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LETTER TO THE EDITOR

Theory of a new type of heavy-electron superconductivity in $PrOs_4Sb_{12}$: quadrupolar-fluctuation mediated odd-parity pairings

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Abstract
It is shown that the unconventional nature of the superconducting state of $PrOs_4Sb_{12}$, 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 the f^2 configuration with a 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 $p_x + ip_y$ are favoured under the magnetic field due to the orbital Zeeman effect, while the 'p'-wave states with twofold symmetry such as p_x 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.

Recently, superconductivity has been found in the heavy electron compound $PrOs_4Sb_{12}$ with the filled skutterudite crystal structure [1]. Since the specific heat jump ΔC at the superconducting transition temperature $T_c = 1.8$ K is quite enhanced as $\Delta C/T_c \simeq 500$ mJ K^{-2} mol^{-1}, heavy quasiparticles are responsible for the Cooper pair formation. Quite recently, a measurement of the longitudinal relaxation rate, $1/T_1$, of NQR at the 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 are also known to be quite unconventional [1, 3]. Unconventional behaviours of $1/T_1$ are summarized as follows.

(1) Pseudo-gap behaviour is seen in $1/T_1T$ at $T_c < T < 2T_c$, in which the resistivity ρ also shows a pseudo-gap behaviour [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 Δ in the low temperature limit as $2\Delta/k_BT_c \simeq 5.3$, although the possibility 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, is not ruled out.

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} ($T_{c2} < T_{c1}$) [3, 4]. It also turned out very recently on the basis of measurements of the angular dependence of the thermal conductivity κ 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 twofold component of κ_z along the z-direction is observed as a function of the angle of the direction of H around the z-axis, while the fourfold 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 the heavy electron superconductor $CeCoIn_5$ where the data can be interpreted by a simple 'd'-wave model [6]. These behaviours suggest that a novel type of heavy electron superconductivity is realized in $PrOs_4Sb_{12}$.

The purpose of this letter is to present a scenario explaining such anomalous behaviours in a unified way on the basis of the crystalline-electric-field (CEF) level, inferred from experiment [1] 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* [1] in the point group T_h is as follows [7]: the lowest level is the non-Kramers doublet $\Gamma_{23}^{\pm}$ ($\Gamma_3^{\pm}$ in the representation of the point group O_h)

$$|\Gamma_{23}^{+}\rangle = \sqrt{\tfrac{7}{24}}(|+4\rangle + |-4\rangle) - \sqrt{\tfrac{5}{12}}|0\rangle, \tag{1}$$

$$|\Gamma_{23}^{-}\rangle = \frac{1}{\sqrt{2}}(|+2\rangle + |-2\rangle), \tag{2}$$

and the first excited state is one of the triplet states $\Gamma_4^{(1)}$ or $\Gamma_4^{(2)}$ (Γ_4 or Γ_5 for O_h), the wavefunction of which has the form

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

where the coefficients $A^{(i)}$ and $B^{(i)}$ are not universal but depend on the details of the CEF parameters [7]. The lowest excitation energy of CEF levels has been estimated as $\Delta_{CEF} \simeq 7$ K [4]. Other excited CEF levels have excitation energies higher than 100 K so that their effects are negligible in the low temperature region of the order of T_c.

While we here adopt the Γ_{23}–Γ_4 CEF level scheme, the possibility of the Γ_1–Γ_4 CEF level scheme cannot be ruled out from the analysis of the static susceptibility and the specific heat [3] alone. Quite recently, a neutron scattering measurement suggesting that Γ_1 is the ground state has been reported [9]. However, recent ultrasonic measurements, using the most suitable probe for searching the CEF ground state, strongly suggest that Γ_{23} is the CEF ground state [10]. So, the assumption of a Γ_{23} ground state still seems valid.

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 χ, 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 $|\pm 1\rangle$ and $|\pm 2\rangle$, 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 of the excited CEF level is broadened such that its spectral weight is approximated by the Lorentzian with the width ΔE, and that the processes across the CEF ground states, (1) and (2), and Γ_4 states are neglected, the imaginary part of the spin-flip susceptibility $\mathrm{Im}\,\chi_\perp(\omega)$ is given simply, in the limit $|\omega| \ll T$, as

$$\mathrm{Im}\,\chi_\perp(\omega) \simeq \text{constant} \times \frac{\omega \Delta E}{\pi T(\omega^2 + \Delta E^2)} \mathrm{e}^{-\Delta_{\mathrm{CEF}}/T}, \tag{4}$$

where the constant is given by a combination of the coefficients A and B in (3), and the Clebsch–Gordan coefficients. Therefore, the NQR/NMR relaxation rate $1/T_1^{\mathrm{CEF}} \approx A_{\mathrm{hf}}^2 T\, \mathrm{Im}\,\chi_\perp(\omega)/\omega$ due to the excited CEF level is given as

$$\frac{1}{T_1^{\mathrm{CEF}}} \simeq \text{constant} \times \frac{1}{\pi \Delta E} \mathrm{e}^{-\Delta_{\mathrm{CEF}}/T}. \tag{5}$$

The width of the 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, $\Delta_{\mathrm{CEF}} \simeq 7$ K is comparable to the bandwidth of heavy electrons, so that ΔE is also expected to be highly renormalized by the correlation effect. Namely, if the temperature is decreased well below $\Delta_{\mathrm{CEF}} = 7$ K, the relaxation processes are gradually killed, leading to the pseudo-gap behaviour (5) in such a temperature region. We have, however, the usual relaxation process due to the quasiparticles of the Fermi liquid in addition. Therefore, the T-dependence of $1/T_1 = 1/T_1^{\mathrm{CEF}} + 1/T_1^{\mathrm{qp}}$ at $T < T_c$ will be a rather complicated one, since both contributions, from the Γ_4 CEF level ($1/T_1^{\mathrm{CEF}}$) and the quasiparticles ($1/T_1^{\mathrm{qp}}$), to $1/T_1$ are decreasing in such a T-region with different T-dependences in general. In particular, one has to be careful in deducing 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 $1/T_1$ [2] although the possibility of the strong coupling effect is not completely ruled out. Another crucial aspect of $\mathrm{PrOs_4Sb_{12}}$ 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 figure 1 [8]. There exists a small FS surrounding the Γ-point whose mass is not large [8] and has been detected by the de Haas–van Alphen experiment [11]. Due to this porous structure of the FS, even the anisotropic pairing state can have a 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 $1/T_1$.

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 pieces of circumstantial evidence 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 $\chi_Q(\boldsymbol{q})$ is expected to be enhanced at large wavevector because the main FS has the nesting tendency as shown in figure 2 which can induce attraction in both the 'd'- and 'p'-wave channels since the spin factor $(\vec{\sigma} \cdot \vec{\sigma}')$ does not exist, in contrast to the case of the spin-fluctuation mechanism [12, 13]. Second, a scenario for the double transition is more easily constructed in the odd-parity pairing with degeneracy

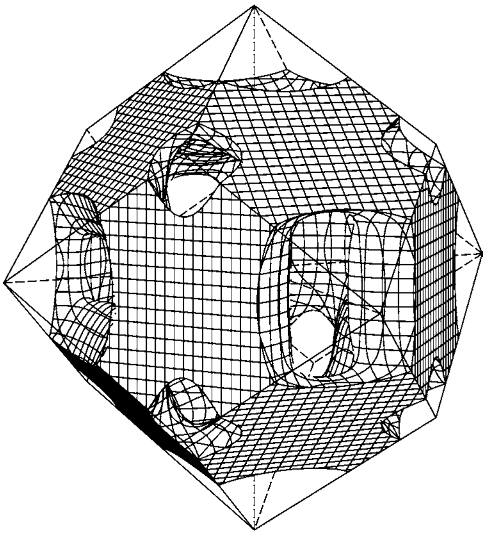

Figure 1. FS of $PrOs_4Sb_{12}$ relevant to the heavy electrons given by band structure calculation [8]. The FS is missing in the [1, 1, 1], [1, 0, 0] and equivalent directions.

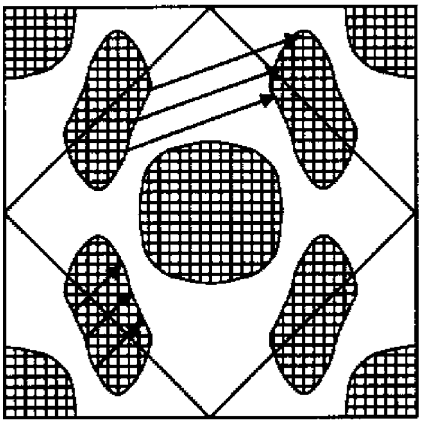

Figure 2. The FS shown in figure 1 cut by the k_x–k_y-plane $k_z = 0$. The nesting tendency in the heavy electron band at $(k_x, k_y) = (\pi/2, \pi/2)$ and $(3\pi/2, \pi/2)$ as shown by arrows, and their equivalent positions, remains in this direction rather robustly for finite $k_z \neq 0$.

due to the time-reversal symmetry than the even-parity pairings. Third, the so-called Maki parameter κ_2 under the magnetic field exhibits no paramagnetic limitation [14].

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 hybridization with the local symmetry of $\Gamma_8^{(1)}$ and $\Gamma_8^{(2)}$ in the cubic representation of the CEF state of the $j = 5/2$ manifold, as discussed by Cox in the context of the quadrupolar Kondo effect [15]. The fact that the heavy quasiparticles contain considerable weight of conduction electrons is a salient feature of the 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 a few per cent [8]. The propagator of the quadrupolar fluctuations $\chi_Q(q, \mathrm{i}\omega_m)$ may be given as

$$\chi_Q(q, \mathrm{i}\omega_m) = \frac{\chi_Q^{\ell\mathrm{oc}}(\mathrm{i}\omega_m)}{1 - g^2\Pi_0(q, \mathrm{i}\omega_m)}, \tag{6}$$

where $\chi_Q^{\ell\mathrm{oc}}$ and Π_0 denote the propagator for local fluctuations of quadrupolar moment, and the polarization function of quasiparticles, respectively, and g is the coupling constant among them.

As shown in figure 2, the FS has a nesting tendency and Π_0 is expected to have peaks at $\vec{q} = (\pi/2, \pi/2, 0)$ and $(\pi/2, 3\pi/2, 0)$, 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 figure 1. Then, the pairing interaction in the static approximation, $\Gamma(\vec{q}) \simeq g^2\chi_Q(q, 0)$, can be parametrized as

$$\Gamma(\vec{q}) = \Gamma_0 - \Gamma_1[\cos(2q_x) + \cos(2q_y)] + \Gamma_2 \cos\frac{q_x}{2}\cos\frac{q_y}{2}$$
$$+ \text{(cyclic permutations of } q_x, q_y, \text{ and } q_z), \tag{7}$$

where the Γ_i are positive constants and Γ_2 is rather smaller than Γ_1. The Γ_2 term represents the effect that the nesting tendency at $\vec{q} = (\pi/2, 3\pi/2, 0)$ is less than that at $\vec{q} = (\pi/2, \pi/2, 0)$ as seen in figure 2. By putting $\vec{q} = \vec{k} - \vec{k}'$, $\Gamma(\vec{q})$ is represented near the peak as follows:

$$\Gamma(\vec{k} - \vec{k}') = \Gamma_0 - \Gamma_1[\cos 2(k_x - k_x') + \cos 2(k_y - k_y')] + \cdots. \tag{8}$$

This gives the attractive interactions in the following channels:

$$\text{‘d’-wave;} \qquad \cos(2k_x) - \cos(2k_y), \text{ etc,} \tag{9}$$

$$\text{‘p’-wave;} \qquad \sin(2k_x), \sin(2k_y), \sin(2k_z). \tag{10}$$

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 figure 2.

The simplest odd-parity states with ‘equal spin pairing’ (ESP) allowed in cubic symmetry are given as follows [16]:

$$\hat{\Delta}_k = \Delta[\mathrm{p}_x(k) + \varepsilon\mathrm{p}_y(k) + \varepsilon^2\mathrm{p}_z(k)]\mathrm{i}(\sigma_y\sigma_x), \tag{11}$$

$$\hat{\Delta}_k = \Delta[\mathrm{p}_x(k) + \mathrm{i}\mathrm{p}_y(k)]\mathrm{i}(\sigma_y\sigma_x). \tag{12}$$

Here, σ_j is the jth component of the Pauli matrix, $\varepsilon \equiv \mathrm{e}^{\mathrm{i}2\pi/3}$, and the $p(k)$ are bases of irreducible representations with ‘p’ symmetry: $\mathrm{p}_x(k) \equiv \sqrt{2}\sin(2k_x)$ etc. These gaps vanish along the directions of [1, 1, 1] or [1, 0, 0], and their equivalent directions. 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 FS of light electrons, detected by the de Haas–van Alphen experiment [11], is closed surrounding the Γ-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

$$\hat{\Delta}_k = \Delta\mathrm{p}_x(k)\mathrm{i}(\sigma_y\sigma_x), \text{ and its equivalent ones.} \tag{13}$$

Such states are less favourable compared to the chiral states (11) and (12) 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 the odd-parity class of ESP with ‘p’ symmetry, it is given as follows [17, 18]:

$$F_{\rm GL}(\Delta_x,\Delta_y,\Delta_z) = F_0 + \Phi(1 - V\Phi)(|\Delta_x|^2 + |\Delta_y|^2 + |\Delta_z|^2) + \tfrac{1}{2}\chi_{\rm diag}(|\Delta_x|^4 + |\Delta_y|^4 + |\Delta_z|^4) + \chi_{\rm off}\{|\Delta_x|^2|\Delta_y|^2 + |\Delta_y|^2|\Delta_z|^2 + |\Delta_z|^2|\Delta_x|^2 + 2[{\rm Re}(\Delta_x\Delta_y^*)]^2 + 2[{\rm Re}(\Delta_x\Delta_y^*)]^2 + 2[{\rm Re}(\Delta_x\Delta_y^*)]^2\}, \tag{14}$$

where the Δ are the coefficients of each (normalized) irreducible representation of the gap, V is the strength of the pairing interaction of 'p' symmetry and

$$\Phi \equiv \sum_k [{\rm p}_x(k)]^2 \frac{\tanh(\xi_k/2T)}{2\xi_k}, \tag{15}$$

$$\chi_{\rm diag} \equiv \sum_k [{\rm p}_x(k)]^4 \left(-\frac{\rm d}{{\rm d}\xi_k^2}\frac{\tanh(\xi_k/2T)}{2\xi_k}\right) > 0, \tag{16}$$

$$\chi_{\rm off} \equiv \sum_k [{\rm p}_x(k){\rm p}_y(k)]^2 \left(-\frac{\rm d}{{\rm d}\xi_k^2}\frac{\tanh(\xi_k/2T)}{2\xi_k}\right) > 0. \tag{17}$$

Since $\chi_{\rm diag} \geqslant \chi_{\rm off}$ due to the Schwarz inequality, the gap (13) cannot minimize $F_{\rm GL}$ in general. When $\chi_{\rm off} < \frac{1}{3}\chi_{\rm diag}$, the gap (11) minimizes $F_{\rm GL}$, while the gap (12) minimizes $F_{\rm GL}$ when $\chi_{\rm diag} > \chi_{\rm off} > \frac{1}{3}\chi_{\rm diag}$.

The low field phase, in the T–H phase diagram [5], having twofold 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, the BW-like state looks inconsistent with the thermal conductivity measurement under the magnetic field [5] and other thermodynamic measurements.

2. Feedback effect

In order for the gap with twofold symmetry such as (13) to be realized, we need a feedback effect. Among these, the following mechanism may be promising. The polarization function Π_0 appearing (6) in the superconducting state is given as

$$\Pi_0(q,0) = \frac{1}{2}\sum_{\vec{k}} \frac{E_{\vec{k}}E_{\vec{k}+\vec{q}} - \xi_{\vec{k}}\xi_{\vec{k}+\vec{q}} + \Delta_{\vec{k}}\Delta_{\vec{k}+\vec{q}}}{E_{\vec{k}}E_{\vec{k}+\vec{q}}(E_{\vec{k}} + E_{\vec{k}+\vec{q}})}, \tag{18}$$

where $E_{\vec{k}} = \sqrt{\xi_{\vec{k}}^2 + |\Delta_{\vec{k}}|^2}$. If the nesting were perfect at $\vec{q} = (\pi/2, \pi/2, 0)$, $(\pi/2, 3\pi/2, 0)$ 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

$$\Pi_0(q,0) = \frac{1}{2}\sum_{\vec{k}} \frac{\xi_{\vec{k}}^2}{(\xi_{\vec{k}}^2 + |\Delta_{\vec{k}}|^2)^{3/2}}. \tag{19}$$

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

$$|\Delta_{\vec{k}}|^2 \propto 2\sin^2(2k_x) \tag{20}$$

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

$$|\Delta_{\vec{k}}|^2 \propto [\sin^2(2k_x) + \sin^2(2k_y)] \tag{21}$$

vanishes only on the lines $(k_x, k_y) = (\pm\pi/2, \pm\pi/2)$, $(\pm\pi/2, \pm\pi)$, $(\pm\pi/2, \pm3\pi/2)$ 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 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 [19, 20], in which the spin-fluctuation spectrum depends on the gap structure of the triplet states.

3. 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

$$H_{so} = -\frac{\mu_B^2}{2\hbar}\frac{m}{m_{band}}\sum_i\sum_{j\neq i}\frac{1}{r_{ij}^3}(\vec{\sigma}_i + \vec{\sigma}_j)\cdot[\vec{r}_{ij}\times[(2\bar{g}-1)\vec{p}_i - 2\bar{g}\vec{p}_j]], \tag{22}$$

where μ_B is the Bohr magneton, m electron mass, m_{band} the band mass and $\bar{g}$ is defined as $\bar{g} \equiv \mu_{eff}/\mu_B$, μ_{eff} being the effective magnetic moment $\mu_{eff} \equiv (6/7)|\langle j_z\rangle|\mu_B$. The appearance of the factor m/m_{band} in (22) can follow from the Ward–Pitaevskii identity [21]. By a procedure similar to that described in [17] 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 [21]:

$$F_{so} = -g_{so}(\mathrm{i}\vec{d}\times\vec{d}^*)\cdot\vec{\ell}, \tag{23}$$

where

$$g_{so} = g_D\frac{m}{m_{band}}\frac{20}{3}(4\bar{g}-1) = g_D\frac{m}{m_{band}}\begin{cases}\dfrac{20}{3}\times\dfrac{37}{7}, & \text{for } \Gamma_8^{(2)};\\[2mm] \dfrac{20}{3}\times\dfrac{5}{7}, & \text{for } \Gamma_8^{(1)},\end{cases} \tag{24}$$

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 the $\Gamma_8^{(2)}$ f^1 CEF state and $\pm 1/2$ for $\Gamma_8^{(1)}$. The free energy due to the dipole–dipole interaction is given as [17]

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

Therefore the spin–orbit interaction, in the non-unitary state with $|\vec{d}\times\vec{d}^*| \simeq 1$, dominates the dipole–dipole interaction, in the unitary state with $|\vec{d}\cdot\vec{\ell}| = 1$, because g_{so} far exceeds g_D in the $\Gamma_8^{(2)}$ band considering (24) and $m/m_{band} \sim \mathcal{O}(10^{-1})$. Following the calculation in the spherical model [17], g_D is given by

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

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

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

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

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

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

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

The free-energy difference between (13) and (12), its non-unitary version with $|\vec{d} \times \vec{d}^*| \neq 0$, is of the order of 10% of $F_{\rm cond}$ in general, and $m/m_{\rm band} \sim \mathcal{O}(10^{-1})$ 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 the splitting of the transition temperature being $(T_{c1} - T_{c2})/T_{c1} \simeq$ several per cent, because state (12) of the non-unitary version is stabilized, due to the spin–orbit interaction (23), against (13), which is a real state and has no spin–orbit coupling such as (23). This splitting width of the double transition is consistent with the experimental observations [3, 4]. In particular, the results by Aoki *et al* [3], suggesting the double transition remains rather robust under the magnetic field, can be explained by the present mechanism.

The chiral state (11) also has intrinsic magnetic moment along the (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 fourfold behaviour is expected.

4. Two phases in T–H phase diagram

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

$$\vec{L}_{\rm in} = \frac{N_{\rm in}}{2}\hbar\vec{\ell}, \tag{30}$$

where $N_{\rm in}$ is the order of the superfluid electron density N_s [22–24], while lively disputes were carried out concerning the size of $N_{\rm in}$, whether $N_{\rm in} \sim \mathcal{O}(N_s)$ or $\mathcal{O}(N_s(T_c/\epsilon_F^*)^n)$ with $n = 1$ or 2, about a quarter of century ago in the context of superfluid ^{3}He [25]. Very recently, the reality of this intrinsic magnetic moment has caused a renewed interest in the magnetic property of the chiral superconducting state of Sr_2RuO_4 [26]. At low enough temperature $T \ll T_c$, the intrinsic magnetic moment is $\vec{M}_{\rm in} \simeq (N/2)\mu_B(m/m_{\rm band})\vec{\ell}$. Therefore, state (12) is stabilized under the magnetic field H over state (13), which has no intrinsic magnetic moment. The transition between the two states occurs when

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

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 mementum in the magnetic field H. We have included in (31) the so-called demagnetization factor N_d which depends on the sample shape. In (31), the energy due to the magnetic field arising from the intrinsic magnetization itself is neglected because it is much smaller than the external field $\simeq H$ 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 in the same order as given by (31), because $N_F \sim N/\epsilon_F^*$, $k_B T_c/\epsilon_F^* \sim 10 \times (m/m^*)$, $m^*/m_{band} \sim 10$ 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 demagnetization factor N_d.

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

5. Conclusion

Before concluding this letter, 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 [27]. This is in marked contrast with the case of heavy electrons based on the f^2 configuration with the singlet CEF ground state [28], 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 are enhanced in proportion to a square of the mass-enhancement factor as observed in UPt_3 [29].

In conclusion, we have proposed a possible scenario to explain the unconventional nature of the superconducting state of $PrOs_4Sb_{12}$, from the view point that the quadrupolar fluctuation is a main origin of its superconductivity. Here, the feed back effect on the quadrapolar fluctuation associated with the characteristic shape of the Fermi surface, the spin–orbit interaction of the triple Cooper pairs, and the Zeeman effect of Cooper pairing cooperatively play crucial roles.

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