

“Back to the Future”—An Account Discovery of Stable Quasicrystals

AN-PANG TSAI*

National Institute for Materials Science, Sengen 1-2-1, Tsukuba 305-0047, Japan

Received August 9, 2002

ABSTRACT

In this Account, I will describe the discoveries of a series of stable quasicrystals in which I participated during the past 15 years. These discoveries led to a paradigm shift in the field of quasicrystals. The story started when I was a graduate student, has continued into the present, and may continue into the future. Of these discoveries, some were made independently by myself and some in collaboration with my colleagues. As it happens, I am the only one related to all of these discoveries, and so it seems appropriate that I tell the stories.

Background

Crystals are composed of identical building blocks called unit cells, each fitting together with its neighbor in the same way on a lattice. By the definition of crystallography, only 1-fold, 2-fold, 3-fold, 4-fold, and 6-fold axes are allowed in crystals. To illustrate the concept of restriction of rotational symmetry in a lattice, consider the two-dimensional lattice in Figure 1a. Using a triangle or a square (also oblique, diamond, and rectangle) as a unit cell, one can form a lattice, and each unit cell has surroundings identical to those of every other unit cell. On the other hand, in Figure 1b, when a unit cell with 5-fold symmetry is used to try to form a lattice, the pentagonal tiles do not fit together to fill the plane, nor do all the pentagonal tiles have the same surroundings as every other tile. The symmetry of crystals has been clearly evident in the symmetry of their diffraction patterns. Since amorphous materials diffract X-rays in only a diffuse ring, it is commonly believed that only crystals could produce a diffraction pattern of spots. Thus, in a system where crystals are defined as being structures based on a lattice, 5-fold symmetry was not allowed in solids. In 1984, the world of solid-state physics was surprised by observations of 5-fold symmetry in an electron diffraction pattern for an Al–Mn alloy, an-

nounced by Shechtman et al.¹ Figure 1c is a typical electron diffraction pattern along a 5-fold axis of a quasicrystal. Note that spots of the pattern appear at 5-fold symmetrical positions and are arrayed in a nonperiodic way with a violation of τ , where $\tau = (1 + 5^{1/2})/2$ is a golden ratio. Detailed investigation showed that the Al–Mn alloy has the symmetry of an icosahedron. Essentially there are two formal definitions of a quasicrystal:² (1) a quasicrystal is a quasiperiodic structure with a crystallographically disallowed rotational symmetry, and (2) a quasicrystal is a structure whose scattering amplitude is given by a discrete sum of Bragg peaks.

After the revolutionary discovery of the Al₆Mn quasicrystal by Shechtman et al., a number of attempts were made to find other quasicrystalline phases by substituting other transition metals for Mn, or by adding metalloids. These attempts led to the discovery of a number of metastable quasicrystals. It was also found that the equilibrium states of the metastable quasicrystals are generally crystalline compounds, called crystalline approximants. A crystalline approximant is a compound whose composition and structural unit are very similar to those of a quasicrystal, but nevertheless it is a crystal. The structures of crystalline approximants have been well defined and have been analyzed locally as icosahedral clusters. Since the quasicrystalline phases could be obtained by conducting rapid solidification from the crystalline approximants, the quasicrystalline phases were realized to be energetically nonequilibrium phases or metastable phases with respect to the corresponding crystalline approximant. The icosahedral glass model was regarded as very promising to describe the structure of quasicrystals, since it could incorporate the icosahedral subunits of the crystalline approximant and could also explain the broad diffraction peaks observed experimentally for all quasicrystals known prior to 1987. However, this picture changed radically after the discovery of a number of stable quasicrystals, starting in 1987.

1986–1989

1. Al–Cu–Fe. Upon reading a paper by Henley and Elser that pointed out the relationship between quasicrystals and certain crystalline compounds,³ I was inspired to search for crystalline compounds with large lattice parameters and local units with 5-fold symmetry. I noted the existence of the crystalline compound, tetragonal Al₇Cu₂Fe₁, with lattice parameters $a = 0.634$ nm and $c = 1.487$ nm.⁴ The structure also contained pentagonal atomic units. Rapid solidification of this composition formed a mixture of a quasicrystalline matrix and an amorphous phase in the grain boundaries. The quasicrystal had a composition close to Al₆₅Cu₂₀Fe₁₅. I then prepared a composition of Al₆₅Cu₂₀Fe₁₅ and performed melt-spinning of the alloy.⁵ As expected, a mostly single quasicrystalline phase with grains of the size of a few tens of micrometers

An-Pang Tsai, born in Taiwan on December 26, 1958, is the Director of the Aperiodic Materials Research Group in the National Institute for Materials Science (NIMS) in Japan. He is also the Research Director of “Quasicrystals Project”, supported by “SORST” of Japan Science and Technology Corporation. He received his B.S. degree from the Department of Metallurgy at Akita University and his Ph.D. degree from the Department of Materials Physics at Tohoku University in 1990. He was an Associate Researcher and then an Associate Professor at the Institute for Materials Research in Tohoku University from 1990 until 1996. In April 1996, he joined the National Research Institute for Metals (NRIM, now NIMS) in Tsukuba. His main research interests include the formation, stability, structure, phase transformations, and physical properties of quasicrystalline and nonequilibrium alloys.

* Fax: +81-298-59-2301. Tel.: +81-298-59-2345. E-mail: aptsai@quasi.nims.go.jp.

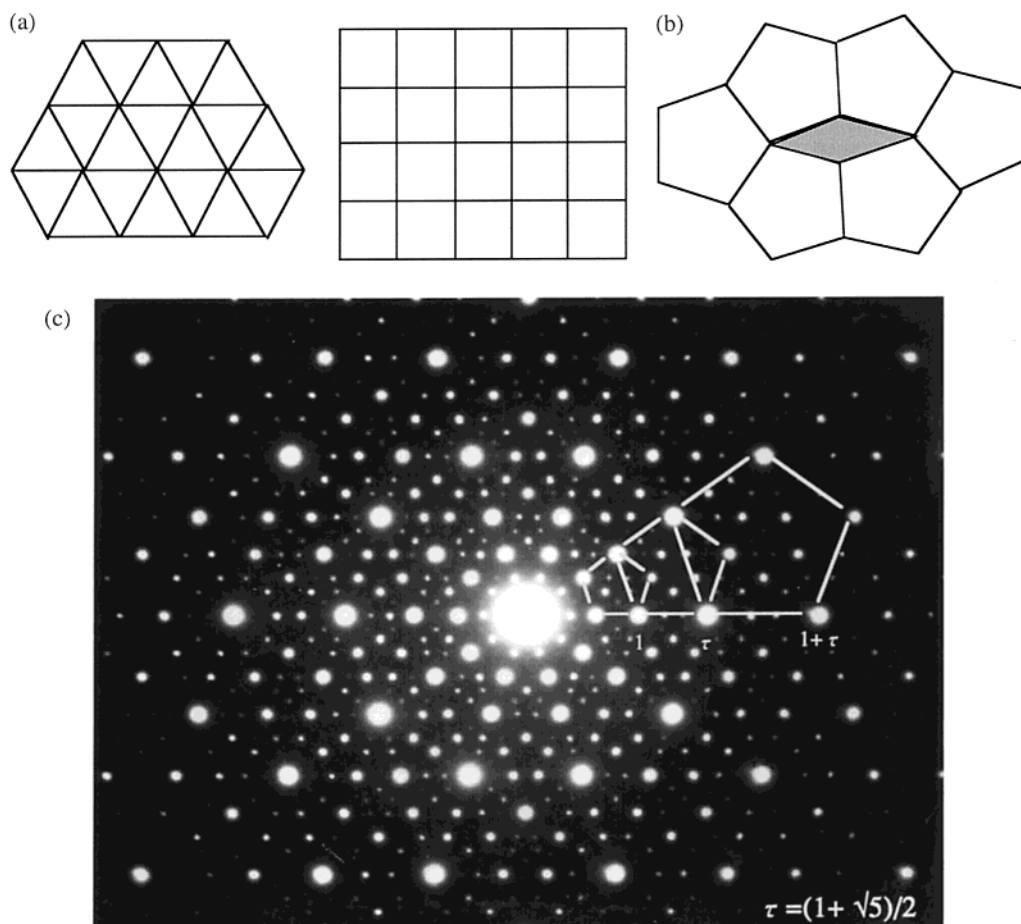


FIGURE 1. Triangle- and square-shaped (a) unit cells can form a lattice, but pentagons (b) cannot due to formation of frustration. (c) An electron diffraction pattern along a 5-fold axis from an Al–Cu–Fe quasicrystal. Note the formation of 5-fold symmetry and nonperiodicity by spots which are disallowed in classic crystallography.

was formed. This was the largest among all the reported quasicrystalline grains to that date. The grain boundaries were filled only with quasicrystalline grains, and there was no trace of precipitate or second phase. The Al–Cu–Fe quasicrystal exhibited surprisingly high resistivity, as large as $\sim 3000 \mu\Omega\cdot\text{cm}$, higher by about 1 order of magnitude than the resistivities of all quasicrystals known at that time.⁵

The large quasicrystalline grains formed in the sample suggested a high propensity for formation of this quasicrystalline alloy. It occurred to me that the quasicrystal might be stable. To check, I performed a powder X-ray diffraction analysis on a sample of as-cast (not rapidly solidified) $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ and found the diffraction peaks of the quasicrystal! The stability of this quasicrystalline phase was proven further by the formation of a faceted pentagonal dodecahedral morphology, as shown in Figure 2, in the bulk alloy obtained by conventional solidification, subsequently annealed at a temperature just below the melting point.⁶ The electron diffraction patterns obtained from an Al–Cu–Fe icosahedral quasicrystal along various directions are shown in Figure 3. The icosahedral quasicrystal gives very sharp diffraction spots in a quasiperiodic array in all directions, indicating that atoms sit at highly ordered but quasiperiodic positions in three dimension. Revisiting the Al–Cu–Fe phase diagram shown in Figure

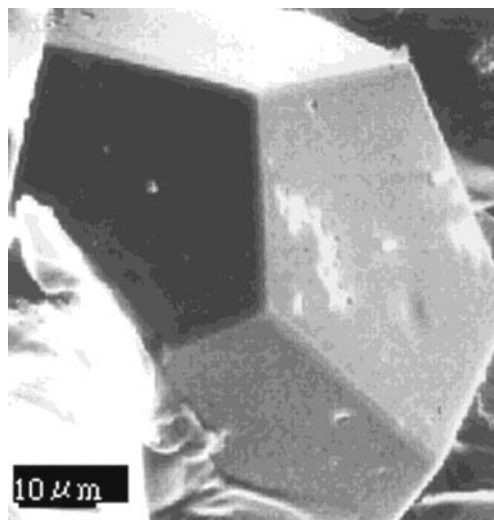


FIGURE 2. Scanning electron microscopy (SEM) micrograph showing a faceted pentagonal dodecahedral morphology of a stable icosahedral grain obtained in a conventionally solidified $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy after annealing at 850°C .⁵

4, it was found that, when the system was being mapped in the 1930s, the Al–Cu–Fe quasicrystal had been observed and labeled as the “ ψ phase” but could not be identified structurally.⁷ This provided the first hint that quasicrystalline phases might more generally be associ-

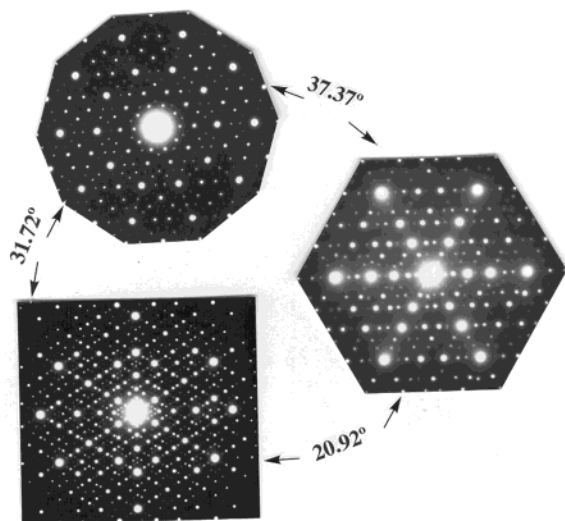


FIGURE 3. Electron diffraction patterns taken with incidences along a direction perpendicular to a pentagonal (5-fold) plane (a), along a direction from the center to a corner (3-fold) (b), and along a direction from the center to an edge center (2-fold) (c) of the pentagonal dodecahedron shown in Figure 1.

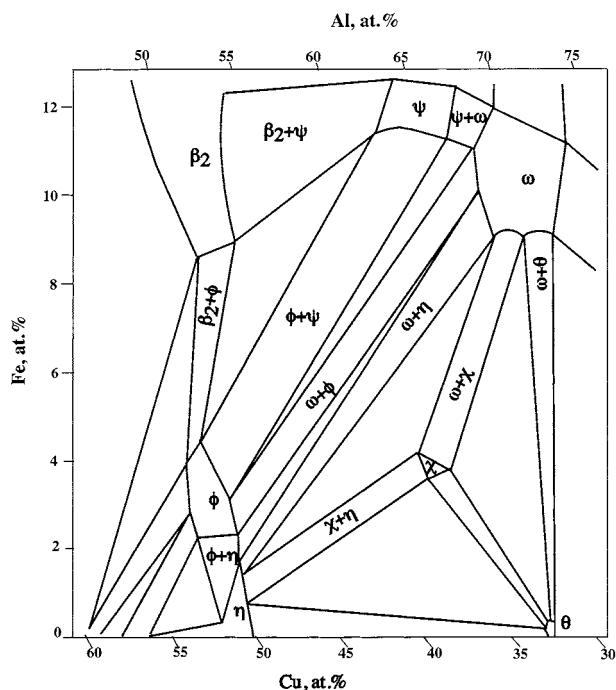


FIGURE 4. Phase diagram of a ternary Al-Cu-Fe system.⁷

ated with structurally unidentified phases in known systems. The stable AlCuLi icosahedral quasicrystal was also discovered by identifying an unknown phase,⁸⁻¹⁰ T_2 , in the phase diagram shown in Figure 5.¹¹

Concurrently, several metastable quasicrystals were obtained by replacing the Fe in Al-Cu-Fe with Mn, Cr, and V, all elements located in the same row on the Periodic Table as Fe. In addition to quasicrystals, a new family of amorphous phases was found unexpectedly in Al-Cu-V, Al-Cu-Y, and Al-Cu-Zr.¹² This was the beginning of the discovery of high-strength Al-based amorphous alloys. However, the replacement did not lead to the formation of stable quasicrystals. I then tested for

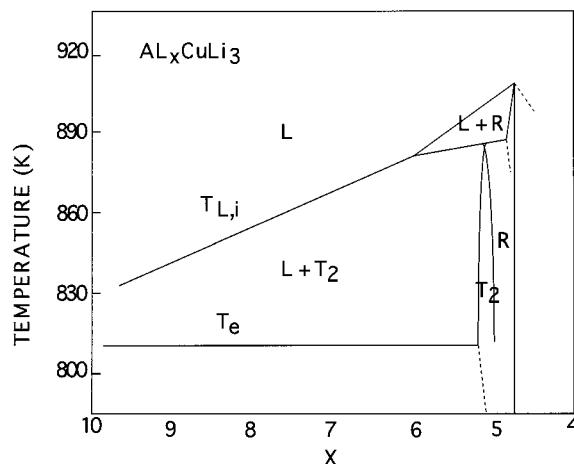


FIGURE 5. Pseudo-binary phase diagram of an Al-Cu-Li system (redrawn from ref 9).

stable quasicrystals by replacing Fe with Ru and Os. Consequently, stable quasicrystalline phases were found in the Al-Cu-Ru and the Al-Cu-Os systems, with the same composition as the Al-Cu-Fe alloy.¹³ Since Ru and Os are located in the same column as Fe in the Periodic Table, their chemistry resembles that of Fe. The principle is very simple, but it took one year for me to reach this conclusion. The discovery of this new group of stable quasicrystals was a milestone in research on quasicrystals, for several reasons.

First, the new stable quasicrystals were shown to possess very sharp diffraction peaks, comparable to those of a crystalline phase, which ruled out the icosahedral glass model for these quasicrystals.¹⁴ The icosahedral glass model relies on local interactions to join the icosahedral clusters in a random way. According to the model, all the icosahedral clusters have the same orientation, but because of random growth, the structure contains a large amount of disorder, manifest in the peak broadening of the diffraction patterns. Crystalline approximants contain icosahedral clusters, which are plausible building blocks for the glass model. In this sense, the quasicrystal can be described as an intermediate state between crystal and amorphous phases. The glass model was, and is, successful in describing quasicrystals in a metastable state, which explains the origins of disorder in these types of quasicrystals. Surprisingly, even the stable Al-Li-Cu quasicrystal discovered in 1986 exhibited the same degree of disorder.¹⁵ However, the stable Al-Cu-Fe quasicrystal, with sharp peaks in its diffraction pattern, could not be explained by the glass model. In turn, this supported the idea that quasicrystals are a new form of *ordered* matter. This gave rise to a controversy, which continues today, about the origin of stability in quasicrystals:¹⁶ whether the Penrose pattern is a ground state for real quasicrystals.

Second, the Al-Cu-Fe quasicrystal exhibited a new type of structure. There are three translation symmetry types of cubic crystals: primitive, body-centered, and face-centered. Since the quasicrystal can be described as a cubic structure in high dimension, a similar variety of lattices is expected in quasicrystals.¹⁷ All the quasicrystals

discovered before Al–Cu–Fe had a primitive cubic lattice in six dimensions. The stable Al–Cu–Fe quasicrystal, in contrast, had a face-centered lattice in six dimensions,¹⁸ demonstrating the structural variety in quasicrystals.

Third, the successful replacement of Fe by Ru and Os suggested that quasicrystals are probably stabilized by electronic structure. These three quasicrystals all exhibited a definite value of the electron/atom (e/a) ratio of 1.75. The valence of Al and Cu is 3 and 1, respectively, and that of Fe is -2.66 according to Raynor.¹⁹ The e/a ratio of Ru and Os is inferred from Fe. This is nothing else but the Hume-Rothery²⁰ rule and was the first plausible mechanism suggested for stabilization of quasicrystals.²¹

Recently, I learned from J. M. Dubois, a scientific leader in quasicrystals and a friend at the CNRS in Nancy, France, that he had prepared the Al–Cu–Fe alloy with similar composition before we found the quasicrystalline phase, but he could not study the samples by transmission electron microscopy (TEM) observation. I was very lucky that I could operate an electron microscope.

2. Al–Ni–Co System. The success in finding new quasicrystals by replacement with an element located in the same column motivated me to replace Cu with Ni in the Al–Cu–TM (TM = transition metal) system. In this trial, several types of decagonal quasicrystals were discovered in melt-spun samples.²² (Decagonal quasicrystals are aperiodic in two dimensions, wherein they display 10-fold symmetry, and periodic in the third dimension.) Among the decagonal quasicrystals, Al–Ni–Co quasicrystals were found to be thermodynamically stable over a wide temperature and compositional range.²³ Recently, decagonal quasicrystalline phases have also been found to be stable at elevated temperatures in Al–Ni–Fe²⁴ and Al–Ni–Ru²⁵ alloys, but Al–Ni–Co remains the most studied decagonal phase, being the subject of more than a thousand papers. Generally, a stable decagonal quasicrystal reveals a faceted decaprisism morphology, as shown in Figure 6. Electron diffraction employing a decagonal quasicrystal reveals patterns as shown in Figure 7.

The discovery of Al–Ni–Co decagonal quasicrystals facilitated enormous progress in the field in several ways. First, the fact that the decagonal phase expands to a wide compositional range at high temperatures has stimulated the study of thermodynamic stability and phase equilibria.²⁶ Second, TEM studies confirmed that several variations in the decagonal structure exist.^{27,28} This has proven very attractive to crystallographers, since the phase transitions and structures of these variations can be studied and compared. Third, a perfect decagonal structure is especially important in solving quasicrystalline structures with complete specification of atomic positions. This is the only quasicrystal to date that allows one to propose a reliable structure model with strict atomic coordination accurate enough to argue about the origin of stability on the basis of the structure model.^{29–31} Fourth, this is the only alloy system in which large-scale single grains of a decagonal phase can be grown.³² The growth of large grains is necessary to elucidate physical properties. And fifth, the physical properties of the decagonal phase are especially

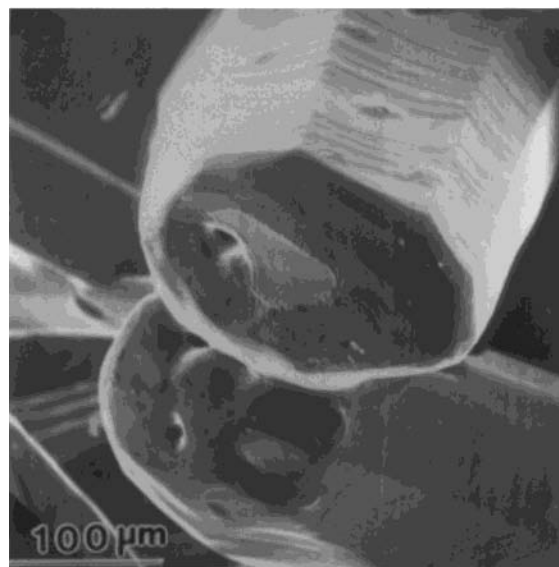


FIGURE 6. SEM micrograph showing a faceted decaprisism morphology of a stable decagonal quasicrystal in a conventionally solidified $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$ alloy.

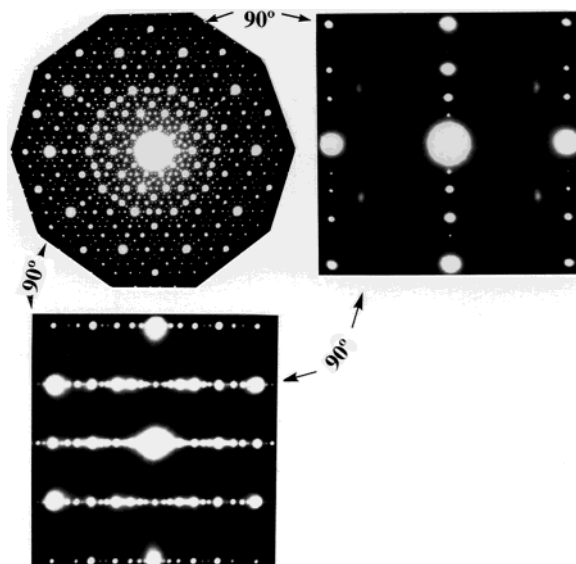


FIGURE 7. Electron diffraction patterns taken with incidences along a direction perpendicular to the decagonal (10-fold) plane and along two directions perpendicular to the 10-fold direction.

intriguing, because the nature of the decagonal phase allows a comparison between a periodic direction and quasiperiodic directions within the same sample.³³

Almost at the same time, K. H. Kuo et al. at the Beijing Electron Microscopy Laboratory discovered the stable decagonal Al–Cu–Co quasicrystal.³⁴ With the replacement of transition metals by Co, Kuo et al. found the decagonal quasicrystal in both quenched samples and bulk samples. On my side, I set up a profile for quick identification of the icosahedral phase from powder X-ray diffraction (XRD) patterns. This allowed any icosahedral phase to be detected quickly, at a glance, from the powder X-ray diffraction (XRD) patterns. The samples for TEM were all checked by powder XRD. However, the XRD of a decagonal phase is completely different from that of an icosahedral phase, and thus, although I had prepared the

decagonal Al–Cu–Co sample, I did not recognize it. I was convinced of the formation of a stable decagonal phase by the observation of a faceted decaprisism morphology in an as-cast Al–Ni–Co sample, as shown in Figure 6. I confirmed its structure by TEM. Turning back to XRD of Al–Ni–Co, I realized that a stable decagonal phase also formed in Al–Cu–Co. Thus, Kuo's discovery was completely independent of ours; our routes were different, but the goal we finally reached was same. One thing I do want to emphasize is that Al–Cu–Fe and Al–Ni–Co were very garden-variety alloy systems, composed of common elements and believed to be understood thoroughly. However, something was still missing, at least before the discovery of the quasicrystalline phases.

1990–1994

1. Al–Pd–Mn Group. In 1990, the year I received a Ph.D. degree, an energetic and active graduate student, Y. Yokoyama, joined the laboratory to begin his master's degree studies. We had agreed on "Formation of Quasicrystals in Al–Pd Systems" as the topic of his thesis.

Empirically, it was known that, by employing rapid solidification, quasicrystals could be formed in a wide compositional range around the stoichiometric composition, as had been proven in the Al–Cu–Fe system. Thus, we chose rapid solidification in order to approach the composition of new quasicrystals. In a systematic investigation, the replacement of Ni and Co by Pd and Mn, respectively, in $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$ and rapid solidification was found to promote formation of an icosahedral phase with sharp diffraction peaks. We then discovered that the addition of Pd to Shechtman's original Al–Mn alloy stabilized the quasicrystallinity and improved the quasiperiodic order.³³ Since I was aware that an e/a of 1.75 prevailed for stable quasicrystals in the Al–Cu–TM system, I designed an alloy of Al–Pd–Mn to have an e/a ratio of 1.75.³⁶ As a result, in 1990, we discovered the stable quasicrystalline phases in Al–Pd–Mn and Al–Pd–Re systems. Interestingly, the new stable quasicrystals had the stoichiometries of $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ and $\text{Al}_{70}\text{Pd}_{20}\text{Re}_{10}$, which were both slightly different from that of Al–Cu–Fe but which showed the same e/a . This suggested the universality of the Hume-Rothery rule for Al-based stable quasicrystals. Similar to Al–Cu–Fe, the stable quasicrystals possessed highly ordered face-centered-cubic lattices in six dimensions. The quasicrystals were thermodynamically stable down to room temperature. The discovery of the Al–Pd–Mn quasicrystal, especially, was another breakthrough, since it was found that single grains could be grown by conventional crystal growth techniques to a single domain size on the order of centimeters,³⁷ without reducing the quasiperiodic order.³⁸ Several research groups around the world have succeeded in producing single quasicrystals larger than a cubic centimeter in this system. A high-quality single quasicrystal on this scale allows almost any type of analysis to be done, including mechanical properties measurements,³⁹ inelastic neutron scattering,⁴⁰ and surface structures⁴¹ of high-symmetry

planes. The Al–Pd–Mn alloy has been used in most of the studies of icosahedral quasicrystals that have been carried out to date. An exciting aspect of the sister alloy, Al–Pd–Re, is that it exhibits high resistivity—comparable to that of doped semiconductors.⁴²

One may note that an element lies between Mn and Re: Tc. I believed that a stable quasicrystal would form in the Al–Pd–Tc alloy. However, Tc is highly radioactive, and it was impossible for me to use it in Japan. However, in 2000, the formation of a stable quasicrystal in Al–Pd–Tc was reported at the Aperiodic 2000 conference in Nijmegen and published almost at the same time.⁴³ This is another piece of clear evidence that the Hume-Rothery rule works for stable quasicrystals.

2. Zn–Mg–RE (RE = Rare Earth Metal) Group. The first evidence of quasicrystals in this system was observed at grain boundaries in commercial Mg alloys.⁴⁴ We noted the paper, and a Ph.D. student, A. Niikura, followed up on the work. As a result, a new group of stable quasicrystals in Zn–Mg–RE (RE = Y, Gd, Tb, Dy, Ho, Er) was reported by Niikura et al. in 1994.^{45,46} The new stable quasicrystal exhibited a face-centered icosahedral lattice, the first time this structure was observed in the Zn–Al–Mg group. [Note: According to constituent elements, quasicrystals are classified into two groups. One is mainly composed of Al and transition metals, and the other is Zn, Mg, Al, etc. but no transition metals. Two groups of quasicrystals contain distinctive atomic clusters, which are the building blocks for the corresponding quasicrystals.] In addition, the stable quasicrystal revealed diffraction peaks with peak widths attaining $\sim 0.004 \text{ \AA}^{-1}$, revealing a highly ordered structure persisting over a long-range. The stoichiometric composition of the new quasicrystals was determined to be close to $\text{Zn}_{60}\text{Mg}_{30}\text{RE}_{10}$. Interestingly, the quasicrystal turned out to be the so-called Z-phase, as shown in Figure 8, which had been reported as a distinct but unidentified phase in this alloy system a few years before the discovery of quasicrystals.⁴⁷ It seems that examining unidentified phases is a viable path to discovering new quasicrystalline alloys. Table 1 lists intermetallic compounds which were unidentified in the original phase diagram but which have been confirmed to be stable quasicrystals. The discovery of the Zn–Mg–RE quasicrystals offered an opportunity to study the intrinsic magnetism inherent in quasiperiodic lattices, since elements with localized f electrons were involved in some of these quasicrystals. As a result, spin-glass-like behavior, together with intriguing magnetic scattering due to antiferromagnetism, has been observed in a single Zn–Mg–Ho quasicrystal.⁴⁸ Compared to all previously known quasicrystal systems, there was another distinctive feature of this system: no crystalline (cubic) compound could be identified as an approximant. However, a related hexagonal compound with a composition close to that of the quasicrystal⁴⁹ became a key to understanding the structure of the quasicrystal. It is now believed that the building block of the Zn–Mg–RE quasicrystal is different from that of the quasicrystals in the Al–Mg–Zn group.⁵⁰

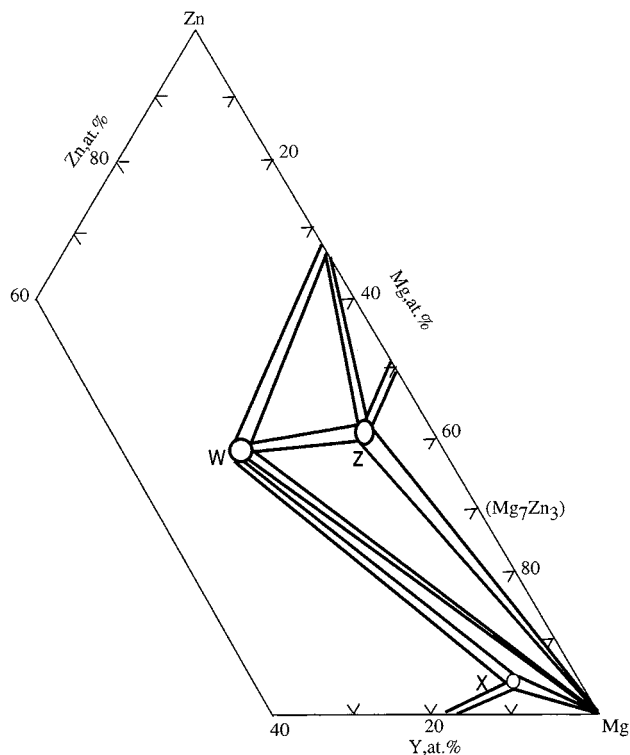


FIGURE 8. Phase diagram of a ternary Zn–Mg–Y system.⁴⁷

Table 1. Compounds Identified To Be Stable Quasicrystals

alloy system	phase	stoichiometry	year indicated	year identified
Al–Li–Cu	T_2	$Al_{5.5}Li_3Cu$	1955	1986
Al–Cu–Fe	ψ	$Al_{65}Cu_{20}Fe_{15}$	1939	1987
Zn–Mg–Y	Z	Zn_6Mg_3Y	1982	1994
Cd–Yb	unknown	$Cd_{5.7}Yb$	1971	2000
Cd–Ca	unknown	$Cd_{17}Ca_3$	1972	2000

1995 to Present

Cd–Mg–RE and Cd–(Yb,Ca) Group. In 1996, I moved to the National Research Institute for Metals at Tsukuba,

Japan (now the National Institute for Materials Science). This provided an opportunity to change my environment and to interact with new scientists. J. Q. Guo was a postdoctoral researcher responsible for preparation of quasicrystals. We tried to prepare Cd–Mg–RE for REs with larger atomic sizes than had existed in the Zn–Mg–RE family. The idea was to replace Zn by Cd in the Zn–Mg–RE system. In 1994, we had tried replacement of Zn with Cd at a composition of $Zn_{50}Mg_{42}RE_8$, and since the composition was far from stoichiometric, we could not find any trace of a quasicrystal.

The main idea was to replace a solvent element by another, a strategy that had never succeeded in another quasicrystalline alloy. Eventually, stable quasicrystals were identified in nine Cd–Mg–RE alloys. We refined the stoichiometry ($Zn_{60}Mg_{30}RE_{10}$) and reached the stable quasicrystal in $Cd_{65}Mg_{20}RE_{15}$.⁵¹ Again, this was very strong evidence that the stability of quasicrystals is governed by the chemistry of the constituent elements. However, the stable quasicrystals in this system possessed an icosahedral structure with a primitive lattice and had a stoichiometric composition close to $Cd_{65}Mg_{20}RE_{15}$, strong departures from the Zn–Mg–RE system. Among nine Cd–Mg–RE alloys, Cd–Mg–Yb was the only one which formed quasicrystals even in an as-cast state.⁵² This led us to check the Cd–Yb phase diagram, where I found Cd_6Yb , a cubic phase with space group $Im\bar{3}$ and lattice parameter $a = 1.564$ nm.⁵³ Since $Im\bar{3}$ is a subgroup of icosahedral symmetry and the lattice parameter is the same as that estimated for a quasicrystal, we suspected that Cd_6Yb could be a crystalline approximant to a quasicrystal. I immediately noted an unknown phase (Figure 9)⁵⁴ with a congruent melting point of 636 °C at a composition of $Cd_{5.7}Yb$. The structure of $Cd_{5.7}Yb$ had been studied and was reported to be an orthogonal unit cell with very large edges, but it did not correspond to any known structure. It dawned on me that $Cd_{5.7}Yb$ was nothing else but an icosahedral quasicrystal! With this conviction, I suggested

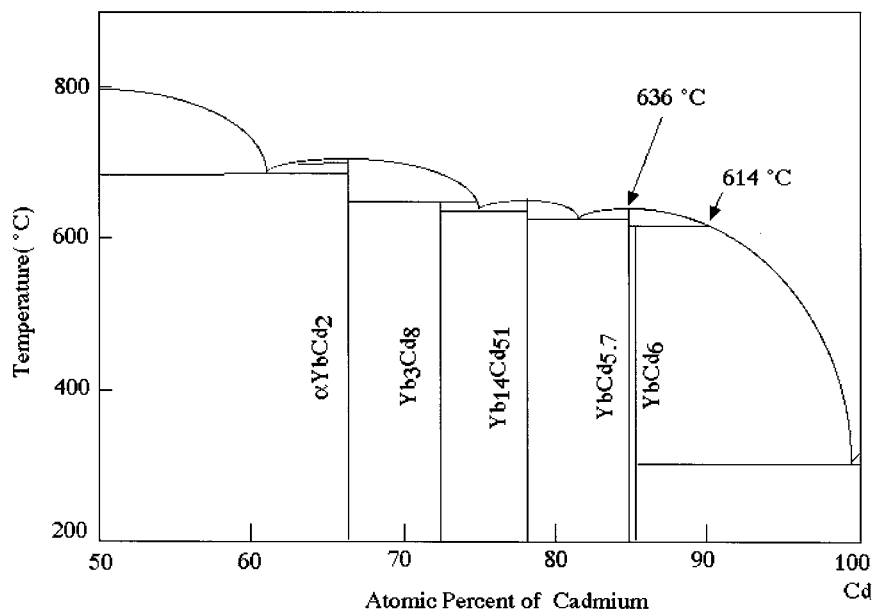


FIGURE 9. Phase diagram of a binary Cd–Yb system (redrawn from ref 51).

preparing the sample and taking the X-ray powder pattern. As expected, $\text{Cd}_{5.7}\text{Yb}$ turned out to be a quasicrystal. Again, as had happened previously, an unknown phase was confirmed to be a stable quasicrystal. This was the first evidence of a thermodynamically stable icosahedral quasicrystal in a binary alloy. We noted a similar phase diagram with an unknown phase in the Cd–Ca system. The unknown phase, $\text{Cd}_{17}\text{Ca}_3$ ($\sim\text{Cd}_{5.7}\text{Ca}$),⁵⁵ whose composition was very close to a Cd_6Ca compound isostructural to Cd_6Yb , was identified as a quasicrystalline phase.⁵⁶ Following the Al–Cu–Li system, $\text{Cd}_{17}\text{Ca}_3$ is the second stable quasicrystal which contains no transition metals or rare earth metals. It is very striking that a stable quasicrystal could form even from such simple elements. This would not have been believed a decade ago. It is hoped that this will open a new frontier for the quasicrystals for the following reasons.

First, the discovery of these quasicrystals destroyed several notions that had arisen over the years, such as the ideas that quasicrystals are found only among metals in the right-hand side of the Periodic Table, and that the icosahedral quasicrystals require at least three different elements.

Second, a binary stable quasicrystal like $\text{Cd}_{17}\text{Ca}_3$, consisting of two simple elements, is simpler for theoretical calculation and allows us to compare it directly with experimental results. This would provide an opportunity to discuss the origins of stability of quasicrystals in three dimensions.⁵⁷

Third, discovery of a ternary stable icosahedral quasicrystal has been inspired by Cd–binary stable quasicrystals, approaching from a Cd_6M -type cubic approximant.⁵⁸ Furthermore, replacement of Cd by half In and half Ag for $\text{Cd}_{84}\text{Yb}_{16}$ and $\text{Cd}_{84}\text{Ca}_{16}$ led to the formation of stable $\text{In}_{42}\text{Ag}_{42}\text{Yb}_{16}$ and $\text{In}_{42}\text{Ag}_{42}\text{Ca}_{16}$ icosahedral quasicrystals.⁵⁹ The values of e/a for the two binary stable icosahedral quasicrystals are 2. I would like to emphasize that in the Periodic Table, In located to the right of Cd is trivalent and Ag located to the left of Cd is monovalent, and thus the values of e/a for two In–Ag quasicrystals were kept at 2. Again, this is straightforward evidence confirming that the stable icosahedral quasicrystal is a Hume-Rothery alloy.

Fourth, the structure of these quasicrystals, as deduced from the approximant, shows that the innermost core in the basic cluster does not have icosahedral symmetry, which is also a noteworthy result.

Discoveries are sometimes not appreciated for their subtlety. This is embodied in a certain proverb which was often quoted by a scientist, Hiroshi Maeda, who discovered the Bi-based superconductors. In his lectures, he often said “Tana kara botanmochi” (a Japanese proverb). It can be translated into English as follows: “Because the first and second prize winners were disqualified, the person who came in third got the gold medal as a windfall.” It seems that making a discovery is just like picking up a windfall because of luck, but Maeda always reminds that we should not forget how much effort was put into reaching third place.

There is a Chinese proverb, “taking a lesson from the past”. It means that “by exploring the old, one becomes able to understand the new”. This may not be the case for the discovery of stable quasicrystals. If quasicrystals were not discovered, we would never understand what the unknown phases are. We learned the past from the future, and this is something like “Back to the Future”!

First of all, I would like to state that if I had not met the following people I would not have been able to experience this exciting series of events. T. Masumoto, my supervisor, allowed me to study quasicrystals for my Ph.D. thesis and, even more importantly, allowed me to continue to study quasicrystals after obtaining my Ph.D. degree. A. Inoue made positive suggestions about my Ph.D. work. Y. Yokoyama was a graduate student who collaborated with me on the Al–Pd–Mn quasicrystals. A. Niikura was a Ph.D. graduate student who collaborated with me on the Zn–Mg–RE quasicrystals. J. Q. Guo was a postdoctoral associate who collaborated on the Cd-based quasicrystals. Drs. T. J. Sato, E. Abe, H. Takakura, K. Saitoh, and A. Singh were not directly involved in the discoveries, but their suggestions were important and were linked to the discoveries. This was a huge collaboration among many colleagues and students. As a scientist, I am very lucky to have had these capable collaborators. I would like to thank CREST-JST for the support of the project for five years. Without this support, I do believe that there would be no late developments on quasicrystals. I shall also keep in mind that if Shechtman had not discovered the quasicrystal, I would not have had the opportunity to study the quasicrystals. Special thank is due to Patricia A. Thiel for her suggestion, encouragement, and critical reading of the manuscript. I am grateful to Jean-Marie Dubois for inviting me to LGS2M, Ecole des Mines de Nancy, where I completed the manuscript and where I shared an office with Patricia A. Thiel.

References

- (1) Shechtman, D.; Blech, I.; Gratias, D.; Cahn, J. W. Metallic phase with long-range orientational order and no translational symmetry. *Phys. Rev. Lett.* **1984**, *53*, 1951–1953.
- (2) Levine, D.; Steinhardt, P. J. Quasicrystals I: definition and structure. *Phys. Rev. B* **1986**, *34*, 596–616.
- (3) Elser, V.; Henley, C. L. Crystal and quasicrystal structures in Al–Mn–Si alloys. *Phys. Rev. Lett.* **1985**, *55*, 2883–2886.
- (4) Bown, M. G.; Brown, P. J. The structure of FcCu_2Al_7 and $\text{T}(\text{Co-CuAl})$. *Acta Crystallogr.* **1956**, *9*, 911–915.
- (5) Tsai, A. P.; Inoue, A.; Masumoto, T. Preparation of a new Al–Cu–Fe quasicrystal with large grain sizes by rapid solidification. *J. Mater. Sci. Lett.* **1987**, *6*, 1403–1405.
- (6) Tsai, A. P.; Inoue, A.; Masumoto, T. A stable quasicrystal in Al–Cu–Fe system. *Jpn. J. Appl. Phys.* **1987**, *26*, L1505–L1507.
- (7) Bradley, A. J.; Goldschmidt, H. J. An X-ray study of slowly cooled iron–copper aluminium alloys. Part II. Alloys rich in aluminium. *J. Inst. Met.* **1939**, *65*, 403–418.
- (8) Hardy, K.; Silcock, J. M. The phase sections at 500C and 350C of aluminum-rich Al–Cu–Li alloys. *J. Inst. Met.* **1955/56**, *24*, 423–428.
- (9) Ball, M. D.; Lloyd, D. J. Particles apparently exhibiting five-fold symmetry in Al–Li–Cu–Mg alloy. *Scr. Met.* **1985**, *19*, 1065–1068.
- (10) Macus, M.; Elser, V. T_2AlLiCu : a stable icosahedral phase? *Philos. Mag.* **1985**, *B54*, L101–L104.
- (11) Chen, H. S.; Kortan, K. R.; Parsey, J. M., Jr. Thermodynamic properties and phase diagram of icosahedral Al–Li–Cu ($\text{Al}_x\text{Li}_3\text{Cu}$). *Phys. Rev.* **1987**, *B36*, 7681–7684.
- (12) Tsai, A. P.; Inoue, A.; Masumoto, T. Formation of Metal–Metal Type Aluminum-based Amorphous Alloys. *Metall. Trans.* **1988**, *19A*, 1369–1370.
- (13) Tsai, A. P.; Inoue, A.; Masumoto, T. New stable icosahedral Al–Cu–Ru and Al–Cu–Os alloys. *Jpn. J. Appl. Phys.* **1988**, *27*, L1587–L1590.
- (14) Stephens, P. W.; Goldman, A. I. Sharp diffraction maxima from an icosahedral glass. *Phys. Rev. Lett.* **1985**, *56*, 1168–1171.

- (15) Heniney, P. A.; Bancel, P. A.; Horn, P. M.; Jordan, J. L.; Laplaca, S.; Angiello, J.; Gayle, F. W. Disorder in Al–Li–Cu and Al–Mn–Si icosahedral alloys. *Science* **1987**, *238*, 660–663.
- (16) Widom, M.; Strandberg, K. J.; Swendsen, R. H. Quasicrystal equilibrium state. *Phys. Rev. Lett.* **1987**, *58*, 706–709.
- (17) Rokhsar, D. S.; Mermin, N. D.; Wright, D. C. Rudimentary quasicrystallography: the icosahedral and decagonal reciprocal lattices. *Phys. Rev.* **1987**, *B35*, 5487–5495.
- (18) Ebalard, S.; Sapepen, F. The body-centered-cubic-type icosahedral reciprocal lattice of the Al–Cu–Fe quasi-periodic crystal. *J. Mater. Res.* **1989**, *4*, 39–43.
- (19) Raynor, G. V. Progress in the Theory of Alloys. *Prog. Met. Phys.* **1949**, *1*.
- (20) Hume-Rothery, W. *J. Inst. Met.* **1926**, *36*, 295.
- (21) Tsai, A. P.; Inoue, A.; Masumoto, T. Quasicrystals as a Hume-Rothery phase—an empirical approach. *Sci. Rep. Res. Inst. (Tohoku Univ.), Ser. A* **1991**, *36*, 99–114.
- (22) Tsai, A. P.; Inoue, A.; Masumoto, T. New Decagonal Al–Ni–Fe and Al–Ni–Co Alloys Prepared by Liquid Quenching. *Mater. Trans., JIM* **1989**, *30*, 150–154.
- (23) Tsai, A. P.; Inoue, A.; Masumoto, T. Stable Decagonal Al–Co–Ni and Al–Co–Cu Quasicrystals. *Mater. Trans., JIM* **1989**, *30*, 463–473.
- (24) Lemmerz, U.; Grushko, B.; Freiburg, C.; Jansen, M. Study of decagonal quasicrystalline phase formation in the Al–Ni–Fe alloy system. *Philos. Mag. Lett.* **1994**, *69*, 141–146.
- (25) Sun, W.; Hiraga, K. Formation and structures of decagonal quasicrystals in the Al–Ni–Ru. *Mater. Sci. Eng., A* **2000**, *294–296*, 147–151.
- (26) Godecke, T.; Ellner, M. Phase equilibria in the aluminium-rich portion of the binary system Co–Al and in the cobalt/aluminium-rich portion of the ternary system Co–Ni–Al. *Z. Metallk.* **1996**, *87*, 855–864; Phase equilibria in the Al-rich portion of the ternary system Co–Ni–Al at 75 and 78 at% Al. *Z. Metallk.* **1997**, *88*, 382–389.
- (27) Ritsch, S.; Beeli, C.; Nissen, H.-U.; Luck, R. Two different superstructures of the decagonal Al–Co–Ni quasicrystal. *Philos. Mag. Lett.* **1995**, *71*, 671–685.
- (28) Tsai, A. P.; Fujiwara, A.; Inoue, A.; Masumoto, T. Structural variation and phase transformations of decagonal quasicrystals in the Al–Ni–Co system. *Philos. Mag. Lett.* **1996**, *74*, 233–240.
- (29) Steinhardt, P. J.; Jeong, H.-C.; Saitoh, K.; Tanaka, M.; Abe, E.; Tsai, A. P. Experimental verification of the quasi-unit-cell model of quasicrystal structure. *Nature* **1998**, *396*, 55–57.
- (30) Abe, E.; Saitoh, K.; Takakura, H.; Tsai, A. P.; Steinhardt, P. J.; Jeong, H.-C. Quasi-unit-cell model for an Al–Ni–Co ideal quasicrystal based on clusters with broken tenfold symmetry. *Phys. Rev. Lett.* **2000**, *84*, 4609–4612.
- (31) Takakura, H.; Yamamoto, A.; Tsai, A. P. The structure of a decagonal Al₇₂Ni₂₀Co₈ quasicrystal. *Acta Crystallogr.* **2001**, *A57*, 576–585.
- (32) Sato, T. J.; Hirano, T.; Tsai, A. P. Single-Crystal Growth of the Decagonal Al–Ni–Co Quasicrystal. *J. Cryst. Growth* **1998**, *191*, 545–552.
- (33) Martin, S.; Hebard, A. F.; Kortan, A. R.; Thiel, F. A. Transport properties of Al₆₅Cu₁₅Co₂₀ and Al₇₀Ni₁₅Co₁₅ decagonal quasicrystals. *Phys. Rev. Lett.* **1991**, *67*, 719–722.
- (34) He, L. X.; Wu, Y. K.; Kuo, K. H. Decagonal quasicrystals with different periodicities along the tenfold axis in rapidly solidified aluminum–copper alloy Al₆₅Cu₂₀M₁₅ (M = Mn, Fe, Co or Ni). *J. Mater. Sci. Lett.* **1988**, *7*, 1284–1286.
- (35) Tsai, A. P.; Yokoyama, Y.; Inoue, A.; Masumoto, T. New icosahedral alloys with superlattice order in the Al–Pd–Mn system prepared by rapid solidification. *Philos. Mag. Lett.* **1990**, *61*, 9–14.
- (36) Tsai, A. P.; Inoue, A.; Yokoyama, Y.; Masumoto, T. Stable Icosahedral Al–Pd–Mn and Al–Pd–Re alloys. *Mater. Trans., JIM* **1990**, *31*, 98–103.
- (37) Yokoyama, Y.; Miura, T.; Tsai, A. P.; Inoue, A.; Masumoto, T. Preparation of a Large Al₇₀Pd₂₀Mn₁₀ Single-Quasicrystal by Czochraski Method and Its Electrical Resistivity. *Mater. Trans., JIM* **1992**, *33*, 97–101.
- (38) de Boissieu, M.; Rurand-Charre, M.; Bastie, P.; Cacabelli, A.; Boudard, M.; Bessiere, M.; Lefebvre, S.; Janot, C.; Audier, M. Centimeter-size single grain of the perfect aluminum–palladium–manganese icosahedral phase. *Philos. Mag. Lett.* **1992**, *65*, 147–153.
- (39) Wollgarten, M.; Beyss, M.; Urban, K.; Liebertz, H.; Koster, U. Direct evidence for plastic deformation of quasicrystals by means of a dislocation mechanism. *Phys. Rev. Lett.* **1993**, *71*, 549–552.
- (40) de Boissieu, M.; Boudard, M.; Bellissent, R.; Quilichini, M.; Hennion, B.; Currat, B.; Goldman, A. I.; Janot, C. Dynamics of the Al–Pd–Mn icosahedral phase. *J. Phys.: Condens. Matter* **1993**, *5*, 4945–4966.
- (41) Gierer, M.; Van Hove, M. A.; Goldman, A. I.; Shen, Z.; Chang, S.-L.; Jenks, C. K.; Zhang, C. M.; Thiel, P. A. Structural analysis of the five-fold symmetric surface of the Al₇₀Pd₂₁Mn₉ quasicrystal by low energy electron diffraction. *Phys. Rev. Lett.* **1997**, *78*, 467–470.
- (42) Akiyama, H.; Honda, Y.; Hashimoto, T.; Edagawa, K.; Takeuchi, S. Toward insulating quasicrystalline alloy in Al–Pd–Re icosahedral phase. *Jpn. J. Appl. Phys.* **1993**, *B32*, L1003–L1004.
- (43) Mikheeva, M. N.; Panvo, Kh. G.; Teplov, A. A.; Khlopkin, M. N.; Chernoplekov, N. A.; Shikov, A. A. Thermodynamic and kinetic properties of an icosahedral quasicrystalline phase in the Al–Pd–Tc system. *Phys. Solid State* **2000**, *42*, 2177–2183.
- (44) Luo, Z.; Zhang, S.; Tang, Y.; Zhao, D. Quasicrystals in as-cast magnesium–zinc–rare earth alloys. *Scr. Metall. Mater.* **1993**, *28*, 1513–1518.
- (45) Niikura, A.; Tsai, A. P.; Inoue, A.; Masumoto, T. Stable Zn–Mg–Rare Earth Face-Centered Icosahedral Alloys with Pentagonal Dodecahedral Solidification Morphology. *Philos. Mag. Lett.* **1994**, *69*, 351–355.
- (46) Tsai, A. P.; Niikura, A.; Inoue, A.; Masumoto, T.; Nishita, Y.; Tsuda, K.; Tanaka, M. *Philos. Mag. Lett.* **1994**, *70*, 169–175.
- (47) Padezhnova, E. M.; Melnik, E. V.; Milyevskiy, R. A.; Dobatkina, T. V.; Kinzhibalo, V. V. Investigation of the Mg–Zn–Y system. *Russ. Metall. (Engl. Transl.)* **1982**, *3*, 185–188.
- (48) Sato, T. J.; Takakura, H.; Tsai, A. P.; Shibata, K. Anisotropic Spin Correlation in the Zn–Mg–Ho Quasicrystal. *Phys. Rev. Lett.* **1998**, *81*, 2364–2367.
- (49) Singh, A.; Abe, E.; Tsai, A. P. A Hexagonal Phase Related to Quasicrystalline Phases in Zn–Mg–Rare-Earth System. *Philos. Mag. Lett.* **1998**, *77*, 95–103.
- (50) Takakura, H.; Shiono, M.; Sato, T. J.; Yamamoto, A.; Tsai, A. P. *Ab Initio* Structure Determination of Icosahedral Zn–Mg–Ho Quasicrystals by Density Modification Method. *Phys. Rev. Lett.* **2001**, *86*, 236–239.
- (51) Guo, J. Q.; Abe, E.; Tsai, A. P. Stable Icosahedral Quasicrystals in Cd–Mg–RE (RE=Rare Earth Element) Systems. *Jpn. J. Appl. Phys.* **2000**, *39*, L770–L771.
- (52) Tsai, A. P.; Guo, J. Q.; Abe, E.; Takakura, H.; Sato, T. J. A stable binary quasicrystal. *Nature* **2000**, *408*, 537–538.
- (53) Palenzona, A. The Ytterbium–Cadmium System. *J. Less-Common Met.* **1971**, *25*, 367–372.
- (54) Massalski, T. B.; Okamoto, H.; Subramanian, P. R.; Kacpzak, L., Eds. *Binary Alloy Phase Diagrams*, 2nd ed.; American Society of Metals: Materials Park, OH, 1990; Vols. 1 and 2, pp 889, 1044.
- (55) Bruzzone, G. The Ca–Cd and Ba–Cd systems. *Gazz. Chim. Ital.* **1972**, *102*, 234–242.
- (56) Guo, J. Q.; Abe, E.; Tsai, A. P. Stable icosahedral quasicrystals in binary Cd–Ca and Cd–Yb systems. *Phys. Rev.* **2000**, *B62*, R14605–R14608.
- (57) Ishii, Y.; Fujiwara, T. Hybridization mechanism for cohesion of Cd-based quasicrystals. *Phys. Rev. Lett.* **2001**, *87*, 206408-1–206408-4.
- (58) Kaneko, Y.; Arichika, Y.; Ishimasa, T. Icosahedral quasicrystal in annealed Zn–Mg–Sc alloys. *Philos. Mag. Lett.* **2001**, *81*, 777–787.
- (59) Guo, J. Q.; Tsai, A. P. Stable icosahedral quasicrystals in the Ag–In–Ca, Ag–In–Yb, Ag–In–Ca–Mg and Ag–In–Yb–Mg. *Philos. Mag. Lett.* **2002**, *82*, 349–352.

AR010013X