Quantum critical behavior in magnetic quasicrystals and approximant crystals

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Abstract. The electronic states of quasicrystals are believed to be critical, neither extended nor localized. To experimentally establish such the critical state remains a formidable challenge. In the Au-Al-Yb quasicrystal, we observed quantum critical phenomena that are characterized by unconventional critical indices similar to those of Yb-based heavy fermions. In contrast, no divergence was observed in the Au-Al-Yb approximant crystal. These results lead us to suggest that the observed quantum criticality is related to the critical state unique to the quasicrystals. Here we review these results, including the recent observation of the superconductivity in the Tsai-type approximant crystal that is isostructural to the Au-Al-Yb approximant, and argue that the quantum criticality of the quasicrystal results from the combined effect of the quasiperiodicity and the electron correlation.

1. Introduction

Quasicrystals (QCs) and heavy fermions have been one of the main topics in solid state physics and developed independently during the last decades. Recently, a new type of the QC was found in which the thermodynamic properties such as the magnetic susceptibility and the specific heat diverge as $T \to 0$ [1], with the critical indices similar to those of YbRh$_2$Si$_2$ and YbAlB$_4$ [2, 3]. Study on this novel QC may shed more light on the basic notions of the quantum criticality in the heavy fermion crystals, and an electronic state unique to the QCs as well.

The QC is a metallic alloy that possesses long-range, aperiodic structures (see Fig. 1(a)) with diffraction symmetries such as $m\bar{3}5$ forbidden to conventional crystals. Figure 1(b) shows the electron diffraction pattern of our QC sample demonstrating 5-fold symmetry. Note that the Bragg spots are very sharp like in the conventional crystals but not like in amorphous materials, confirming the presence of some kind of the long-range ordering in the QC. Because of this unique structure, we expect the existence of the so-called critical state that is neither extended nor localized. This novel electronic state has long been pursued by experimentalists but has not been established yet. As a promising candidate of the QC critical state, the valence fluctuation QC, Au$_{51}$Al$_{34}$Yb$_{15}$, has attracted much attraction; while the QC shows the quantum critical phenomenon, its corresponding periodic crystal called the approximant crystal (AC; see Fig. 1(c)) shows no such divergence and only heavy Fermi liquid behavior at low temperatures [1].

The QC and AC of the present interest consist of atomic decorations (i.e., icosahedral clusters of atoms) called Tsai-type cluster, which is composed of a concentric arrangement of multiple
Figure 1. Geometric structure of the Tsai-type quasicrystal (QC) and approximant crystal (AC) [1]. (a) Aperiodic array of icosahedrons in the QC. (b) Diffraction pattern of the QC studied here. (c) Body-centered cubic array of the icosahedrons in the AC. (d) Tsai-type cluster composed of a concentric arrangement of multiple shells.

shells (Fig. 1(d)). At the center of the first shell, there is a polyhedron that consists of 4 atoms in total and points in a various direction. The second shell is a dodecahedron that is composed of mixed Au/Al atoms. The third shell is an icosahedron with Yb ions on the vertex. The fourth and fifth shell are an icosidodecahedron and triacontahedron, respectively. In the recently discovered Au-Ge-Yb superconducting ACs [4], there are two types of the crystal structure; one contains the tetrahedron as described above [5], and the other contains the single Yb atom at the center of the dodecahedron [6]. These Tsai-type clusters are arranged quasiperiodically in the QC (Fig. 1(a)), while in the 1/1 AC, they are arranged periodically to form a body-centered cubic (bcc) structure (space group: Im3) (Fig. 1(c)).

Before describing the geometrical relationship between the QC and the AC, we present the prescription to construct the quasiperiodicity from the conventional lattice [7]. Figure 2(a) illustrates the square lattice in the plane of $X_1$ and $X_2$. Let us separate the two dimension (2D) space into two orthogonal subspaces, $X_{\parallel}$ (“physical space”) and $X_{\perp}$ (“complementary space”), by rotating the original set of the axes by some angle $\theta$ such that $\tan \theta = 1/\tau$ (where $\tau = (1+\sqrt{5})/2$ is the golden ratio). In order to produce atoms in the physical space, we introduce the atomic basis (sometimes called “acceptance region”, “superatom”, or “hyperatom”) as represented by the heavy line segments perpendicular to $X_{\parallel}$. The intersection of the basis segments with the $X_{\parallel}$ axis locates the position of atoms in the physical space. We find that the atomic density along $X_{\parallel}$ is described by a Fibonacci sequence of long ($L$) and short $(S)$ interatomic spacings, $L, S, L, L, \cdots$, corresponding to the quasiperiodicity in the QC. It may be understood that by extending this prescription, an aperiodic array of atoms in 3Ds can be obtained from a periodic lattice, “hypercrystal”, in 6Ds.

Now we show that the AC structure results from introducing a “linear phason strain” in the QC hypercrystal, using a simple example shown in Fig. 2(b). The “phason displacement” $w$ is a displacement of the atomic basis along the $X_{\perp}$ axis, and the “phason strain” is defined by $dw/dX_{\parallel}$; then, the linear phason strain is characterized by a constant $A$ such that
Figure 2. (a) Construction of an aperiodic array of atoms in 1D from a periodic square lattice in 2Ds. $X_1$ and $X_2$ axes denote the square lattice. The physical space ($X_\parallel$) represents a 1D cut through the 2D periodic lattice. The sequence of $L$ and $S$ on the $X_\parallel$ axis corresponds to the Fibonacci sequence. (b) Construction of AC from QC. The light-gray symbols in the upper panel denote the atomic basis on the square lattice of the QC. By inducing the linear phason strain $w$ shown in the lower panel, the periodic sequence with a period $LS$ ($L$ and $S$ being the length between the black atomic bases) emerges on the $X_\parallel$ axis.

$w = AX_\parallel$ as shown in the lower panel. The constant $A$ is expressed in terms of the Fibonacci sequence as $A = (F_{n+1} - F_n)/(F_{n+1} + F_n)$, where $F_n$ is a successive Fibonacci number; $F_0 = 0, F_1 = 1, F_2 = 1, F_3 = 2, \cdots$. In the case of Fig. 2(b), $A$ corresponds to $n = 1$, which gives rise to the displacement from the light-gray to black segments shown in the upper panel, and the resulting arrangement of the atomic basis along the $X_1$ becomes periodic, $L, S, L, S, \cdots$. This is just a regular crystal with the unit cell of $LS$, and called 1/1 AC. In the case of $n = 2$, the interatomic spacings become periodic again, but the unit cell is $LSL$. This is called 2/1 approximant; the number 2 and 1 corresponds to the number of $L$ and $S$ in the unit cell, respectively. Note that the higher order AC (characterized by the larger $n$) has the larger unit cell size. As a result, in an ideal case, the QC is regarded geometrically as a limit of the rational AC with the infinitely large unit cell, in other words, the AC approaches the QC as $A \to 0$.

The 3D AC is characterized by the conventional cubic lattice parameter $a_{3D}$ as usual, whereas the 3D QC is characterized by the 6D lattice parameter $a_{6D}$. (For our case, the Au-Al-Yb QC and AC have $a_{6D} = 0.7448$ nm and $a_{3D} = 1.4500$ nm, respectively.) These lattice parameters are connected by the relation, $a_{3D} = Ba_{6D}$, where $B = \sqrt{2/(\tau + 2)(F_{n+1} + F_n)}$. For the 1/1 AC, $B$ is approximately equal to 1.946. For the higher order ACs, the same relation holds but $B$ takes a different value from the above number. Remembering these in mind, we discuss the physical properties of the QCs and ACs in the next section.

2. Results and Discussion

Figure 3(a) shows the inverse magnetic susceptibility of Au$_{49}$Al$_{34}$Yb$_{17}$ QC (referred to as Au-Al-Yb QC hereafter) as a function of temperature [1, 8], which shows a Curie-Weiss form above $\sim100$ K. The linear slope yields the effective moment as $p_{\text{eff}} = 3.91 \mu_B$ per Yb ion (where $\mu_B$ is the Bohr magneton). This value is smaller than that of the free Yb$^{3+}$ ion, $4.54 \mu_B$, indicating that the Yb-ion of the QC is in between Yb$^{3+}$ and Yb$^{2+}$, in agreement with X-ray absorption near edge structure experiments [9].

As $T \to 0$, the magnetic susceptibility of the QC shows the quantum critical behavior, $\chi \propto T^{-0.51}$, at $H = 0$ as shown in Fig. 3(b). The electronic specific heat coefficient also shows
the divergent behavior \([1]\), \(C/T \propto -\ln T\), where \(C\) is specific heat.

One may think that this unconventional low-\(T\) behavior might be caused by the random occupation of the Au and Al atoms in the Tsai-type clusters \([10]\). To examine this possibility, we measured the susceptibility of the 1/1 AC, \(\text{Au}_{49}\text{Al}_{36}\text{Yb}_{15}\), whose composition is very similar to that of the QC. Note that it also contains the same type of randomness as the QC \([11]\). While the AC shows the intermediate valence nature \((p_{\text{eff}} = 3.96\mu_B)\) at high temperatures similarly to the QC (Fig. 3(a)), it shows a tendency to saturate at low temperatures in contrast to the QC (Fig. 3(c)). (The specific heat also shows the Fermi liquid feature at low temperatures \([1]\), in contrast to the divergent feature in the QC mentioned above.) If the non-Fermi liquid behavior of the QC would be due solely to the randomness, then the similar divergence should be observed in the AC. However, this is not the case. Therefore, it is very unlikely that the unusual low-\(T\) behavior of the QC is caused by the randomness.

Instead, the quantum criticality of the QC seems to be reasonably ascribed to the presence of the quasiperiodicity, because it is absent in the AC. However, one may think that in the case of the QC, the quantum critical point would appear accidentally at ambient pressure. To check this possibility, we measured the high-pressure magnetic susceptibility. For the QC, the divergent behavior survives at the highest pressure accessible in the present experiment \((\sim 2.8\ \text{GPa})\) (not shown here). In contrast, the AC shows the heavy-fermion like feature: The low-temperature susceptibility increases with pressure, and at a high pressure exceeding 2 GPa, a cusp-like anomaly emerges at a very low temperature below 100 mk (not shown here). It is open whether this is ascribed to the long-range ordering or the spin-glass like transition, but we failed to find in the AC the quantum critical point where the susceptibility diverges as \(T \to 0\).

The different response to the hydrostatic pressure between the QC and the AC implies that the quantum criticality even at ambient pressure is not fortuitous but inherent to the QC, and confirms that the quasiperiodicity plays a role in the emergence of the quantum criticality of the QC.

The question to be addressed here is if all the QCs would show the quantum criticality. To examine this, we prepared the Tm-based samples isostructural to the Yb-based ones, and measured the magnetic susceptibility \([12]\). The temperature dependences of the Au-Al-Tm
Figure 4. Temperature dependence of magnetic susceptibility of the Au-Al-Tm QC and AC [12]. (a) The inverse dc magnetic susceptibility measured at \( H = 500 \) Oe. (b) Ac magnetic susceptibility measured at zero dc field at low temperatures. Note that the broad peak emerges at \( T_f \approx 0.43 \) and 0.28 K for the QC and the AC, respectively.

QC and AC are shown in Fig. 4(a). The \( 1/\chi(T) \) curve shows the linear behavior over a wide temperature range, and the slope above \( \sim 150 \) K yields \( p_{\text{eff}} = 7.8 \) and 7.4 \( \mu_B/\text{Tm} \) for the QC and the AC, respectively. These \( p_{\text{eff}} \) values are close to the free ion value of Tm\(^{3+} \) (7.54 \( \mu_B \)), indicating that their 4\( f \) electrons are localized in the real space. At low temperatures, both the QC and AC show a transition into a spin-glass like state as suggested by a broad peak at a temperature \( T_f \) below 1 K (Fig. 4(b)). Note that the specific heat also shows a broad peak at a temperature close to \( T_f \) [12]. It should be mentioned that the Curie-Weiss behavior continues to low temperatures down to \( T_f \). From these results, we conclude that the valence fluctuation is also needed for the emergence of the quantum criticality in the Yb-based QC.

The importance of the valence fluctuation as a result of the hybridization effect may be confirmed from the substitution effect of the constituent elements on the physical properties. We prepared the \( \text{Au}_{44}\text{Ga}_{41}\text{Yb}_{15} \) and \( \text{Ag}_{47}\text{Ga}_{38}\text{Yb}_{15} \) AC, which were found to belong to the 1/1 AC with the lattice constant of \( a_{3D} = 1.4527 \) and 1.4687 nm, respectively. As may be expected from the fact that these lattice constants are larger than that of the Au-Al-Yb AC, 1.4500 nm, the two substituted ACs possess no localized magnetic moment and hence their Yb valence is divalent. From this observation, we suggest that the Au-Al-Yb QC and AC are located near the border of the divalent and trivalent states of the Yb ion [8].

We also synthesized \( \text{Au}_{64.0}\text{Ge}_{22.0}\text{Yb}_{14.0} \) and \( \text{Au}_{63.5}\text{Ge}_{20.5}\text{Yb}_{16.0} \), which are referred to as Au-Ge-Yb(I) and Au-Ge-Yb(II), hereafter. Our structure analysis showed that the Au-Ge-Yb(I) is a Tsai-type 1/1 AC with \( a_{3D} = 1.4724 \) nm [4]. For Au-Ge-Yb(II), we were unable to give a structure model due to the lack of a single phase sample, but it was reported by Gebresenbut et al. that Au-Ge-Yb(II) is also a Tsai-type 1/1 AC [6]. These two ACs have a slight difference in the crystal structure as mentioned in Introduction: The cluster center of the Au-Ge-Yb AC(I) is a tetrahedron, while in the Au-Ge-Yb AC(II), a single Yb ion occupies the cluster center; as a result, 12 and 13 Yb ions are contained in the Tsai-type cluster in the Au-Ge-Yb AC(I) and AC(II), respectively. We note that the Au-Ge-Yb AC(I) and AC(II) show superconductivity below 0.68 and 0.36 K, respectively. From a detailed analysis of the magnetism, we found that while the Yb ions on the vertex of the icosahedron are divalent, the cluster-center Yb ion is likely of intermediate valence. These results suggest that the hybridization effect plays an important role in the physical properties of the materials investigated here. The interplay between the
magnetism and the superconductivity remains to be resolved in the future.

Let us study the magnetic field effect on the Au-Al-Yb QC. As was shown in Figs. 3(b) and (c), the application of uniform magnetic field $H$ suppresses the growing of the magnetic susceptibility with lowering temperature in both the QC and the AC, resulting in a field-induced Fermi liquid state below a characteristic temperature $T^*$ with an enhanced Pauli susceptibility.

According to our preliminary measurements, the strong sensitivity to the magnetic field was also observed at high pressures. Such the magnetic field effect is often observed in the heavy fermions, and the AC is considered as a heavy fermion system. Therefore, the nonmagnetic ground state such as the Kondo state is likely formed in the QC.

Finally we summarize the characteristics of the Au-Al-Yb QC comparing the ACs. In the 3D space of the temperature, pressure, and magnetic field, the QC is located on the “quantum critical line” at $T = 0$ (see the heavy line on the $P$ axis in Fig. 5(a)). (Note that the quantum critical line running on the zero temperature plane in the phase diagram might be ubiquitous as was theoretically discussed to study a novel high-pressure phase of the itinerant electron ferromagnet ZrZn$_2$ [13]; it may be interesting to compare the experimentally obtained phase diagram of ZrZn$_2$ [14] with the present result.) This results in the plot of $T^*$ vs. $a_{6D}$ (Fig. 5(b)) in which the QC takes a route as indicated by the thick arrow: Here, the application of the hydrostatic pressure decreases $a_{6D}$ like the conventional lattice parameter $a_{3D}$. Remembering that $a_{6D} \propto a_{3D}$, the Au-Al-Yb AC moves as indicated by the thin arrow. Then, we find that the traces of the QC and the AC do not cross each other. Other ACs than the Au-Al-Yb AC occupy a position of high $T^*$ values, reflecting that they behave like a conventional metal. This viewgraph may help us to distinguish the Au-Al-Yb QC with the Yb-based ACs. We consider that this difference comes from the difference in the periodicity/quasiperiodicity and the stable/unstable valence, which allows us to conclude that the unconventional quantum criticality of the Au-Al-Yb QC is caused by the combined effect of the quasiperiodicity and the strong electron correlation.

We speculate the material dependence of the quantum critical behavior as shown in Fig. 5(c), in which the QC is located at a limit of zero linear phason strain. To confirm this speculation would give a direct evidence for the above conclusion. The search for the higher-oder ACs like the 2/1 AC is a challenging work in the future.

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**Figure 5.** (a) Schematic illustration of $T$-$P$-$H$ phase diagram of the Au-Al-Yb QC. The hatched plane marks $T^*$ below which the Fermi liquid is observed. (b) Schematic illustration of the characteristic temperature $T^*$ (or the transition temperature $T_f$ into a short-range or long-range ordered state) as a function of the 6D lattice parameter $a_{6D}$. (c) $T^*$ as a function of the inverse of the 3D lattice parameter $a_{3D}$. Note that the QC can be regarded as the AC with $a_{3D} \to \infty$. 
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