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$PuCoGa_5$ and related materials

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Abstract

Temperature dependencies of the nuclear spin-relaxation rate and specific heat of $PuCoGa_5$ and isostructural $PuRhGa_5$ are consistent with their superconductivity being unconventional. A simple model of hybridization between localized f-electrons and itinerant conduction-band electrons gives a framework for interpreting basic similarities and differences between these Pu-based superconductors and their Ce-based analogs. This model also provides a rationale for the correlation between T_c and a characteristic spin-energy scale in these materials.

Keywords: Superconductivity; Heavy fermions; Spin dynamics

1. Introduction

The Bardeen–Copper–Schrieffer (BCS) theory of superconductivity predicts the opening of a gap in the electronic density of states when superconductivity develops. Because this gap exists over the entire Fermi surface, physical properties, such as specific heat and nuclear spin-relaxation rate, decrease exponentially with decreasing temperature below T_c. This prediction is very well established in a large number of conventional superconductors in which pairs of itinerant electrons with equal but opposite spin and momentum are formed through an attractive interaction mediated by lattice excitations [1]. In contrast to these dominant cases, a few but growing number of superconductors exhibit a power-law dependence of physical properties below T_c, which can be understood if the superconducting gap goes to zero over parts of the Fermi surface. The terminology 'unconventional' is applied loosely to superconductivity found in these materials that exhibit physical properties qualitatively distinct from those of 'conventional' superconductors. A more precise definition of unconventional is that the wave-function symmetry of superconducting electron pairs breaks additional symmetries, e.g., rotational or mirror symmetries, of the crystal lattice [2]. The s-wave symmetry of electron pairs in a conventional superconductor does not break these symmetries, but superconductivity mediated by magnetic excitations can produce pairs with higher net angular momentum that do and that by their symmetry require the superconducting gap to vanish at points or lines on the Fermi surface [2]. In the absence of a microscopic theory of magnetically mediated superconductivity, it is non-trivial and rarely unambiguous to establish that superconductivity is indeed unconventional. Instead, it often is inferred from a body of evidence, such as power-laws below T_c and corresponding evidence for magnetic fluctuations above T_c. With this definition, the high-T_c superconductors based on copper-oxide are unconventional as are certain Ce- and U-based intermetallic compounds, called heavy-fermion materials. As will be discussed, the first Pu-based superconductors $PuCoGa_5$ [3] and $PuRhGa_5$ [4] (Pu1 1 5s) appear to belong to this class of unconventional heavy-fermion superconductors.

2. Effective mass and hybridization

An enhanced Sommerfeld coefficient of specific heat, γ, characteristic of heavy-fermion compounds is also found in some materials based on Pu; however, the largest values of γ in these Pu materials do not reach those of Ce- and U-based heavy-fermion superconductors in which γ ranges from several 100 to about 1000 mJ/(mol K^2). Table 1 lists Pu materials with the largest Sommerfeld coefficients. Quite generally, the magnitude

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Table 1
Properties of five Pu-based compounds with the largest Sommerfeld coefficients of specific heat γ

Compound	γ	Reference
$PuAl_2$	260	[5]
Pu_4PdSb_{12}	>225	[6]
$PuBe_{13}$	210	[7]
$PuGa_3$	205[a]	[8,9]
	100[b]	[8]
$PuRh_2$	145	[9]
$PuCoGa_5$	80	[3]
$PuRhGa_5$	50	[10]
$CeRhIn_5$	450	[11]
$CeCoIn_5$	250	[12]

$PuCoGa_5$, $PuRhGa_5$, $CeCoIn_5$ and $CeRhIn_5$ are included for comparison. Values of γ are in mJ/mole-Pu K^2 or mJ/mole-Ce K^2 for Pu- and Ce-based materials, resectively.
[a] Hexagonal phase.
[b] Trigonal phase.

of γ is proportional to the electronic density of states at the Fermi energy $N(E_F)$ or equivalently to the effective mass m^* of itinerant electrons. (Crudely, $\gamma = 1$ mJ/(mol K^2) implies $m^* \approx m_e$, the mass of a free electron.) One way in which m^* can be enhanced is for a material to be tuned close to a magnetic quantum-critical point. Precisely at the critical point where a second-order magnetic transition is tuned to $T = 0$, m^* diverges, but m^* also can be very large over a range of parameters, such as chemical composition or pressure, near the quantum-phase transition [13]. Invariably, heavy-fermion superconductivity in Ce- and U-based materials develops very close to or even coexists with magnetism. This is one reason to suspect that they are close to a quantum-critical point and that attendant magnetic fluctuations are involved in producing an unconventional superconducting state within a band of heavy-mass itinerant charge carriers. Aside from this special condition for a large m^*, $N(E_F)$ can be enhanced significantly through hybridization of conduction-band electrons with localized f-electrons. Hybridization broadens the f-electron level to a width Γ and mixes f-electron character into $N(E_F)$ such that the f-electron density of states at E_F is given approximately by $N_f(E_F) = (N/\pi\Gamma)\sin^2(\pi n_f/N)$, where N is the degeneracy of the f-level, n_f the number of f-electrons in the f-shell, and $\Gamma = \pi\langle V_{kf}\rangle^2 N_0(E_F)$ [14]. $\langle V_{kf}\rangle$ is the matrix element that mixes conduction and f-electron wave functions into the bare density of states $N_0(E_F)$ in the absence of hybridization. In the simplest limit of a trivalent Ce ion in a crystal-field doublet ground state, which is typical of Ce-based heavy-fermion materials, $N = 2$ and $n_f \cong 1$, and the expression for $N_f(E_F)$ corresponds to a spin-1/2 Kondo state in which there is a resonance in the density of states at E_F that dominates all other contributions to $N(E_F)$.

The dependence of $N_f(E_F)$ on degeneracy and n_f provides a plausible reason why the largest γ values in Pu compounds are smaller than in Ce heavy-fermion systems. Consider two identical tetragonal compounds, one made with Pu and the other with Ce, that have the same matrix element $\langle V_{kf}\rangle$ and the same f-valence state 3+. Because they are composed of the same elements, except the f-element, $N_0(E_F)$, and, consequently, Γ will be essentially the same in both. The Ce ion will experience crystal-field splitting, so that $N = 2$ for $n_f = 1$, but Pu^{3+} has $n_f = 5$ and crystalline electric field effects are rare in Pu materials, so $N = 6$. With these additional conditions, the expression for $N_f(E_F)$ predicts that the f-density of states at E_F in the Pu material will be at most 75% of that in the corresponding Ce compound. Besides assuming Russell–Saunders coupling, the most significant caveat in the comparison above is that $\langle V_{kf}\rangle$ is independent of the f-element. Because the 5f-wave functions of Pu are more spatially extended than the 4f-wave functions of Ce, mixing is stronger in Pu compounds, with a corresponding quadratic decrease in $N_f(E_F)$.

$PuCoGa_5$, $PuRhGa_5$, $CeCoIn_5$ and $CeRhIn_5$ form in the same $HoCoGa_5$ (1 1 5) tetragonal structure and are nominally isoelectronic [3,4,11,12]. A comparison of $PuCoGa_5$ to $CeCoIn_5$ and $PuRhGa_5$ to $CeRhIn_5$ allows a qualitative estimate of the difference in $\langle V_{kf}\rangle$, neglecting a relative minor distinction between isovalent Ga and In in these materials. Taking $N_f(E_F) \propto \gamma$, then $\langle V_{kf}\rangle_{(PuCoGa_5)}/\langle V_{kf}\rangle_{(CeCoIn_5)} \sim [(0.75)(\gamma_{CeCoIn_5})/(\gamma_{PuCoGa_5})]^{1/2} \sim 1.5$ and $\langle V_{kf}\rangle_{(PuRhGa_5)}/\langle V_{kf}\rangle_{(CeRhIn_5)} \sim [(0.75)(\gamma_{CeRhIn_5})/(\gamma_{PuRhGa_5})]^{1/2} \sim 2.6$. An approximately factor of two larger matrix element for f-mixing with conductions electrons in the Pu versus the isostructural Ce1 1 5 materials is not unreasonable and within this simple picture accounts for the smaller values of γ and m^* in the Pu1 1 5s. (This conclusion is affected only weakly by preceding assumptions about ground state degeneracy.) The corresponding hybridization $\Gamma \sim \langle V_{kf}\rangle^2$ then is ~2.3–6.8 times stronger in the Pu1 1 5 than the Ce1 1 5 compounds. This hybridization sets the width of the f-level as well as density of states at E_F and is a characteristic energy scale for spin/charge fluctuations [14]. If the energy scale of Γ becomes comparable to or greater than crystal-field splitting, evidence for crystal-field effects will be washed out, and consequently, the larger Γ in $PuCoGa_5$ and $PuRhGa_5$ provides a plausible reason why clear evidence for crystal-field effects is not seen in the Pu1 1 5s but is found in the Ce1 1 5s. Likewise, stronger hybridization in the Pu1 1 5 compounds also may be one reason why their normal state effective moment is reduced from its Hund's rule value.

3. Superconductivity

It is instructive to extend this comparison between Pu1 1 5 and Ce1 1 5 compounds to a discussion of their superconductivity. $CeRhIn_5$ is typical of Ce-heavy-fermion systems in which applied pressure induces superconductivity from an ambient-pressure antiferromagnetic state [11]. The relationship between antiferromagnetism and superconductivity in $CeRhIn_5$ is shown in the vertical plane of Fig. 1 [15]. For a range of pressures $P \leq P_1$, antiferromagnetism and superconductivity coexist, but once T_c becomes equal to T_N, evidence for a Néel state disappears. However, applying a magnetic field induces magnetic order that coexists with superconductivity for $P_2 > P > P_1$, as illustrated by open squares in the horizontal H–P plane. A linear extrapolation of the line of field-induced magnetic

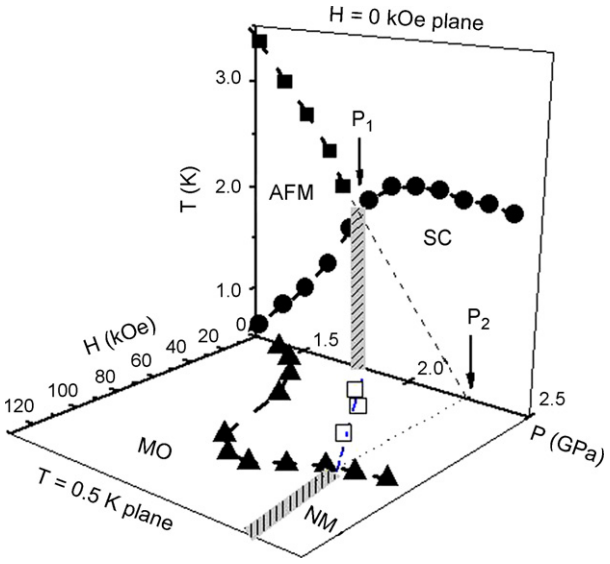

Fig. 1. Temperature–pressure–magnetic field phase diagram of $CeRhIn_5$ [15]. The relationship between antiferromagnetic order (AFM) and pressure-induced superconductivity (SC) shown in the vertical T–P plane is typical of behavior found in Ce-based heavy-fermion systems. The horizontal H–P plane shows the evolution of the upper critical magnetic field $H_{c2}(P, T = 0.5\,\mathrm{K})$, solid triangles, and field values, open squares, at which magnetic order is induced inside the superconducting state. deHass-vanAlphen measurements show that m^* diverges at P_2 [16]. In the normal state above H_{c2}, there is a transition from magnetic order (MO) to paramagnetism (NM) at P_2.

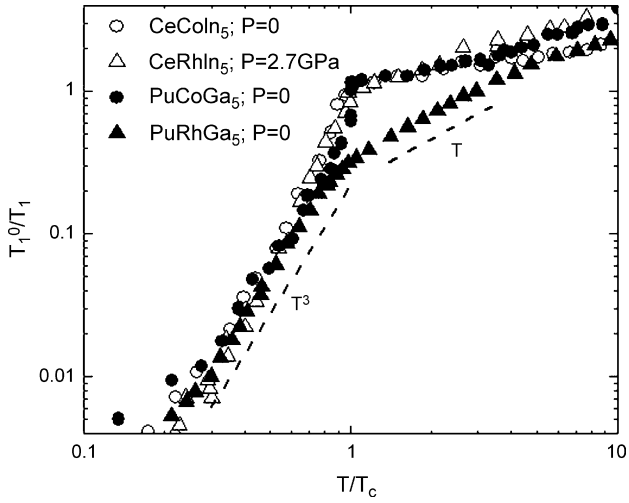

Fig. 2. Nuclear spin-relaxation rate $1/T_1$ normalized by a material-dependent constant rate $1/T_1^0$ as a function of temperature divided by the superconducting transition temperature T_c. The value of $1/T_1^0$ is taken as $1/T_1$ at T_c for $CeCoIn_5$, $CeRhIn_5$ and $PuCoGa_5$ data; whereas, this normalization constant is the value of $1/T_1$ at the onset of the possible pseudogap temperature ~25 K in $PuRhGa_5$. $CeCoIn_5$ (Ref. [19]); $CeRhIn_5$ at 2.7 GPa (Ref. [20]), $PuCoGa_5$ (Ref. [21]); $PuRhGa_5$ (Ref. [22]).

transitions intersects the upper critical field boundary ($H_{c2}(P, T)$) at P_2, where there is a magnetic to non-magnetic transition. P_2 appears to be a genuine quantum-critical point, as evidenced by deHaas–van Alphen experiments that find m^* diverging as P_2 is approached from either lower or higher pressures [16]. At P_2, dHvA frequencies increase abruptly and above P_2 correspond closely to those of isostructrural $CeCoIn_5$ [16], which is superconducting at atmospheric pressure with nearly the same T_c as $CeRhIn_5$ at P_2. Thermodynamic, transport and dHvA studies of $CeCoIn_5$ also suggest that it is close to but slightly beyond a quantum-critical point at $P = 0$ so that qualitatively it would be located in $CeRhIn_5$'s phase space somewhere above P_1 [17]. These results, together with $CeCoIn_5$'s smaller unit cell volume, imply that f-electron mixing with conduction-band electrons is stronger in $CeCoIn_5$ than in $CeRhIn_5$ at atmospheric pressure. Because both Ce1 1 5 compounds have a crystal-field doublet ground state [18], the expression for $N_f(E_F)$ also gives at atmospheric pressure $\Gamma_{CeCoIn_5} \approx 1.8\Gamma_{CeRhIn_5}$.

Evidence that superconductivity is unconventional in $CeRhIn_5$ under pressure and in $CeCoIn_5$ at atmospheric pressure comes from nuclear spin-relaxation measurements that are summarized in Fig. 2 [19,20]. Below T_c, the relaxation rate $1/T_1$ decreases approximately as T^3, which contrasts to the exponential decrease expected for a conventional s-wave superconductor but is consistent with the existence of lines of zeroes in an unconventional superconducting gap. Above T_c, $1/T_1$ increases as $T^{1/2}$ for $CeRhIn_5$ and as $T^{1/4}$ for $CeCoIn_5$. These unusual temperature dependences are predicted for relaxation dominated by spin fluctuations near an antiferromagnetic instability [23]. To the extent these data indicate that superconductivity in the Ce1 1 5s is unconventional and mediated by magnetic fluctuations, $PuCoGa_5$'s superconductivity also is unconventional and magnetic in origin. This is established from the comparison in Fig. 2 of $1/T_1$ data for $PuCoGa_5$, which also follow a T^3 dependence below T_c and a weak power-law dependence above T_c [21]. On the other hand, $1/T_1 \propto T^3$ for $PuRhGa_5$ below T_c, again the temperature expected for an unconventional superconducting gap with line nodes, but above T_c is approximately linear in temperature to two to three times T_c before it approaches the temperature dependence of $PuCoGa_5$ and the Ce1 1 5s [22]. This Korringa-like relaxation, where $1/(T_1T)$ is a constant, emerges in $CeCoIn_5$ at pressures $P > 2$ GPa where it has been tuned well away from a quantum-critical point [20]. As with $CeCoIn_5$ at high pressures, the $1/T_1 \propto T$ behavior in $PuRhGa_5$ may indicate strong f-mixing with conduction electrons and the absence of significant magnetic fluctuations above T_c, which is consistent with $\Gamma_{PuRhGa_5} \approx 1.6\Gamma_{PuCoGa_5}$ estimated from the expression for $N_f(E_F)$. However, the implied stronger hybridization in $PuRhGa_5$ compared to $PuCoGa_5$ is just opposite to the case of Ce1 1 5s in which the Co member is more hybridized than the Rh member. An alternative interpretation for the Korringa-like relaxation in $PuRhGa_5$ is that it arises from two contributions to $1/T_1$, one from magnetic fluctuations near a antiferromagnetic instability and another from the opening of pseudogap below ~25 K [24]. If a pseudogap does exist, it would reduce the intrinsic, hybridization-induced density of states at E_F and lead to an overestimate of hybridization. In this scenario, it is possible that $\Gamma_{PuRhGa_5} < \Gamma_{PuCoGa_5}$ or equivalently that $PuRhGa_5$ is even closer to a magnetic instability than $PuCoGa_5$. Presently available data prevent a distinction between these two possible interpretations; however, it may be relevant that $1/T_1 \propto T$ behavior is observed in $CeRhIn_5$ at pressures just below P_1 and is attributed to pseudogap formation [25]. Irrespective of detailed understanding of

the temperature dependence of $1/T_1$ above $PuRhGa_5$'s T_c, the $1/T_1 \propto T^3$ below T_c in $PuCoGa_5$ and $PuRhGa_5$ as well as evidence [26] for a power-law temperature dependence in specific heat below T_c in the Pu1 1 5s are consistent with an unconventional superconducting gap with line nodes.

Whether this unconventional gap arises because superconductivity is mediated by magnetic fluctuations remains an open question, just as it does for almost all superconductors that are suspected to have a magnetic origin. Moriya and Ueda, however, have shown that T_c is linearly related to a characteristic energy scale T_0, which measures the energy spread of wavevector dependent spin fluctuations, and that the same linear relationship holds for Ce- and U-based heavy-fermion superconductors as well as for the high-T_c cuprates [27]. Because these two classes of materials are leading contenders for magnetically-mediated superconductivity, this observation is highly suggestive that magnetic fluctuations play a role in producing their superconductivity. More recently, Curro et al. have found that the Ce1 1 5s and $PuCoGa_5$ follow this same linear proportionality between T_c and T_0 and, further, that T_0 for $PuCoGa_5$ is about five times larger than in the Ce1 1 5s [21]. The factor of five difference in characteristic energy scale T_0 falls squarely within the estimated range of characteristic hybridization energies $\Gamma_{Pu1\,1\,5} \sim (2.3–6.8)\Gamma_{Ce1\,1\,5}$. With Γ setting the effective bandwidth of f-electrons, it is reasonable to associate Γ with T_0, which leads to the conclusion that T_c in these compounds is influenced by the effective f-bandwidth determined by mixing f and conduction-band electrons.

4. Summary

The model of hybridization used here is strictly applicable only to an isolated ion and completely ignores lattice effects that are essential for a more realistic description of 5f-electron physics in these materials. In Ce heavy-fermion materials, such as the Ce1 1 5s, there is no doubt that the 4f-electron is localized near room temperature, but this is less clear in Pu compounds where 5f-electrons are balanced close to a localized/itinerant boundary. In the limit of strong hybridization and with the 5f-level close to E_F, 5f-electrons assume itinerant character, and in this case, fluctuations in the 5f-valence configuration will become important but also will carry with them spin fluctuations [14]. This limit raises the possibility that superconductivity in the Pu1 1 5s could be mediated by valence fluctuations, which has been suggested theoretically [28]. Though valence fluctuations cannot be ruled out in the Pu1 1 5s, this seems to be an unlikely scenario for Ce1 1 5 superconductivity. The difference between Ce1 1 5 and Pu1 1 5 compounds is primarily a difference in energy scale, which is reflected quite clearly by their roughly order of magnitude different T_cs. The simple model of hybridization between localized f-electrons and itinerant conduction-band electrons gives a framework for interpreting basic similarities and differences between Pu1 1 5 and Ce1 1 5 compounds and a plausible rationale for the correlation between T_c and characteristic spin-energy scale in these materials. Instead of providing a precise description of all relevant physics, ideas discussed here are intended ideally to motivate critical experiments and theory that will lead to a much better understanding of $PuCoGa_5$ and related materials.

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