LETTER TO THE EDITOR

A theory of new type of heavy-electron superconductivity in PrOs$_4$Sb$_{12}$: quadrupolar-fluctuation mediated odd-parity pairings

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Abstract. It is shown that unconventional nature of superconducting state of PrOs$_4$Sb$_{12}$, a Pr-based heavy electron compound with the filled-Skutterudite structure, can be explained in a unified way by taking into account the structure of the crystalline-electric-field (CEF) level, the shape of the Fermi surface determined by the band structure calculation, and a picture of the quasiparticles in $f^2$-configuration with magnetically singlet CEF ground state. Possible types of pairing are narrowed down by consulting recent experimental results. In particular, the chiral “p”-wave states such as $p_x + ip_y$ is favoured under the magnetic field due to the orbital Zeeman effect, while the “p”-wave states with two-fold symmetry such as $p_z$ can be stabilized by a feedback effect without the magnetic field. It is also discussed that the double superconducting transition without the magnetic field is possible due to the spin-orbit coupling of the “triplet” Cooper pairs in the chiral state.

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Recently, the superconductivity has been found in heavy electron compound PrOs$_4$Sb$_{12}$ with the crystal structure of the filled Skutterudite [4]. Since the specific heat jump $\Delta C$ at the superconducting transition temperature $T_c=1.8$K is quite enhanced as $\Delta C/T_c \simeq 500$ mJ/K$^2$mole, heavy quasiparticles are responsible for the Cooper pair formation. Quite recently, a measurement of the longitudinal relaxation rate, $1/T_1$, of NQR at Sb site has been performed and very unusual temperature ($T$) dependence was revealed both for $T < T_c$ and $T > T_c$ [2], while the normal state properties had been known to be also quite unconventional [3, 4]. Unconventional behaviors of $1/T_1$ are summarized as follows: 1) Pseudo gap behavior is seen in $1/T_1T$ at $T_c < T < 2T_c$, in which the resistivity $\rho$ also shows a pseudo-gap behavior [1]. 2) There is no trace of the coherence (Hebel-Slichter) peak around $T = T_c$ at all. 3) $1/T_1$ appears to exhibit an exponential $T$-dependence below $1.3T_c$, giving the superconducting gap $\Delta$ in the low temperature limit as $2\Delta/k_BT_c \simeq 5.3$, although a possibility is not ruled out that the crossover to the $T^3$-dependence begins to be observed at around $T \simeq T_c/3$ the lowest temperature covered by experiments.

Very recently, the anomaly of specific heat near $T_c$ has been observed, which suggests a double transition at $T = T_{c1}$ and $T_{c2}$ ($T_c < T_{c2}$) [3, 4]. It also turned out very recently on the basis of measurements of the angular dependence of the thermal conductivity $\kappa$ under the magnetic field $H$ [5] that there exist at least two different superconducting phases in the $T$-$H$ phase diagram. In the low-field phase, the 2-fold component of $\kappa_z$ along the $z$-direction is observed as a function of the angle of the direction of $H$ around the $z$-axis, while the 4-fold one is observed in the high-field phase. The phase boundary approaches the lower critical temperature $T_{c2}$ as $H \to 0$. This is in marked contrast with the case of a heavy electron superconductor CeCoIn$_5$ where the data can be interpreted by a simple “d”-wave model [6]. These behaviors suggest that a novel type of heavy electron superconductivity is realized in PrOs$_4$Sb$_{12}$.

The purpose of this letter is to present a scenario explaining such anomalous behaviors in a unified way on the basis of the crystalline-electric-field (CEF) level, inferred from the experiment [4] and theoretical study [7], a topology of the Fermi surface (FS) offered from the band structure calculations [8], and a picture of the quasiparticles of $f^2$-based heavy electrons with a non-Kramers (non-magnetic) doublet CEF ground state.

The CEF level scheme proposed by Bauer et al. [4] in the point group $T_h$ is as follows [7]: The lowest level is the non-Kramers doublet $\Gamma^{\pm}_{23}$ ($\Gamma^+_{3}$ in the representation of the point group $O_h$)

$$|\Gamma^{\pm}_{23}\rangle = \sqrt{\frac{7}{24}}(|+4\rangle + |-4\rangle) - \sqrt{\frac{5}{12}}|0\rangle,$$  

and the first excited state is one of the triplet states $\Gamma^{(1)}_4$ or $\Gamma^{(2)}_4$ ($\Gamma_4$ or $\Gamma_5$ for $O_h$),
wavefunction of which has the form

$$\left| \Gamma_4^{(i)} \right> = \begin{cases} A_1^{(i)} (| - 4 > - |4 >) + A_2^{(i)} (| - 2 > - |2 >), \\ B_1^{(i)} | \mp 3 > + B_2^{(i)} | \mp 1 > + B_3^{(i)} | \pm 1 > + B_4^{(i)} | \pm 3 >, \end{cases}$$

where the coefficients $A^{(i)}$'s and $B^{(i)}$'s are not universal but depend on the details of the CEF parameters [7]. The lowest excitation energy of CEF levels has been estimated as $\Delta_{CEF} \simeq 7K$ [4]. Other excited CEF levels have excitation energies higher than 100K so that their effects are negligible in the low temperature region of the order of $T_c$. However, the possibility of $\Gamma_1$-$\Gamma_4$ CEF level scheme, with $\Delta_{CEF} \simeq 7K$, cannot be ruled out only from the analysis of the static susceptibility and the specific heat [3]. The ultrasonic measurements performed quite recently strongly suggest that the $\Gamma_{23}$ is the CEF ground state [9].

Around $T \sim 10$K, these lowest excited CEF levels give considerable contribution not only to the thermodynamic quantities, such as the specific heat $C$ and the magnetic susceptibility $\chi$, but also to the NQR relaxation rate $1/T_1$, since the “spin-flip” process can occur among the states forming $\Gamma_4^{(i)}$, e.g., between $| \pm 1 >$ and $| \pm 2 >$, giving the NQR relaxation. It is noted that each CEF level broadens due to the hybridization with the conduction electrons so that the energy conservation law is satisfied in the NQR or NMR relaxation process. Indeed, if we assume that the energy level of excited CEF level is broadened such that its spectral weight is approximated by the Lorentzian with the width $\Delta E$, and that the processes across the CEF ground states, (1) and (2), and $\Gamma_4$'s are neglected, the imaginary part of the spin-flip susceptibility $\text{Im} \chi_{\perp}(\omega)$ is given simply, in the limit $|\omega| \ll T$, as

$$\text{Im} \chi_{\perp}(\omega) \simeq \text{const.} \times \frac{\omega \Delta E}{\pi T(\omega^2 + \Delta E^2)} e^{-\Delta_{CEF}/T},$$

where const. is given by a combination of the coefficients $A$’s and $B$’s in (3), and the Clebsch-Gordon coefficients. Therefore, the NQR/NMR relaxation rate $1/T_1^{CEF} \approx A_{5d}^2 T \text{Im} \chi_{\perp}(\omega)/\omega$ due to the excited CEF level is given as

$$\frac{1}{T_1^{CEF}} \simeq \text{const.} \times \frac{1}{\pi \Delta E} e^{-\Delta_{CEF}/T}$$

The width of CEF level arises from the hybridization between f- and conduction electrons and is of the order of the width of the renormalized quasiparticle band. In the present case, $\Delta_{CEF} \simeq 7K$ is comparable to the bandwidth of heavy electrons, so that $\Delta E$ is also expected to be highly renormalized by the correlation effect.

Namely, if the temperature is decreased well below $\Delta_{CEF} = 7K$, the relaxation processes are gradually killed, leading to the pseudo-gap behavior [5] at such temperature region. We have, however, the usual relaxation process due to the quasiparticles of the Fermi liquid in addition. Therefore, $T$-dependence of $1/T_1 = 1/T_1^{CEF} + 1/T_1^{qp}$ at $T < T_c$ will be rather complicated one, since both contributions, from $\Gamma_4$ CEF level ($1/T_1^{CEF}$) and the quasiparticles ($1/T_1^{qp}$), to $1/T_1$ are decreasing
in such $T$-region with different $T$-dependence in general. In particular, one has to be careful in drawing the structure of the superconducting gap from the $T$-dependence of $1/T_1$ at $T_c/4 < T < T_c$.

In this Letter, we discuss the nature of the gap structure specific to the present system. First of all, it may be reasonable to assume that the strong on-site repulsion, the possible origin of the heavy electron state, cannot be avoided in a manifold of the conventional $s$-wave pairing state. This is also consistent with the absence of the coherence peak in $1/T_1$ although the possibility of the strong coupling effect is not completely ruled out. Another crucial aspect of PrOs$_4$Sb$_{12}$ uncovered by the band structure calculation is that the FS of the heavy electron band is missing in the directions of [1,0,0] and [1,1,1] and their equivalents as shown in Fig. 1. There exists a small FS surrounding the Γ-point whose mass is not heavy and has been detected by the de Haas-van Alphen experiment. Due to this porous structure of FS, even the anisotropic pairing state can have finite gap over the FS. However, even with such FS features being taken into account, the anisotropy of the gap due to such features of FS does not seem to fully explain the exponential-like $T$-dependence of $1/T_1$.

**Odd-parity pairing due to quadrupolar fluctuations**

We adopt here the odd-parity pairing to explain the unconventional nature of the superconducting state mentioned above. There are at least three circumstantial evidences for favouring the odd-parity pairing. First, the pairing interaction should be mainly mediated by the mode which gives rise to mass enhancement of quasiparticles, the quadrupolar fluctuations in the present case. Quadrupolar susceptibility $\chi_Q(q)$ is expected to be enhanced at large wave vector because the main FS has the nesting tendency as shown in Fig. 2 which can induce the attraction in both the “$d$”- and “$p$”-wave channel since the spin factor $(\vec{\sigma} \cdot \vec{\sigma}')$ does not exist in contrast to the case of spin-fluctuation mechanism. Second, a scenario for the double transition is more easily constructed in the odd-parity pairing with degeneracy due to the time-reversal symmetry than the even-parity pairings. Third, the so-called Maki parameter $\kappa_2$ under the magnetic field exhibits no paramagnetic limitation.

As mentioned above, the pairing is also expected to be induced by exchanging the quadrupolar fluctuations of the non-Kramers doublet $\Gamma_{23}^\pm$. The quadrupolar coupling between essentially localized $4f^2$-states and the quasiparticles containing considerable weight of the conduction electrons, arises through the hybridisation with the local symmetry of $\Gamma_8^{(1)}$ and $\Gamma_8^{(2)}$ in the cubic representation of CEF state of $j = 5/2$-manifold, as discussed by Cox in the context of the quadrupolar Kondo effect. The fact that the heavy quasiparticles contains the considerable weight of conduction electrons is a salient feature of $f^2$-based heavy electron state, which is in marked contrast with the $f^1$- or $f^3$-based ones where the quasiparticles are dominated by $f$-electrons. It is also consistent with the result of band structure calculation which shows that the $f$-component of the heaviest band at FS is only several %. The propagator of the
quadrupolar fluctuations $\chi_Q(q, i\omega_n)$ may be given as

$$\chi_Q(q, i\omega_n) = \frac{\chi_Q^{loc}(i\omega_n)}{1 - g^2 \Pi_0(q, i\omega_n)},$$

where $\chi_Q^{loc}$ and $\Pi_0$ denote the propagator for local fluctuations of quadrupolar moment, and the polarisation function of quasiparticles, respectively, and $g$ is the coupling constant among them.

As shown in Fig. 2, the FS has a nesting tendency and $\Pi_0$ is expected to have peaks at $\vec{q} = (\pi/2, \pi/2, 0)$, and $\vec{q} = (\pi/2, 3\pi/2, 0)$, and their equivalent positions. It is noted that the FS is rather flat in the $z$-direction near the nesting position as can be seen in Fig. 1. Then, the pairing interaction in the static approximation, $\Gamma(\vec{q}) \simeq g^2 \chi_Q(q, 0)$, can be parameterised as

$$\Gamma(\vec{q}) = \Gamma_0 - \Gamma_1 [\cos(2q_x) + \cos(2q_y)] + \Gamma_2 \cos \frac{q_x}{2} \cos \frac{q_y}{2} + (\text{cyclic permutations of } q_x, q_y, \text{ and } q_z),$$

(7)

where $\Gamma_i$'s are positive constants and $\Gamma_2$ is rather smaller than than $\Gamma_1$. The term of $\Gamma_2$ represents the effect that tendency of the nesting at $\vec{q} = (\pi/2, 3\pi/2, 0)$ is less than that at $\vec{q} = (\pi/2, \pi/2, 0)$ as seen in Fig. 2. By putting $\vec{q} = \vec{k} - \vec{k}'$, $\Gamma(\vec{q})$ is represented near the peak as follows:

$$\Gamma(\vec{k} - \vec{k}') = \Gamma_0 - \Gamma_1 [\cos 2(k_x - k'_x) + \cos 2(k_y - k'_y)] + \cdots$$

(8)

This gives the attractive interactions in the following channels:

- “d’-wave; $\cos(2k_x) - \cos(2k_y)$, etc.,
- “p”-wave; $\sin(2k_x)$, $\sin(2k_y)$, $\sin 2k_z$,

(9) (10)

Among these states, $\sin(2k_x)$ and its equivalents, $\sin(2k_y)$ and $\sin(2k_z)$, will be the most favourable ones because they have maximum amplitude on the FS. Indeed, other states have more nodes on the FS as seen in Fig. 2.

The simplest odd-parity states with “equal-spin-pairing” (ESP) allowed in cubic symmetry are given as follows:

$$\hat{\Delta}_k = \Delta [p_x(k) + \varepsilon p_y(k) + \varepsilon^2 p_z(k)] i(\sigma_y \sigma_x),$$
$$\hat{\Delta}_k = \Delta [p_x(k) + ip_y(k)] i(\sigma_y \sigma_x),$$

(11) (12)

Here, $\sigma_j$ is the $j$-th component of the Pauli matrix, $\varepsilon \equiv e^{i2\pi/3}$, and $p(k)$’s are bases of irreducible representations with “p”-symmetry: $p_x(k) \equiv \sqrt{2} \sin(2k_x)$, etc.. These gaps vanish along the direction of [1,1,1] or [1,0,0], and its equivalent direction. However, since there exists no FS in those directions, $1/T_1$ exhibits an exponential $T$-dependence in the lowest temperature region in spite of the anisotropic gap. It is noted that the Fermi surface of light electrons, detected by the de Haas-van Alphen experiment [11], is closed surrounding the $\Gamma$-point and these gaps have nodes at points on this FS. However, since $1/T_1$ is proportional to the square of the density of states at the Fermi level, the effect of such light electrons should hardly be seen by the $T$-dependence of $1/T_1$. 


Other possible states in the odd-parity manifold are
\[ \hat{\Delta}_k = \Delta p_x(k)i(\sigma_y\sigma_x), \text{ and its equivalent ones.} \] (13)
Such states are less favourable compared to the chiral states (1 1) and (1 2) in the so-called weak-coupling case where the feedback effect is not taken into account. This can be seen from the structure of the GL free energy. For instance, in the case of odd-parity class of ESP with “p”-symmetry, it is given as follows [16, 17]:
\[
F_{GL}(\Delta_x, \Delta_y, \Delta_z) = F_0 + \Phi(1 - V\Phi)(|\Delta_x|^2 + |\Delta_y|^2 + |\Delta_z|^2) \\
+ \frac{1}{2}\chi_{\text{diag}}(|\Delta_x|^2 + |\Delta_y|^2 + |\Delta_z|^2) \\
+ \chi_{\text{off}}\left\{ |\Delta_x|^2|\Delta_y|^2 + |\Delta_y|^2|\Delta_z|^2 + |\Delta_z|^2|\Delta_x|^2 \right\} \\
+ 2[\text{Re}(\Delta_x\Delta_y^*)]^2 + 2[\text{Re}(\Delta_x\Delta_z^*)]^2 + 2[\text{Re}(\Delta_y\Delta_z^*)]^2, \] (14)
where \( \Delta \)'s are the coefficient of each (normalized) irreducible representation of the gap, \( V \) is the strength of pairing interaction of “p”-symmetry, and 
\[
\Phi \equiv \sum_k |p_x(k)|^2 \frac{\tanh(\xi_k/2T)}{2\xi_k}, \] (15)
\[
\chi_{\text{diag}} \equiv \sum_k |p_x(k)|^4 \left( -\frac{d}{d\xi_k^2} \frac{\tanh(\xi_k/2T)}{2\xi_k} \right) > 0, \] (16)
\[
\chi_{\text{off}} \equiv \sum_k |p_x(k)p_y(k)|^2 \left( -\frac{d}{d\xi_k^2} \frac{\tanh(\xi_k/2T)}{2\xi_k} \right) > 0. \] (17)
Since \( \chi_{\text{diag}} \geq \chi_{\text{off}} \) due to the Schwarz inequality, the gap (13) cannot minimize \( F_{GL} \) in general. In case \( \chi_{\text{off}} < \frac{1}{3}\chi_{\text{diag}} \), the gap (11) minimizes \( F_{GL} \), while the gap (12) minimizes \( F_{GL} \) in case \( \chi_{\text{diag}} > \chi_{\text{off}} > \frac{1}{3}\chi_{\text{diag}} \).

The low-field phase, in the \( T-H \) phase diagram [5], having 2-fold symmetry is consistent with the gap (13), which cannot be realized in the weak-coupling theory. This is also the case in the singlet manifold. The so-called BW-like state is known to be the most stable state in the weak-coupling approximation, and there is no reason in principle to rule out its possibility from the first. However, BW-like state looks inconsistent with the thermal conductivity measurement under the magnetic field [5] and other thermodynamic measurements.

**Feedback effect**

In order that the gap with 2-fold symmetry such as (13) to be realised, we need a feedback effect. Among them, the following mechanism may be promising. The polarisation function \( \Pi_0 \) appearing (3) in the superconducting state is given as
\[
\Pi_0(\vec{q}, 0) = \frac{1}{2} \sum_{\vec{k}} \frac{E_{\vec{k}}E_{\vec{k}+\vec{q}} - \xi_{\vec{k}}\xi_{\vec{k}+\vec{q}} + \Delta_{\vec{k}}\Delta_{\vec{k}+\vec{q}}}{E_{\vec{k}}E_{\vec{k}+\vec{q}}(E_{\vec{k}} + E_{\vec{k}+\vec{q}})}, \] (18)
where \( E_{\vec{k}} = \sqrt{\xi_{\vec{k}}^2 + |\Delta_{\vec{k}}|^2} \). If the nesting were perfect at \( \vec{q} = (\pi/2, \pi/2, 0) \), and \( \vec{q} = (\pi/2, 3\pi/2, 0) \), and their equivalent positions, the following relations would hold,
\( \xi_{\vec{k}+\vec{q}} = -\xi_{\vec{k}} \), \( \Delta_{\vec{k}+\vec{q}} = -\Delta_{\vec{k}} \), and \( E_{\vec{k}+\vec{q}} = E_{\vec{k}} \), for \( \vec{k} \) near the FS. Then, the expression, (18), would be reduced to

\[
\Pi_0(q, 0) = \frac{1}{2} \sum_{\vec{k}} \frac{\xi_{\vec{k}}^2}{(\xi_{\vec{k}}^2 + |\Delta_{\vec{k}}|^2)^{3/2}}
\]

(19)

Then, the polarisation mediating the pairing interaction depends on the type of pairing itself. Indeed, the pairing (13) is expected to give larger (19) than the pairing (12), because the gap function of (13)

\[
|\Delta_{\vec{k}}|^2 \propto 2\sin^2(2k_x)
\]

(20)

vanishes on the planes, \( k_x = 0, \pm \pi/2, \pm \pi \), and \( \pm 3\pi/2 \), which pass through near the FS, while the gap function (12)

\[
|\Delta_{\vec{k}}|^2 \propto [\sin^2(2k_x) + \sin^2(2k_y)]
\]

(21)

vanishes only on the lines, \( (k_x, k_y) = (\pm \pi/2, \pm \pi/2), (\pm \pi/2, \pm \pi), (\pm \pi/2, \pm 3\pi/2) \), etc., which are located away from the FS. Although the explicit band structure calculation is hard in practice for the moment, the tendency mentioned above is expected to remain valid. Therefore, the state (13) may be stabilized against (12) by the feedback effect. In the BW-like state, \( \Pi_0(q, 0) \), (19), is suppressed more severely than in the state (12), and is destabilized against (13).

This kind of feedback effect is an analogue of that due to the ferromagnetic spin-fluctuation mechanism discussed in superfluid \(^3\)He \cite{18, 19}, in which the spin-fluctuation spectrum depends on the gap structure of the triplet states.

**Double transition due to spin-orbit coupling**

The spin-orbit interaction \( H_{so} \) due to the mutual Coulomb interaction between electrons and relative motion is given by

\[
H_{so} = -\frac{\mu_B^2 m}{2\hbar m_{\text{band}}} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}^3} (\vec{\sigma}_i + \vec{\sigma}_j) \cdot [\vec{r}_{ij} \times [(2\vec{g} - 1)\vec{p}_i - 2\vec{g}\vec{p}_j]]
\]

(22)

where \( \mu_B \) is the Bohr magneton, \( m \) electron mass, \( m_{\text{band}} \) the band mass, and \( \vec{g} \) is defined as \( g \equiv \mu_{\text{eff}}/\mu_B, \mu_{\text{eff}} \) being the effective magnetic moment \( \mu_{\text{eff}} \equiv (6/7)|\langle j_z \rangle|\mu_B \). The appearance of the factor \( m/m_{\text{band}} \) in (22) can follows from the Ward-Pitaevskii-identity \cite{20}. By the procedure similar to that described in Ref. \cite{16} for the dipole interaction, the interaction (22) leads to the spin-orbit free energy \( F_{so} \) for Cooper pairs which is spin triplet and chiral, such as (12), with the pair angular momentum \( \hbar \vec{\ell} \) as follows \cite{20}:

\[
F_{so} = -g_{so} (\vec{d} \times \vec{d}^\ast) \cdot \vec{\ell},
\]

(23)

where

\[
g_{so} = g_D \frac{m}{m_{\text{band}}} \times \frac{20}{3} (4\vec{g} - 1) = g_D \frac{m}{m_{\text{band}}} \times \begin{cases} 
\frac{20}{3} \times \frac{37}{7}, & \text{for } \Gamma_{8}^{(2)}; \\
\frac{20}{3} \times \frac{5}{7}, & \text{for } \Gamma_{8}^{(1)}.
\end{cases}
\]

(24)
where \( g_D \) is the strength of the dipole coupling in the “ESP”-superconducting state, and we have used \( \langle j_z \rangle = \pm 11/6 \) for quasiparticles consisting of \( \Gamma_8^{(2)} \) f1-CEF state, and \( \pm 1/2 \) for \( \Gamma_8^{(1)} \). The free energy due to the dipole-dipole interaction is given as 

\[
F_D = -\frac{3}{5} g_D |(\vec{d} \cdot \vec{\ell})|^2. \tag{25}
\]

Therefore the spin-orbit interaction, in the non-unitary state with \( |\vec{d} \times \vec{d}^\ast| \approx 1 \), dominates the dipole-dipole interaction, in the unitary state with \( |\vec{d} \cdot \vec{\ell}| = 1 \), because \( g_{so} \) far exceeds \( g_D \) in \( \Gamma_8^{(2)} \)-band considering (24) and \( m/m_{\text{band}} \sim \mathcal{O}(10^{-1}) \). Following the calculation in the spherical model \[16\], \( g_D \) is given by

\[
g_D = \frac{F_{\text{cond}}}{1 - T/T_c} \times 3.1 \mu_{\text{eff}}^2 N_F \left[ \ln \left(1.14 \epsilon_c/k_B T_c\right) \right]^2, \tag{26}
\]

where \( N_F \) is the density of states (DOS) of the quasiparticles, and \( F_{\text{cond}} \) is the condensation free energy

\[
F_{\text{cond}} = -N_F \frac{4(\pi k_B T_c)^2}{7 \zeta(3) \kappa} \left(1 - \frac{T}{T_c}\right)^2, \tag{27}
\]

where \( \kappa \) is the average of square of the magnitude of normalized gap function over the FS. The second factor in (26) is estimated as

\[
3.1 \mu_{\text{eff}}^2 N_F \left[ \ln \left(1.14 \epsilon_c/k_B T_c\right) \right]^2 \simeq \left( \frac{\mu_{\text{eff}}}{\mu_B} \right)^2 \times 1.4 \times 10^{-3}, \tag{28}
\]

where we have assumed that the renormalized Fermi energy is \( \epsilon_F \simeq 10^4/300 \) K, the number density of quasiparticles \( N/V = 2/(2/\sqrt{3} r_{\text{Pr-Pr}})^3 \), \( r_{\text{Pr-Pr}} \) being the distance between two nearest Pr ions. Therefore, the spin-orbit coupling \( g_{so} \), \[24\], is estimated as

\[
g_{so} = \frac{F_{\text{cond}}}{1 - T/T_c} \frac{m}{m_{\text{band}}} \times \begin{cases} 
\frac{20}{3} \times \frac{37}{7} \times 1.4 \times 10^{-3} = 4.9 \times 10^{-1}, & \text{for } \Gamma_8^{(2)}; \\
\frac{20}{3} \times \frac{5}{7} \times 1.4 \times 10^{-3} = 6.6 \times 10^{-2} & \text{for } \Gamma_8^{(1)},
\end{cases} \tag{29}
\]

The free-energy difference between \[13\] and \[12\], its non-unitary version with \( |\vec{d} \times \vec{d}^\ast| \neq 0 \), is of the order of 10% of \( F_{\text{cond}} \) in general, and \( m/m_{\text{band}} \sim \mathcal{O}(10^{-1}) \) according to the band structure calculation \[8\]. Therefore, if the stable state is \[13\] due to the feedback effect as discussed above, there occurs a double transition with splitting of the transition temperature being \( (T_{c1} - T_{c2})/T_{c1} \simeq \text{several }\% \), because the state \[12\] of non-unitary version is stabilized, due to the spin-orbit interaction \[23\], against \[13\] which is real state and has no spin-orbit coupling such as \[23\]. This width of splitting of double transition is consistent with the experimental observations \[3, 4\]. Especially, the results by Aoki et al \[3\], suggesting the double transition remains rather robustly under the magnetic field, can be explained by the present mechanism.

The chiral state \[11\] has also intrinsic magnetic moment along (1,1,1) direction, so that it can also give rise to the double transition as above. However, this state gives
the angular dependence of the thermal conductivity opposite to the observation in the high-field phase \[5\] although the 4-fold behaviour is expected.

Two phases in T-H phase diagram

Finally, the multiphase diagram in \(T-H\) plane determined by the thermal conductivity measurements under the magnetic field \[5\] may be understood as follows: A crucial point is that the triplet state \((12)\) has the intrinsic magnetic moment \(\vec{M}_{\text{in}}\) associated with the intrinsic angular momentum \(\vec{L}_{\text{in}}\) as \(\vec{M}_{\text{in}} = \mu_B (m/m_{\text{band}}) \vec{L}_{\text{in}} / \hbar\), where \(m^*\) is the effective mass of heavy quasiparticles, and \(\vec{L}_{\text{in}}\) is given as

\[
\vec{L}_{\text{in}} = \frac{N_{\text{in}}}{2} \hbar \ell, \tag{30}
\]

where \(N_{\text{in}}\) is the order of the superfluid electron density \(N_s\) \[21, 22, 23\], while the lively disputes were performed concerning the size of \(N_{\text{in}}\), whether \(N_{\text{in}} \sim \mathcal{O}(N_s)\) or \(\mathcal{O}(N_s \cdot (T_c/\epsilon_F)^n)\) with \(n = 1\) or \(2\), about a quarter of century ago in the context of superfluid \(^3\)He \[24\]. Very recently, the reality of this intrinsic magnetic moment has caused a renewed interest in the magnetic property of the chiral superconducting state of \(\text{Sr}_2\text{RuO}_4\) \[25\]. At low enough temperature \(T \ll T_c\), the intrinsic magnetic moment is \(\vec{M}_{\text{in}} \simeq (N/2) \mu_B (m/m_{\text{band}}) \vec{L}\). Therefore, the state \((12)\) is stabilized under the magnetic field \(H\) over the state \((13)\), which has no intrinsic magnetic moment. The transition between the two states occurs when

\[
N_F (k_B T_c)^2 \times 10^{-1} \sim N \frac{m}{m_{\text{band}}} \mu_B H \left(1 - \frac{N_d}{4\pi}\right), \tag{31}
\]

where the left-hand side represents the difference of the condensation energy between the two superconducting phases at \(T \ll T_c\), and the right-hand side the energy gain in the chiral state \((12)\) with the intrinsic angular momentum in the magnetic field \(H\). We have included in \((31)\) the so-called the demagnetisation factor \(N_d\) which depends on the sample shape. In \((31)\), the energy due to the magnetic field arising from the intrinsic magnetisation itself is neglected because it is much smaller than the external field \(\approx H\) in question. The magnetic field giving the phase boundary between low- and high-field phases, determined by the thermal conductivity, roughly agrees with the present estimation is in the same order as given by \((31)\), because \(N_F \sim N/\epsilon_F^*, k_B T_c/\epsilon_F^* \sim 10 \times (m/m^*), m^*/m_{\text{band}} \sim 10\), and \(N_d \sim 10^{-1}\). A crucial prediction of the present scenario is that the phase boundary in the \(T-H\) plane is dependent on the sample shape through the demagnetisation factor \(N_d\).

The angular dependence of the thermal conductivity \(\kappa_z\) reported in Ref. \[5\] may also be explained by the present scenario. If the state \((13)\), \(\Delta_k \propto p_x(k)\), is realised in the low-field phase due to the boundary effect, which works to align the extension of pair wavefunction, \(\kappa_z\) takes maximum (minimum), when the magnetic field \(\vec{B}\) is \(\vec{B} \parallel \hat{x}\) (\(\vec{B} \parallel \hat{y}\)), in consistent with Ref. \[5\]. This can be understood by applying the argument similar to Ref. \[6\]. If a type of the state \((12)\) is realized in the high-field phase, the free energy takes minimum when the quantisation axis of intrinsic angular momentum is parallel to \(\vec{B}\) for which \(\kappa_z\) is minimum \[6\]. Therefore, when the direction of \(\vec{B}\) is
rotated by angle $\phi$ from the $x$-axis in the plane perpendicular to $z$-axis, $\kappa_z$ increases and reaches maximum at $\phi = 45^\circ$ above which the stable quantisation axis changes from $x$- to $y$-axis, and then $\kappa_z$ decreases up to $\phi = 90^\circ$ where the stable configuration is reached again. Namely, the 2-fold dependence of $\kappa_z(\phi)$ taking maximum at $\phi = 0^\circ$ can be possible in the low-field phase, and the 4-fold one taking minimum at $\phi = 0^\circ$ and $\phi = 90^\circ$ in the high-field phase [5].

In conclusion, it is remarked that the magnetic susceptibility, both longitudinal and transverse, can be enhanced by electron correlations even if the mass enhancement arises from the degeneracy due to the non-Kramers doublet, i.e., electric quadrupolar moment, provided that there exists a perturbation which breaks the particle-hole symmetry, such as the repulsion among conduction electrons, as shown by the numerical renormalization group calculations for the impurity model [26]. This is in marked contrast with the case of heavy electrons based on $f^2$-configuration with the singlet CEF ground state [27], where the static susceptibility along the easy axis due to quasiparticles is not enhanced while the NMR/NQR relaxation rates given by the dynamical transverse susceptibility is enhanced in proportion to a square of the mass-enhancement factor as observed in UPt$_3$ [28].

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Figure 2. Fermi surface shown in Fig. 1 cut by the $k_x$-$k_y$ plane $k_z = 0$. The nesting tendency in the heavy electron band at $(k_x, k_y) = (\pi/2, \pi/2)$ and $(3\pi/2, \pi/2)$ as shown by arrows, and their equivalent positions, remains in the direction rather robustly for finite $k_z \neq 0$.

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