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Author(s)	Kitagawa, S.; Ikeda, H.; Nakai, Y.; Hattori, T.; Ishida, K.; Kamihara, Y.; Hirano, M.; Hosono, H.
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Metamagnetic Behavior and Kondo Breakdown in Heavy-Fermion CeFePO

S. Kitagawa,[1,2,*] H. Ikeda,[1,2] Y. Nakai,[1,2,†] T. Hattori,[1] K. Ishida,[1,2] Y. Kamihara,[2,3] M. Hirano,[4] and H. Hosono[4,5]

[1]*Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*
[2]*TRIP, JST, Sanban-cho building, 5, Sanban-cho, Chiyoda, Tokyo 102-0075, Japan*
[3]*Departments of Applied Physics and Physico-Informatics, Keio University, Kanagawa, 223-8522, Japan*
[4]*Frontier Research Center, Tokyo Institute of Technology, Yokohama, 226-8503, Japan*
[5]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, 226-8503, Japan*

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We report that nonmagnetic heavy-fermion (HF) iron oxypnictide CeFePO with two-dimensional XY-type anisotropy shows a metamagnetic behavior at the metamagnetic field $H_M \simeq 4$ T perpendicular to the c axis and that a critical behavior is observed around H_M. Although the magnetic character is entirely different from that in other Ce-based HF metamagnets, H_M in these metamagnets is linearly proportional to the inverse of the effective mass, or to the temperature where the susceptibility shows a peak. This finding suggests that H_M is a magnetic field breaking the local Kondo singlet, and the critical behavior around H_M is driven by the Kondo breakdown accompanied by the Fermi-surface instability.

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Metamagnetism is represented by a sudden increase in magnetization with increasing an applied field. In heavy-fermion (HF) systems, $CeRu_2Si_2$ with the tetragonal $ThCr_2Si_2$ structure shows the metamagnetic behavior at about 7.7 T when a magnetic field (H) is applied parallel to the c axis. Although various experiments as well as theoretical studies have been carried out [1,2], the mechanism is still controversial. In order to understand the metamagnetic behavior in HF systems, it might be desired to investigate new metamagnetic compounds.

The iron oxypnictide CeFePO is a related material of the iron-based superconductor LaFePO [3,4]. They possess the same two-dimensional layered structure, stacking Ce(La)O and FeP layers alternately. Brüning *et al.* reported that CeFePO is a magnetically nonordered HF metal with a Sommerfeld coefficient $\gamma = 700$ mJ/(mol K^2) [5]. At present, it is difficult to synthesize large single crystals of CeFePO for NMR measurements, but ^{31}P-NMR can probe in-plane and out-of-plane magnetic response separately using c-axis aligned polycrystalline samples. Here we report novel metamagnetic behavior observed in $H \perp c$, and suggest that metamagnetism of Ce-based HF compounds is driven by Kondo breakdown (drastic reduction of c-f hybridization) as clarified experimentally.

The polycrystalline CeFePO was synthesized by solid-state reaction [4]. Basic properties are consistent with the previous report [5]. To measure anisotropic magnetic properties of CeFePO, the samples were uniaxially aligned using a magnetic field [6]. The polycrystalline CeFePO was ground into powder, mixed with stycast 1266, and was rotated in the external field of 1.4 T while the stycast cures. The c axis of the sample is nicely aligned, which is shown from the angle dependence of ^{31}P-NMR spectra (see in the inset of Fig. 1), and ^{31}P-NMR measurement was performed on the sample.

Figure 1 shows H-swept NMR spectra in $H \parallel c$ and $H \perp c$ obtained at 31.4 MHz and various temperatures (T). The resonance peak for $H \parallel c$ is almost T independent, but the peak for $H \perp c$ shows the characteristic T dependence originating from $\chi(T)$. The Knight shift $K_{\perp(\parallel)}$ was determined from the peak field of the ^{31}P NMR spectrum obtained in H perpendicular (parallel) to the c axis. $K = 0$ was determined by reference material H_3PO_4. $K_i(T, H)$ ($i = \perp$ and $\parallel$), which is the measure of the local susceptibility at the nuclear site, is defined as

$$K_i(T, H_{\rm res}) = \left(\frac{H_0 - H_{\rm res}}{H_{\rm res}}\right)_{\omega=\omega_0} \propto \frac{M_i(T, H_{\rm res})}{H_{\rm res}}, \qquad (1)$$

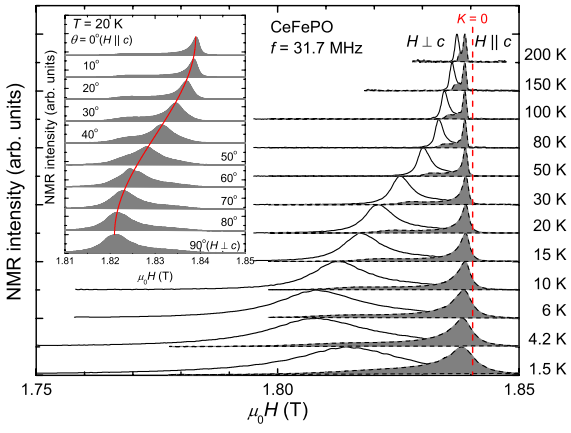

FIG. 1 (color online). (Main panel) T dependence of H-swept NMR spectra at 31.7 MHz for $H \perp c$ (solid line) and $H \parallel c$ (broken line). $K = 0$ was determined by reference material H_3PO_4. (Inset) Angle dependence of H-swept NMR spectra at 31.7 MHz measured at 20 K. θ is the angle between magnetic field and c axis. Solid line is corresponding to fitting line.

where $H_{\rm res}$ are magnetic fields at resonance peaks, H_0 and ω_0 are the resonance field and frequency of bare ^{31}P nucleus and have the relation of $\omega_0 = \gamma_n H_0$ with gyromagnetic ratio γ_n, and $M_i(T, H_{\rm res})$ is the magnetization under $H_{i,\rm res}$ ($i = \perp$ and $\parallel$) at T. $K_\parallel$ is almost independent of T and H, whereas $K_\perp$ shows strong T dependence originating from the Curie-Weiss behavior of $\chi(T)$ above 10 K as shown in Fig. 2(a). The anisotropic Knight shift suggests that static spin properties possess XY-type spin anisotropy. It should be noted that $K_\perp$ exhibits H dependence below 4 K and above 2 T, indicative of a nonlinear relation between $M_\perp$ and H. Using the hyperfine coupling constant $^{31}A_{\rm hf} = 0.2$ T$/\mu_B$, which is estimated from the plot between isotropic component of K and $\chi(T)$ above 10 K (not shown), we can plot $M_i(H)$ against H in Fig. 2(b). $M_\perp(H)$ becomes superlinear against H at 0.1 K, which is the hallmarks of metamagnetism, whereas $M_\parallel(H)$ is linear up to 6.2 T, which is again highly anisotropic.

Next, we focus on T and H dependence of low-energy spin dynamics probed with the nuclear spin-lattice relaxation rate ($1/T_1$). $1/T_1$ of ^{31}P was measured at each resonance peak by the saturation-recovery method, and was uniquely determined by a single component in whole measured range. The inset of Fig. 3 shows T dependence of $1/T_1T$ at low field $\mu_0 H \simeq 0.6$ T parallel and perpendicular to the c axis. Below 1.5 K, $1/T_1T$ as well as K along both directions becomes constant, indicative of the formation of a Fermi-liquid (FL) state of heavy electrons. In general, $1/T_1$ probes spin fluctuations perpendicular to applied H, and thus $1/T_1$ in $H \parallel c$ and $H \perp c$ are described as

$$
\begin{aligned}
(1/T_1)_{H\parallel c} &= 2(\mu_0\gamma_n)^2 \sum_q |H_\perp(q, \omega_{\rm res})|^2 \\
&\propto 2A^2 \sum_q |S_\perp(q, \omega \sim 0)|^2, \quad \text{and} \\
(1/T_1)_{H\perp c} &= (\mu_0\gamma_n)^2 \sum_q [|H_c(q, \omega_{\rm res})|^2 + |H_\perp(q, \omega_{\rm res})|^2] \\
&\propto A^2 \sum_q [|S_\parallel(q, \omega \sim 0)|^2 + |S_\perp(q, \omega \sim 0)|^2].
\end{aligned} \tag{2}
$$

Here $|X(\omega)|$ denotes the power spectral density of a time-dependent random variable $X(t)$, and A is assumed to be q independent due to the metallic state. From these equations, we can decompose spin fluctuations along each direction as shown in the main panel of Fig. 3. $\sum_q |S_\perp(q, \omega \sim 0)|^2$ is dominant at low T, since $(1/T_1T)_{H\parallel c}$ is almost twice larger than $(1/T_1T)_{H\perp c}$. This indicates that the spin dynamics also possess XY-type anisotropy. The XY-type spin fluctuations have the predominance of ferromagnetic (FM) correlations as inferred from the Korringa relation between $(1/T_1T)_{H\parallel c}$ and $K_\perp$ in low-T FL state, which is consistent with the previous ^{31}P-NMR result [5] and with the experimental facts that CeFePO is close to FM instability [7,8].

The evolution of the spin dynamics against H was investigated for both directions. Figure 4 shows T dependence of $(1/T_1T)_{H\perp c}$ below 4 T (approximately the metamagnetic field, $H_{\rm M}$) (a) and above 4 T (b). Although $(1/T_1T)_{H\parallel c}$ does not depend on H up to 6.2 T as shown in the inset of Fig. 3, $(1/T_1T)_{H\perp c}$ changes significantly by H as shown in Figs. 4(a) and 4(b). H dependence of

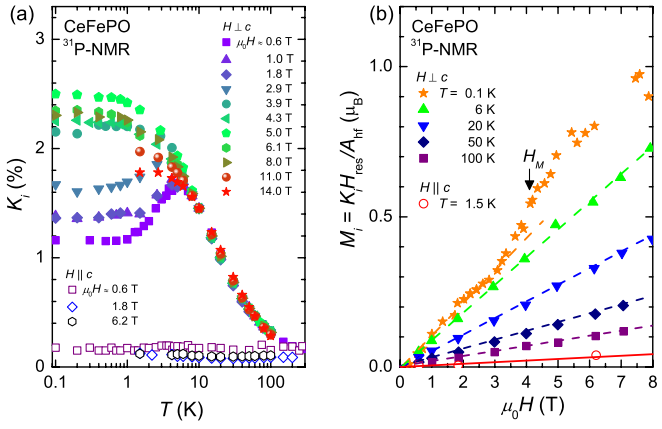

FIG. 2 (color online). (a) T dependence of the Knight shift determined at the peaks of $H \perp c$ and $H \parallel c$ spectra obtained at various H. Strong anisotropy of Knight shift suggests that static spin properties possess XY-type spin anisotropy. (b) H dependence of magnetization $M_i(H)$ ($i = \perp$ and $\parallel$) using the relation of $M_i(H) = K_i(H)H_{\rm res}/A_{\rm hf}$. Solid and broken lines are guide to eyes. $M_\perp(H)$ suddenly increases with increasing H and deviates from linear relation in the field range of 3–5 T, which is a definition of a metamagnetic behavior, while such a behavior was not observed in $M_\parallel(H)$ up to 6.2 T and down to 1.5 K.

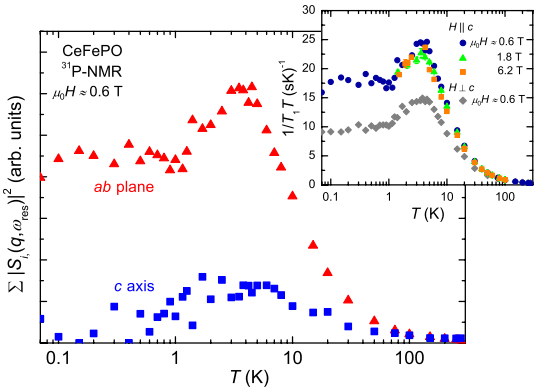

FIG. 3 (color online). (Main panel) T dependence of low-energy spin fluctuations parallel and perpendicular to the c axis at $\simeq 0.6$ T evaluated with $1/T_1T$ measured in $H \perp c$ and $H \parallel c$ [see Eq. (2)]. The in-plane spin fluctuations are dominant at low T, suggesting that the spin dynamics also possess XY-type anisotropy. (Inset) T dependence of $1/T_1T$ at 10.3 MHz ($\simeq 0.6$ T) for $H \perp c$ and at 10.3 MHz ($\simeq 0.6$ T), 31.7 MHz ($\simeq 1.8$ T), and 107.2 MHz ($\simeq 6.2$ T) for $H \parallel c$. $(1/T_1T)_{H\parallel c}$ is independent of H up to 6.2 T.

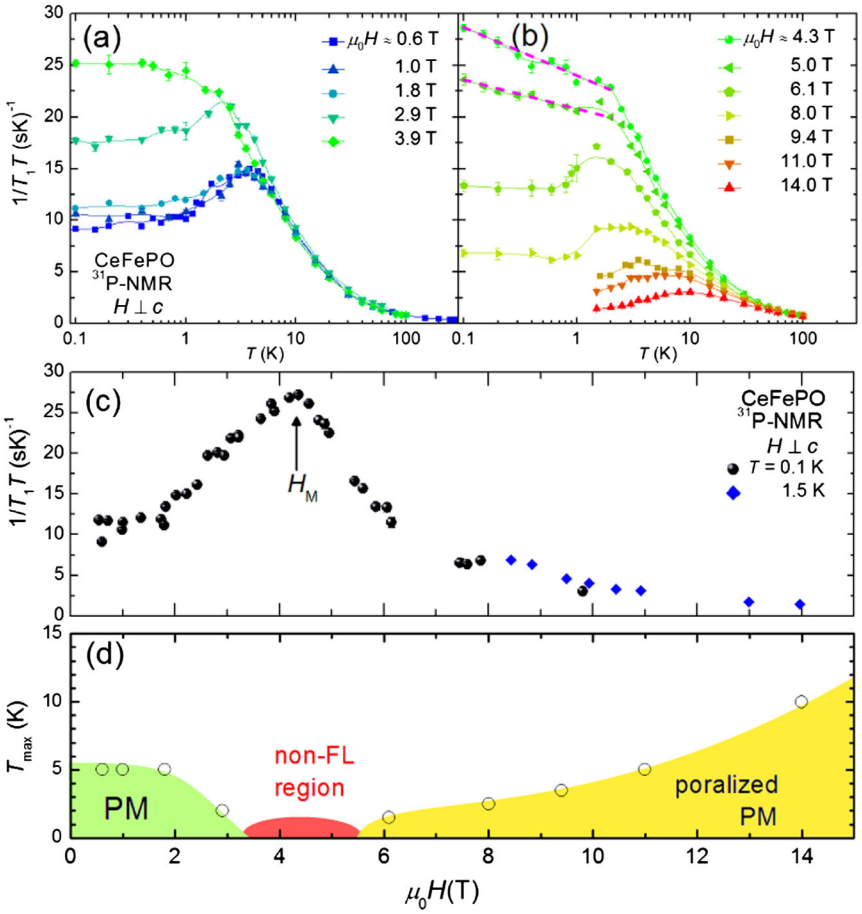

FIG. 4 (color online). T dependence of $(1/T_1T)_{H\perp c}$ below 4 T (a), and above 4 T (b). (c) H dependence of $(1/T_1T)_{H\perp c}$ at low T. $(1/T_1T)_{H\perp c}$ shows a distinct maximum at around H_M, indicating the enhancement of $N(E_F)$ related to metamagnetic anomaly. (d) H-T phase diagram defined by T_{max} where $(1/T_1T)_{H\perp c}$ shows a maximum. Non-FL behavior characterized by continuous increase in $(1/T_1T)_{H\perp c}$ with decreasing T [broken lines are shown in (b)] was observed in a narrow field region intervening between low-field paramagnetic (PM) state and high-field polarized PM state above 6 T.

$(1/T_1T)_{H\perp c}$ at 0.1 and 1.5 K is shown in Fig. 4(c). $(1/T_1T)_{H\perp c}$ shows a distinct maximum at H_M, suggesting that the enhancement of the density of states (DOS) is related to metamagnetic behavior. If we assume that $1/T_1T \propto N(E_F)^2$, $N(E_F)$ at H_M is almost 1.5 times larger than $N(E_F)$ at 0 T. However, it is noteworthy that non-FL behavior characterized by a continuous increase in $(1/T_1T)_{H\perp c}$ with decreasing T was observed down to 100 mK [$(1/T_1T)_{H\perp c} \sim -\log T$] in 4.3 T $< \mu_0 H < 5$ T intervening between low-field paramagnetic (PM) state and high-field polarized PM state above 6 T. In the high-field polarized state, $(1/T_1T)_{H\perp c}$ decreases with increasing H and $(1/T_1T)_{H\perp c}$ at 14 T shows almost the same value as (LaCa)FePO [$\simeq 1.5$ (s K)$^{-1}$] without $4f$ electrons [9]. The H variation of $(1/T_1T)_{H\perp c}$, reflecting the evolution of DOS at the Fermi level with H, strongly suggests the evolution of the Fermi surfaces (FSs) by H. It is noted that such a significant H dependence was not reported in the previous specific-heat measurement [5]. This would be because the magnetic field is applied in the various angles against the c axis, and suggests that the metamagnetic behavior would be observed when H is exactly perpendicular to the c axis.

To investigate such evolution of FSs by H, we performed the *ab initio* band-structure calculation in the paramagnetic state of CeFePO by using the WIEN2K package [10]. FSs in the low-field region are composed of itinerant Ce $4f$ electrons as shown in Fig. 5(a). The large FS shows the characteristic neck structures around X-R at the Brillouin zone boundary, at which boundary electrons have small Fermi velocity or heavy electron mass. The orbital character is dominated by the $j_z = \pm 1/2$ component in the $j = 5/2$ multiplet of $4f$ orbitals, as seen in Figs. 5(a) and 5(c) [11]. These features of Fermi surface imply that the low-field HF state possesses the small q magnetic correlations and their in-plane component is much larger than the out-of-plane component, in good agreement with the experimental results. The band calculation also shows that applied field pinches off the neck FSs around R and X in order, that is, "the field-induced Lifshitz transition" appears. This is accompanied by a drastic change in DOS at the Fermi level, which can be a driving force for the

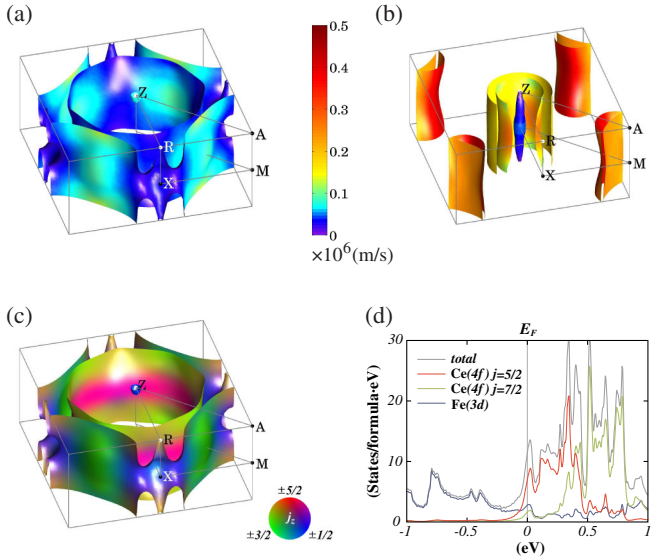

FIG. 5 (color online). Fermi surfaces (FSs) calculated with the *ab initio* band-structure calculation as Ce-4f electrons are itinerant (a), or localized (b), where the Fermi velocity is mapped on the FSs. (c) shows the FS colored by the j_z character in the $j = 5/2$ multiplet of $4f$ orbitals, where j is the total angular momentum. (d) the partial density of states. The Fermi level corresponds to 0 eV.

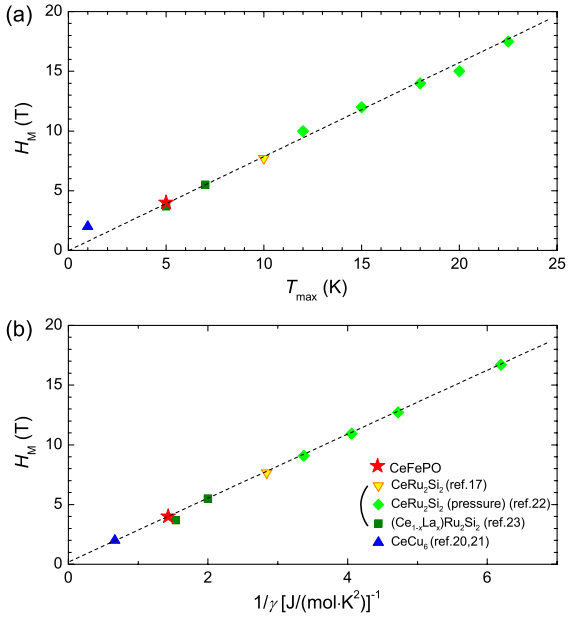

FIG. 6 (color online). (a) Values of metamagnetic fields are plotted against $T_{\max}$ determined from a maximum in static susceptibility (a) or inverse of Sommerfeld coefficient γ at $H = 0$ (b) in CeFePO, $CeCu_6$, and $CeRu_2Si_2$ with pressurized and La-doped system. Broken lines are a guide to eyes. A linear relation holds between two quantities, although three compounds possess quite different crystal structures and magnetic properties, indicating that H_M is linked with the local Kondo singlet energy $T_{\max}$.

metamagnetic transition and non-FL behavior around H_M [12,13]. With applying higher H, $4f$ electrons are localized, and thus the FSs become small. The resultant FSs are shown in Fig. 5(b), familiar in the iron-based superconductors [14]. Thus the scenario of the field-induced Lifshitz transition can link with the nature in the metamagnetic transition in CeFePO.

Here, we compare the present results with $CeRu_2Si_2$, one of the most well-known metamagnetic compounds. Although both compounds show similar T and H dependence of Knight shift and $1/T_1T$ in H parallel to the magnetic easy axis [15], as well as the similar H-T phase diagram defined by $T_{\max}$ [16] as shown in Fig. 4(d), magnetic properties are quite different. For example, magnetic easy axis is different between CeFePO and $CeRu_2Si_2$: CeFePO possesses two-dimensional XY-type spin anisotropy, whereas $CeRu_2Si_2$ possesses Ising-type spin anisotropy [17]. As a result, the ground states of the crystal-field level are different and their metamagnetic behavior is observed in different directions. In addition, dominant magnetic fluctuations in CeFePO differ from those in $CeRu_2Si_2$. It is reported that $CeRu_2Si_2$ is located close to antiferromagnetic instability accompanied with FM fluctuations [18,19].

Figure 6 shows the relationship between the metamagnetic field H_M and the temperature where the bulk susceptibility shows a maximum $T_{\max}$ or inverse of Sommerfeld coefficient γ at $H = 0$ for $CeCu_6$, CeFePO, and $CeRu_2Si_2$ with doped and pressurized systems [5,17,20–23]. It deserves mention that the linear relation holds between the two quantities, notwithstanding that the three compounds possess totally different crystal structures and magnetic properties. Since $T_{\max}$ is regarded as a Kondo temperature T_K and roughly speaking, the relation of $\gamma T_K = \text{const}$ holds in the HF state, these facts indicate that H_M is merely related to the local Kondo singlet energy $T_{\max}$ and is not linked with the magnetic fluctuations originating from the intersite coupling between neighboring Ce ions and/or the nesting between the ''large'' FS. The experimental fact that H_M is linearly proportional to T_K in Fig. 6 strongly suggests that the metamagnetic behavior is linked with the Kondo breakdown [24]. Therefore, in the Ce-based metamagnets, the Kondo breakdown and the Fermi-surface instability accompanied by the drastic change of DOS occur almost simultaneously around H_M, which can induce novel non-FL behavior.

In summary, we performed ^{31}P-NMR in the uniaxially aligned CeFePO and found that CeFePO possesses two-dimensional XY-type FM fluctuations, and shows metamagnetic behavior when H is applied to $H \perp c$ below 5 K, accompanied with non-FL behavior around metamagnetic field $H_M \simeq 4$ T. As far as we know, this is a first example that the metamagnetic behavior occurs in a nonmagnetic Ce-based HF compound with the XY-type spin anisotropy. From the band calculation and the comparison with other Ce-based metamagnets, we

claim that H_M is a magnetic field breaking the local Kondo singlet, which is determined with the intrasite coupling between Ce-4f and conduction electrons, and that the FSs change drastically due to the Kondo breakdown.

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*shunsaku@scphys.kyoto-u.ac.jp

†Present address: Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan.

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