新量子臨界性を圧力下で示す

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New quantum criticality revealed under pressure

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Unconventional quantum critical phenomena observed in Yb-based periodic crystals such as YbRh\textsubscript{2}Si\textsubscript{2} and $\beta$-YbAlB\textsubscript{4} have been one of the central issues in strongly correlated electron systems. The common criticality has been discovered in the quasicrystal Yb\textsubscript{15}Au\textsubscript{51}Al\textsubscript{34}, which surprisingly persists under pressure at least up to $P = 1.5$ GPa. The $T/H$ scaling where the magnetic susceptibility can be expressed as a single scaling function of the ratio of the temperature $T$ to the magnetic field $H$ has been discovered in the quasicrystal, which is essentially the same as that observed in $\beta$-YbAlB\textsubscript{4}. Recently, the $T/H$ scaling as well as the common criticality has also been observed even in the approximant crystal Yb\textsubscript{14}Au\textsubscript{51}Al\textsubscript{35} under pressure. The theory of critical Yb-valence fluctuation gives a natural explanation for these striking phenomena in a unified way.

1. Introduction

Quantum critical phenomena in itinerant-electron systems have attracted much attention in condensed matter physics. By changing the control parameter of the system, the continuous transition temperature of the ordered state can be suppressed to 0 K, at which a quantum critical point (QCP) is realized. Pressure is one of the most important control parameters, which can change the electronic state to tune the system to the QCP. Near the QCP, a non Fermi-liquid behavior emerges in a series of physical quantities such as resistivity $\rho(T)$, specific heat $C(T)$, magnetic susceptibility $\chi(T)$, and NMR relaxation rate $(T_1 T)^{-1}$, which are referred to as quantum critical phenomena. Quantum criticality emerging near the magnetic QCP in itinerant electron systems has been well understood from the spin fluctuation theory developed by Moriya,\cite{Moriya1, Moriya2, Moriya3, Moriya4} which has been endorsed by the renormalization group theory developed by Hertz\cite{Hertz} and Millis\cite{Millis} (see Table I).

On the other hand, an unconventional quantum criticality has been observed in the Yb-based metal YbCu$_{5-x}$Al$_x$ near $x = 1.5$\cite{Takagi, Watanabe} (see Table I), where a sharp Yb-valence crossover has been observed.\cite{Watanabe} A similar unconventional criticality has been also observed in the heavy-electron metals YbRh$_2$Si$_2$\cite{Kimura, Stievater} and $\beta$-YbAlB$_4$,\cite{Kondo, Kondo2} as listed
Table I. Quantum criticality of conventional and unconventional types. 3d AF denotes a conventional three-dimensional antiferromagnetic criticality. Unconventional criticality observed in Yb-based periodic crystals and the quasicrystal Yb$^{15}$Au$^{51}$Al$^{34}$. CVF denotes the quantum criticality of critical valence fluctuations (CVF) emerging in the temperature region $T > T_0$ with $T_0$ being the characteristic temperature of CVF. $\zeta$ takes the value for $0.5 \leq \zeta \leq 0.7$ depending on the material and temperature range (see Ref. 15 for details).

| Theory and material | $\rho(T)$ | $C(T)/T$ | $\chi(T)$ | $1/(T_1T)$ | Refs. |
|---------------------|-----------|-----------|------------|-------------|-------|
| 3d AF               | $T^{3/2}$ | const.$-T^{1/2}$ | const.$-T^{1/4}$ | $T^{-3/4}$ | 1,4,7,8 |
| YbCu$_{4.5}$Al$_{1.5}$ | $T^{1.5} \to T$ | $- \log T$ | $T^{-0.66}$ | * | 9,10 |
| YbRh$_2$Si$_2$      | $T$       | $- \log T$ | $T^{-0.6}$ | $T^{-0.5}$ | 11,12 |
| $\beta$-YbAlB$_4$   | $T^{1.5} \to T$ | $- \log T$ | $T^{-0.5}$ | * | 13,14 |
| Yb$^{15}$Au$^{51}$Al$_{34}$ | $T$       | $- \log T$ | $T^{-0.51}$ | $T^{-0.51}$ | 17,18 |
| CVF                 | $T$       | $- \log T$ | $T^{-\zeta}$ | $T^{-\zeta}$ | 15,16 |

in Table I. As a possible origin of the unconventional criticality, the theory of critical Yb-valence fluctuation, which gives a unified explanation for the measured quantum critical phenomena (see Table I), has been proposed.\textsuperscript{15,16}

Recently, common unconventional quantum critical phenomena have been discovered in the Yb-based quasicrystal Yb$^{15}$Au$^{51}$Al$_{34}$ at the ambient pressure $P = 0$ and zero magnetic field $H = 0$\textsuperscript{17,18} (see Table I). Surprisingly, the quantum criticality persists even under pressure at least up to $P = 1.5$ GPa.\textsuperscript{17} Recently, the common quantum criticality has been observed in the approximant crystal Yb$_{14}$Au$_{51}$Al$_{35}$ when pressure is tuned.\textsuperscript{19} Interestingly, a new type of scaling called “$T/H$ scaling” has been discovered in the pressurized approximant crystal and quasicrystal,\textsuperscript{20} where magnetic susceptibility is expressed as a single scaling function of the ratio of the temperature $T$ to the magnetic field $H$.\textsuperscript{19} This behavior is essentially the same as that observed in the periodic crystal $\beta$-YbAlB$_4$.\textsuperscript{14} Furthermore, the $T/H$ scaling behavior has also been observed even in the approximant crystal when pressure is tuned.\textsuperscript{19} The theory of critical valence fluctuation (CVF) has been shown to give a natural explanation for these striking phenomena in a unified manner.

In this paper, a new type of quantum criticality arising from the CVF is reviewed, mainly focusing on new aspects of quantum critical phenomena revealed under pressure. In Sect. 2, the CVF theory will be explained. An experimental indication of valence instability will be discussed in Sect. 3. The paper will be summarized in Sect. 4.
2. Theory of critical valence fluctuation (CVF)

As the simplest minimal model for the Ce- and Yb-based heavy-electron systems, we consider the extended periodic Anderson model

\[
\mathcal{H}_{\text{EPAM}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \varepsilon_f \sum_{i\sigma} n_{i\sigma}^f + \sum_{\mathbf{k}\sigma} \left( V_{\mathbf{k}} f_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \text{h.c.} \right) + U \sum_i n_{i\uparrow}^f n_{i\downarrow}^f
\]

with \( n_{i\sigma}^f = f_{i\sigma}^\dagger f_{i\sigma} \) and \( n_{i\sigma}^c = c_{i\sigma}^\dagger c_{i\sigma} \). The first line is the so-called periodic Anderson model. The conduction electron with the energy band \( \varepsilon_{\mathbf{k}} \) and the f electron with the f level \( \varepsilon_f \) hybridizes with the hybridization \( V_{\mathbf{k}} \). The onsite Coulomb repulsion between f electrons is denoted by \( U \) in the 4th term. The second line indicates the interorbital Coulomb repulsion between f and conduction electrons, \( U_{fc} \), which plays an important role of inducing the first-order valence transition. For example, in the Ce metal that exhibits the \( \gamma-\alpha \) transition, there are 4f and 5d bands at the Fermi level. Since both the 4f and 5d orbitals are located at the same Ce site, \( U_{fc} \) has a considerable value and cannot be neglected (see Ref. 22 for details).

Actually, theoretical calculations based on \( \mathcal{H}_{\text{EPAM}} \) [Eq. (1)] have shown that the first-order valence transition occurs for a sufficiently large \( U_{fc} \) and the corresponding \( T-P \) phase diagram is illustrated in Fig. 1(a). In Fig. 1(a), the first-order valence transition terminates at the critical end point (CEP), from which the valence-crossover line extends. As \( U_{fc} \) decreases, the critical temperature decreases, which corresponds to the cases from Figs. 1(a)-1(d). When the critical temperature is located at \( T = 0 \) K, the quantum CEP is realized, which is called the quantum critical point (QCP) of the valence transition [see Fig. 1(c)]. At the QCP, the CVF diverges, which can cause the instability of the electronic state. Indeed, the superconducting correlation has been shown to be enhanced in the Kondo regime near the QCP by theoretical calculations in \( \mathcal{H}_{\text{EPAM}} \). The CVF-mediated superconductivity is favorably compared with the pressure-induced superconductivity in CeCu₂Si₂, CeCu₂Ge₂, and CeCu₂(Si₁₋ₓGeₓ)₂ (see Ref. 33 for details).

2.1 Mode-mode coupling theory of critical valence fluctuations

To clarify the quantum critical phenomena of the CVF arising from the QCP of the valence transition, we have constructed the mode-mode coupling theory of CVF by taking into account the local correlation effects of f electrons due to the on-site Coulomb repul-
Fig. 1. Schematic phase diagrams of valence transition and crossover in the temperature $T$ and pressure $P$ phase diagram. The first-order valence transition (solid line) terminates at the critical end point (CEP) (solid circle), from which the valence-crossover line (dashed line) extends. As $U_{fc}$ in the extended periodic Anderson model [Eq. (1)] decreases, the critical temperature decreases, corresponding to the cases from (a) to (d). In (c), the quantum CEP, i.e., quantum critical point (QCP), is realized.
Fig. 2. (Color online) Concentric shell structures of Tsai-type cluster, which is the core structure of quasicrystal and approximant crystal. (a) 1st shell, (b) 2nd shell, (c) 3rd shell, (d) 4th shell, and (e) 5th shell. In (b) and (d), Al/Au mixed sites are framed in red. In (c), the number indicates the $i$-th Yb site.

both show the same criticality.\textsuperscript{15,34)} Then, a huge Wilson ratio appears. Note that, in the region $T < \sim T_0$, electronic resistivity behaves as $\rho(T) \sim T^{1.5}$ in dirty systems and $\rho(T) \sim T^{5/3}$ in clean systems.\textsuperscript{15)} This gives a unified explanation for the unconventional quantum criticality observed in Yb-based metals, as shown in Table I.\textsuperscript{16,35)}

2.2 Robust quantum criticality in quasicrystal $\text{Yb}_{15}\text{Au}_{51}\text{Al}_{34}$ under pressure

To get insight into the mechanism of the robust quantum criticality in $\text{Yb}_{15}\text{Au}_{51}\text{Al}_{34}$ under pressure, let us start with analyzing the lattice structure of the quasicrystal. The quasicrystal consists of an Yb-Au-Al cluster with concentric shell structures from the 1st to 5th shells, as shown in Figs. 2(a)-2(e), respectively. In the 3rd shell, there are 12 Yb atoms. In the 1st, 2nd, and 4th shells, Al/Au mixed sites exist. Namely, the Al or Au atom is located with the existence ratio of Al/Au being 7.8%/8.9% (1st shell), 62%/32% (2nd shell), and 59%/41% (4th shell).\textsuperscript{36)} In Figs. 2(b) and 2(d), the Al/Au mixed sites framed in red are illustrated as a representative case following the existence ratio. There also exists an approximant crystal with the periodic arrangement of the body-centered cubic (bcc) structure of the Yb-Au-Al cluster with the concentric shell structures shown in Figs. 2(a)-2(e).\textsuperscript{36)}

As discussed in Sect. 2.1, the locality of the CVF mode is considered to be the key origin of the emergence of the new type of quantum criticality. Namely, the charge transfer between the Yb site and the surrounding atoms is considered to play a key role, which is essentially local. Hence, let us concentrate on the Yb-Au-Al cluster.

A recent measurement performed by replacing Al with Ga in the quasicrystal has revealed that the quantum critical behavior in physical quantities disappears.\textsuperscript{37)}
Fig. 3. (Color online) Contour plot of valence susceptibility $\chi_v$ for (a) $i = 1$, (b) $i = 2$, (c) $i = 3$, (d) $i = 4$, (e) $i = 5$, and (f) $i = 6$ calculated for the Yb-Au-Al cluster.\(^{38}\) In each white region, the CVF diverges at the QCP of valence transition. (g) Total valence susceptibility $\chi_v = \sum_{i=1}^{12} \chi_{vi}$ suggests that conduction electrons at Al sites contribute to the quantum critical state. Hence, we consider the extended Anderson model with the f orbital at the Yb site and the conduction orbital at the Al site on the Yb-Au-Al cluster as the simplest minimal model.\(^{38}\) This model has essentially the same structure as the extended periodic Anderson model with the $U_{fc}$ term $H_{EPAM}$ [Eq. (1)], which exhibits the quantum valence criticality.

By using the slave-boson mean-field theory for $U = \infty$, we determined the ground-state phase diagram of the Yb-Au-Al cluster for a typical parameter set of heavy electrons.\(^{38}\) The result of the contour plot of the valence susceptibility for each f site indicated as the $i$-th site in Fig. 2(c), $\chi_{vi} = -\frac{\partial n_f^i}{\partial \varepsilon_f}$, is shown in Figs. 3(a)-3(f), representing the CVF in the phase diagram of the f-level $\varepsilon_f$ and interorbital Coulomb repulsion $U_{fc}$. We see that the valence QCPs appear as spots, which are located inside the white islands. This is because the strength of the f-c hybridization at each f site differs owing to the Al/Au mixed sites. The contour plot of the total valence suscep-
tibility $\chi_v = \sum_{i=1}^{12} \chi_{vi}$, is shown in Fig. 3(g). An important result is that the valence QCPs appear as spots in the phase diagram, whose critical regions are overlapped to be unified, giving rise to a wide quantum critical region.

When pressure is applied to Yb compounds, the f level $\varepsilon_f$ in the hole picture decreases and $U_{fc}$ increases generally. Hence, when applying pressure follows the line located in the enhanced CVF region, a robust quantum criticality appears under pressure. The emergence of a wide critical region also gives a natural explanation for why quantum criticality appears without tuning the control parameters in this material.38)

### 2.3 Same criticality in approximant crystal by pressure tuning

In Sect. 2.2, we analyzed the fundamental nature of the Yb-Au-Al cluster, which is the core structure of both the quasicrystal and approximant crystal. Essentially, the local nature of the CVF offers an interesting possibility that the same criticality appears in the approximant crystal when pressure is tuned.38)

By further considering outer concentric shells to the Yb-Au-Al cluster shown in Fig. 2, the quasicrystal is constructed, where the valence QCPs are expected to appear as widespread and condensed spots like, for instance, the Andromeda Galaxy. On the other hand, in the approximant crystal, the Yb 12 cluster is periodically arranged, giving rise to 24 valence QCP spots in the bulk limit at most, since 24 Yb atoms are located inside the bcc unit cell. Hence, the quantum critical region in the quasicrystal is expected to be larger than that in the approximant crystal.39)

Recently, these theoretical predictions have actually been observed experimentally.19) When pressure is applied to the approximant crystal Yb$_{14}$Au$_{51}$Al$_{35}$ and is tuned to $P = 1.96$ GPa, the magnetic susceptibility has been discovered to exhibit the quantum critical behavior $\chi \sim T^{-0.5}$, which is the same as that in the quasicrystal Yb$_{15}$Au$_{51}$Al$_{34}$. It has also been observed that the quantum critical region in the $T$-$P$ phase diagram is much wider in the quasicrystal than in the approximant crystal.19)

The emergence of the common quantum criticality in the quasicrystal and approximant crystal suggests that its key origin is the Yb-Au-Al cluster with the strong locality of the CVF as the underlying mechanism because essentially the “local” CVF does not depend on the details of lattice structures. Namely, the emergence of the quantum valence criticality itself does not depend on the periodic crystal or quasicrystal, while the extent of the critical regions in their phase diagrams can be different as noted above. The significance of the Yb-Au-Al cluster is also reinforced by the experimental fact
that the simple Kondo disorder scenario due to the Al/Au mixed sites is incompatible with the robustness of the critical exponent under pressure.\textsuperscript{17} The appearance of the common criticality even in the pressurized approximant crystal also offers serious difficulties in the Kondo disorder scenario for the quasi periodicity.\textsuperscript{40,41} It remains to be resolved whether the quantum critical behavior of physical quantities such as $\chi(T)$, $C(T)/T$, $\rho(T)$, and $(T_1 T)^{-1}$ listed in Table I can be explained by the Kondo disorder scenario in a unified manner.

In the approximant crystal, the magnetically ordered phase has been observed for $P \gtrsim P_c = 2$ GPa.\textsuperscript{19} However, the magnetic order is considered to be a secondary effect on the unconventional criticality since there exists no magnetic order anywhere in the $T$-$P$ phase diagram from $P = 0$ at least up to $P = 1.5$ GPa in the quasicrystal.\textsuperscript{17} Theoretically, it has been shown that the valence-crossover pressure $P_v^*$, which is defined as the pressure at the dashed line in Figs. 1(c) and 1(d), coincides with the magnetic transition pressure $P_c$ in $\mathcal{H}_{\text{EPAM}}$ in the case of a rather small f-c hybridization strength in Eq. (1).\textsuperscript{26,28} The $T$-$P$ phase diagram of the approximant crystal is in agreement with this result.

2.4 Valence-crossover “region” in Yb- and Ce-based quasicrystals

When the magnetic field is applied to $\mathcal{H}_{\text{EPAM}}$ [Eq. (1)] the valence QCP starts to shift to the smaller-$U_{\text{fc}}$ direction in the ground-state phase diagram of the $\varepsilon_{\text{f}}$-$U_{\text{fc}}$ plane.\textsuperscript{22,34} Hence, when the system is located in the Kondo regime close to the valence QCP for $U < U_{\text{QCP}}$, a field-induced valence-crossover line is expected to appear, as shown in
Fig. 4(a). As \( H \) varies across \( T^*_v \), crossover from the Kondo regime with a relatively larger \( n_f \) (\( \lesssim 1 \)) to the mixed-valence regime with a relatively smaller \( n_f \) occurs. This valence-crossover effect arising from the CEP occurs in addition to the ordinary Zeeman effect, which increases \( n_f \) monotonically to reach the \( n_f = 1 \) state to earn the Zeeman energy. Hence, a negative contribution to the monotonic increase in \( n_f \) is expected to be marked at the \( T^*_v \) line in Fig. 4(a), especially for lower temperatures, since the effect of finite temperature easily makes the valence crossover be smeared out.

On the other hand, in the quasicrystal \( \text{Yb}_{15}\text{Au}_{51}\text{Al}_{34} \), the valence QCPs are densely condensed, giving rise to a valence-crossover region with a certain width, as shown in Fig. 4(b).

\(^{39}\) In this case, the valence-crossover-induced negative contribution to the monotonic increase in \( n_f \) by the Zeeman effect occurs in a certain \( H \) region. Note here that the absolute values of the \( n_f \) changes, caused by the valence crossover and Zeeman effect, respectively, depend on the details of each material. Hence, at least, some counter effect to the monotonic increase in \( n_f \) ordinarily seen as the Zeeman effect is expected to be conspicuous for a certain \( H \) region, especially for low temperatures.

### 2.5 \( T/H \) scaling in pressurized approximant crystal and quasicrystal

To clarify the origin of quantum critical phenomena commonly observed in the quasicrystal and pressurized approximant crystal, we have constructed the periodic Anderson model for the approximant crystal with 4f electrons at Yb sites and 3p electrons at Al sites.\(^{42}\) Namely, we consider the system with the periodic arrangement of the bcc structure of the Yb-Au-Al cluster (see Fig. 2), which was discussed in Sect. 2.2. As the first step of analysis, we consider the case where Al/Au mixed sites framed in red in Figs. 2(b) and 2(d) are occupied by Al and the orbital degeneracy of electrons is neglected. The transfer integral of 3p electrons between the nearest-neighbor (N.N.) Al sites is set to be \( t_2 \) [see Fig. 2(b)] and the f-c hybridization between 4f and 3p electrons at the N.N. Yb and Al sites on the 3rd shell [see Fig. 2(c)] and 2nd shell [see Fig. 2(b)] is set to be \( V_0 \). The transfer integral of 3p electrons between the N. N. Al sites on the 5th shell [see Fig. 2(e)] is set to be \( t'_5 \). The other transfers and f-c hybridizations between the different shells are set so as to follow the distance dependence 1/\( r^{\ell+\ell'+1} \) with the azimuthal quantum numbers \( \ell \) and \( \ell' \) (see Ref. 42 for details).\(^{43-45}\)

By using the slave-boson mean-field theory for the strong limit of Coulomb repulsion between f electrons, \( U = \infty \), for a typical parameter set of heavy electrons at half filling, the band structure is calculated.\(^{42}\) In Fig. 5(a), the density of states of each of the 4f
and 3p electrons on the 2nd to 4th shells, respectively, $D(\varepsilon)$, for the parameters $t_2 = 1.0$, $t'_5 = 0.2$, $V_0 = 0.13$, $\varepsilon_f = -0.4$, and $U = \infty$ is shown, which simulates the pressurized approximant crystal. Because of the strong Coulomb repulsion between 4f electrons, the renormalized f level is raised up to the vicinity of the Fermi level $\varepsilon_F$, giving rise to the heavy quasiparticle band.\cite{42} Hence, the dominant contribution to the density of states at the Fermi level originates from 4f electrons at Yb sites on the 3rd shell [see Fig. 2(c)] and the next leading contribution originates from 3p electrons at Al sites on the 4th shell [see Fig. 2(d)]. This is due to the largest f-c hybridization reflecting the shortest Yb-Al distance (see Yb and Al sites indicated by arrows in Figs. 2(c) and 2(d), respectively).

Indeed, we found that the charge-transfer fluctuation between the 4f electron at Yb on the 3rd shell and the 3p electron at Al on the 4th shell is greatly enhanced.\cite{42} A remarkable result is that an almost dispersionless charge-transfer fluctuation mode appears around $q = 0$, which is ascribed to strong local correlation effect for f electrons.\cite{42} To clarify how the local charge-transfer fluctuation affects the quantum criticality, let

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{(Color online) (a) Densities of states of 4f electrons on the 3rd shell (red) and 3p electrons on the 2nd shell (blue), 4th shell (green), and 5th shell (black) in the Yb-Au-Al cluster in the pressurized approximant crystal. The parameters are set as $t_2 = 1.0$, $t'_5 = 0.2$, $V_0 = 0.13$, $\varepsilon_f = -0.4$, and $U = \infty$ at half filling.\cite{42} The horizontal dashed line indicates the Fermi level $\varepsilon_F$. (b) $T/h$ scaling at the QCP of valence transition at $U_{fc} = 0.0192$ for parameter set in (a).\cite{42} The inset shows the data range in the $T$-$h$ phase diagram to which scaling applies.}
\end{figure}
us focus on the charge-transfer mode. Then, we apply the recently developed mode-mode coupling theory of CVF under a magnetic field\cite{46} to the present system. Namely, starting from the periodic Anderson model with the interorbital Coulomb repulsion $U_{fc}$ and the Zeeman term with the magnetic field $h$, we have derived the self-consistent renormalization (SCR) equation for the CVF.\cite{42} By solving the valence SCR equation at the QCP, which is identified to be $U_{fc} = 0.0192$ for the same parameter set used in Fig. 5(a), we found that the $T/h$ scaling

$$y = h^{1/2} \phi \left( \frac{T}{h} \right)$$

appears over four decades in $T/h$, as shown in Fig. 5(b). The dashed line indicates the least-square fit of the data in the large-$T/h$ region, $y/h^{1/2} = c(T/h)^{\zeta}$, which gives the exponent $\zeta = 0.5$. Then, the solution of the valence SCR equation turns out to have $y \sim T^{0.5}$ dependence. Hence, the magnetic susceptibility $\chi$, as well as the valence susceptibility $\chi_v$, shows the criticality as $\chi \propto \chi_v \propto y^{-1} \sim T^{-0.5}$. This result indicates that the magnetic susceptibility in the pressurized approximant crystal exhibits $\chi \sim T^{-0.5}$ for the zero-field limit and also the $T/H$ scaling behavior Eq. (4) as observed in the quasicrystal\cite{17} and also in the pressurized approximant crystal.\cite{19} Now, the characteristic temperature of CVF defined by Eq. (3) is evaluated to be $T_0 \sim 10^{-4}$ in the unit of $t_2$, which is comparable to the lowest temperature [see inset in Fig. 5(b)]. By the detailed analysis of the mechanism of the $T/H$ scaling in $\beta$-YbAlB$_4$,\cite{46} it turned out that the emergence of $T/H$ scaling is ascribed to the presence of the small characteristic temperature $T_0$.

Then, let us discuss the quasicrystal from the viewpoint of the infinite limit of the unit cell size of the approximant crystal. Now, the small $T_0$ is realized by the small coefficient $A$, due to the strong locality of the charge-transfer mode [see Eq. (2)] and the small Brillouin zone $q_B$ reflecting the large unit cell. In reality, the $3p_x$, $3p_y$, and $3p_z$ energy bands of Al and the 6s energy band of Au are considered to exist. Those conduction bands are folded into the small Brillouin zone, and hybridizations between them give rise to many splits into the bonding and antibonding bands.\cite{47} Therefore, the conduction bands themselves already have the flat nature. The hybridization between f and their conduction bands is expected to further promote the locality of CVF. The quasicrystal corresponds to the infinite limit of the unit cell size of the approximant crystal. Thus, the quasicrystal is regarded as the system with the small limit of the Brillouin zone. Hence, the characteristic temperature of CVF in the quasicrystal, $T_0$, is
considered to be at least lower than the measured lowest temperature so that, in the low temperature region, $T_T' > T > T_0$, the quantum valence criticality is manifested in a series of physical quantities as $\chi \sim T^{-0.5}$, $(T_1T)^{-1} \sim T^{-0.5}$, $\rho \sim T$, and $C/T \sim -\log T$ (see Table I).

3. Experimental indication of valence instability

To clarify the origin of the unconventional quantum criticality listed in Table I definitely, the experimental identification of the QCP of the valence transition is highly desired. In YbCu$_{5-x}$Al$_x$, it has been observed that the Yb valence crossover occurs near $x = 1.5$.9)

To obtain the evidence of the valence QCP, materials have been examined by measuring the Yb valence and magnetic susceptibility under extreme conditions of low temperature, high pressure, and strong magnetic field. Recently, the evidence of the CEP of the first-order valence transition has been obtained in YbNi$_3$Ga$_9$ by Matsubayashi et al.48)

In YbRh$_2$Si$_2$, a careful measurement by NMR at low temperatures under a magnetic field has been performed by Kambe et al., in which a signature of the phase separation of two heavy-electron states was reported.49) This suggests that relatively larger and smaller Yb valence states coexist, indicating the close proximity to the first-order Yb valence transition.

Consequences of these experimental indications of valence instability will be discussed in the following subsections.

3.1 Discovery of CEP of the first-order valence transition in YbNi$_3$Ga$_9$

By constructing the $T$-$P$-$H$ phase diagram of YbNi$_3$Ga$_9$, the CEP of the first-order valence transition has been discovered in the paramagnetic metal phase.48) It is also observed that the magnetic susceptibility is enhanced toward the CEP, which detects the signature of the simultaneous divergence of the valence and uniform magnetic susceptibilities at the CEP predicted from the CVF theory.15,22,34) It is found that the first-order valence transition surface extends to the magnetically ordered phase for the $P > P_c \approx 9$ GPa region, giving rise to the first-order magnetic transition surface. Namely, the first-order valence transition is considered to terminate the magnetic order, which has been theoretically shown to occur in $H_{\text{EPAM}}$.16,26) Interestingly, the “critical end line”, which connects the CEPs of the valence transition $T_{\text{CEP}}(P,H)$ in the $T$-$P$-$H$ phase diagram,48) seems to be continued to the “tricritical line”, which connects the
tricritical points of the magnetically ordered phase $T_{TCP}(P, H)$ (see Fig. 4 in Ref. 48).

It is also interesting to identify the location of the quantum CEP defined by $T_{CEP}(P_{QCP}, H_{QCP})=0$, i.e., the QCP of the valence transition, in the $T$-$P$-$H$ phase diagram. By tuning the pressure and magnetic field to $P_{QCP}$ and $H_{QCP}$, respectively, the temperature dependence of physical quantities such as $\rho(T)$, $C(T)/T$, $\chi(T)$, and $(T_1 T)^{-1}$ can be observed. At the QCP, the criticality of the CVF theory listed in Table I is expected to appear. Such measurements are highly desired and are left for future studies.

3.2 Signature of coexistence of two-component heavy electron states in YbRh$_2$Si$_2$

Recently, in YbRh$_2$Si$_2$, NMR measurement has revealed that two heavy-electron states coexist at low temperatures under a magnetic field.$^{49}$ This suggests that the phase separation of higher and lower valences of Yb occurs, which can be naturally understood if this material is located closely to the first-order valence transition. Actually, it has been shown theoretically that the CEP of the first-order valence transition can be induced by applying a magnetic field to the $\mathcal{H}_{EPAM}$. This implies that the CEP is raised to approach 0 K [see Fig. 1(d)] and eventually appears on the $T > 0$ side [see Fig. 1(b)] by applying a magnetic field, even if the CEP is located on the $T < 0$ side for zero magnetic field. In reality, the first-order valence transition line is expected to be surrounded by the phase-separated region of the relatively higher and lower valence states of Yb owing to extrinsic effects such as lattice defect and impurity incorporation, which are inevitable in real materials. The experimental fact that the coexistence region expands in the $T$-$H$ phase diagram as $H$ increases$^{49}$ is in agreement with this picture.

4. Summary

The theory of CVF is shown to exhibit a new universality class of quantum criticality. The quantum valence criticality gives a unified explanation for the unconventional criticality observed in Yb-based periodic crystals and also the robustness of the criticality observed in the Yb-based quasicrystal under pressure. The CVF theory has shown the emergence of the common quantum criticality even in the approximant crystal by pressure tuning and the wider quantum critical region in the quasicrystal than in the approximant crystal in the $T$-$P$ phase diagrams. These predictions have actually been observed by recent experiments. The CVF theory also predicts that the valence-crossover region appears in the quasicrystal under a magnetic field.
By constructing the periodic Anderson model on the approximant crystal, we have recently found that the charge-transfer fluctuation between the 4f electron at Yb on the 3rd shell and the 3p electron at Al on the 4th shell in the Yb-Au-Al cluster is dominant, which shows a strong local character. By applying the mode-mode coupling theory to this mode, we have shown that the small characteristic temperature $T_0$ of the CVF emerges so that the quantum valence criticality and $T/H$ scaling behavior appear. This gives a unified explanation for the common criticality in the approximant crystal under pressure and the quasicrystal. These results suggest that a new class of universality is formed irrespective of periodic crystal and quasicrystal because of the strong locality of CVF.

As an experimental indication of valence instability, the evidence of the critical point of the first-order valence transition has recently been observed in the $T$-$P$-$H$ phase diagram of YbNi$_3$Ga$_9$.

High-pressure measurements have been playing key roles in revealing these new aspects of quantum critical phenomena, which are also expected to play significant roles in future studies toward the complete understanding of new quantum critical phenomena.

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