Research Overview
Quasicrystals and their physical properties
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1. Introduction
The history of mankind is often classified as Stone age, Bronze age, Iron age, and Silicon age. The main role here is solid, and in most cases it is crystalline. The quasicrystals studied by the present author are new solid states recognized in 1984 and have been expected as new functional materials due to the specificity of the structure. We have been studying quasicrystals with a primary focus on the structure and contributing to the establishment of a new concept called quasicrystals.

As is well known, crystals are formed by the periodic arrangement of atoms. This periodicity is reflected in the band structure and is the basis of the properties of each substance. On the other hand, in quasicrystals, atoms are arranged obeying unexpected rules such as "regular but not periodic". Regularity of the quasicrystal is related to "geometric progression" in the ideal state, while the periodicity of the crystal is to "arithmetic progression". The common ratio of the geometric progression is a certain irrational number like golden ratio. This special regularity is called "quasiperiodicity".

"How electrons behave at quasiperiodic potential" is an important issue. From the theoretical calculations of one- and two-dimensional systems, it is expected that a special state appears, which is not similar to the extended state in a crystal nor to the localized state in an amorphous. (This is called "critical state".) Therefore, electronic properties inherent to quasicrystals are expected, and have been searched for a long time. However, no clear indication of them was found before the observation of the quantum criticality in Au-Al-Yb quasicrystal (see Section 3.).

Furthermore, quasicrystals are also different from crystals in terms of rotational symmetry. In crystals, rotational symmetry is limited to those that are compatible with periodicity. On the other hand, in the case of quasicrystals, "high symmetry" such as 12-fold symmetry, which is not permitted in crystals, is possible in the reciprocal space (see Figure 1). Such symmetry is thought to reflect on the electronic structure through the shape of pseudo-Brillouin zone, which affects physical properties and also phase stability.

When trying to conduct experimental research from these viewpoints, it is a problem that "Quasiperiodicity close to the ideal can be formed in real material?". With this problem in mind, we have carried out the following two themes: "A new series of icosahedral quasicrystal" and "A new dodecagonal quasicrystal". Below, the results of research after...
2. New series of icosahedral quasicrystals in Zn-, Cu and Au-based alloys

In 2000 new stable quasicrystal, Cd-Yb, was reported by the group of Prof. A.P. Tsai (Tohoku Univ.). Stimulated by this discovery, we explored quasicrystals and reached a new series. They are Zn-M-Sc alloys with M=Mg, Mn, Fe, Co, Ni, Pd, Ag, Pt and Au. This series includes many stable quasicrystal phases. We also found the first Cu-based quasicrystals in Cu-Al-Sc and Cu-Ga-Mg-Sc alloys, the latter of which is a stable phase. Furthermore, ternary Au-based quasicrystals were also discovered.

Among others, the structural integrity of Zn-Mg-Sc quasicrystal (Figure 2) was extremely high, and the diffraction peaks measured using synchrotron radiation had the same sharpness as the crystal. This fact indicates that quasiperiodicity is realized with the same degree of completeness as periodicity in a real matter. (It should be noted that this is true only for some selected quasicrystals.)

The presence of a series of quasicrystals indicates that these quasicrystals have "diversity as alloy" capable of element substitution. From this diversity, crude conditions necessary for forming this type of quasicrystals was known. They are conditions for the atomic size relation and the valence-electron concentration e/a. They correspond to the famous conditions known as Hume-Rothery rules of crystalline alloys. The condition for the valence-electron concentration is explained by the formation of a pseudo gap resulting from the interaction between the Fermi-surface and the pseudo-Brillouin zone with the "sphere like shape". In this way, physical property control by element substitution, or material design, became possible to a certain extent. The results mentioned in the next section is this application example.

On the other hand, "approximant crystals" having a composition similar to quasicrystals are often formed in these alloys; for example, Au51Al35Yb14 approximant for Au51Al34Yb15 quasicrystal. An approximant is composed of local structural unit, called cluster, similar to that included in the corresponding quasicrystal. The approximant can be used as a reference material in structural studies of quasicrystals and physical properties.

For details, see the following reference.


3. Valence-fluctuating quasicrystal and its quantum criticality

As described above, in the quasicrystal, a critical electronic state has been expected. On the other hand, in the alloy containing a rare earth element in the valence fluctuating state, the problem of itinerant/localized state of the 4f electron has been studied from the viewpoint of magnetism and
strongly correlated electron system. One may think that it is interesting if a quasicrystal that combines both properties is formed. The first quasicrystal satisfying this condition is Au$_{51}$Al$_{34}$Yb$_{15}$ alloy discovered by our research group. In the preceding study, we have found Yb-containing quasicrystals in Zn-Mg-Yb and Ag-Ga-(Mg)-Yb alloys. However, in these alloys valency of Yb is +2, and they show no interesting magnetic properties. Intermediate valency +2.6 of Yb in the Au-Al-Yb quasicrystal was found by fortunate coincidence.

By collaboration with Deguchi/Stao group of Nagoya University, it has been clarified that Au-Al-Yb quasicrystal exhibits specific temperature dependence of magnetism, electronic specific heat, and electrical resistance at cryogenic temperatures. Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi$. The magnetic susceptibility $\chi$ rapidly increase at the low-temperature side at $T^{-0.51}$, and appears to diverge at $T=0$ in the case of magnetic field $H\sim0$. Actually, as seen in the inset, $\chi^{-1}$ has a linear relationship with $T^{0.51}$, and the straight line passes through the origin. This is the dependence different from the Curie low proportional to $T^{-1}$. In addition, divergence tendency was also observed in the temperature dependence of the electronic specific heat coefficient. Furthermore, although the divergence of the magnetic susceptibility is suppressed by the application of the magnetic field, it does not depend on the pressure (see the inset of Figure 3). These experimental results show that a unique quantum critical state "insensitive to pressure" occurs in the Au-Al-Yb quasicrystal. As pressure usually changes the degree of $s$-$f$ hybridization, such insensitivity to pressure is not an example in crystal.

On the other hand, in the Au-Al-Yb approximant crystal having a composition similar to that of the quasicrystal, the susceptibility shows a finite value at the limit of $T=0$. This indicates occurrence of "Heavy fermion" similar to that observed in ordinary valence-fluctuating crystals. Recent research has further revealed that the temperature dependence of the magnetic susceptibility of the approximant is greatly affected by the application of pressure, and that it also shows quantum criticality at approximately 2 GP. This clear difference between the approximant and the quasicrystal suggests that the unique quantum criticality is a phenomenon inherent to a quasicrystal.

For details, please refer to the following two papers.

4. Dodecagonal quasicrystals

In 1985, the authors found the first "dodecagonal quasicrystal" in Ni-Cr alloy particles of about 1000 Å in diameter. This is a "two-dimensional quasicrystal" with a 12-fold symmetry axis as well as quasiperiodicity in the plane perpendicular to the axis. This is the third kind of quasicrystal following the icosahedral and the decagonal quasicrystals*. However, as of around 1990, the dodecagonal quasicrystals were limited to the fine particles and some other rapidly quenched alloys, and the research in the metal field came to a dormant state.

* This result was cited as reference 13 in the official document of the Nobel Prize in Chemistry 2011 "Scientific background on the Nobel Prize in Chemistry 2011: The Discovery of Quasicrystals".

On the other hand, recently, dodecagonal quasicrystals have been discovered one after another in ceramics such as mesoporous silica, polymers such as micelle-forming dendrimer and ABC star polymer, and surfaces such as very thin layer of BaTiO3 on Pt (111). By these discoveries, the universality of the dodecagonal order in the material world has become clear. Then, we resumed research on alloys around 2010. The target is a stable metallic dodecagonal quasicrystal with structural quality comparable to the ordinary crystal.

A new alloy was searched experimentally starting from two kinds of approximant known in Mn-Cr-Si alloy, which are respectively high- and low-temperature phases. As a result, a new dodecagonal quasicrystal was discovered as an alloy containing 1 at.% of Ni (Figure 4). The conventional dodecagonal quasicrystals in alloys are formed through non-equilibrium treatment such as quenching, whereas this quasicrystal is formed by aging from β-Mn type crystal. Therefore, it can be said that this is one step closer to the stable quasicrystal. A high resolution electron microscope image is presented in Figure 4. Tiling of squares and equilateral triangles (edge length 4.6 Å) is observed, which is the feature of the dodecagonal quasicrystal. The squares and triangles further form regular dodecagons as indicated in the figure. However, as a result of detailed analysis, it became clear that quasiperiodicity was kept only within a limited range of about 100 Å in diameter. It is still an unsolved problem to synthesize dodecagonal quasicrystals with high degree of structural perfection. This result was published in the following paper.

* Phason space analysis and structure modeling of 100 Å-scale dodecagonal quasicrystal in Mn-based alloy, T. Ishimasa, S. Iwami, N. Sakaguchi, R. Oota and M. Mihalkovič, Phil. Mag. 95 3745-3767 (2015).
5. Other important result: Dynamical flexibility in Zn₆Sc approximant

In the series of quasicrystals and their approximants mentioned in Section 2, we studied both static and dynamical structures, as well as physical properties such as magnetism. Among them, the most important result is dynamical flexibility related to the central structure of the cluster. In the case of Zn₆Sc approximant, this is the rotation like motion of the Zn tetrahedron in THz order (see Figure 5). This movement is similar to the rattling, except that the four Zn atoms move together holding the shape of the tetrahedron. At low temperature below approximately 150K, the movement stops and an ordered structure is formed. This new phenomenon named dynamical flexibility was clarified from the results of X-ray structure analysis at low temperature as well as neutron quasi-elastic scattering experiment at higher temperature. It is surprising that such a dynamical phenomenon occurs inside a hard and brittle intermetallic compound. For details, please refer to the following two papers.