THE THIRTY-NINTH HONDA MEMORIAL LECTURE

Studies on Atom Clusters by Ultra-High Voltage Electron Microscopy[†]

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When the number of constitutive atoms decreases to $10^3 \sim 10^5$, depending on the bonding mode and binding strength, the materials show different behavior from bulk ones as if they are new materials. These ultra-fine blocks are named "atom clusters" whose behavior is closely related to the many body effect of constitutive atoms.

Recently, an ultra-high voltage electron microscope "micro-laboratory" has been developed, in which the material behavior can be widely changed *in-situ* and the identification and characterization of materials in the atomic scale can be done. Various studies on the atom clusters have been carried out by this method.

In the present report, the anomalous behavior of these atom clusters is shown from the experimental results, and is discussed in terms of the formation of hybrid orbitals of valence electrons. Furthermore, the relationship between the so called "magic number" of micro-clusters and "magic size" of atom clusters is discussed.

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I. Introduction

Recent studies have shown that the materials markedly change their behavior when their size decreases to a certain value in the nanometer scale. Most of these anomalous phenomena of materials cannot be understood simply from the fact that the surface area relatively increases against the volume of materials with decreasing size⁽¹⁾⁻⁽⁸⁾.

Recently, atomic arrangements in localized regions such as the atomistic structure of ultra-fine materials, the atomic reconstruction of surface, etc., have been clarified by using various experimental methods⁽⁹⁾.

On the other hand, there are many phenomena suggesting the existence of the long range force (LRF) in the materials, *e.g.*, the formation of ordered lattice with a large spacing, the Ostwald type of crystals growth and so on. Total sum of LRF acting on each individual atom is quite large, because the number of neighboring atoms around each atom increases proportionally to the third power of a distance from the atom. And thus, the atomistic structure of materials is determined by the sum of these LRF even when the attenuation of LRF itself rapidly occurs. It is easily expected that both the atomistic and electronic structures of materials become so sensitive to the size of materials when the materials become smaller than the effective radius of LRF. Practically, the

materials consisting of $10^3 \sim 10^5$ atoms show a variety of anomalous behavior as if different new materials from bulk ones⁽⁶⁾⁻⁽⁸⁾. The number of constitutive atoms of such materials coincides with those of polymers in the small-number group and those of proteins in the large-number group, respectively. Both of these ultra-fine organic and inorganic materials show anomalous behavior, *i.e.*, the ultra-fine inorganic materials also behave like neo-molecules. This is one of the reasons why the ultra-fine inorganic materials are named "atom clusters" (AC)⁽⁶⁾⁻⁽⁸⁾.

In the present report, the anomalous behavior of these AC is described based mainly on the experimental results obtained by the ultra-high voltage electron microscope "micro-laboratory"⁽⁷⁾, and the physical meaning of the critical size of AC is discussed from a view point of the formation of hybrid orbitals.

II. Anomalous Behavior of Atom Clusters

The electronic structure of atoms markedly changes by the charge transfer when plural atoms interact with each other. Theoretical estimations of them have been carried out when the number of constitutive atoms is less than about $50^{(5)-(9)}$, but it becomes very difficult even in such

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small AC when the valence electrons increase in numbers. Therefore, in the present report, the behavior of AC will be discussed mainly on the basis of the experimental results.

As mentioned above, remarkable changes appear in the behavior when the materials become smaller than the corresponding critical sizes. Here, the critical size is named the “magic size” (d_M) of AC⁽⁶⁾⁻⁽⁸⁾. The value of d_M is a function of the surrounding condition of AC which is classified into the following two types; (a) embedded and (b) isolated ones. The behavior of each type of AC is shown below.

1. AC embedded in solids and/or liquids

The crystalline→amorphous transition (amorphization) is a typical example of the embedded AC. The present author and his coworkers have succeeded in making amorphous solids of both intermetallic compounds⁽¹⁰⁾⁻⁽¹²⁾ and ceramics⁽¹³⁾ by the high-energy electron irradiation induced atom-displacement (EII-AD) method. The EII-AD method has great advantages compared with other methods, such as liquid quenching, ion implantation and mixing, neutron mixing and others, in making non-equilibrium phases as follows: (a) Specimen damage and temperature rise of the specimens are extremely small. (b) Implanted depth of foreign atoms can easily be controlled in a wide range from the atomic scale to the 1 mm scale. (c) Ultra-fine fabrication in the 1 nm scale can be carried out. (d) Conditions of the specimen treatment are precisely controlled. (e) Foreign-atom implantation can be made from any place inside the solid as

well as the surface. Furthermore, in the EII-AD method, the details of the amorphization process can be continuously observed in the atomic scale by the electron microscopy. Namely, the EII-AD method is an indispensable tool for studying the amorphization process, and thus the method has widely been applied to examine the possibility of amorphization in more than 60 intermetallic compounds and more than 30 ceramics. Figure 1 is an example showing the amorphization process in a Ni-50 at%Ti alloy induced by electron irradiation at 2 MV and 170 K⁽⁶⁾. Here it is to be noted that this alloy can hardly be amorphized by the conventional liquid quenching method. High-resolution electron micrographs (c), (b) and (a) in Fig. 1 correspond to the beginning of amorphization, the partly amorphized stage and the completely amorphized one, respectively. The bright spots in (c) and dark ones in (b) represent atom-chains whose direction is perpendicular to the specimen surface. It should be noted in Fig. 1(b) that periodic arrays of the spots can be observed in very limited regions, as indicated with a white circle. Namely, the periodic arrays of atom-chains are observed only in regions whose size is larger than the critical one. The critical size for a Ni-50 at%Ti alloy is about 3 nm in diameter, as seen in Fig. 1(b).

Table 1 is parts of the experimental results obtained by the EII-AD method showing amorphization of intermetallic compounds⁽¹⁴⁾. In Table 1, various parameters, which have been considered up to date to determine amorphization, are listed at the upper part, and marks Am and No. Am show the compounds in which amorphization and no amorphization occur respectively. All the

Fig. 1 Crystalline→amorphous transition induced by electron irradiation at 2 MV and 170 K in a Ni-50 at%Ti alloy⁽⁶⁾. Each corresponding optical diffraction pattern is shown at the upper-left corner of the micrograph. A white circles in (b) shows the magic size of this alloy.

Table 1 Relationships between amorphization and various parameters in intermetallic compounds⁽¹⁴⁾. Marks Am and No. Am show the compounds in which amorphization and no amorphization occur respectively. Mark Δ shows an electronegativity difference between the two elements.

Compounds	Crystal structure	Transformation temp. (K)	Atomic size ratio	Δ	Extent of solubility (at%)	
Am	NiTi	B2	1583	1.18	0.2	< 1
	NiTi ₂	Eg ₃	1536	1.18	0.2	none
	Co ₂ Ti	C15	1523	1.18	0.1	none
	Fe ₂ Ti	C14	1700	1.16	0.1	5~6
	Mn ₂ Ti	C14	1598	1.13	0.2	7~8
	Cu ₃ Ti ₂	Os ₂ Al ₃	1143	1.15	0.3	none
	Cu ₄ Ti ₃	Cu ₄ Ti ₃	1191	1.15	0.3	none
	CuTi	B11	1177	1.15	0.3	4
	CuTi ₂	C11 _b	1288	1.15	0.3	3
	CuZr	CuZr	713	1.25	0.4	—
	Cu ₁₀ Zr ₇	Zr ₇ Ni ₁₀	—	1.25	0.4	—
	Zr ₂ Ni	C16	1413	1.28	0.3	none
	Nb ₇ Ni ₆	D8 ₅	1568	1.18	0.1	4
	MoNi	tetra.	1635	1.16	0.2	3
	Zr ₂ Al	C16	1523	1.12	0.1	none
No. Am	Ni ₃ Ti	DO ₂₄	1926	1.18	0.2	none
	FeTi	B2	1590	1.16	0.1	3
	CoTi	B2	1573	1.18	0.1	none
	Cr ₂ Ti	C15	1423	1.16	0	5
	Cu ₄ Ti	ZrAu ₄	1143	1.15	0.3	2
	Ni ₃ Al	Li ₂	1668	1.14	0.3	7
	NiAl	B2	1911	1.14	0.3	14
	CuZn	B2	1175	1.04	0.3	3
	Nb ₃ Sn	Al5	2393	1.10	0.2	8
	V ₃ Si	Al5	2208	1.02	0.1	1
	Zr ₃ Al	Li ₂	1248	1.12	0.1	none

parameters mentioned here appear reasonable ones, but actually none of them corresponds directly to amorphization, as can be recognized from Table 1. The result is probably due to selection of the specimens used. Namely, up to date, these parameters have been checked in the selected specimens which were already clarified their amorphization. This fact shows the followings: (a) In order to make clear the general rules controlling such a complex phenomenon as amorphization, the specimens themselves must also be selected from various crystals whose amorphization has not been made clear. (b) Amorphization must be carried out under accurately controlled conditions. Necessary conditions for amorphization, such as the dose rate and the accelerating voltage of electrons, the temperature and the reflecting condition of the specimen, etc., are accurately controlled in the EII-AD method, so that the amorphization can easily and exactly be checked in every kinds of the specimens. Therefore, the EII-AD method is considered to be superior to any other methods⁽¹⁴⁾.

Amorphization by the EII-AD method is very sensitive to the specimen temperature, and always occurs at low temperatures, as shown in Fig. 2⁽¹⁵⁾. Figure 2 shows the total dose of electrons necessary for amorphization as a function of the specimen temperature, in which marks A and C show the amorphous and crystalline materials re-

Fig. 2 Temperature dependence of crystalline $\rightleftharpoons$ amorphous transition⁽¹⁵⁾.

spectively. Furthermore, T_{am} shows the critical temperature below which amorphization occurs, and T_{cr} the critical one above which the crystallization of amorphous materials occurs only by heat treatment without electron irradiation. Namely, crystalline materials (C) change to amorphous ones (A) by electron irradiation when the specimen temperature is kept lower than T_{am} , but amorphization does not occur at temperatures higher than T_{am} . In the temperature range higher than T_{am} , amorphous materials (A) are crystallized in reverse by electron irradiation when the total dose of electrons reaches the solid line⁽¹⁵⁾. Namely, the crystallization temperature of amorphous materials under electron irradiation almost coincides with T_{am} which is considerably lower than T_{cr} . This is due to electron irradiation induced diffusion of atoms. Furthermore, Fig. 2 also shows that the total dose of electrons for amorphization rapidly decreases at first and reaches a constant value gradually when the specimen temperature decreases lower than T_{am} ⁽¹⁰⁾⁻⁽¹²⁾. Here, it is noted in Fig. 2 that the temperature of crystalline-amorphous transition, T_{am} , is clearly defined. The value of T_{am} is generally about 273 K in the intermetallic compounds⁽¹⁰⁾⁻⁽¹²⁾, and corresponds to a temperature at which mobility of vacancies is frozen.

Based on the experimental results obtained in both intermetallic compounds and ceramics, it is concluded that amorphization is determined by the following three general rules⁽⁶⁾⁽¹¹⁾:

Rule I: The crystal must be divided into ultra-fine blocks whose size is smaller than the corresponding magic size. When the material consists of more than two phases, each of these phases must be divided into their corresponding magic sizes.

Rule II: At least one of the constitutive atoms must take two or more coordination numbers, i.e., bonding modes, at the same time. Furthermore, amorphization becomes easier when the different constitutive atoms take a large separation in the periodic table, i.e., as the difference in the bonding mode increases.

Rule III: The material must be kept at low temperatures, i.e., lower than T_{am} , below which vacancies do not move. Under this condition, the following relationship

between the interatomic distance (D) and the coordination number (N) plays an important role⁽¹⁶⁾;

$$D = D_0 - \alpha \ln(i/N), \quad (1)$$

where D_0 : the interatomic distance at the maximum coordination number; i : the number of valence electrons; α : a positive empirical factor. The interatomic distance decreases in the vicinity of each individual vacancy because of the decrease of the coordination number, so that the periodic array of atoms is disturbed there. Thus, amorphization easily occurs along the lattice imperfections, such as dislocation lines, grain boundaries, interfaces and free surfaces^{(10)–(12)}, because the regular coordination number of the periodic array is not satisfied in these regions.

The above mentioned rules for amorphization must be satisfied in any other methods for amorphization such as liquid-quenching, vapour deposition, chemical reaction and others. For example, a Zr_3Al crystal is amorphized by absorbing H_2 -gas at about 600 K⁽¹⁷⁾⁽¹⁸⁾. In this process, two kinds of stable Zr-hydrides, i.e., γ (f.c.t.) and δ (f.c.c.) phases, are formed, but no Al-hydride is formed. Namely, in this case, Zr-atoms have two kinds of bonding modes at the same time against H-atoms. On the other hand, Al-blocks themselves must be smaller in size than the corresponding d_M , and they also divide those two types of Zr-hydrides into ultra-fine blocks

whose size is smaller than the corresponding d_M . This is the reason why amorphization of the Zr–Al system becomes difficult as the number of Al-atoms increases as in the case of a Zr_2Al crystal, and finally amorphization does not occur in a ZrAl crystal.

Furthermore, the Zr–Al crystals is also amorphized by absorbing O_2 -gas⁽¹⁵⁾⁽¹⁷⁾. In this process, two kinds of stable oxides, i.e., ZrO_2 and Al_2O_3 are formed, and thus O-atoms have two kinds of the bonding modes against both Zr- and Al-atoms so that they divide each other into the corresponding AC, whose size is smaller than each d_M . Therefore, amorphization most easily occurs when two elements Zr and Al are equal in the number of atoms, i.e., in a ZrAl crystal, as expected from Rule I.

As mentioned above, amorphization takes place in materials consisting of more than two elements in general. Even when the material consists of one kind of elements, however, amorphization is also expected to occur at the transformation temperature when the temperature is sufficiently low to suppress migration of the vacancies, because Rules II and III are also satisfied under this condition.

Another example of the embedded AC is the crystal nucleus formed by the reverse process of amorphization⁽⁶⁾⁽⁷⁾. Figure 3 is an example of crystal nucleation in an amorphous (Al_2O_3 - ZrO_2) composite^{(6)–(8)}, in which the lattice fringes appear in crystallized regions of ZrO_2 . In the

Fig. 3 Lattice fringes appearing in the crystal nuclei of ZrO_2 in an amorphous (Al_2O_3 - ZrO_2) composite⁽⁶⁾. Dotted and solid circles correspond to partly crystallized regions and the magic size of ZrO_2 crystals, respectively. The specimen was annealed at 1213 K for 1.8 ks.

specimen used for Fig. 3, ZrO_2 crystals are formed first. The incubation time for the growth is very large in the crystal nucleus of ZrO_2 and Al_2O_3 because of the low diffusion velocity of these elements, and thus the nucleus of each crystal takes the same size practically after a certain time of annealing in the specimens. Therefore, the maximum size of blocks in which the lattice fringes can be observed was decided as the nucleus size of ZrO_2 in Fig. 3. In Fig. 3, the partly crystallized region and the crystal nucleus corresponding to the magic size of ZrO_2 are indicated with a dotted and a solid circle respectively. It is noted in Fig. 3 that the diameter of solid circle, i.e., the nucleus size, is about 6 nm in diameter, and that the orientation of lattice fringes are different from each other in general when the solid circles are separated from each other, as seen in four solid circles on the right-hand side. On the contrary, their orientations coincide with each other when the solid circles slightly overlap each other, as seen in three solid circles on the middle left side. These facts mean that the coalescence among the embedded AC easily occurs when they contact each other. This is the same process as sintering of the isolated AC, as mentioned later.

According to the Rules of amorphization, the atomistic structure of AC can be estimated as follows⁽⁶⁾⁻⁽⁸⁾:

(a) The zigzag atom-chains are formed from the peripheral regions of AC along the radial direction, because the binding strength increases around atoms whose coordination number decreases by eq. (1). As a result, the interaction force among the zigzag atom-chains decreases like the van der Waals potential. (b) The atomic reconstruction occurs along the tangential direction of AC. (c) Since amorphous materials consist of these zigzag atom-chains, their density remarkably decreases down to 10^{-2} in the number density of vacancies, while the density is only 10^{-3} in vacancies even at the melting point. (d) When the Rules of amorphization are not satisfied, these zigzag atom-chains are not formed directly in AC but the similar atomic arrangements to the zigzag atom-chains result dynamically from the soft phonon mode in AC.

On the other hand, foreign-atom implantation by the EII-AD method has been developed⁽⁶⁾⁽¹⁸⁾⁽¹⁹⁾, and the size and distribution of embedded AC are exactly controlled by combination of this method and heat treatments⁽²⁰⁾.

2. AC isolated in gases and/or vacuum

When AC are kept in vacuum or gases, d_M of them becomes larger than those of the embedded ones because of the increased surface energy, as mentioned later. The isolated AC are convenient to study the anomalous behavior of AC themselves, and many interesting results have been obtained. A typical example is a phenomenon called "spontaneous alloying" or "spontaneous mixing" of the isolated AC⁽²¹⁾⁽²²⁾, as shown in Fig. 4. Figure 4(a) shows Au-atom clusters (Au/AC) which were vapour-deposited at room temperature on an amorphous carbon film. After that, Cu-atoms were vapour-deposited in vacuum onto the Au/AC at sub-zero temperatures,

i.e., below room temperature. Then Au-Cu alloys formed instantly, as seen in Fig. 4(b). At the same time, all the diffraction rings of Au/AC in Fig. 4(a') expand immediately after Cu-atoms are vapour-deposited, as seen in (b'), but any new diffraction rings of Cu-crystals do not appear; i.e., Cu-atoms are completely dissolved into the Au/AC to form nearly homogeneous solid solutions whose chemical composition is a function of not only the amount of vapour-deposited Cu-atoms but also the size and temperature of Au/AC.

The anomalous phenomenon mentioned above in the Au/AC also occurs instantly even at very low temperatures such as 165 K when the size of Au/AC is about 4 nm in diameter⁽²¹⁾. The same spontaneous alloying has been observed in various combinations of the different elements⁽²²⁾. And thus, this phenomenon is practically used for a new type of alloying method which can not be imagined from the current diffusion concept.

A mechanism of the spontaneous alloying can be recognized by using the similar model to the intercalation, as shown in Fig. 5. Here, the interatomic distance in AC is lengthened by more than a few %, especially at the peripheral regions, as expected from remarkable decrease of the melting temperature⁽²³⁾. Furthermore, the zigzag atom-chains are formed in AC along the radial direction, and the atomic reconstruction occurs along the tangential direction on the surface layers, as mentioned before. As a result of these facts, the phonon mode becomes extremely soft, especially at the peripheral regions. Figure 5 shows the atomistic structure of peripheral regions of AC whose relative displacement among constitutive atoms is a little bit exaggerated for clarity. Here, the zigzag atom-chains in Fig. 5 correspond to a real atomic arrangement in amorphous AC, and they are also caused dynamically by the soft phonon mode along each atom-chain consisting of a kind of elements. The atom-chains themselves in both cases always vibrate with a high-frequency to expand their interspacings by the soft phonon mode even at low temperatures. The negative charge is stored at the concaved parts of the atom-chains and the positive charge at the convexed parts in Fig. 5. Since the solute atoms with a large electronegativity against the solvent atoms are ionized negatively in the vicinity of the surface of AC, they are easily absorbed into AC by the interaction with the positive charge inside AC. When electronegativity of solute atoms is smaller than that of solvent atoms, they are absorbed into AC by the interaction with the negative charge inside AC.

When crystalline blocks of ordered structures become smaller than 3–5 nm in diameter, the order→disorder transition rapidly occurs so that the atomistic structure of compounds becomes unstable. The phenomenon is also due to the spontaneous mixing of solute atoms in AC, because d_M of these crystals is 3–5 nm in diameter, as mentioned later⁽⁶⁾⁽⁷⁾. Furthermore, there are other anomalous behavior of AC as follows: (a) Sintering among AC rapidly occurs even at sub-zero temperatures⁽²⁴⁾. (b) AC themselves easily change their own shapes under a very small applied force⁽²⁴⁾⁽²⁵⁾. Coalescence

Fig. 4 Spontaneous mixing of Cu-atoms into Au-atom clusters at 300 K⁽²²⁾. Micrographs (a) and (b) were taken before and after vapour-deposition of Cu-atoms onto Au-atom clusters. Diffraction patterns (a') and (b') correspond to micrographs (a) and (b), respectively.

among three embedded AC in Fig. 3 is an example of such sintering, as mentioned before. Fact (b) is also closely related with the atomistic structure of AC⁽⁶⁾⁽¹⁸⁾.

Furthermore, the secondary defects of point defects, i.e., a sort of AC in a reverse sense, induced by electron irradiation in f.c.c. crystals frequently cause hop-flip motion along the close-packed plane during irradiation, as seen in Fig. 6 (horizontal lines result from the scanning mode of TV system). Figure 6 shows successive stages of the hop-flip motion of the vacancy-type secondary defects in a Cu-crystal during electron irradiation at 2 MV and room temperature⁽²⁶⁾. It is noted in Fig. 6 that the real size of defects is smaller than that in the diffraction contrast, and that the hop-flip motion always takes place along the {111} planes, as indicated with arrows. Furthermore, the motion frequently occurs when the size of defects is considerably smaller than d_M of Cu-crystals. These facts will be discussed later.

III. Estimation of the Magic Size, d_M , in Various Materials

As mentioned above, the magic size of AC can be determined experimentally by both amorphization of crystalline materials and the crystallization of amorphous

materials. In the latter case, d_M , which corresponds to the crystal nucleus, can be determined more accurately than that in amorphization, because the lattice fringes in crystallized regions are not disturbed by electron irradiation in this method compared with that of amorphization by the EII-AD method, as seen in Fig. 3. The magic size of various materials can be accurately determined not only by the crystal nucleation in various crystals, liquids and vapours, but also by both the order-disorder transition and decomposition of various compounds. Because all of these phenomena always take place when the size is smaller than the corresponding d_M ⁽⁷⁾.

The magic size, however, should be defined as the critical size at which the materials behavior, such as sintering speed, alloying speed, and other physical parameters (except the mechanical strength and the magnetization) markedly changes⁽⁷⁾.

By observing the phenomena mentioned above, the magic size of various materials has been determined as a function of the bonding modes, binding force and the surrounding conditions, as shown in Table 2⁽⁶⁾⁽⁷⁾. Most of the magic sizes of the embedded AC shown in Table 2 were directly measured by observing the amorphization and crystal nucleation processes, and the others were estimated by comparing both the bonding mode and the

Fig. 5 Mechanism of spontaneous mixing of foreign atoms into atom clusters. Figures (a) and (b) correspond to the cases in which electronegativity of foreign atoms is higher and lower than that of the host-atoms in AC, respectively.

binding strength of unknown materials with those of known ones. On the other hand, most of the magic size of the isolated ones in Table 2 were also directly obtained from their critical size at which sintering speed abruptly increases, and the others were also estimated from difference in both the bonding mode and binding strength of materials in the same way mentioned above. Here, it is noted that the magic size is not necessarily correlated

Table 2 Magic size of various atom clusters as a function of the bonding mode, the binding strength and the surrounding condition.

Magic size (nm ϕ)		Bonding mode of materials
Isolated	Embedded	
20–10	8–4	Metallic and ionic bonding
10– 5	5–3	Intermetallic compounds
5– 2	3–1	Covalent and diamond bonding

with amorphization. Namely, all of the general rules must be satisfied to cause amorphization even when the material is smaller than the magic size.

It is also noted in Table 2 that the magic size in each group decreases not only with increasing the degree of covalent bonding but also with decreasing the coordination number⁽⁶⁾⁽⁷⁾. For example, the magic size of the isolated AC can be estimated to be $\phi 15 \sim 20$ nm in f.c.c. metals, $\phi 10 \sim 15$ nm in b.c.c. metals, $\phi 15 \sim 20$ nm in Al_2O_3 , and $\phi 3 \sim 5$ nm in TiC and SiC, respectively. In the embedded AC, it is about $\phi 2$ nm in Si and about $\phi 1$ nm in diamond.

IV. Discussions

In the present report, it was shown that AC show various anomalous phenomena as if they are new materials, and that the magic size, d_M , is clearly defined as the critical one at which the material behavior markedly changes. Physical meaning of the magic size of AC is discussed in terms of the many body potential.

1. Effect of surface and/or interface on the behavior of materials

It is well known that the surface has a different behavior from that of the interior of materials. When the number of atoms consisting of the surface (S) becomes larger than that of the interior (I) of materials, the material behavior is considered to be quite different from that of bulk ones irrespective of the sort of materials⁽³⁾⁽⁴⁾. Ultra-fine materials whose values of I/S are smaller than unity

Fig. 6 Hop-flip motion of the vacancy-type secondary defects in a Cu-crystal under electron irradiation at 2 MV⁽²⁶⁾.

have been named the “micro-clusters”⁽³⁾⁽⁴⁾. This condition is satisfied when the number of constitutive atoms becomes smaller than about 5×10^2 atoms. As shown in Table 2, however, the actual values of d_M depends on the kind of constitutive atoms. Namely, they change from $\phi 1$ nm to $\phi 20$ nm, which correspond to $10^3 \sim 10^5$ atoms, depending on both the bonding mode and the binding strength. The difference between the theoretical and the actual values of the magic size is considered to be mainly due to the following two factors⁽⁶⁾⁽⁷⁾:

(a) Size effect on both the specific volume free energy difference ($\Delta\epsilon_v$) and the specific surface energy (γ_s) of AC: In AC of radius r , both $\Delta\epsilon_v$ and γ_s become very sensitive to the size when $2r < d_M$, as shown experimentally in the nucleation process of recrystallization⁽²⁷⁾⁽²⁸⁾. Furthermore, both of them are closely related to each other⁽⁶⁾.

(b) Effects of both the bonding mode and the binding strength on the value of d_M : The many body effect can be estimated from difference in the binding strength between diatomic molecules and bulk materials, as shown in Table 3⁽²⁹⁾. In Table 3, it is shown that the many body effect relatively increases with increasing ratio of the latter against the former. Namely, the metallic and ionic bondings are the most sensitive to the many body potential. The ratio decreases in the covalent bonding, and becomes smaller than unity in the molecular bonding.

Now, the effective radius of LRF is assumed to be Λ , as shown in Fig. 7. When the radius of AC becomes just 2Λ , the bonding potential ($\Delta\epsilon_v$) resulting from the many body potential takes the same amount as that of bulk material (Q) at the center atom, and gradually decreases to that of the matrix along the radial direction, as shown in Fig. 7(a)⁽⁶⁾⁽¹¹⁾. In case the radius of AC increases more than Λ , as shown in Fig. 7(b), the equi-potential region of Q expands to take the periodic array of atoms, as shown with a horizontal hatching in Fig. 7(b). According to this model, d_M is considered to correspond to 2Λ . The value of $d_M/2$ varies depending on the sort of constitu-

Table 3 Binding strength in diatomic molecules and the corresponding bulk materials⁽²⁹⁾. Each block in the table corresponds to the metallic, ionic, covalent and molecular bonding, respectively.

Constitutive atoms	Bonding strength (Kcal/mol)	
	Diatomic molecule	Bulk materials
Al-Al	44.5	78
Ti-Ti	33.8	112
Ag-Ag	39	68
Au-Au	53.8	88
U-U	53	126
Au-Al	77.9	—
Na-Cl	98	183
Ag-Cl	81.6	205
Ag-Br	70	200
Ag-I	56	200
B-B	71	134
C-C	145	171
Si-Si	78	107
Ge-Ge	65	90
H-H	104	52
O-O	119	59
S-S	101	66
P-P	117	79

tive atoms in the range from about 2 nm to 4 nm in the embedded AC of metals, and thus the cause of such large LRF must be considered, while they are reasonably recognized in the inorganic AC of Columdum type whose Madelung constant is larger than 20. The physical meaning of such large Λ in metallic bonding is discussed in the following sections.

It is shown in Fig. 6 that the secondary defects of vacancies, i.e., a sort of voids, in a Cu-crystal make the hop-flip motion under electron irradiation. Now, the diameter of void is assumed to be about a half of d_M , i.e., Λ , of Cu-crystals, and then all atoms located on the surface of void take a sufficiently large sum of LRF, which is

Fig. 7 Relationship between the magic size and the effective radius of long range force (Λ).

very close to that of the periodic array of Cu-crystals, from the neighboring atoms, as recognized in Fig. 7(a). As a result, the bonding potential of these atoms becomes extremely smaller than that of the free surface, as expected from Fig. 7(a). Since the close-packed plane of the crystal shows the minimum potential barrier for the surface migration of atoms, the surface diffusion of atoms is expected to rapidly occur along the close-packed plane under such a small applied force as electron irradiation. This is considered to be a reason why the void can rapidly change its position under the condition mentioned above.

2. Atomistic and electronic structures of AC

(1) Atomistic structures of ultra-fine AC

Recently, it has been shown that the materials take different atomistic structures from those of bulk ones when the number of constitutive atoms (n) is very small, i.e., smaller than about $10^{(5)(9)}$. Here, such ultra-fine AC are named “micro-atom clusters” (micro-AC). A typical example is the case of Co/micro-AC⁽⁵⁾. The atomistic structure of Co/micro-AC takes a triangle one at $n=3$, a tetrahedron one at $n=4$, an icosahedral one at $n=12$, and then an atom occupies at the core of icosahedral structure at $n=13$. Another example is Cu/micro-AC⁽³⁰⁾ in which the atomistic structure is a linear one at $n=4$, polyhedral ones at $n \geq 5$, and an icosahedral with an atom at the core at $n=13$. Silicon and other micro-AC take the similar closed-shell structures of atoms when the constitutive atoms reaches at least 13 in the number⁽⁴⁾. Namely, the materials do not take their own periodic structures in general until the number of constitutive atoms reaches at least more than 13. When the constitutive atoms take a stable molecular structure like C₆₀, the critical number for taking the periodic structure will be higher.

These facts mentioned above suggest that the van der Waals potential is still important in these micro-AC.

(2) Excitation energy necessary for formation of the crystal structure in AC

The periodic structures of metallic crystals is determined by the Engel's relationship in general⁽³¹⁾. An isolated atom takes the ground state of electrons which is different from that of the crystal in general. Thus, the valence electrons of each individual atom must be excited to the energy level corresponding to the electronic structure of crystal. Table 4 shows some examples of such excitation in Na-, Mg- and Al-crystals⁽³¹⁾. In Table 4, it is noted that 335 kJ/mol is necessary for the valence electrons to be excited from ($3s^2$) to ($3s^1, 3p^1$) in Mg-atoms in a h.c.p. structure, and 347 kJ/mol from ($3s^2, 3p^1$) to ($3s^1, 3p^2$) in Al-atoms in a f.c.c. structure. Furthermore, according to the Engel's relationships, the excitation of valence electrons from the s-state to the d-state is also necessary for metals with b.c.c. structures in general, as shown in Table 5.

As mentioned above, in order to establish each crystal structure, the valence electrons of each individual atom

Table 4 Excitation from the ground state to the energy level corresponding to the electronic structure of crystal⁽³¹⁾. The table shows the excitation energies for Na-, Mg- and Al-crystals, respectively.

Element	Na		Mg		Al	
	3s	3p	3s	3p	3s	3p
Ground state	⋯⊗	○○○	⋯⊗	○○○	⋯⊗	○○○
Bonding state	⋯⊗	○○○	⋯⊗	○○○	⋯⊗	○○○
Excitation energy [kJ/mol]		0		335		347
The number of s- and p-electrons		1		2		3
Crystal structure		bcc		hcp		fcc

Table 5 Crystal structures of Fe, Ti and Zr as a function of electronic structures by the Engel's relationship.

Fe: K, L, $3s^2, 3p^6, 3d^6, 4s^2$ $4s^2, 3d^6 \rightarrow 4s^1, 3d^7$ (b.c.c.) $\rightarrow 4s^1, 3d^5, 4p^2$ (f.c.c.)
Ti: K, L, $3s^2, 3p^6, 3d^6, 4s^2$ $4s^2, 3d^2 \rightarrow 4s^1, 3d^3$ (b.c.c.) $\rightarrow 4s^1, 3d^2, 4p^1$ (h.c.p.)
Zr: K, L, M, $4s^2, 4p^6, 4d^2, 5s^2$ $5s^2, 4d^2 \rightarrow 5s^1, 4d^3$ (b.c.c.) $\rightarrow 5s^1, 4d^2, 5p^1$ (h.c.p.)

must be excited from the ground state to the necessary one corresponding to the periodic structure of atoms. This is the formation of the hybrid orbital of valence electrons corresponding to the crystal structure. The activation energy of excitation is a few hundred kJ/mol, i.e., a few eV/atom, in general, as mentioned above.

Here, the thermal energy kT (k : Boltzmann constant) is very small compared with that for the formation of hybrid orbital in general, i.e., less than 20 kJ/mol even at $T=1000$ K. This means that the many body potential is necessary for the formation of hybrid orbital, and that the value of d_M of AC is not sensitive to the temperature, i.e., it is almost constant in a wide temperature range of a few hundred K. From the same reasoning, it is concluded that the size of crystal nucleus, which corresponds to AC of d_M in diameter, in crystalline materials is not so sensitive to the degree of super-cooling either.

(3) Formation of the hybrid orbital by the many body potential

As mentioned above, the formation of hybrid orbitals is necessary for all metallic elements in order to take their own crystal structures. Recently, the many body effect has been calculated in some simple cases⁽³²⁾. The results show that the width of each energy band of electrons increases with increasing the number of constitutive atoms, i.e., increase of the many body potential. Namely, the upper level of each band increases but the lower one decreases with increasing the many body potential. When the lower level of the upper energy band coincides with the Fermi energy of the valence electrons, the charge transfer becomes possible to form the hybrid orbitals. The change of energy level due to the many body potential, however, must be larger than a few hundred kJ/mol, and thus the number of neighboring atoms must

increase at least more than 13 in metallic elements, as mentioned before.

3. Various effects on the formation of hybrid orbital

In the present report, the value of d_M under various conditions are shown in Table 2. Based on these data, the critical number (n_c) of constitutive atoms for the formation of hybrid orbital can be roughly estimated.

(1) Effect of the free surface and/or interface on the formation of hybrid orbital

Now, a material consisting of one kind of atoms is assumed to take a nearly random close-packing structure whose coordination number is about 12. Under this condition, the hybrid orbital corresponding to its own crystal structure is considered to be formed when the number of neighboring atoms reaches the critical one, n_c , which corresponds to the number of atoms filled up a sphere of radius r_c .

On the other hand, the atomistic and electronic structures near the surface and/or interface of AC are markedly changed because of the discontinuity of atomistic structures through the surface layer. This is the cause of the surface and/or interfacial energy. Therefore, all neighboring atoms around the center atom is strongly affected by the surface structures so that the formation of hybrid orbital becomes difficult even inside the sphere of radius r_c . In order to establish the necessary hybrid orbital inside the sphere of radius r_c , each atom located on the spherical surface at distance r_c from the center should be surrounded with the same number of atoms (n_c) as that of the center atom, to the first approximation. Namely, it is considered that a buffer zone whose thickness is r_c^* is necessary to relieve the surface effect on the formation of hybrid orbital, as shown in Fig. 8.

Under this condition, d_M of the isolated AC can be expressed by

$$\begin{aligned} d_M(\text{isolated AC}) &= 2\Lambda = 2(r_c + r_c^*) + a \\ &= (4P + 1)a, \end{aligned} \quad (2)$$

where a is an atomic diameter, $r_c \approx r_c^*$ and $P = r_c/a$.

Since the surface effect is considered to be proportional to the surface energy, $(r_c + r_c^*)$ in the embedded AC is assumed to be a half of that of isolated AC, because the interfacial energy is about a half of the surface one in general⁽³³⁾. Namely, d_M of the embedded AC can be expressed by

$$d_M(\text{embedded AC}) = 4Pa/2 + a = (2P + 1)a. \quad (3)$$

(2) Shape effect on the formation of hybrid orbital

As mentioned above, the formation of hybrid orbital is strongly affected by the surface and/or interface. The effect of the surface and/or interface on the value of d_M also depends on the shape of AC. Typical shapes of AC are classified into the following three types; two-dimensional, one-dimensional and extremely fine three-dimensional, i.e., so called zero-dimensional ones, as shown in

Fig. 8 Necessary condition for the formation of hybrid orbital in an atom cluster. Spheres of radius r_c and $(r_c + r_c^*)$ correspond to the critical number of atoms for the formation of hybrid orbital under no effect and the effect of the surface and/or interface of AC, respectively.

Figs. 9(a), (b) and (c).

The two-dimensional AC consist of a sufficiently large amount of constitutive atoms along the two-dimensional atomic plane, and thus both the spacing and relative shift among these atomic planes are affected by the surface. The relative shift causes the two-dimensional lattice strain, such as the atomic reconstruction on the surface and the formation of dislocations along the interface, and then the effect of surface will be considerably relieved in a few atomic layers even when the change of spacing among atomic planes is taken into account.

In the case of one-dimensional AC, the atom-chains along the close-packed direction can also be shifted relatively even on the close-packed planes as well as the change of spacing by the surface effect. Therefore, the surface effect markedly increases so that the affected range expands into a wide region. Furthermore, in the case of zero-dimensional AC, not only each atom-chain is relatively shifted three-dimensionally but also their spacing is also widely changed by the surface effect, because the surface effect extremely increases three-dimensionally to expand the affected range. This is considered to result in the formation of zigzag atom-chains.

As mentioned above, it is considered that the atomistic structure also strongly depends on the shape of AC, and that the value of n_c in AC increases as the relative shift among atom-chains becomes complex and large. When the number of constitutive atoms becomes $10^3 \sim 10^5$, it is very difficult now to calculate the surface and interface effect accurately. Here, the surface effect is roughly assumed to be proportional to the ratio of surface area against the volume of AC. The value of ratio becomes 1:2:3 in the two, one and zero-dimensional AC, as shown in Fig. 9. Furthermore, in addition to the rough assumption, eqs. (2) and (3) are considered to be also applicable. Under such conditions, d_M of these three-shapes of AC

Shape of AC	Two-dimensional	One-dimensional	Zero-dimensional
Surface/Volume Ratio	$2 \times t^2 / t^3 = 2/t$	$2\pi(t/2)t / \pi(t/2)^2 t = 4/t$	$4\pi(t/2)^2 / 4/3\pi(t/2)^3 = 6/t$

Fig. 9 Shape effect on the atomistic structure of atom clusters. Figures (a), (b) and (c) show the two-, one- and zero-dimensional atom cluster respectively, and the ratio of surface area against volume of each atom cluster is listed in the lower table.

can be estimated for various constitutive atoms, as shown in Table 6 in which the atomic diameter is varied from 0.25 ~ 0.35 nm.

By comparing these values in Table 6 with actually estimated values, i.e., d_M of the zero-dimensional AC, in Table 2, both the value of P in eqs. (2) and (3) and the corresponding d_M of two- and zero-dimensional AC can be estimated.

In the case of embedded AC, i.e., $d_M = (2P + 1)a$, the value of P for various metals and alloys is estimated as follows: It is 1 ~ 2 for intermetallic compounds, 1.5 ~ 2.5 for b.c.c. metals and 2.5 ~ 3.5 for f.c.c. metals respectively when the atomic diameter varies from 0.3 to 0.35 nm in diameter. The magic size (d_M) of two-dimensional AC sandwiched with other crystals can also be estimated from these data, i.e., it is 3 ~ 5, 4 ~ 6 and 6 ~ 8.5 atomic layers for intermetallic compounds, b.c.c. and f.c.c. metals, respectively.

By the same method, P of the isolated AC having various shapes can also be estimated from Table 6.

Estimation of the value of P has been carried out so roughly, but the estimated values themselves seem to be reasonable. And thus, it is considered that the effective radius of LRF (Λ) is determined by the parameters mentioned above, and that d_M of various shapes of AC can be estimated from those obtained with one shape of AC. Furthermore, d_M of crystalline materials corresponds to the crystal nucleus size, and thus various nucleus sizes involving the martensite crystals can also be estimated by the same method.

(3) Relationship between the magic size (d_M) and the magic number of AC

As mentioned in the present report, the formation of necessary hybrid orbital is hardly possible when the number of constitutive atoms of AC becomes very small, i.e., in micro-AC. In such micro-AC, so called "the magic

number" has been frequently observed⁽³⁾⁻⁽⁵⁾. On the other hand, "the magic size" is defined as the critical size at which the number of constitutive atoms, i.e., the many

Table 6 Estimation of the magic size as a function of $P(=r_c/a)$ in the two- and zero-dimensional atom clusters. In the table, $d_M^2(e)$ and $d_M^2(i)$ show the magic sizes of the two-dimensional embedded and isolated atom clusters, and $d_M^0(e)$ and $d_M^0(i)$ those of the zero-dimensional embedded and isolated atom clusters, respectively.

P	0.5	1	1.5	2	3	4	5	6	7	8
The number of atomic layers										
$d_M^2(e)$	2	3	4	5	7	9	11	13	15	17
$d_M^2(i)$	3	5	7	9	13	17	21	25	29	33
$a = \phi 0.25$ nm										
$d_M^2(e)$	0.5	0.7 ₅	1	1.2 ₅	1.7 ₅	2.2 ₅	2.7 ₅	3.2 ₅	3.7 ₅	4.2 ₅
$d_M^2(i)$	0.7 ₅	1.2 ₅	1.7 ₅	2.2 ₅	3.2 ₅	4.2 ₅	5.2 ₅	6.2 ₅	7.2 ₅	8.2 ₅
$d_M^0(e)$	1.5	2.2 ₅	3	3.7 ₅	5.2 ₅	6.7 ₅	8.2 ₅	9.7 ₅	11.2 ₅	12.7 ₅
$d_M^0(i)$	2.2 ₅	3.7 ₅	5.2 ₅	6.7 ₅	9.7 ₅	12.7 ₅	15.7 ₅	18.7 ₅	21.7 ₅	24.7 ₅
$a = \phi 0.3$ nm										
$d_M^2(e)$	0.6	0.9	1.2	1.5	2.1	2.7	3.3	3.9	4.5	5.1
$d_M^2(i)$	0.9	1.5	2.1	2.7	3.9	5.1	6.3	7.5	8.7	9.9
$d_M^0(e)$	1.8	2.7	3.6	4.5	6.3	8.1	9.9	11.7	13.5	15.3
$d_M^0(i)$	2.7	4.5	6.3	8.1	11.7	15.3	18.9	22.5	26.1	29.7
$a = \phi 0.35$ nm										
$d_M^2(e)$	0.7	1.0 ₅	1.4	1.7 ₅	2.4 ₅	3.1 ₅	3.8 ₅	4.5 ₅	5.2 ₅	5.9 ₅
$d_M^2(i)$	1.0 ₅	1.7 ₅	2.4 ₅	3.1 ₅	4.5 ₅	5.9 ₅	7.3 ₅	8.7 ₅	10.1 ₅	11.5 ₅
$d_M^0(e)$	2.1	3.5 ₅	4.2	5.2 ₅	7.3 ₅	9.4 ₅	11.5 ₅	13.6 ₅	15.7 ₅	17.8 ₅
$d_M^0(i)$	3.1 ₅	5.2 ₅	7.3 ₅	9.4 ₅	13.6 ₅	17.8 ₅	22.0 ₅	26.2 ₅	30.4 ₅	34.6 ₅

body potential, reaches a sufficient value for the formation of necessary hybrid orbital. Namely, the magic size of crystalline materials corresponds to the nucleus one.

Figure 10 shows the relationship between the magic number and the magic size. Suppose isolated atoms taking the ground state interact with one another to form an ultra-fine AC. In this case, the closed-shell structure of valence electrons is formed when the total number of valence electrons becomes 8, 20, 40, 58, 70, ...⁽³⁴⁾. The closed-shell structure of electrons, however, does not appear so clearly when each atom has many valence electrons, but the closed-shell structure of constitutive atoms is formed at 13, 55, 147, ... in the number of atoms⁽³⁵⁾. The closed-shell structure of atoms is also formed in AC taking the closed-shell structures of electrons when the number of constitutive atoms increases⁽³⁶⁾.

When the number of atoms increases so that the size of AC approaches to d_M , the corresponding hybrid orbital is formed at the center by the many body potential, and then the hybridized region expands to the peripheral regions of AC because of decreasing the volume free energy difference. After that, the many body potential reaches a fixed value corresponding to that of the crystal inside AC except the peripheral regions. This is the formation of crystal nucleus which can grow further easily.

On the contrary, when the size of AC becomes smaller than the corresponding magic size, the hybrid orbital is rapidly decomposed from the surface and/or interface, and contribution of the van der Waals potential increases in the bonding potential among the atoms as the number

of constitutive atoms decreases. As a result, the behavior of bulk materials including various physical parameters, such as the periodic array of atoms, the diffusion coefficient, the magnetic strength, the electric resistivity, the rigidity of modulus and so on, markedly change as the size of AC decreases from d_M .

The closed-shell structures of both electrons and atoms are stable at the corresponding magic numbers of atoms in the ultra-fine AC⁽³⁴⁾⁻⁽³⁶⁾. However, when the number of electrons and/or atoms deviates from these magic numbers, the surface reactions such as the catalysis and other chemical reactions become very active, especially in the former case. Therefore, the ultra-fine AC, whose behavior is determined by the magic number, may well be called "micro-AC" in AC group, as mentioned before.

V. Conclusions

In the present report, the anomalous behavior of embedded and isolated types of AC was shown, and discussed from a view point of the many body potential. The relationship between the magic size and the magic number of AC was also discussed. Namely, the former corresponds to the nucleus size of crystals, and the latter the formation of closed-shell structures of valence electrons and/or atoms.

The behavior of AC is determined by distribution of the local bonding potential in AC, as recognized in Fig. 7(a). Since a spherical AC is considered to consist of multi-layered spherical shells, the local bonding poten-

Fig. 10 Relationship between the magic number and the magic size. The magic number corresponds to the formation of closed-shell structures of both valence electrons and constitutive atoms. The magic size corresponds to the crystal nucleus in which the hybrid orbital of the crystal is formed.

tial varies from that of the centered atom to that of the surrounding matrix. Suppose AC and the matrix crystal consist of A- and B- atoms respectively, and the former is embedded into the latter. Then, the behavior of AC of A-atoms changes from that of the crystal of A-atoms to that of the crystal of B-atoms when the bonding potential of the centered A-atom reaches that of the corresponding crystal (Q), as seen in Fig. 7. Namely, any behavior ranging between those of A- and B-crystals can be realized at a part of the embedded AC of A-atoms. This means that theoretically various new materials consisting of different elements from those in the periodic table can be realized infinity in local regions of AC.

When the materials consisting of different kinds of AC they also show anomalous behavior, which is different from those of A- and B-crystals, depending on the bonding potential of the centered atom of each individual AC. Amorphous materials are one of such cases.

Furthermore, new methods for making new functional materials are realized by using the anomalous behavior of AC as follows⁽⁶⁾⁽⁸⁾⁽¹⁸⁾: A new type of crystal growth, rapid and low temperature sintering, a new alloying method, formation of various non-equilibrium phases such as amorphous materials and super-saturated solid solutions, and others.

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REFERENCES

- (1) *Ultra-Fine Particles*, a special issue of Solid State Physics, AGNE Publ. 1984.
- (2) *Ultra-Fine Particles—Science and Its Applications*, Jpn. Chemical Soc., the Elements of Chemistry, No. 48 (1985).
- (3) *Micro-Clusters*, ed. A. Sugano, a special issue of Butsuri, Phys. Soc. Jpn. (1987).
- (4) T. Kobayashi: *Frontiers of Physics*, No. 16 (1986), 57; A. Sugano: *ibid*, No. 25 (1989), 64.
- (5) O. Kajimoto: *Chemistry of Clusters*, Baifuh-Kan Publ., 1992.
- (6) H. Fujita: *Mater. Trans., JIM*, 31 (1990), 523.
- (7) H. Fujita: *Ultramicroscopy*, North-Holland Phys. Publ., 39 (1991), 369.
- (8) H. Fujita: *Surface*, 29 (1991), 209.
- (9) S. Tsukada: *Introduction of Surface Physics*, Tokyo Univ. Publ., 1989.
- (10) H. Mori and H. Fujita: *Jpn. J. Appl. Phys.*, 21 (1982), L494.
- (11) H. Fujita: *J. Electr. Microsc. Techn.*, 3 (1986), 45.
- (12) H. Mori and H. Fujita: *Proc. JIMIS-5 "Non-Equilibrium Solid Phases of Metals and Alloys"*, Suppl. Trans. JIM, 29 (1988), 93.
- (13) H. Fujita: *Electron Microscopy*, Electr. Microsc. Soc. Jpn., 23 (1988), 103.
- (14) H. Fujita: *Proc. New Materials '88, 2nd Int. New Materials Conf.*, Osaka, (1988), 274.
- (15) H. Fujita: *Proc. 11th Int. Cong. on Electr. Microsc.*, Kyoto, 2 (1986), 1025.
- (16) L. Pauling (trans. M. Koizumi): *Theory of Chemical Bonding*, Kyoritsu Publ., (1960), 210; 363.
- (17) H. Fujita: *J. Electr. Microsc. Techn.*, 3 (1986), 243.
- (18) H. Fujita: *ISIJ International*, 30 (1990), 70.
- (19) H. Fujita: a special issue "Micro-Laboratory", AGNE Publ., No. 9 (1993), 2.
- (20) H. Fujita and H. Mori: *Proc. JIMIS-5 "Non-Equilibrium Solid Phases of Metals and Alloys"*, Suppl. Trans. JIM, 29 (1988), p. 37.
- (21) H. Mori, M. Komatsu, K. Takeda and H. Fujita: *Phil. Mag. Lett.*, 63 (1991), 173.
- (22) H. Yasuda, H. Mori, K. Takeda and H. Fujita: *Proc. DIMAT-92, Defect and Diffusion Forum*, 95-98 (1993), p. 697.
- (23) D. A. Buffet and J. P. Boel: *Phys. Rev.*, A13 (1976), 2289.
- (24) K. Takayanagi, Y. Tanishiro, K. Kobayashi, K. Akiyama and K. Yagi: *Jpn. J. Appl. Phys.*, 26 (1987), L957.
- (25) S. Iijima: *J. Electr. Microsc.*, 40 (1985), 246; *Phys. Rev. Letters*, 56 (1986), 616.
- (26) H. Fujita, T. Sakata and H. Fukuyo: *Jpn. J. Appl. Phys.*, 21 (1982), L235.
- (27) H. Fujita: *J. Phys. Soc. Jpn.*, 16 (1961), 397.
- (28) H. Fujita: *J. Phys. Soc. Jpn.*, 26 (1969), 1437.
- (29) J. A. Kerr: *CRC Handbook of Chemistry and Physics*, 71th Edition, CRC Press, (1990/1991), p. 9-86.
- (30) J. Demuyck, M. M. Rohmer, A. Strich and A. Veillard: *J. Chem. Phys.*, 75 (1981), 3443.
- (31) For example, G. C. Pimentel and R. D. Spratly (trans. H. Chihara and T. Ohnishi): *Chemical Bonding*, Tokyo Kagaku-Dojin Publ., (1982), p. 255.
- (32) *ibid*, (1982), p. 255; 248.
- (33) G. A. Somorjai: *Chemistry in Two-Dimensions—Surfaces*, Cornell Univ. Press, (1981), p. 31.
- (34) W. D. Knight, W. A. de Heer and W. A. Saunders: *Z. Phys.*, D-3 (1986), 109.
- (35) W. Miehe, O. Kandler, T. Leisner and O. Echt: *J. Chem. Phys.*, 91 (1989), 5940.
- (36) T. P. Martin, T. Bergmann, H. Gohlich and T. Lange: *J. Phys. Chem.*, 95 (1991), 6421.