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Study on the Phase Transition Behavior of Ni Nano-Clusters Using Molecular Dynamics Simulation

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Structural phase transition of Ni nanocluster from cuboctahedron to icosahedron at 1100 K is investigated by means of molecular dynamics simulation. Radial distribution function and potential energy of each atom are calculated to study the transition phenomena in detail. At 1100 K, potential energy of interior atoms in the cluster is increased before the transition, while the periodicity of a_0 in the radial distribution function is broken. Thus the interior atoms partially lose its crystallinity in advance of the transition. Rather potential energy of the surface starts to decrease relatively so much by changing the surface structure to icosahedron at/after the transition. Consequently, the system energy is decreased. Minimizing surface energy enables Ni nano cluster to drive the transition. In addition, the interior energy is increased to as much as that of icosahedron prior to the transition.

Keywords: Ni Nanoclsuter, Molecular Dynamics, Phase Transition.

1. INTRODUCTION

Metal nanoclusters have received much attention for their possibility in wide applications[1,2] such as a catalyst,[3] self-assembly[4] or a building block for novel nano-materials,[5] and a deposited material for films.[6] The nanoclusters has large surface-to-volume ratio so that total surface energy is more comparable to the interior energy of the system, which could result in different structure and properties to a macroscopic bulk phase.[7] For instance, various structures such as noncrystalline structures like icosahedron (Ih) and decahedron (Dh), or truncated face-centered-cubic (fcc) structure like cuboctahedron (Ch) are exhibited unlike a bulk structure.[8–11]

In this article, we employ classical MD simulations and study phase transition behavior of Ni nanoclusters. Initially Ch Ni cluster containing 561 atoms are transformed into Ih at a temperature $T = 1100$ K within our simulation time. Both Ch and Ih share same number of particles and have only small energy difference about $E = 0.02$ eV/atom, corresponding to about $T = 300$ K, for 561 atoms. This condition makes it available the solid-to-solid transition before melting transition (melting temperature, $T_m = 1725$ K for the Ni bulk). Our wonder is how such structural transition can occur spontaneously during a random thermal process. As a first step to find a relevant description, we investigate in detail the evolution of atomic configurations around the transition. To monitor the phase transition, the radial distribution function (rdf) $g(r)$ and change of the potential energy, E in the surface and the interior are calculated.

2. CALCULATION METHODS

The accuracy of MD simulation is largely dependent on the reliability of interatomic potential in use. We utilized embedded atom method (EAM) scheme for describing structural and kinetic behaviors of Ni.[12] EAM potential is well known force field for the metallic system and it has verified its reliabilities by numerous simulation works. Among the Ni potentials, we applied Voter-Chen's EAM potential to this work after rigorous benchmark on lattice constants, mechanical properties, surface energies, and thermodynamic stability.[13] The initial structure of Ni nanocluster was set to cuboctahedron which is basically face centered cubic (fcc) lattice, but having six (100) and eight (111) surfaces. In order to find energetically favorable structure between Ih, Ch, and fcc spheres, we calculated 0 K energy for various kinds of sizes of Ni nanoclusters up to 20 shells, which composed of 28741 atoms.[14] All atom movements were performed by constant NVE integration to update position and velocity in each time step. Temperature of the system was controlled by a temperature

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rescaling method every 100 MD time step. During heating or cooling processes, the rates maintain as 1×10^{-2} K/fs or 2×10^{-3} K/fs. To investigate the Ch-to-Ih transition behavior of Ni cluster, particularly on 561 atoms, constant temperature simulation has performed at $T = 1100$ K. The temperature was reached by stepwise heating from 300 K to eliminate rate dependence and maintained at least 400 ps. In this time period, structural or energetic properties such as kinetic energy, potential energy, surface energy, and radial distribution function (rdf) were computed with respect to the simulation time. All calculations were performed by using LAMMPS code.[15]

3. RESULTS

Figure 1 shows the variations of the internal energy at 0 K between Ih and Ch clusters with respect to number of particles, N. We obtain the 0 K energies by minimization calculation in LAMMPS from geometrically perfect structures. From the viewpoint of energetics, Ih is more stable structure than Ch at small size. However as the cluster size increases, there is a crossover around $N = 5083$, 5.2 nm in diameter, at which Ch becomes more stable than Ih. Ih cluster is surrounded by 20 triangular (111) faces, energetically most stable surface in fcc structures. However, Ch has 6 square (100) faces, which show energetically less favorable than (111) faces. Thus, the relatively large energy difference before the crossover mainly comes from the surface energy difference between them, and the effect is much more significant as N is smaller due to large surface-to-volume ratio.

To avoid the dependence of heating rate, simulated annealing in step-wise fashion is introduced as shown in Figure 2. Temperature jumps 200 K from the initial $T = 300$ K every 10^4 steps. System is sufficiently equilibrated within the duration under our rescaling temperature scheme. After 4×10^4 steps, equilibrating the system at $T = 1100$ K, the potential energy of the system gradually increases up to the transition around 4.7×10^4 steps or 47 ps.

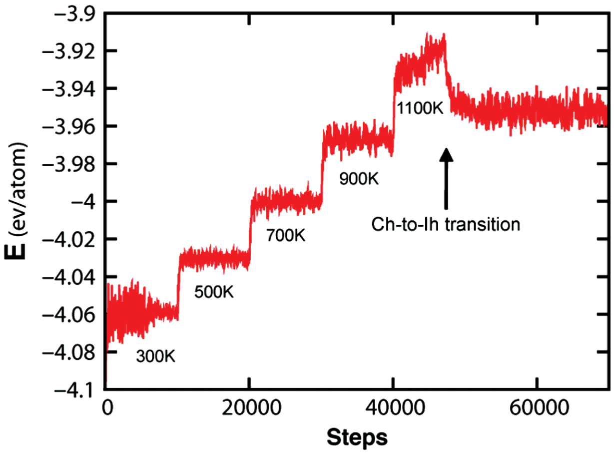

Fig. 2. Annealing scheme in our simulation. Temperature jumps every 10000 steps to 200 K. In this energy curve, the transition from Ch to Ih occurs around 47000 steps where steep decline of internal energy appears.

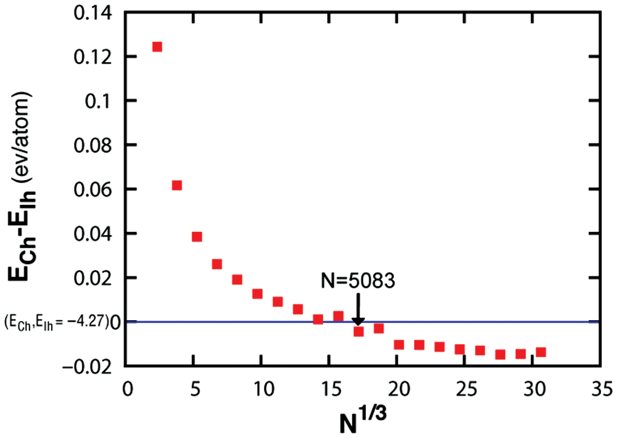

Fig. 1. Comparison of internal energies between Ch and Ih at $T = 0$ K. Ih clusters are energetically more stable than Ch clusters when the number of particles. N are smaller than 5083.

Figure 3 shows atomic configurations and potential energy of surface atoms. The colors of each atom represent their potential energy. The initial Ch (Fig. 3(a)) and final Ih (Fig. 3(d)) surface structure is clearly characterized by potential energy according to vertices, edges and faces, respectively. Through annealing by a rate 2×10^{-3} K/fs, spatial ordering of surface atoms wander and some atoms, mainly edge atoms, are excited, but still maintained Ch structure (Fig. 3(b)). After the transition (Fig. 3(c)), five-fold symmetry is appeared on vertices and edge atoms are energetically stabilized. Cooling by the same rate with

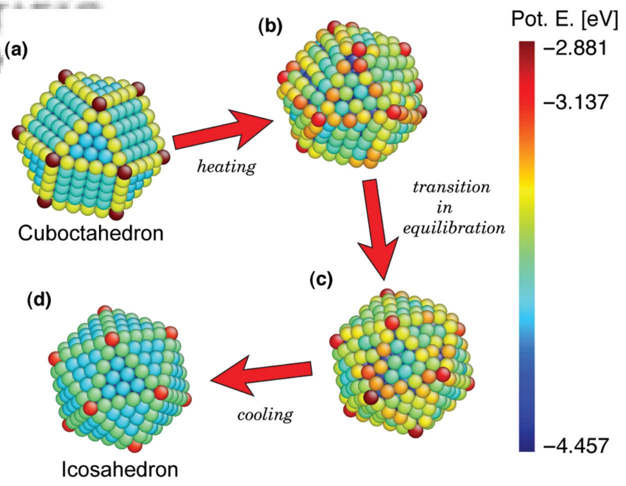

Fig. 3. Representative atomic configuration during heating-equilibrating at $T = 1100$ K-cooling procedure. The heating/cooling rate is 2×10^{-3} K/fs. The initial Ch cluster transforms into the Ih cluster in the equilibrating steps. Then the Ih structure becomes geometrically perfect by cooling to 0 K. Atoms are colored according to their potential energies.

the annealing, some defect sites are cured and perfect Ih structure is obtained. We note when the rate is much faster, say 1×10^{-2} K/fs, the defects are remained and the cluster does not reach perfect Ih.

The geometrical ordering of atoms is represented by the radial distribution functions in Figure 4. The rdf at each time is calculated with quenched cluster to 0 K for ignoring thermal noise, thus clarifying peaks. Initial Ch peaks locate at typical positions such as $(1/2^{0.5})\ a_0$, a_0 $(= 3.52$ Å for Ni), $(6^{0.5}/2)\ a_0$, $2^{0.5}\ a_0$, and etc. because of its crystallinity. Compared with Ih, peaks of Ih lie at slight different positions with smaller magnitude. In particular, 4th peak differs significantly. At $t = 40$ ps, peaks still share nearly same position with Ch. At $t = 46.7$ ps, just before the transition, the Ni cluster still maintain Ch structure however the peaks are clearly broadened and decreased in height. Especially 2nd peak almost disappeared, which means break of a_0 periodicity in the system already. At $t = 47.7$ ps, just after the transition, five-fold symmetry is appeared in the surface as shown in Figure 3(c). The peaks are slightly translated and well fitted with Ih. The 2nd peak is revived in its height and placed close to that of Ih. The 4th peak in the inset of Figure 4 is clearly moved and agreed with Ih, thus it demonstrates well the Ch-to-Ih transition.

We also investigate potential energy change before and after the Ch-to-Ih transition with the quenched clusters used in Figure 4. E_{surf} takes into account of the total potential energy per atom of the surface, consisting of 252 atoms (about 45% in total atoms) in the most outer shell. Rest of atoms contributes to the interior potential energy E_{int}. Before the transition (corresponding to $t = 46.7$ ps), total energy of the system E_{tot} in Figure 5 is increased by virtue of annealing from 300 K to 1100 K. It is intriguing that the rise of E_{tot} comes from E_{int} rather than E_{surf}, which slightly decreases. At/after the transition, E_{surf} becomes to decrease highly, amounted as 0.04 eV since the surface structure transforms into the Ih. However, E_{int} is very slightly decreased by about 0.002 eV. Thus E_{tot} decreases due to mainly E_{surf}.

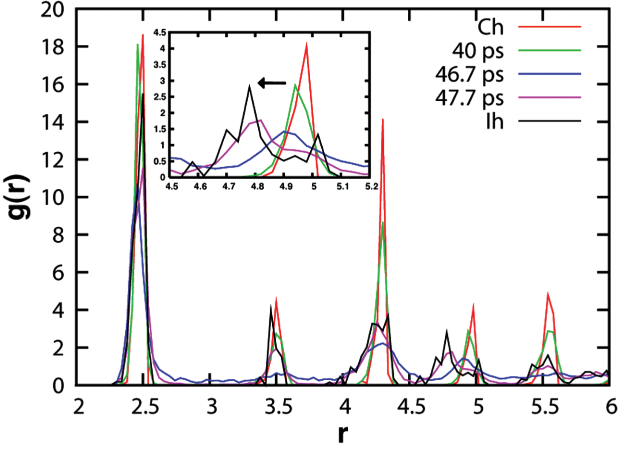

Fig. 4. The radial distribution function $g(r)$ calculated from the minimized atomic configurations at different times. Initial Ch structure alters into Ih structure around $t = 47$ ps. Inset clearly shows Ch peak is shortened and broadened before the transition, and new peak appear well fitted with that of Ih.

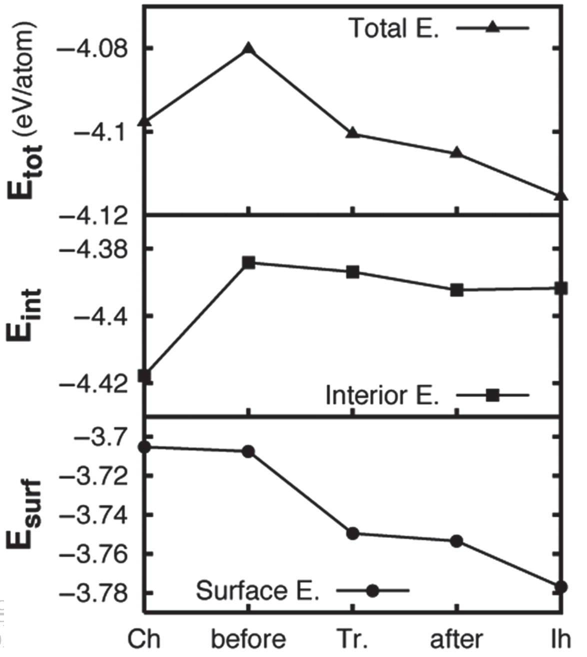

Fig. 5. Potential energy change around transition. Before transition, surface energy very slightly decreases however interior energy increases relatively high, which result in total energy rise as well. During and after transition, the surface energy decreases much than the interior energy, and total energy decreases due to the surface energy decrease.

4. SUMMARY AND DISCUSSION

We understand the Ch-to-Ih transition in Ni nanocluster in terms of evolution of both rdf and energy. 0 K energy of Ih is smaller by about 0.02 eV (corresponding to about 300 K) than initial Ch structure. Also, surface energy of Ih alone is lowered by about 0.07 eV (corresponding to about 800 K) when compared with Ch. In spite of such energetically unstableness of Ch, transition to Ih cannot occur spontaneously in room temperature because the energy of interior atoms in Ih is larger by 0.04 eV as shown in Figure 5. Thus for activating the transition, annealing is needed that increase E_{int}. When the interior energy of the system reaches close to E_{int} of Ih -4.39 eV, finally surface-induced minimization of energy is working on. If not surface and interior would be separated, which cost big energy pay. The transition temperature 1100 K is nothing but activation energy of interior atoms. Just before the transition, Ni cluster lose its own crystallinity and prepare to accept new structural order of the Ih.

One might wonder how the (100) surfaces in Ch are twinned as (111) surfaces in Ih without external mechanical interactions. In Figure 3, magnitude of the potential energy is ranked as the order of vertices, edges, faces and interiors. Thus we guess different thermal expansion rate under certain temperature between surface and interiors or more locally among vertices, edges and faces, which would induce stress in lateral direction. To figure out such mechanism, further analysis such as atom-resolved Lindemann index[16] and accumulated strain energy[11] on surface is required.

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