Size Effect on the Atomistic Structure of Metallic Atom Clusters

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The atomistic structure of metallic atom clusters is discussed based on the experimental results with the following conclusions: (1) When ultrafine particles of metals become smaller than the critical sizes corresponding to the nucleus size of the crystals, they behave as atom clusters and their atomistic structure changes as a function of the number of constituent atoms, *i.e.*, the many-body potential. (2) Icosahedrons are formed first and change to the cuboctahedral structure before such atom clusters take the final crystal structures. (3) The phonon mode of these atomistic structures is very much softened, and thus the zigzag atom-chains are formed dynamically around the average position of atoms even in the cuboctahedral structure. (4) The hybrid orbital corresponding to the final crystal structure is formed when atom clusters grow to the critical size. As a result, the binding strength sufficiently increases along a certain crystal axis such as the $\langle 110 \rangle$ in the fcc structure and the $\langle 111 \rangle$ in the bcc one, so that atomic rearrangement can occur within the ultrafine particles, including disappearance of multi-twin in Au particles, to take the bonding state of crystals.

1. Introduction

Recent studies have shown that materials anomalously change their behavior when they become smaller than the critical sizes, which correspond to the size of crystal nuclei, on the nanometer scale.[1-6] Most of the anomalous behavior cannot be understood by a simple consideration that the ratio of surface vs. volume of materials increases with decreasing their size. Practically, the critical size of spherical particles varies from ϕ 1 nm to 20 nm, which corresponds to the number of constituent atoms from above 10^2 to 10^5, reflecting differences in the bonding mode, the binding strength and the surrounding conditions.[2,4] These critical sizes have been estimated by various methods, and named "the magic size (d_M)", as shown in Table 1.[2,4] Here, ultrafine particles whose size is smaller than the critical one are named "atom clusters". It should be emphasized in Table 1 that so called nano-materials on the nanometer scale anomalously change their behavior when their size is smaller than the corresponding d_M, *i.e.*, in atom clusters, but that they show the same behavior as those of bulk ones except a large ratio of surface vs. volume when they become larger than their d_M.

In the present report, the size effect on atomistic structures of atom clusters are discussed based on the experimental results, and corelated with the anomalous behavior of atom clusters.

2. Experimental Results on Atom Clusters

Many experimental results have been obtained on the behavior of atom clusters as follows:

(1) There are two typical types of electronic structures; *i.e.*, one is the ground state of free atoms and the other the bonding state of crystals. The former changes to the latter as the number of constituent atoms increases.[2,5]

(2) It has been concluded from so called the magic number of constituent atoms that all metallic elements form 13-atoms icosahedrons at the beginning of formation of atom clusters.[7]

(3) Binding strength increases along a certain direction in metal crystals, as expected from existence of the Burgers vector along the $\langle 110 \rangle$ in the fcc structure and the $\langle 111 \rangle$ in the bcc one. This shows formation of hybrid orbitals having considerably high covalency in the bonding state.[4,6]

(4) Various alloys and ceramic crystals are amorphized by high energy electron irradiation when they are divided into ultrafine blocks whose size is smaller than the critical one (d_M).[1,2]

(5) Spontaneous mixing of foreign-atoms instantly occurs into atom clusters.[8] Intermetallic compounds also change to solid solutions when their size becomes smaller than the critical one.[9]

(6) Atom clusters easily change their shapes with an extremely small applied stress,[10] and sintering among them quickly occurs like a liquid phase.[11]

(7) During crystallization of amorphous materails, the reverse process of the spontaneous mixing of foreign atoms occurs, and results in formation of homogeneous nucleus size of crystals. The critical size of crystal nuclei is exactly the same as d_M for amorphization of the crys-

Table 1 The magic size (d_M) of atom clusters as a function of the bonding mode, binding strength and surrounding conditions. The table is partly corrected from the previous report[4] based on the recent experimental results.

Magic size (ϕnm)		Bonding mode of materials
Isolated	Embedded	
20–8	8–4	Metallic and ionic bonding
6–3	4–2	Intermetallic compounds
3–1.5	2–1	Covalent and diamond bonding

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tals.[12]

(8) The melting point markedly decreases when the size of the ultrafine particles decreases smaller than a certain value.[13,14]

(9) The following two evidences are also closely related to the formation of the hybrid orbitals: a) Debye temperature of Au ultrafine particles markedly decreases when the size becomes smaller than about ϕ 15 nm.[15] b) In the Raman shift of ultrafine particles of Si, only single broad peak appears first, and then a sharp peak newly appears when the size reaches a critical one. After that, the latter increases in intensity with increasing the size, but the former decreases at the same time.[15]

(10) It is expected from item (1) that physical properties, such as optical, electric, magnetic ones $etc.$, and their chemical properties, such as chemical reaction, catalysis $etc.$, are also remarkably changed in atom clusters.[2-6]

Based on these results, atomistic structures of atom clusters and their related phenomena are discussed in the following sections.

3. Anomalous Behavior of Ultrafine Particles Showing Multi-Wave Lattice Fringes

Figure 1 is high resolution electron micrographs showing the size effect on the atomistic structure of Au-atom clusters. It is noted in a-series of Fig. 1 that the lattice fringes show wavy and weak contrast when the size of atom clusters is smaller than about ϕ 2 nm. These wavy fringes often show spot-like contrast, and they change to a liquid-like contrast by a slight change of the orientation of atom clusters. From these results, the spot-like contrast in atom clusters of this size is considered to be related to atom-chains of the icosahedral structure unit which will be discussed later.

Multi-wave lattice fringes corresponding to a fcc-type structure clearly appear in Au ultrafine particles when their size becomes larger than about ϕ 3 nm, as seen in b- and c-series of Fig. 1. Two kinds of structures appear in this size, $i.e.$, one consists of a single domain and the other is multi-twinned ones. The latter is considered to result from growth of the Mackay-type icosahedron which are formed so frequently in Au ultrafine particles. Facet structures, however, are not clear even when the size increases to about ϕ 3 nm. These facts mean that Au ultrafine particles take a fcc-type structure when their size reaches to about ϕ 3 nm. Here, it is noted that these Au ultrafine particles show the anomalous behavior as atom clusters, such as the spontaneous mixing of various foreign atoms, when their size is smaller than about ϕ 15 nm.[8] Furthermore, most of the multi-twinned structure of Au ultrafine particles disappear or change to only single twinned domain when the particle size becomes more than about ϕ 15 nm, as seen in usual Au fine particles. The twin boundaries taking a five-fold node are not only thermaly stable but also atomic misfit at the boundaries is easily relieved by rearrangement of atoms nearby by the continuity of both atomistic and electronic structures through boundaries. Therefore, these twin boundaries are considered to hardly disappear at low temperatures at which self-diffusion scarcely occurs.

The paradoxial results mentioned above are considered to result from changing bonding mode during growth of these ultrafine particles, as discussed later.

4. Atomistic Structures as a Function of Local Bonding Potential within Atom Clusters

4.1 Initial stage of atom clusters

The interaction force among atoms taking the ground state mainly results from the van der Waals potential, and thus at the beginning of formation of atom clusters an icosahedron consisting of 13-atoms of the same element (hereafter denoted as the icosahedron) is generally formed first at least in metallic elements.[7] On the other hand, there are other types of atom clusters consisting of 13-atoms such as an fcc-type one, a bcc-type one et $al.$ Figure 2 shows a relationship between the icosahedron and the fcc-type atom cluster. In these atom clusters, a bonding potential (u) between two adjacent atoms can be assumed to be proportional to d^{-6}, where d is an interatomic distance, and the total potential energy (U_T) among them can be relatively compared with each other by taking the total sum of the interatomic distance among all constituent atoms.[6,17]

Here, substitute the size of the core-atom for an interatomic distance between the core-atom and the nearest neighbors. Then, the values of U_T for these three types of atom clusters are obtained as a function of the size of the core-atom, as shown in Table 2.[6,17] In Table 2, the value of U_T of the fcc-type atom cluster is lower than that of the icosahedron when the size of core-atom (d^*) is the same as that of the surrounding atoms (d_o).

It has been shown that the icosahedron of metallic elements are practically formed at the initial stage of atom clusters. This means that the icosahedron becomes more stable than the fcc-type arrangement at ambient temperature.[7] In order to realize this condition, the size of the core-atom in the icosahedron must be shrinked more than about 3%, as shown in Table 2. When d^* decreases to $0.973d_o$, the value of U_T of the icosahedron takes $-0.601U_o$, where U_o is an arbitrary unit, that is the same as that for the fcc-type arrangement, $i.e.$, cuboctahedron. However, in order to contact all peripheral atoms of the icosahedron each other, d^* must be decreases further to $0.902d_o$, as almost satisfied in most quasi-crystals.

Furthermore, it is noted in Table 2 that the fcc-type atom cluster shows the minimum total potential (U_T) compared with any other type atom clusters, such as bcc-type and monoclinic ones, when the center-atom takes the same size as those of surrounding ones.

Distribution of the local bonding potential within the icosahedron is also estimated by the same way.[6,17] The result shows that the bonding potential at contact points between the core-atom and each of its neighbors is stronger than that between adjacent peripheral atoms. Furthermore, each peripheral atom directly contacts only with the core-atom, and thus the size of the core-atom, $i.e.$, an interatomic distance between them, considerably decreases because of remarkable decrease of the coordination number of the former, as suggested by Pauling.[18] As a result, the negative charge density increases around the core-atom, $i.e.$, occurrence of the polarization, so that d^* decreases. Thus, it is considered that the size of the core-atom of the icosahedron of metallic elements
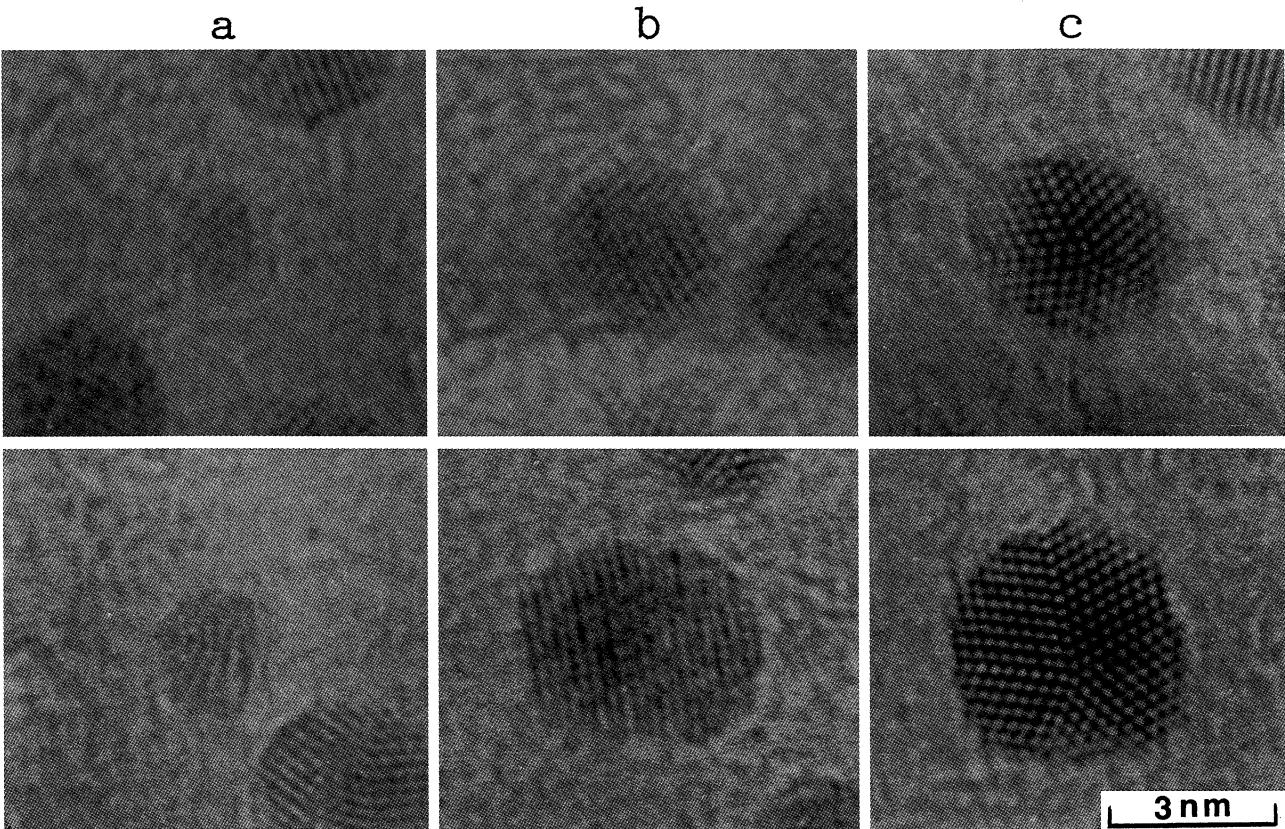
Fig. 1   High resolution electron micrographs showing the size effect on the atomistic structure of Au ultrafine particles deposited on amorphous carbon films. Multi-wave lattice fringes appear in these ultrafine particles when their size becomes larger than about ϕ 3 nm, but those particles show anomalous behavior as atom clusters.

Table 2   Size effect of the core-atom on the total potential energy of three types, *i.e.*, the icosahedron, fcc-type and bcc-type, of atom clusters consisting of 13 atoms.

Type of 13-atoms atom cluster	Icosahedron			FCC-type	BCC-type
	$d^* = d_o$	$d^* = 0.973d_o$	$d^* = 0.902d_o$		
Estimated U_T (arbitrary unit)	-0.55_5	-0.60_1	-0.75_0	-0.60_1	-0.48_8

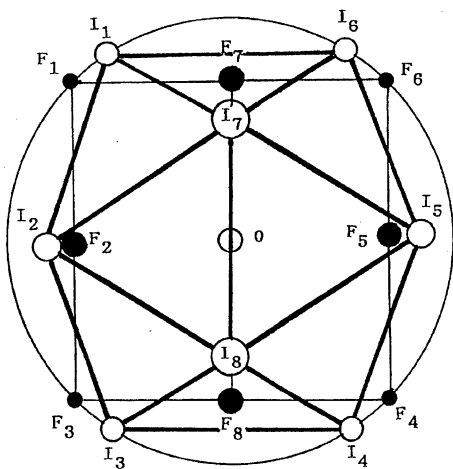d_o: A diameter of constituent atoms, d^*: A diameter of the core-atom.

Fig. 2   Two types of atom clusters consisting of 13 atoms. Markes I and F show atom positions of the icosahedron and a fcc-type atom cluster respectively.

actually decreases more than about 3% by the polarization around the core-atom.

4.2   Transition from the icosahedral structure unit to cuboctahedral one

The results mentioned above show that the icosahedron also has the following characteristics: (i) Gaps exist among the peripheral atoms in general even when the core-atom decreases considerably in size, because the value of d^* in the icosahedron consisting of the same atoms is difficult to be reduced as much as about 10%. (ii) The fcc-type atom clusters consisting of 13-atoms, *i.e.*, cuboctahedron, have a similar atomistic structure to that of the icosahedron, as shown in Fig. 2.

In these characteristics, item (i) shows that formation of the second zone of the icosahedron becomes difficult in general as a simple expansion of the first zone even in metallic elements, because gaps exist among adjacent constituent atoms of the first zone. Furthermore, item (ii) means that the transition between the icosahedron to a cuboctahedron easily occurs by a simple shear displacement along the surface of a sphere whose radius is an interatomic distance between the core-atom and the nearest neighbors, as shown in Fig. 2.

Namely, the transition spontaneously occurs without thermal diffusion only when the number of constituent atoms, *i.e.*, the many body potential, increases to a certain value, because d^* approaches that of the neighboring ones (d_o) by homogenizing the many-body potential.

Interaction force among the icosahedrons themselves is not so strong, because their bonding force mainly results from the van der Waals potential. Furthermore, growth of the icosahedron is difficult by item (i), while the van der Waals potential of the icosahedron itself increases with increasing size of an atom group.[19] Thus, these icosahedrons are connected with each other by either of face-, edge- or vertex-sharings. Figures 3(a) and (c) show schematic illustrations of atomistic structures of peripheral and the center regions within an atom cluster of nearly d_M in size. Here, open circles in (a) show vacant sites in the icosahedral structure unit, and a three-dimensional illustration in (b) shows a transition process from the icosahedral structure unit to the cuboctahedral one. The most probable arrangement of these icosahedral structure units is shown in Fig. 3(a) in which the zigzag atomic arrangements are formed by connecting these icosahedral structure units. In the center region, however, the atomistic structure becomes nearly straight along the close-packed $\langle 110 \rangle$ direction in the cuboctahedral structure unit by the many body potential, as shown in Fig. 3(c). Here, it is noted that constituent atoms within the cuboctahedral structure unit are also easily diplaced along the surface of the sphere shown in Fig. 2 by the thermal agitation. And thus, they are oscilated around each average position along the $\langle 110 \rangle$ direction to form the zigzag atom-chains dynamically even in the cuboctahedrall structure unit.

4.3 Distribution of the bonding potential within an atom cluster and the corresponding phonon mode

The ground state of electrons of free atoms smoothly changes to the bonding state of crystals as the number of constituent atoms increases.[5,6] Therefore, the bonding potential at the center region becomes close to the bonding state when the size of an atom cluster increases to nearly d_M, but that of the peripheral regions is still far from the bonding state. As a result, the bonding potential within an atom cluster varies from the center to the peripheral regions, as shown at the lower side in Fig. 4(a), and the corresponding local surface energy is illustrated as a function of the local bonding potential, as shown at the upper side in Fig. 4(a).[2–6] In Fig. 4(a), curve 0 and curves 1, 2, 3, $\cdots$ show distribution of the local bonding potentials, which are determined by the local many body potential, before and after the hybrid orbital is formed in the center region respectively. Each individual atom in the center region of the icosahedron are displaced with a rather high frequency by the thermal agitation (kT), but the zigzag atom-chains are vibrated as a whole with a low frequency by kT. The phonon displacement increases with increasing distance from the center of an atom cluster, as shown in Fig. 4(b) which corresponds to the shaded stage, curve 1, in Fig. 4(a). The thermal displacement of atoms increases with decreasing local bonding potential within atom clusters as well as temperature rise, as recognized from Fig. 4(b), and thus the phonon mode is remarkably softened in peripheral regions of an atom cluster. It was shown in Fig. 1 that facet struc-
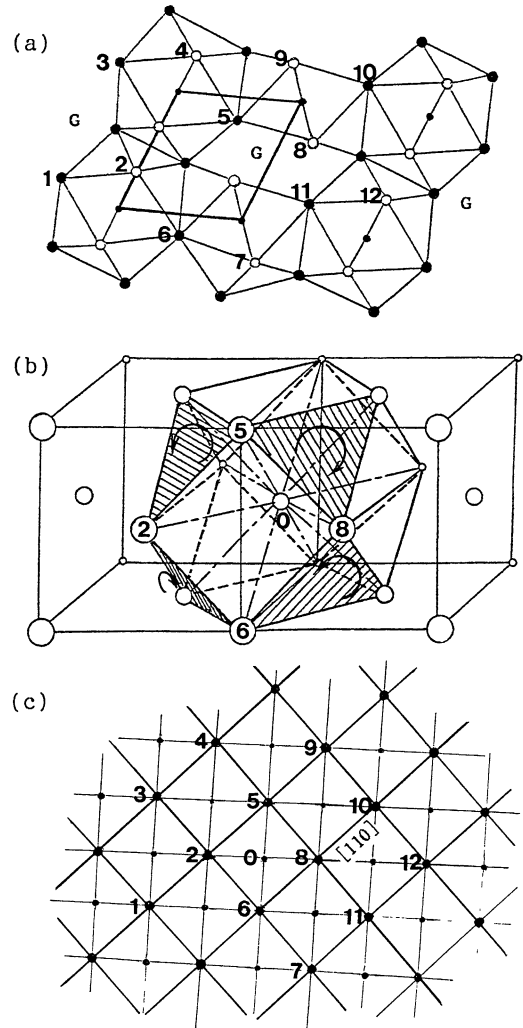

Fig. 3 Transition from the icosahedral structure unit (a) to the cuboctahedral one (c). (a) and (c) correspond to the peripheral regions and the center region of an atom cluster, in which filling up degrees of atoms are about 0.64 and less than 0.74 respectively. (b) shows a transition process from (a) to (c) by rotating triangles of atoms, as indicated with arrows. Mark **G** in (a) shows gaps among zigzag atom-chains, and an open circle in (a) a vacant site which is either atom site of a pair of atoms located in directions perpendicular to positions I_7 and I_8 in Fig. 2.

tures are not formed in Au ultrafine particles of ϕ 3 nm in size notwithstanding appearance of the multi-wave lattice fringes. This is considered to be due to remarkable softening of the phone mode in the peripheral regions. Furthermore, the melting point of atom clusters also markedly decreases with decreasing their size by the Lindeman's criterion of melting, as already known.[13,14]

4.4 Formation of intermediate atomistic structures within atom clusters before taking the final crystal structures

It was mentioned in Section 3 that multi-twinned domains disappear when Au ultrafine particles become larger than about ϕ 15 nm in size. Here, it should be noted that the electronic structure within an atom cluster changes from the ground state to the bonding state as the number of constituent atoms increases. This means that there are intermediate stages between these two typical electronic structures. In the case of Au-atom cluster, s-σ bond is considered to be formed with
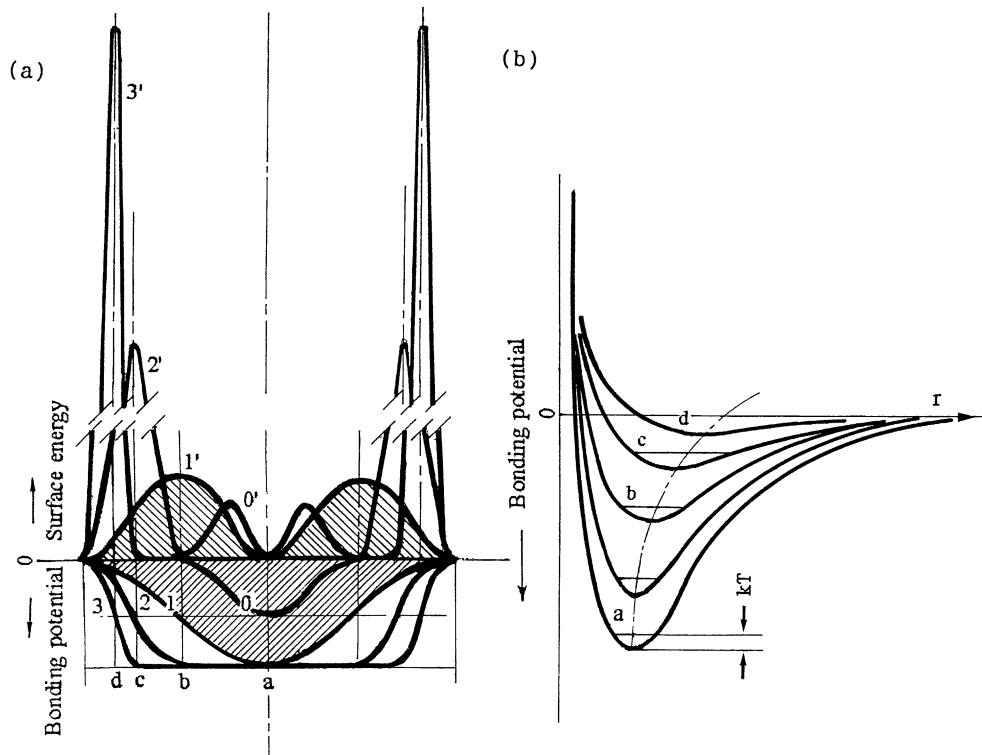
Fig. 4   Effect of the many body potential on local atomisitic structures within atom clusters. Distribution of both the local bonding potential and the corresponding local surface energy within an atom cluster is shown as a function of the number of constituent atoms of atom clusters in (a). (b) shows the corresponding phonon mode, *i.e.*, displacement of atoms by the thermal energy (kT), within an atom cluster taking a shaded stage, curve 1, in (a). Apparent size of an atom cluster will be expressed by the half-value diameter of each potential curve.

one s-electron of the outermost shell, but it is very weak in the binding strength because of both a weak bonding potential of s-orbital and a large coordination number of the center-atom, *i.e.*, about 12. When the number of constituent atoms is around 13, the energy bands of electrons do not overlap sufficiently each other among adjacent atoms, because the many body potential is not enough.

On the other hand, the center region takes the cuboctahedral structure unit first when the many body potential increases sufficiently to increase the size of center-atom more than about $0.97d_0$, but such structure is delayed to realize in peripheral regions. Furthermore, the second zone of the icosahedron frequently consists of atoms depositing onto each center of triangles of the first zone, ans thus other types of intermediate structures such as the dodecahedral-type structure or something like that are also possible to be formed by mixing these different local structures.

The cuboctahedral structure nuit, however, is formed by the geometrical condition determined by the size of center-atom in an atom cluster, and thus the energy bands of valence electrons in constituent atoms do not overlap sufficiently yet. When the size of each atom cluster reaches d_M, the energy bands of valence electrons overlap each other, and the metallic orbital of the free electrons is formed first. After that, the corresponding hybrid orbitals whose covalency is considerably large along the close-packed direction are formed when the overlapping degree of the energy bands becomes sufficient,[2–6] and the bonding state of crystals is completed.[6] This stage corrsponding to the crystal nucleation.[12]

Since the binding strength among constituent atoms is very

weak in the cuboctahedral structure unit, these constituent atoms are easily rearranged like recrystallization by the considerably high binding strength of the hybrid orbital, so that the multi-twinned structure disappears as the hybrid orbital expands all over an atom cluster.

In the case of fcc crystals, the intermediate atomistic structures, *i.e.*, cuboctahedral ones, show the same atomic arragement as that of the final crystal structure, and thus both of them are rather difficult to be discriminated. Therefore, existence of the intermediate atomistic structure must be checked on other metallic elements taking different final crystal structures from fcc-type ones, such as bcc and monoclinic structures.

As mentioned in Table 2, the cuboctahedral type (fcc-type) structure takes the minimum total potential in various atom clusters consisting of 13-atoms. And thus, it is considered that the fcc-type atom clusters appear before the final crystal structures are formed even when their final atomistic structures are different from the fcc-type one. Actually, metallic element in takes a fcc-type structure before taking the final monoclinic crystal.[20] Furthermore, it has been reported that various ultrafine particles of other elements also show such intermediate structures as fcc-type or dodecahedral-type ones before taking the final crystal structures; for example, (a) ultrafine particles of Fe take an intermediate structure like a fcc-type one,[21] and (b) those of bcc-type elements such as V, Nb, Ta, Mo, W *etc.* also take such intermediate structures as dodecahedral or fcc-type ones.[21]

From these results, it is concluded that all metallic elements always take the intermediate structures in the course of transi-

tion between the icosahedral structure nuit and the final crystal structures. The situation will also be the same in most elements taking the icosahedron at the initial stage of atom clusters.

Besides facts mentioned above, the bonding potential within each atom cluster decreases as a whole before taking the final crystal structure completely, especially in peripheral regions, as shown in Fig. 4. Under this condition, the dislocation core is hardly formed because of a weak constraint force from the neighboring atoms, and thus shear displacement among close packed atom-chains and/or planes occurs before the dislocation core is formed. Therefore, shape change of each atom cluster is easily carried out by an extremely small applied stress, as shown by Iijima.[10] Since atomic displacement also takes place along lowest potential valleys among constituent atoms, the deformation process becomes similar to movement of the partial dislocation. Furthermore, the zigzag atom-chains in Fig. 3 are not only thermally oscilated but also easily displaced by an extremely small force such as the weak Coulomb force caused by local charge transfer, and thus the average potential of saddle point for diffusion remakably decreses within each atom cluster, as expected from the spontaneous mixing phenomenon.[4]

5. Summary and Conclusions

In the present report, atomistic structures of metallic atom clusters are discussed based on the experimental results, and correlated to anomalous behavior of atom clusters. The results obtained are summarized as follows:

(1) The icosahedron consisting of 13-atoms of metals is formed at the initial stage of an atom cluster by decreasing diameter of the center-atom more than about 3%. The icosahedrons are connected to form the icosahedral structure nuit as the number of constituent atoms increases. The phonon mode is very much softened in these atomic arrangements.

(2) The atomistic structure of an atom cluster is a function of the number of constituent atoms. When the many body potential reaches a certain value, the center-atom increases in size more than 97.3% of those of neighbors so that the center region of each atom cluster changes to the cuboctahedral structure.

(3) As a result, intermediate atomistic structures between the icosahedral structure and the cuboctahedral one are formed locally and/or as average ones. The zigzag atom-chains are always formed dynamically by the soft phonon mode around the average position of atoms even in the cuboctahedral structure. As a result, ultrafine particles taking cuboctahedral structures still belong to atom clusters.

(4) When the number of constituent atoms increases, the energy bands of valence electrons in each atom overlap to form the metallic orbital first, and followed by formation of the corresponding hybrid orbitals. The covalency of these hybrid orbitals are considerably high, and thus the zigzag atom-chains become rigidly straight along the $\langle 110 \rangle$ in the fcc structure and the $\langle 111 \rangle$ in the bcc one, respectively, as expected from existence of the Burgers vectors.

(5) The lattice fringes sharply appear in Au ultrafine particles when their size increases to about ϕ 3 nm, but they result from such intermediate atomistic structures as the cuboctahedral one. Actually, multi-twinned structures of such Au particles disappear when the size increases to more than about ϕ 15 nm. The phenomenon can be recognized reasonably to be due to rearragement of constituent atoms in multi-twinned domains by considerably strong binding strength of the hybrid orbitals.

(6) Other metallic elements taking different atomistic structures in crystalline state, such as bcc and monoclinic ones, also take the intermediate structures like the cuboctahedral structure or something like that before the final crystal structure is formed.

Since free surfaces of materials is considered to be two-dimensional atom clusters,[4] their behavior can also be discussed from a veiw point of the anomalous behavior of the spherical atom clusters mentioned in the presenet report. The crystal nucleation of materials was also made clear in terms of the hybridization of atom clusters.[12]

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