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Spontaneous Alloying and Collective Motions of Surface Atoms in Metal Cluster

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Dynamics of surface atoms penetrating into microclusters is investigated in connection with the spontaneous alloying phenomenon (SA) in metal microclusters. The SA is a signature of an unexpectedly fast diffusion of solute atoms (Cu) which is deposited on the surface of host nano-sized Au cluster at room temperature. An attempt to elucidate the atomistic mechanism of dynamics which is closely related to the SA in microclusters is presented. We put our focus upon two types of atomic rearrangements which are termed as a *gliding motion* and a *cornering slipping motion*, respectively. We analyze the frequency of these characteristic collective motions by means of an isothermal molecular dynamics(MD) simulation. It is confirmed that majority of the surface rearrangement of a cluster belongs to these two types. In particular, the *gliding motion* of 3 atoms are observed at frequent intervals. We point out that collective motion of the groups of atoms which are sufficiently large are often accompanied with *cornering slipping motion*.
Key words: microcluster, molecular dynamics, simulation

1 INTRODUCTION

A number of interesting static and dynamical properties of micro clusters have been reported by many authors during last two decades[1]. In 1992 Yasuda and Mori(YM) discovered a very interesting phenomenon manifesting the dynamical activity of microclusters by using transmission electron microscope. They observed that the solute atoms (e.g. Cu-atom) deposited on the surface of nano-sized metal cluster (e.g. Au-cluster) on a substrate are promptly absorbed into the host cluster. A highly concentrated and homogeneously mixed alloyed cluster is formed at room temperature[2]. Such a rapid alloying process is often called *spontaneous alloying*(SA). To understand the dynamics of SA, Shimizu, Sawada and Ikeda (SSI) examined numerical simulations by using two-dimensional (2D) Morse cluster[3, 4]. By using isothermal MD simulation, we confirm that the atomic diffusion in a cluster obeys an Arrhenius-like law[5]. We paid our attention upon the diffusive atomic motion along the following two directions: One is the diffusion along the radial direction of a cluster (radial diffusion) and the other is that along the cluster surface (surface diffusion). The numerical results strongly suggest that the diffusion process observed in the SA is not a manifestation of a straightforward radial diffusion mediated by interstitial sites or vacancies, but an accumulation of active surface motion. In fact there exist a wide variety of collective surface motion which has relatively low energy barrier on multidimensional potential energy surface(PES). SSI numerically located a number of the reaction paths connecting one local minimum and another on PES, and pointed out the presence of a lot of types of complicated collective motions which correspond to the reaction path with sufficiently low-lying saddle points on PES. [6]. In this paper we present a detailed analysis on the collective motions of atoms on a cluster surface. Our purpose is to pick up the characteristic surface rearrangements which are found in term of the reaction path analysis and to quantify how frequently they appear in isoenergetic dynamics. Our goal is to resolve the most important elementary process controlling the SA from the viewpoint of dynamics.

2 MODEL AND METHOD

The potential part of our model Hamiltonian $H = \sum_{i=1}^{N} \frac{1}{2m}\boldsymbol{p}_i^2 + \sum_{i<j} V\left(|\boldsymbol{q}_i - \boldsymbol{q}_j|\right)$, is the Morse potential which was used in the previous paper: [4] $V(r) = \epsilon\left\{e^{-2\beta(r-\sigma)} - 2e^{-\beta(r-\sigma)}\right\}$, A cluster contains 67 atoms($N = 67$). We choose $\beta = 1.3588\text{Å}^{-1}$, $\epsilon = 0.3429$ eV and $\sigma = 2.866$Å, which correspond Cu atom[7]. The temperature of the system is defined by $T(t) = \frac{2E_K(t)}{(2N-3)k_B}$, where $E_K(t) = \sum_{i=1}^{N} \boldsymbol{p}_i^2/2m$ is the total kinetic energy of the cluster at the time t and N is the number of constituent atoms. Isoenergetic dynamics is employed to simulate the time evolution of the cluster M_{67}. The temperature of the system T is set to 600 K which is below the melting point. The hopping rearrangement of individual atoms is detected by monitoring the displacement at every time interval which is predetermined. In case that several atoms move to the same direction all at once, the group of these moving atoms is termed as a *colony*. The collective motion of atoms are analyzed in terms of scrutinizing the behavior of colonies.

3 A QUALITATIVE ASPECT OF COLLECTIVE MOTIONS

According to atomic motions the configurational space, we classify the surface atomic motion into 2 types.

(A) gliding motion

(B) cornering slipping motion

The TYPE(A) is closely related to the diffusion toward the radial direction of a cluster. In Fig.1 a collective motion classified as TYPE(A) is displayed. In these snapshots, after 9 surface atoms at the left-hand side glide over the surface, the 4 atoms at the right hand also move upward.

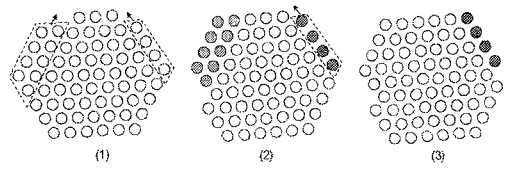

Figure 1: Configuration snapshots of the cluster atoms for the M_{67}. This is an example of serial *gliding motion*, which is the simplest collective motion of surface atoms.

Fig.1 illustrate the successive occurrence of the collective rearrangements which is termed as a gliding motion. As will be mentioned below, a gliding motion of surface atoms forming a train is frequently observed in isothermal dynamics. However, TYPE(A) does not contribute to push the surface atoms into the core of cluster. In that sense, a gliding motion does not directly affect the radial diffusion of surface atoms. In Fig.2 an example of the TYPE(B) motion

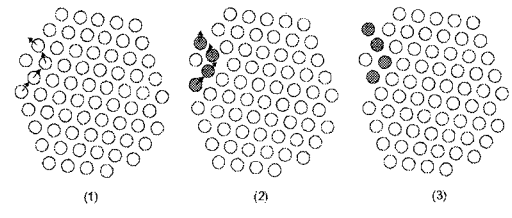

Figure 2: Configuration snapshots of the cluster atoms for the M_{67}. This is an example of *cornering slipping motion*, which is related to radial diffusion. The atoms which are going to rearrange are shaded and encircled by the dotted line. The direction of the atomic movement is denoted by the arrows.

which is termed as the cornering slipping motion is depicted. During the present motion the 4 atoms pass through the beneath of the surface with retaining the surface atoms at the corner. The TYPE(B) is often observed during the MD simulation as well as TYPE(A). Unlike the TYPE(A), the TYPE (B) is considered to be an elementary process where surface atoms are pushed into the inside of a cluster. Thus, we may say that TYPE(B) is directly contribute to the radial diffusion of surface atoms.

During the long time evolution, the process TYPE(A) and (B) may interfere in each other in the following way. Fig.3 shows an example where TYPE(A) and (B) occur successively. The successive events in Fig.3 are possible to be decomposed into 3 steps. In other words, the while process in Fig.3 is completed by climbing over 3 saddle points on the PES. The 2nd saddle is supposed to imply relatively high energy barrier, because about 9 atoms are involved to attain the rearrangement. In fact it is rare to find out an avalanche of atomic rearrangements like the present case in the lower temperature region, even though it is an efficient process to mix surface atom with core atoms. At $600K$ an large-scale rearrangement exemplified in Fig.3 occurs at an average of 1 time per 1 ns. The most promising process which contributes to the mass transport between the inside and the outside of the cluster seems to be the cornering slipping motion which implies sufficiently low energy barrier.

In the followings we quantify how often the collective atomic rearrangements, which are represented by TYPE(A) and (B), occur during the dynamics.

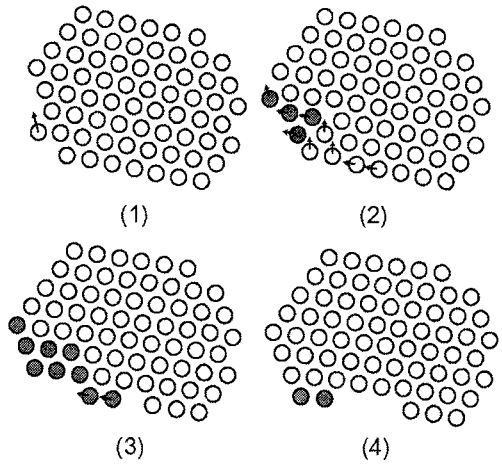

Figure 3: The snapshots of the cluster atoms for the M_{67}. This is an example of successive occurrence of *gliding and cornering motion*.(1)A single atom glides over the flat surface.(2)(3) (7+2) atoms begin to migrate over the corner of the cluster surface. (4) 2 atoms glide over the cluster surface again.

4 A QUANTITATIVE ASPECT OF COLLECTIVE MOTIONS

In the present section we put our focus on a statistical aspect of collective motion of surface atoms. We evaluate how many atoms are involved in a single atomic rearrangement. In Fig.4, the frequency distribution of the number of atoms which are involved in a single rearrangement motion of surface atoms. It is evident that a single rearranging event prefers to be accompanied with 3 atoms. The result seems to contradict

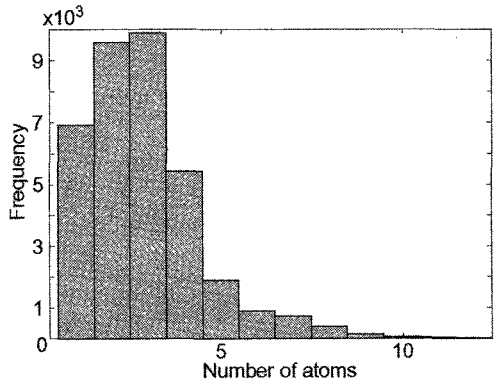

Figure 4: A histogram for the number of the atoms which are moved concurrently during a single rearrangement.

a naive consideration that a single atom is the easiest to move from the energetic viewpoint. However, assuming that a single atom hops along the cluster surface, a single atom has to be located on the cluster surface prior to the hop. The possibility to generate a single surface atom which is almost isolated and free to move is considerably small. On the hand, 2 or 3 atoms are relatively easy to generate due to characteristic length of edge of the cluster shape. Because the cluster M_{67} forms an almost hexagonal shape and its edge consists of 4 or 5 atoms, the cluster tends to have 2 or 3 atoms forming a train on its surface during the isomerization process. In that sense the location of the peak in the histogram depends on the cluster size.

As demonstrated in Fig.1, the *colony* which is denoted by dotted line may move almost simultaneously in the spatially separated places in a cluster. Fig.5

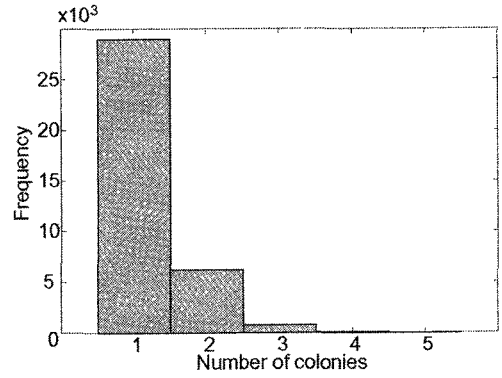

Figure 5: A histogram for the number of the colonies whose constituent atoms move simultaneously.

demonstrate how many colonies move almost simultaneously during a MD simulation. The event where i colonies move all at once is denoted by C_i. Fig.5 implies that the colony tends to move as a single. The number of the event where a few colonies move simultaneously decreases rapidly. It is a direct outcome of the fact that it costs high energy to rearrange few colonies including many surface atoms.

Fig.6(A) shows the frequency of the event where the colony containing i atoms exhibits the gliding motion(gray line) and the cornering slipping motion(thick line), respectively. The frequency of the event where the colony exhibits the cornering slipping motion(TYPE(B)) considerably rare, although TYPE(B) is an elementary process which plays a significant role in pushing surface atoms into the core. Fig.6(B) exhibit the ratio between the accumulated number of colonies which is involved by the cornering slipping motion and the accumulated total number of colonies. Since the length of the edge of the present model M_{67} contains about 5 surface atoms, the rel-

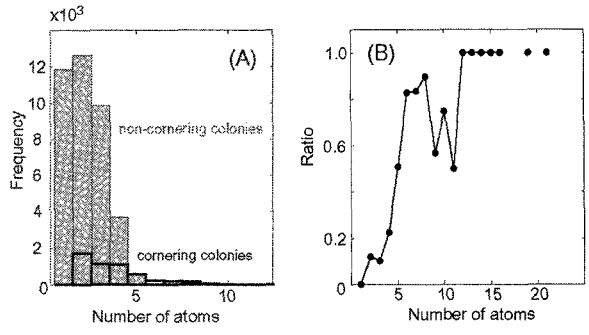

Figure 6: (A) A histogram for the frequency of the event where the colony containing i atoms exhibits the gliding motion is denoted by a gray line. The horizontal axis is the number of the atoms in a colony C_i^j, where $j = s$ or c. While $j = s$ implies that the colony is involved by a gliding motion. $j = c$ represents that the colony is involved is involved by the cornering slipping motion. A histogram for the frequency of the event where the colony containing i atoms exhibits the cornering slipping motion is also denoted by a thick line. (B)The horizontal axis indicates the number of atoms in a colonies. The vertical axis represents the ratio between the accumulated number of colonies, which is involved by the cornering slipping motion, and the accumulated total number of colonies, which appear in the isothermal MD.

atively large colonies which consist of more than 5 atoms are necessarily accompanied with the cornering slipping motion. This is a reason for the increasing trend of the ratio in Fig.6(B). The ratio exhibits a decreasing trend about the colony size 9,10, and 11. This behavior is not statistically reliable, since the insufficient sample number is taken into account.

5 CONCLUSION

We characterize the collective surface motion which appears in isothermal MD simulation by evaluating the frequency of occurrence of the atomic rearrangements represented by TYPE (A) and (B). It is found that the majority of the surface rearrangements belongs to these two types. In particular, we verified that the colonies consisting of 3 atoms are frequently observed during isothermal dynamics. The most of the colonies which consists of less than 5 atoms are involved by the movement represented by TYPE(A). For small colonies the movement TYPE(B) is also frequent to occur below the melting point. However the frequency of TYPE(A) overwhelms that of TYPE(B) in the ratio, although TYPE(B) plays a key role to mix the surface atom with the core atoms efficiently. Consequently the most frequent events which are picked up in the model M_{67} is a gliding motion of 3 atoms forming a train.

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