Roles of critical valence fluctuations in Ce- and Yb-based heavy fermion metals

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Abstract

The roles of critical valence fluctuations of Ce and Yb are discussed as a key origin of several anomalies observed in Ce- and Yb-based heavy fermion systems. Recent development of the theory has revealed that a magnetic field is an efficient control parameter to induce the critical end point of the first-order valence transition. Metamagnetism and non-Fermi liquid behavior caused by this mechanism are discussed by comparing favorably with CeIrIn5, YbAgCu4 and YbIr2Zn20. The interplay of the magnetic order and valence fluctuations offers a key concept for understanding Ce- and Yb-based systems. It is shown that suppression of the magnetic order by enhanced valence fluctuations gives rise to the coincidence of the magnetic-transition point and valence crossover point at absolute zero as a function of pressure or magnetic field. The interplay is shown to resolve the outstanding puzzle in CeRhIn5 in a unified way. The broader applicability of this newly clarified mechanism is discussed by surveying promising materials such as YbAuCu4, β-YbAlB4 and YbRh2Si2.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In this paper, we discuss the roles of critical valence fluctuations of Ce and Yb as a key origin of several anomalies observed in the Ce- and Yb-based heavy fermion systems. Recent development of the theory and experiments have revealed that the valence fluctuations appear ubiquitously by tuning the control parameters of the magnetic field and pressure, giving rise to broader consequences than previously recognized. First, we briefly survey accumulated experiments on the anomalies related to the valence transition and its fluctuations, and explain how the theoretical understanding has been achieved so far. Then, we discuss the recent development of theory and experimental results focusing on the prototypical materials.

The valence transition is an isostructural phase transition with a valence of the material element showing a discontinuous jump. A typical example is known as the $\gamma$–$\alpha$ transition in Ce metal [1], where the first-order valence transition (FOVT) occurs in the temperature–pressure ($T$, $P$) phase diagram while keeping the fcc lattice structure, as shown in figure 1(a).

The critical end point (CEP) of the FOVT is located at ($T$, $P$) = (600 K, 2 GPa). The valence of Ce changes discontinuously between Ce$^{3.03+}$ ($\gamma$ phase) and Ce$^{3.14+}$ ($\alpha$ phase) at $T = 300$ K [2]. YbInCu4 is also well known as a prototypical material for the isostructural FOVT [3, 4], where, as $T$ decreases, the Yb valence changes discontinuously from Yb$^{7.97+}$ to Yb$^{7.84+}$ at $T = 42$ K [5]. As diverging density fluctuations in the liquid–gas transition, valence fluctuations diverge at the CEP of the FOVT. When the temperature of the CEP is suppressed by controlling the material parameters and enters the Fermi degeneracy regime, diverging valence fluctuations are considered to be coupled to the Fermi-surface instability. This multiple instability is considered to be a key mechanism for understanding anomalies observed in Ce- and Yb-based heavy fermion systems. Such phenomena have been detected in CeCu2Ge2 [6] and CeCu2Si2 [7], where remarkable enhancement of the superconducting transition temperature appears at the pressure $P$ larger than $P_c$, corresponding to the antiferromagnetic (AF) quantum critical point (QCP) (see figure 1(b)), and in CeCu2(Si$_x$Ge$_{1-x}$)$_2$, where two separate domes of the superconducting phase have been found under pressure [8]. In these materials, near $P = P_c$, remarkable anomalies such as the $T$-linear resistivity and enhancement of the residual resistivity have been observed, which clearly exhibit the distinct behavior of resistivity near $P = P_c$ [6–8]. Furthermore, these materials show that the coefficient $A$ obtained by the $T^2$ fitting to the lowest-$T$ regime of the resistivity decreases by 2–3 orders of magnitude when $P$ increases across $P = P_c$. 


Theoretically, it has been pointed out that enhanced Ce-valence fluctuations are the possible origin of the anomalies near $P = P_c$ in the CeCu$_2$(Si/Ge)$_2$ systems \cite{9}. It has also been pointed out that the sudden drop of the coefficient $A$ at $P = P_v$ can be understood as a sharp change of the valence of Ce on the basis of the Gutzwiller arguments in the periodic Anderson model \cite{10}. It has also been shown that enhanced valence fluctuations cause the $T$-linear resistivity \cite{7} and enhancement of residual resistivity \cite{11}. The emergence of the superconducting dome near $P \sim P_v$ in figure 1(b) has been explained by the valence-fluctuation-mediated superconductivity shown by the slave-boson mean-field theory taking account of the Gaussian fluctuations in the periodic Anderson model \cite{10}. The density-matrix renormalization group (DMRG) calculation applied to the same model in one spatial dimension has also shown the enhancement of the superconducting correlation in the same parameter regime \cite{12}. Pairing symmetry of density-fluctuation (i.e. valence-fluctuation)-mediated superconductivity has also been analyzed on the basis of the phenomenological model \cite{13}.

Furthermore, a recent NQR measurement in CeCu$_2$Si$_2$ has detected a change of the Cu-NQR frequency near $P = P_v$, suggesting that the Ce valence changes near $P = P_v$ \cite{14}. Detailed measurement of the $T$ dependence of the specific heat and the upper critical field in CeCu$_2$Si$_2$ under pressure concluded that the pairing symmetries of the superconducting phases near $P = P_c$ and $P_v$ are different, suggesting that a pairing mechanism different from the antiferromagnetic spin-pairing mechanism \cite{15}. For a detailed summary of the theory and related experiments up to this stage, readers can refer to \cite{16} and also \cite{17}.

Recent development of the theory of the quantum critical end point (QCEP) of the FOVT has revealed that valence fluctuations play a key role in the other Ce- and Yb-based heavy fermion systems more ubiquitously. We discuss the crucial roles of valence fluctuations in the following sections. In section 2, we discuss the properties of the valence transition and valence crossover of Ce or Yb by comparing theoretical phase diagrams with Ce- and Yb-based systems. In section 3, we discuss the fact that the QCEP of the FOVT can be induced rather easily by applying the magnetic field to the Ce- and Yb-based systems, which causes various anomalies such as metamagnetism and non-Fermi liquid behavior. We discuss that this mechanism gives a unified explanation for CeRhIn$_5$, YbAgCu$_4$ and YbIr$_2$Zn$_20$. In section 4, we discuss the interplay of magnetic order and valence fluctuations, giving rise to a coincidence of the magnetic transition and sharp valence crossover at $T = 0$ K, as shown in figure 1(c). We show how this interplay resolves the outstanding puzzle in CeRhIn$_5$ and also in YbAuCu$_4$. The summary and outlook are given in section 5. The broader applicability of the present mechanism is discussed by surveying promising materials such as $\beta$-YbAlB$_4$ and YbRh$_2$Si$_2$.

2. Model and phase diagrams

2.1. Minimal model for Ce- and Yb-based heavy fermions exhibiting valence transition

We consider the simplest minimal model, which describes an essential part of the physics in Ce- and Yb-based heavy fermion systems exhibiting valence transition, as follows:

$$\mathcal{H} = \mathcal{H}_c + \mathcal{H}_f + \mathcal{H}_{hyb} + \mathcal{H}_{Uc},$$

where $\mathcal{H}_c = \sum_{\sigma} \epsilon_f n_{f\sigma}^f + U \sum_{i=1}^N n_{c\uparrow}^{\ast} n_{c\downarrow}^{\ast}$ represents the conduction band, $\mathcal{H}_f = \sum_{\sigma} \epsilon_f n_{f\sigma}^f + U \sum_{i=1}^N n_{c\uparrow}^{\ast} n_{c\downarrow}^{\ast}$ the f level of onsite Coulomb repulsion $U$ for f electrons, $\mathcal{H}_{hyb} = V \sum_{\sigma} (f_{\sigma}^c c_{\sigma}^{\ast} + c_{\sigma}^{\ast} f_{\sigma}^c)$ the hybridization $V$ between f and conduction electrons, and $\mathcal{H}_{Uc} = U_{c} \sum_{i=1}^N n_{c\uparrow} n_{c\downarrow}$ the Coulomb repulsion $U_{c}$ between f and conduction electrons. The $U_{c}$ term is a key ingredient for explaining the valence transition as well as the various anomalies caused by enhanced Ce- or Yb-valence fluctuations \cite{10, 12, 16, 18, 17}; the $T$-linear resistivity and residual resistivity peak have also been shown theoretically by the model equation (1) \cite{7, 11}.

2.2. Ground-state and finite-T phase diagrams

Figure 2(a) shows the schematic ground-state phase diagram for paramagnetic states drawn on the basis of the DMRG.
calculation in one spatial dimension \(d = 1\) [12] and the calculation by the dynamical mean-field theory (DMFT) in infinite spatial dimensions \(d = \infty\) [19] applied to the model equation (1). Here, the filling \(n = (n_f + n_c)/2\) with \(n_a = \sum_{\sigma} \sum_{\alpha} \langle a^\dagger_{\alpha\sigma} a_{\alpha\sigma}\rangle / N\) for \(a = f\) or \(c\) with \(N\) being the number of lattice sites is set slightly smaller than 1 (half-filling), which describes typical Ce- and Yb-based heavy fermion metals.

The FOVT line (solid line) terminates at the QCEP (filled circle) and sharp valence crossover occurs (thick dashed line). When \(\varepsilon_f\) is deep enough, the Kondo state with \(n_f = 1\) is realized. As \(\varepsilon_f\) increases across the FOVT and valence crossover line, the mixed valence (MV) state with \(n_f < 1\) is realized\(^1\). At the QCEP, the valence fluctuation \(\chi_v = -\partial n_v / \partial \varepsilon_f\) diverges and at the valence crossover line, enhanced valence fluctuation appears [12, 18]. We note that the slave-boson mean-field theory for \(d = 1\) [12], \(d = 2\) [20] and \(d = 3\) [21, 18] also gives essentially the same phase diagram as figure 2(a). This is because the valence transition and its fluctuation are caused by the atomic Coulomb interaction \(U_{fc}\) in equation (1), which is ascribed to the local origin. Hence, the essential feature of the phase diagram for the valence transition does not depend on the spatial dimension. As shown by the shaded region in figure 2(a), near the QCEP of the FOVT, the superconducting phase is shown to appear by the shaded region in figure 2(a), near the QCEP of the FOVT surface, giving rise to the large Fermi surface (see also figure 6(b)). This is naturally understood in terms of the

\[\begin{align*}
\varepsilon_f & = 1
\end{align*}\]

\(^{1}\) We refer to a spatially uniform and quantum mechanically valence-fluctuating state with \(n_f < 1\) as mixed valence. We refer to the state with larger \(n_f\) than that in the mixed valence state at the FOVT and valence crossover as the Kondo state. Note that, in the intermediate-coupling regime, \(n_f\) in the Kondo state is smaller than 1 [12, 18].

2.3. Correspondence to Ce- and Yb-based materials

As shown in figure 2(a), the Kondo (MV) state with \(n_f \approx 1\) (\(n_f < 1\)) is realized for deep (shallow) \(\varepsilon_f\) for a fixed \(U_{fc}\). In Ce systems, the \(n_f = 1\) state corresponds to Ce\(^{3.0+}\) with a 4f\(^t\)-electron configuration per Ce site. In Yb systems, where Yb\(^{3.0+}\) has a 4f\(^{13}\)-electron configuration per Yb site, the hole picture is useful, so that the \(n_f = 1\) state corresponds to Yb\(^{3.0+}\) with a 4f\(^t\)-hole configuration per Yb site.

When we apply pressure to the Ce (Yb) compounds, \(\varepsilon_f\) increases (decreases), since negative ions approach the tail of the wavefunction of 4f electrons (holes) at the Ce (Yb) site. The hybridization \(V\) and inter-orbital Coulomb interaction \(U_{fc}\) also increase. In the case of Ce metal, 4f and 5d electrons are located at the same Ce site, which makes \(U_{fc}\) large [1]. In figure 2(a), the dashed line with an arrow (A) represents the route for applying the pressure to Ce metal. Hence, the cutout for the large \(U_{fc}\) including the \(T\) axis labeled by (A) in figure 2(b) corresponds to the \(T–P\) phase diagram of Ce metal shown in figure 1(a). Namely, the large critical end temperature...
$T \sim 600$ K in Ce metal is naturally understood from a large $U_{fc}$ due to its onsite origin in figure 2(b).

On the other hand, in the case of Ce (Yb) compounds with conduction electrons supplied from elements other than Ce (Yb), the Coulomb repulsion between the 4f electron at the Ce (Yb) site and the conduction electron $U_{fc}$ is weaker in general because of its inter-site origin. Hence, applying pressure to the Ce compounds corresponds to the route represented by the dashed line with arrows in figure 2(a). The cutout for such a moderate $U_{fc}$ labeled by (B) in figure 2(b) is considered to correspond to the $T-P$ phase diagrams of most of the Ce-based compounds. Although the magnetically ordered phase is not shown in figures 2(a) and (b) for simplicity of explanation here, the cutout (B) corresponds to figure 1(b) (or figure 1(c)). Namely, in CeCu$_2$(Si/Ge)$_2$ systems, the AF phase is located in the Kondo regime with a certain interval to the valence crossover pressure $P_v$ in figure 1(b), where the valence crossover temperature $T^*_c(P)$ covered by the superconducting dome corresponds to the cutout of figure 2(b). When we take into account the magnetic order in the phase diagram, depending on the strength of the c–f hybridization $V$ (and also $U_{fc}$ and $U_{fc}$) in equation (1), the location of the magnetic–paramagnetic phase boundary changes. Hence, the relative position of $P_v$ and $P_c$ changes as shown in figures 1(b) and (c).

The interplay of the magnetic order and valence crossover (or transition) is quite important in understanding the actual phase diagrams of Ce- and Yb-based systems, which will be discussed in section 4.

Here, we remind the readers of the fact that, even at the $\gamma-\alpha$ transition in Ce metal, the magnitude of the valence jump is about 0.10 [2], as is in the case of YbInCu$_4$ [5], as remarked in section 1. We note that the magnitude of the valence change at the valence crossover for moderate $U_{fc}$ is smaller than that at the FOVT for large $U_{fc}$, which is expected to be of the order of 0.01. Actually, such a tiny change of Yb valence has been observed at the valence crossover temperature $T = T^*_c \sim 40$ K in YbAgCu$_4$ [34], which will be discussed in section 3.3.

### 3. Field-induced valence crossover

#### 3.1. Theoretical results

As shown in section 2, the valence transition is essentially ascribed to the charge degrees of freedom and it is nontrivial how the magnetic field affects the valence transition. Recently, theoretical studies have clarified that the QCEP of the FOVT as well as the sharp valence crossover is induced by applying a magnetic field [18]. The slave-boson mean-field theory applied to the model equation (1) in $d = 3$ with the Zeeman term $-h \sum_i (S_i^c + S_i^f)(h \equiv g \mu_B H)$ has shown that the FOVT surface and the valence crossover surface move as shown in figure 3(a) [21, 18]. On the locus with an arrow illustrated in figure 3(a), the magnetic susceptibility $\chi = \partial m / \partial h$ with $m = \sum_i (f_i^c \alpha_i f_i^c + f_i^c \beta_i f_i^c - c_i^\dagger c_i^\dagger - c_i^\dagger c_i) / N$ diverges. Namely, metamagnetism occurs. The DMRG calculation applied to the same model in $d = 1$ has also shown that the field-induced extension of the QCEP of the FOVT to the MV regime actually occurs, giving rise to the metamagnetism [21]. This finding is quite important and hence we put special emphasis on this result: at the QCEP of the FOVT, not only the valence fluctuation, i.e. charge fluctuation, but also the magnetic susceptibility diverges.

Furthermore, this result indicates that, even in the intermediate-valence materials, which do not show any valence transition at $H = 0$, the QCEP of the FOVT is induced by applying the magnetic field $H$. An important point here is that, as shown in figure 2(b), most of the Ce- and Yb-based compounds are located in the region for a moderate $U_{fc}$, but not in the region for a large $U_{fc}$ causing the FOVT. Hence, in the Ce- and Yb-based compounds, the valence crossover temperature $T^*_c(H)$ with strong valence fluctuations can emerge in the $T-H$ phase diagrams. Here, the magnitude of the characteristic field to make $T^*_c(H)$ emerge depends on how close the location of the material is to the QCEP of the FOVT in the phase diagram. When the material is located close to the QCEP, metamagnetism as well as non-Fermi...
liquid behavior is expected to be observed by applying even a small magnetic field. In the following sections of 3.2, 3.3, and 3.4, we discuss the possible relevance of this mechanism to experimental observations.

3.2. Metamagnetism and non-Fermi liquid behavior in CeIrIn5

CeIrIn5 is a heavy fermion metal, which shows a superconducting transition at \( T = 0.4 \) K at ambient pressure [22]. When pressure is applied, the superconducting transition temperature increases in spite of the fact that the In-NQR relaxation pressure is applied, the superconducting transition temperature of CeIrIn5 is located at the valence crossover regime indicated by the black square in figure 3(b). At \( H = 0 \), the slope of the valence crossover line (dashed line) becomes steeper, which crosses the black square point at \( H = H_c \) [27]. This fact and the above observations of (i)–(iii) suggest that non-Fermi liquid behavior begins prominent: (i) convex behavior appears in the valence crossover line (dashed line) becomes steeper, which crosses the black square point at \( H = H_c \) [27]. The properties of (i) and (ii) are consistent with the theoretical results of critical valence fluctuations in [7] and [11], respectively, as explained in section 1. The property of (iii) is also consistent with a theory recently developed for quantum valence criticality, which has shown that evaluation of the quasiparticle self-energy for one valence-fluctuation exchange process gives the low-\( T \) specific heat as \( C/T \sim -\log T \) in a certain-\( T \) regime [29].

Figure 4. \( T-H \) phase diagram in CeIrIn5 [28]. For \( T < T_{FL} \), Fermi liquid behavior appears in specific heat data [27].

Recent measurement of the de Haas–van Alphen (dHvA) effect has confirmed that the Fermi surface topology remains essentially the same between the \( H < H_c \) regime and the \( H > H_c \) regime. This is also consistent with the metamagnetism caused by the field-induced QCEP of the FOVT: as explained in detail in figure 2(a) in section 2.2, the Fermi surface volume basically does not change at the FOVT and valence crossover so long as a system remains in a paramagnetic state (of course, in the case of the FOVT (valence crossover), the lattice constant shows a discontinuous (continuous) change, which gives a change of the wavenumber itself). We also note that no evidence of the folded Brillouin zone below and above \( H_c \) has been obtained by the dHvA measurement in CeIrIn5 [28]. This result indicates that the field-induced AF-ordered phase is unlikely to be realized at \( H_c \), although the possibility of the magnetic-breakdown effect in the dHvA measurement should be carefully examined.

We also note that CeIrIn5 and CeCoIn5 have almost the same Fermi surfaces according to the band structure calculations [30] and the dHvA measurements [31]. Both materials have a quite similar level scheme of the crystalline electric field (CEF) [32]. However, in CeCoIn5, the crossover line (or first-order transition line) accompanied by the non-Fermi liquid behavior as shown in figure 4 does not appear in the \( T-H \) phase diagram. We note here that, by applying pressure to CeCoIn5, residual resistivity and the \( T^2 \) coefficient \( \alpha \) of the low-\( T \) resistivity drop drastically [33]. These observations suggest that the QCEP of the FOVT, or the sharp valence crossover point, exists on a slightly negative pressure side in the \( T-P \) phase diagram of CeCoIn5. Actually, the experimental fact of the emergence of the \( T \)-linear resistivity and logarithmic divergence of the specific heat \( C/T \sim -\log T \) at low temperatures and ambient pressure in CeCoIn5 does not contradict this point of view [29].

These results indicate that a viewpoint of the closeness to the QCEP of the FOVT is important for understanding the Ce115 systems in addition to the conventional view based on the competition between the Kondo effect and the RKKY interaction. Indeed, this viewpoint offers us a key to resolving the outstanding puzzle in CeRhIn5 as well, which will be discussed in section 4.1. Since the superconducting correlation has been shown to develop near the QCEP of the FOVT theoretically (see figures 2(a) and 3(b)) [10, 12], the proximity to the QCEP seems to control the occurrence of the unconventional superconductivity in CeIrIn5.

To examine our theoretical proposal, it is desirable to measure the valence change of Ce at the crossover line \( T_v^* \) (or first-order transition line) in figure 4. The x-ray
adsorption spectra for direct observation of the Ce valence, the NQR measurement for the electric-field gradient, the ultrasonic measurement and the X-ray diffraction and/or thermal expansion measurement for the lattice-constant change are highly desirable.

3.3. Enhanced magnetic susceptibility and metamagnetism in YbAgCu$_4$

As noted in section 1, YbInCu$_4$ shows the FOVT at $T = T_c = 42$ K [3, 4]. When In is replaced by other elements, the FOVT has not been observed. However, anomalous behavior which seems to be related to valence fluctuations has been observed in YbAgCu$_4$ [34]. In YbAgCu$_4$, uniform magnetic susceptibility has a broad peak at $T = 40$ K. Below $T = 40$ K, the volume expansion occurs [35] simultaneously with a sharp valence crossover from Yb$^{3+}$ for $T > 40$ K to Yb$^{3.7+}$ for $T < 40$ K [34], indicating that negative volume expansion occurs as $T$ increases to approach $T = 40$ K. Namely, the uniform magnetic susceptibility is enhanced at the valence crossover temperature $T = T^*_v$. The volume expansion for $T > 40$ K, as shown by the black dashed line in figure 3(a) [18, 17]. Hence, the broad peak of the magnetic susceptibility is considered to be caused by the valence fluctuations developed at the valence crossover surface. YbAgCu$_4$ shows a metamagnetism in the low temperature limit around $H = 40$ T [34]. This can also be naturally understood from the field-induced valence crossover surface shown in figure 3(a). Namely, the location of YbAgCu$_4$, indicated by the black circle in figure 3(b) is at a distance of about $H = 40$ T from the valence crossover line close to the QCEP at $H = 0$. For more details, the readers can refer to [17] and [18].

3.4. Enhanced magnetic susceptibility and metamagnetism in YbIr$_2$Zn$_{20}$

Recently, behaviors similar to those of YbAgCu$_4$ have been observed in YbIr$_2$Zn$_{20}$ [36]. The uniform magnetic susceptibility has a peak at $T = T^*_v = 7.4$ K accompanied by the volume expansion for $T < T^*_v$. Since the unit-cell volume with the Yb$^{3.0+}$ ($4f^6$ hole configuration) state is larger than that with the Yb$^{3.6+}$ ($4f^5$ hole configuration) state, this observation suggests that the enhancement of the magnetic susceptibility is caused by the enhanced Yb valence fluctuations associated with the valence change of Yb. This viewpoint is consistent with the fact that the thermal expansion coefficient is negative for $T < T^*_v$ [36].

Recently, it has been found that YbIr$_2$Zn$_{20}$ shows a metamagnetism at $H \sim H_m = 10$ T [36]. Near the metamagnetic field $H_m$, enhancement of the cyclotron mass of electrons has been observed by the dHvA measurement. The specific-heat constant $C/T$ and the $T^2$ coefficient of the resistivity at low temperatures also indicate the mass enhancement of electrons at $H = H_m$. Furthermore, residual resistivity has a peak at $H = H_m$. The temperature region where the low-$T$ resistivity shows the $T^2$ dependence becomes narrower in the vicinity of $H = H_m$, which suggests a tendency of the $T$-linear resistivity near $H = H_m$. All these observations are naturally explained by the field-induced valence crossover discussed in section 3.1. Although the mass enhancement and the residual resistivity peak suggest a clear signature of the Yb valence fluctuations developed when $H$ approaches $H_m$, the experimental fact that the resistivity has a $T^2$ dependence at the lowest temperatures even at $H = H_m$ implies that YbIr$_2$Zn$_{20}$ at ambient pressure is located at the valence crossover regime. Namely, YbIr$_2$Zn$_{20}$ seems to be located at a similar position to that of YbAgCu$_4$, indicated by the black circle in figure 3(b). The distance from the valence crossover line close to the QCEP at $H = 0$ seems to be about $H \sim 10$ T in YbIr$_2$Zn$_{20}$, since the metamagnetic field is about $H_m \sim 10$ T. Indeed, a steep volume shrinkage has been observed at $H \sim H_m$ [36], which indicates that the Yb valence sharply increases at $H = H_m$. The dHvA measurement has concluded that the Fermi surfaces do not change at $H = H_m$ from the fact that the dHvA frequencies show no change across $H_m$ [36]. This is also consistent with the mechanism of the field-induced valence crossover, since the Fermi surface volume is essentially unchanged at the valence crossover so long as the system remains in the paramagnetic state as discussed in section 2.2 and also in section 3.2.

When pressure is applied to YbIr$_2$Zn$_{20}$, the metamagnetic field $H_m$ can be tuned to approach $H = 0$ T [37]. This seems to be consistent with the location of YbIr$_2$Zn$_{20}$ mentioned above, since applying pressure makes $U_{c1}$ large because of the reduction of the distance between wavefunctions of 4f and conduction electrons and also makes $\epsilon_f < 0$ small (i.e. $\epsilon_f$ large) in the hole picture. Here, we should note that the panel of the cutout shown in figure 2(b) is drawn for the Ce compounds. In the case of Yb compounds, the panel tilts with a certain angle with the opposite sign to the $\epsilon_f$ axis. The observation of the quantum criticality at the QCEP of the FOVT by tuning the control parameters of the pressure and/or magnetic field is an interesting future issue [38]. Systematic measurements in YbX$_2$Zn$_{20}$ (X = Ir, Co and Rh) are highly desirable for a unified understanding of the effect of the critical valence fluctuations.

4. Interplay of magnetic order and valence fluctuations

In the preceding sections, we have discussed the nature of the QCEP of the FOVT in a paramagnetic phase and how it is controlled by applying the pressure and/or magnetic field. In Ce- and Yb-based heavy fermion systems, however, the magnetic order can also occur. The interplay of the magnetic order 2 We note that each material has different strength of c–f hybridization V. Hence, the locus of the QCEP under the magnetic field depends on V in figures 3(a) and (b), strictly speaking. To avoid confusion by drawing each locus (thick line with an arrow) for each material, we just drew one locus and schematic locations of CeIrIn$_5$, YbAgCu$_4$ and YbAuCu$_4$, respectively, in figure 3(b).
order and Ce or Yb valence fluctuations offers a key concept for understanding these systems. Below we focus on CeRhIn$_5$ as a prototypical material to demonstrate how such an interplay plays a crucial role in understanding the puzzling behaviors.

4.1. CeRhIn$_5$

CeRhIn$_5$ is a heavy fermion metal [39] which undergoes an AF transition at $T_N = 3.8$ K with the ordered vector $Q = (1/2, 1/2, 0.297)$ at ambient pressure [40]. When pressure is applied, the AF-ordered phase changes to the paramagnetic and superconducting phase at $P = P_c \sim 2$ GPa, as shown schematically in figure 5 [41–46]$^3$. This material has attracted much attention since accumulated experiments offer an outstanding puzzle, whose significant features are summarized as follows: (i) the Sommerfeld constant $\gamma_e \sim 50$ mJ mol$^{-1}$ K$^{-2}$ in the AF state at $P = 0$ is about ten times larger than $\gamma_e = 5.7$ mJ mol$^{-1}$ K$^{-2}$ in LaRhIn$_5$ [39, 44]. (ii) The Fermi surfaces similar to those in LaRhIn$_5$ in the AF phase for $P < P_c \sim 2.35$ GPa change to Fermi surfaces similar to those in CeCoIn$_5$ in the paramagnetic phase for $P > P_c$ by the dHvA measurement performed under the magnetic field $H \sim 15$ T [44]. (iii) The cyclotron mass of electrons shows an enhancement toward $P = P_c$: the cyclotron mass of the $\beta_2$ branch, whose Fermi surface has a cylindrical shape, changes from $6m_0$ at $P = 0$ to $60m_0$ at $P \lesssim P_c$ and the signal is not detected for $P > P_c$, probably because of a too heavy mass, $\sim 100m_0$ [44]. (iv) The $T$-linear resistivity emerges prominently near $P = P_c$ [41, 42, 45]. (v) The residual resistivity has a peak at $P \sim P_c$ [41, 42, 45]. (vi) The superconducting phase exists in a wide pressure region around $P = P_c$ [41–43].

Because of the dHvA measurement noted above (ii), one might succumb to the temptation to believe a scenario in which the localized to itinerant transition of f electrons happens at $P = P_c$ [47, 48]. However, this scenario encounters a serious difficulty in explaining the experimental fact (i) above: the AF state with a ten times mass enhancement at $P = 0$ strongly suggests that the heavy quasiparticles contribute to the formation of the AF state, indicating the existence of the c–f hybridization even in the AF phase for $P < P_c$. Hence, the theoretical explanation for resolving a series of puzzles outlined above (i)–(vi) in a natural and unified way has been desired.

First of all, let us point out that the transport anomalies above (iv) and (v) and the robust superconducting phase (vi) are quite similar to the observations in the CeCu$_2$(Si/Ge)$_2$ systems [6–8] introduced in section 1. Emergence of the $T$-linear resistivity prominent at $P = P_c$ in figure 1(b), at which the residual resistivity has a peak, covered with

\begin{equation}
\nu = \frac{2}{3} \left( \frac{c}{m_0} \right)
\end{equation}

Figure 5. Schematic $T$–$P$ phase diagram of CeRhIn$_5$ [41, 42]. The shaded region represents the superconducting phase.

Figure 6. (a) Ground-state phase diagram in the $\varepsilon_f$–$U_{fe}$ plane of the model equation (1) for $V = 0.2$ and $U = \infty$ at $n = 0.9$ (see the text) [20]. The FOVT (solid line with triangles) terminates at QCEP (filled circle). Valence crossover with enhanced valence fluctuations occurs at the dashed line with open circles. The solid line with filled squares represents the antiferromagnetic (AF)–paramagnetic (PM) boundary. Occupied (solid lines) and empty (gray lines) bands in the periodic Anderson model at $n = (n_f + n_c)/2 = 0.9$ are shown in the paramagnetic phase (b) and in the AF-ordered phase (c). In (c), the gray dashed line indicates the energy band of the conduction band, $E_k$ at $n_f = 0.8$. The black dashed line is a guide for the eyes, indicating that the Fermi surface in the AF-ordered phase with finite c–f hybridization coincides with the small Fermi surface where f electrons are completely localized.
the superconducting phase in the wide pressure region is
the common feature in CeCu$_2$Ge$_2$ [6], CeCu$_2$Si$_2$ [7] and
CeCu$_2$(Ge$_x$Si$_{1-x})_2$ [8]. Since the $T$-linear resisitvity and
residual resistivity peak appear at the AF-paramagnetic
boundary in CeRhIn$_5$, $P_c \approx P_v$ seems to be realized in figure 5.
As will be shown below, this is actually the case realized in the
model equation (1) for realistic parameters for CeRhIn$_5$, which
naturally resolves the above puzzles (i)-(vi) [20].

Figure 6(a) shows the ground-state phase diagram of the
model equation (1) without the magnetic field on the square
lattice obtained by the slave-boson mean-field theory [49],
which enables us to treat the AF order and valence transition
or fluctuations on an equal footing. Here, we set small
which enables us to treat the AF order and valence transition
or fluctuations suppress the AF order. Then the AF order is
suddenly cut around
fluctuations in the $T$-$P$ phase diagram for $P_c < P_v$, (b) Enhanced valence fluctuations at $P_v$ suppress the AF order, giving rise to the
AF transition of the first order at $P = P_c$ shown by the vertical thick line [20].

We have also shown that the Fermi surface calculated for
$V = 0.2$ in the AF phase at $n = (n_t + n_c)/2 = 0.9$ is nearly
the same as the small Fermi surface without c-f hybridization
where electrons for $n_t = 1$ are located at the localized f level
and the conduction band is filled up with all extra electrons for
$n_c = 0.8$ [20]. This naturally explains the dHvA measurement
(ii) above. In the paramagnetic phase in figure 6(a), the large
Fermi surface, which counts the f-electron numbers in the
total Fermi volume, i.e. $n_f$, is realized, as shown in figure 6(b). In the AF phase, the lower and upper hybridized
bands are folded, as shown in figure 6(c). Since the lower
folded hybridized band is completely filled, the Fermi surface
becomes the same as that of the conduction electrons at the
filling $n_c$. Hence, we stress that the small Fermi surface appears
in the AF phase with finite c-f hybridization, $\langle f_{k\sigma}^\dagger c_{k\sigma} \rangle \neq 0$.

The mass enhancement observed by the dHvA measurement
(iii) above is also quantitatively reproduced by the same
model equation (1) under the magnetic field $H = 15$ T [20].
Namely, the mass enhancement of the two-dimensional-like
Fermi surface of the $p_z$ branch from $6m_0$ at $P = 0$ to $60m_0$
$P \approx 6P_c$ [44], which is well reproduced by the present mechanism,
which shows that the total density of states at the Fermi level
increases near the AF-paramagnetic boundary in figure 6(a).
This is because when the pressure is applied to the AF state,
i.e. when $\varepsilon_f$ increases, the gap between the original lower
hybridized band and the folded band increases as in figure 6(c).
Then, the f-electron-dominant flat part of the folded lower
hybridized band approaches the Fermi level, giving rise to the
increase in the density of states. In the paramagnetic phase,
as $\varepsilon_f$ approaches the AF-paramagnetic boundary in figure 6(a),
i.e. as $\varepsilon_f$ decreases, $n_f$ increases to approach 1, which is in
the so-called Kondo regime. Hence, the density of states at the Fermi level increases. Thus, the reason why the mass enhancement occurs toward the AF-paramagnetic boundary $P = P_c$ in CeRhIn$_5$ is naturally explained.

This result is quite consistent with a recent experiment on the effective mass of electrons [41]: Knebel et al applied a magnetic field to CeRhIn$_5$, whose magnitude is the same as $H = 15$ T used in the dHvA measurement [44]. After the disappearance of the superconductivity, the $T^2$ dependence of the resistivity appears at lowest temperatures. Knebel et al found that the $\sqrt{A}$ with $A$ being the coefficient of the $T^2$ term scales nicely with the cyclotron mass of the $\beta_2$ branch under pressure for $0 \leq P \leq P_c$, i.e. $\sqrt{A}/m^* = $ const. scaling holds [41]. This scaling indicates that the mass enhancement towards $P = P_c$ is essentially caused by the effect of the energy band dispersion of quasiparticles [50]. We also note that about a ten-times mass enhancement at $P = 0$ is also reproduced by the same model equation (1) [20], which is quite consistent with the experimental fact (i) above. Formation of the heavy quasiparticles via the c–f hybridization naturally explains the mass enhancement even inside the AF phase.

As shown in figure 6(a), $P_c \approx P_s$ is a consequence of the suppression of the AF order by enhanced valence fluctuations for moderate $U_{fc}$, e.g. $U_{fc} \approx 0.5$, which is a realistic parameter for CeRhIn$_5$, giving rise to the $T$-linear resistivity and the residual resistivity peak at the AF-paramagnetic boundary. Hence, the experimental facts (iv) and (v) are naturally explained. Since the superconducting phase was shown to be realized around $P_c$ [10, 12], as shown in figure 1(b), (vi) above is also consistently explained (see figures 5 and 7(b)). Hence, all of the above experimental observations (i)–(vi) are naturally explained in a unified way.

We note that local correlation effects of 4f electrons give rise to the large ordered moment of the AF order: only about 10% reduction of the full ordered moment for the Kramers doublet of the lowest CEF level is realized even near the AF-paramagnetic boundary. This is, as we will discuss in section 4.2, because $P_c \approx P_s$ is realized in CeRhIn$_5$, if the above correspondence holds, this implies that, on the slightly negative pressure side in the $T$–$P$ phase diagram of CeCoIn$_5$, the QCEP or sharp Ce valence crossover point, i.e. $P = P_c$, exists, which is the same conclusion stated in section 3.2.

The interplay of the magnetic order and enhanced valence fluctuations plays an important role not only in CeRhIn$_5$ but also in other materials. One such example is YbAuCu$_4$, which will be discussed in section 4.2.
5. Summary and outlook

In this paper, the roles of critical valence fluctuations in Ce- and Yb-based heavy fermion metals are discussed. Recent development of theory and experiment has revealed that critical Ce and Yb valence fluctuations play a key role in several anomalies in this family of materials. The magnetic field is shown to be a useful control parameter to induce the quantum critical end point (QCEP) of the first-order valence transition (FOVT). As a prototypical material, metamagnetism and non-Fermi liquid behavior in CeRhIn₅, YbAgCu₄ and YbIr₂Zn₂₀ are shown to be naturally explained by the mechanism of the field-induced valence crossover. The interplay of the magnetic order and Ce or Yb valence fluctuations is a key mechanism for understanding anomalous behavior in Ce- and Yb-based heavy fermion systems. It is shown that the interplay resolves the outstanding puzzle in CeRhIn₅. The origin of the transport anomalies and drastic change of the Fermi surface accompanied by the mass enhancement of electrons is naturally explained by the interplay in a unified way. A special emphasis is put on the fact that a small Fermi surface generally appears by the folding of the hybridized band in the AF phase in the periodic Anderson model. The unified explanation for CeIn₅ and CeRhIn₅ strongly suggests that the viewpoint of the closeness to the QCEP of the FOVT is indispensable in understanding the Ce₁₁₅ systems. As another prototypical material where the interplay occurs, the T−H phase diagram of YbAuCu₄ is discussed. The proximity to the QCEP of the FOVT is a key concept for understanding Ce- and Yb-based heavy fermion systems as an underlying mechanism.

In an outlook, recently synthesized materials, YbIr₂Zn₂₀, YbCo₂Zn₂₀ and YbRh₂Zn₂₀ are promising materials, which are expected to show the properties caused by the Yb valence fluctuations by tuning the control parameters of the magnetic field and pressure. Recently, in β-YbAlB₄, where the superconductivity was first discovered among Yb-based compounds [58], evidence of strong Yb valence fluctuations has been reported [59]. Further study to clarify the role of the valence fluctuations in the unconventional criticality as well as the origin of the superconductivity is an interesting future problem. We point out that the T−H phase diagram in YbRh₂Si₂ [55], where unconventional criticality has attracted much attention in correlated electron systems [56], is closely similar to that in YbAuCu₄ (see figure 8). Hence, there exists a possibility that the critical Yb valence fluctuation plays a key role in the origin of the unconventional criticality in YbRh₂Si₂. Thus, it is quite important to examine the possibility of whether the Yb valence change takes place at the crossover temperature T⁺(H), whose origin has not yet been clarified experimentally in the T−H phase diagram. The experimental fact that YbRh₂Si₂ shows a huge mass enhancement even at H = 0 such as γₑ ∼ 1.7 J mol⁻¹ K⁻² deep inside the AF phase [57] indicates that heavy quasiparticles form the AF-ordered state as in CeRhIn₅. The Co-NQR measurement in Yb(Rh₁₋ₓCoₓ)₂Si₂ and/or the direct observation of the Yb valence by x-ray adsorption measurement at the crossover temperature T⁺(H) are highly desirable. As noted in section 2.3, the magnitude of the valence change is expected to be of the order of 0.01 in most of the Ce and Yb compounds. Hence, high accuracy measurement which can detect the tiny change of the valence is a challenging future problem, which will open new avenues of study in this field.

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