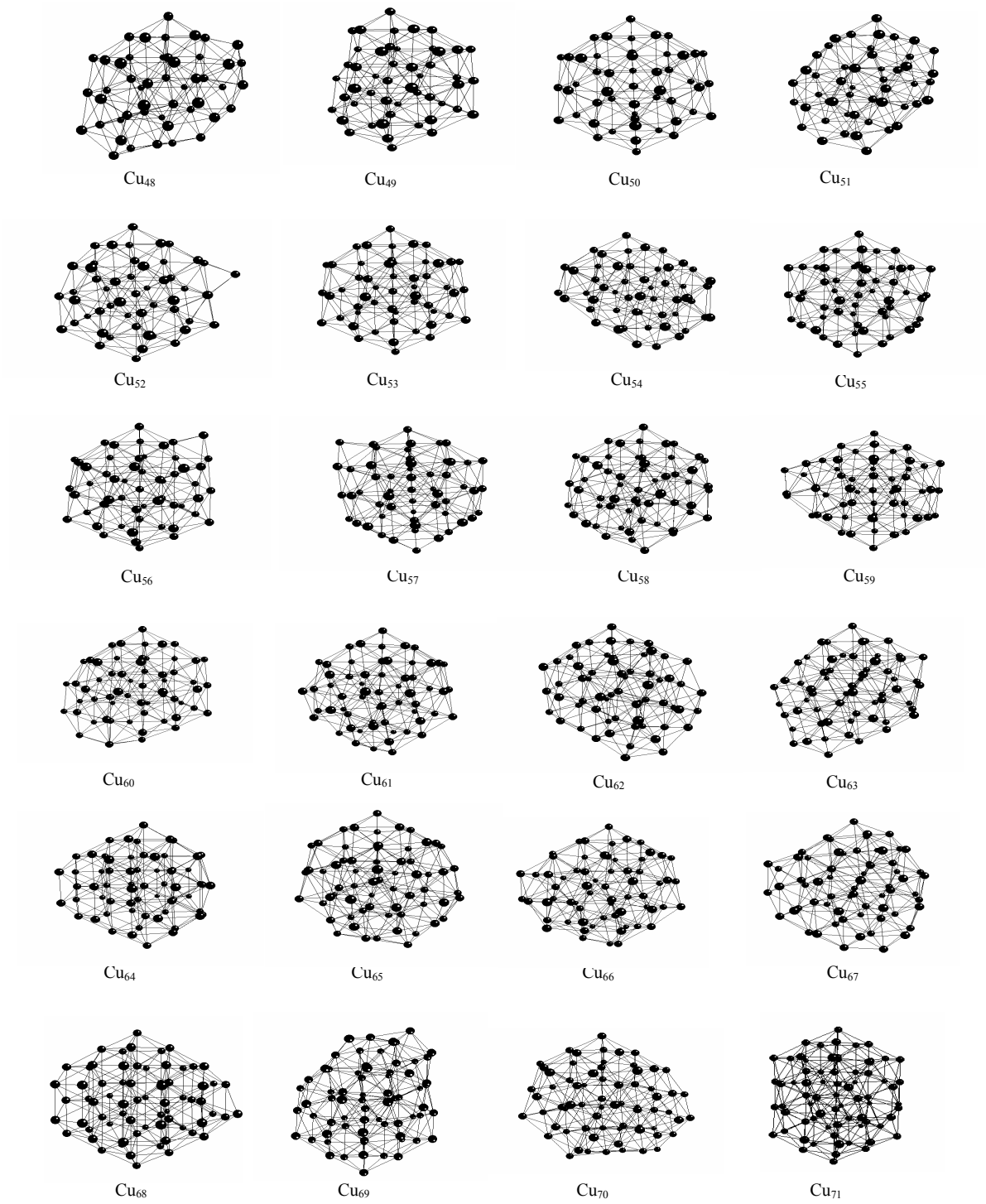

Figure 2. The minimum energy geometries of the most stable copper clusters n=48-71.

The average nearest-neighbor distance for the Cu clusters n = 21-71 vary between 2.5143Å and 2.5339Å. As the cluster size increases, the average nearest-neighbor distance approaches the bulk value (the bulk value is 2.56Å for the fcc copper crystal [23]). Obtained results for binding energies from10 up to 56 atoms of the cluster are agree with calculated values by Darby et al [21] using many body Gupta potentials for these size of the copper clusters.

In order to investigate the relative stabilities of the clusters we consider here the evolution of the binding energy per atom (the average interaction energy), E_a, the first difference energy, $\Delta E^{(1)}$, and the second difference energy, $\Delta E^{(2)}$, which are defined in terms of the total interaction energy of the cluster (Figures 3-5).

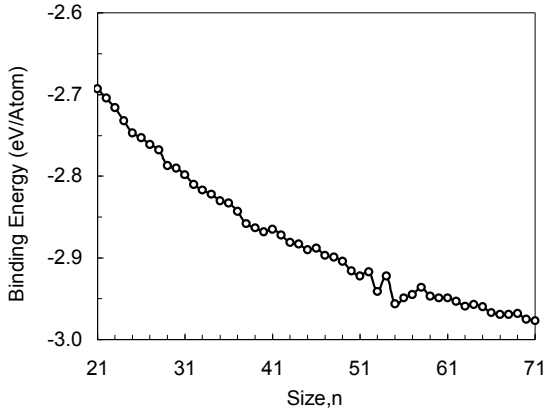

Figure 3. The binding energy per atom, $E_a=E_n/n$, as a function of the cluster size, n.

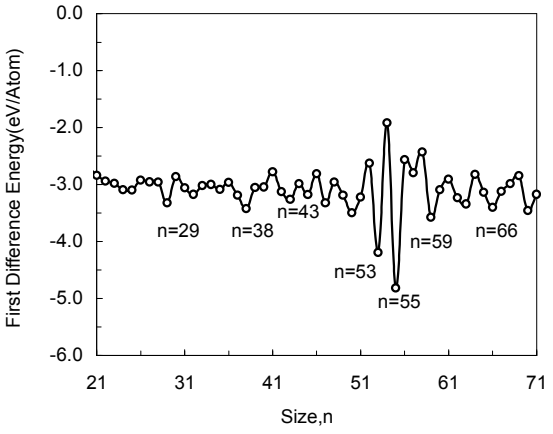

Figure 4. The first difference energy $\Delta E^{(1)}=E_n-E_{n-1}$ and as a function of the cluster size, n.

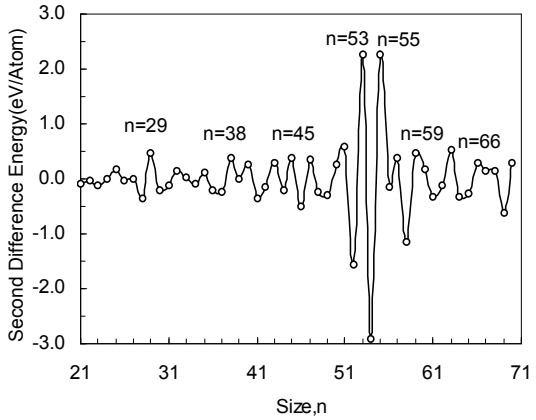

Figure 5. The second difference energy $\Delta E^{(2)}=E_{n+1}-2E_n+E_{n-1}$ as a function of the cluster size, n.

These energies are defined in terms of the total interaction energy of the cluster, $E_a=E_n/n$, $\Delta E^{(1)} = E_n - E_{n-1}$, $\Delta E^{(2)} = E_{n+1} - 2E_n + E_{n-1}$.

The average interaction energy per atom as a function of cluster size is in Figure 3. The energy difference by adding one atom, namely, the first difference $\Delta E^{(1)}$ in Figure 4, and the second difference energy $\Delta E^{(2)}$ as a function of cluster size are shown in Figure 5. Some clusters are especially stable as illustrated in Figures 3-5 where a peak indicates that the cluster's stability is enhanced relative to the neighboring clusters. In the limit of very large clusters both E_a and $\Delta E^{(1)}$ will approach the cohesive energy of the corresponding bulk solid. The extent to which E_a and $\Delta E^{(1)}$ differ is a signature of how different the clusters are from their bulk limit in terms of stability. The second difference energy $\Delta E^{(2)}$ is the difference in energy between the two fragmentation paths $X_{n+1} \rightarrow X_n + X$ and $X_n \rightarrow X_{n-1} + X$. If $\Delta E^{(2)}$ is positive, it means that the dissociation of X_{n+1} into X_n leaving one atom free is more favorable than the dissociation of X_n into X_{n-1} ; so $\Delta E^{(2)}$ is nothing but a measure of the stability of the clusters [16].

The peaks in Figures 3-5 indicate that n= 53 and 55 are the most stable clusters. The average bond lengths <d> for these cluster sizes are 2.5135 Å and 2.5161Å, respectively. In the limit of very large clusters both E_a and $\Delta E^{(1)}$ will approach the cohesive energy (–3.4 eV/atom) for Cu crystal. The lowest energy structure of the Cu_{38} cluster, $Cu_{38}^{(1)}$ has a fcc-like truncated octahedron form which is different from those of the other sizes (Figures 1 and 2). This geometry was reported in ref.21.

From Figure 3 one may say that the clusters with n = 29, 38, 39, 40, 43, 53, 55, 70 and 71 seem to be relatively more stable; from Figure 4 the clusters with the number of atoms 29, 38, 43, 53, 55, 63 and 70 seem to be relatively more stable; peaks in Figure 3 indicate that the sizes of n = 29, 38, 40, 53, 55, 63 and 71 seem to be relatively more stable. One may conclude that the common numbers in these three groups might be the magic numbers for the copper clusters studied in this

paper. The common numbers are n = 29, 38, 53, and 55. Adding further an icosahedral shell over size 13, cluster with 55 atoms is obtained as seen in Figures 3-5.

4. ACKNOWLEDGEMENTS

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