

# Superconductivity in Heavy Fermion Materials

Shailaj Kumar Shrivastava



**Abstract:** The heavy fermion materials have small superconducting transition temperature and large specific heat corresponding to large effective masses. In these materials the superconductivity co-exists with ferromagnetic or antiferromagnetic order at low temperature. It shows phenomena like magnetic instabilities, quantum critical points (QCP), non-fermi liquid (NFL) and unconventional superconductivity. By comparing the superconducting properties, phase diagram and effect of magnetic field and pressure of heavy fermions based on uranium, cerium, and praseodymium, the basic physics behind pairing mechanism can be imagined. This paper aims to present remarkable findings in superconductivity of various heavy fermion materials.

**Keywords:** Cerium, heavy fermion superconductors, Praseodymium, Unconventional superconductivity, Uranium.

## I. INTRODUCTION

The heavy fermion materials have rare earth (usually Ce) or actinide element (usually U) in which f electron shell are not fully filled. The interaction of the localized magnetic moments with the momenta and spin of outer shell electrons of the other constituent metal atoms are very strong [1]. The critical temperature of these materials is less than 2.0K. They have magnetic field penetration depth  $\lambda$  in excess of several thousand Å and the values of coherence length  $\xi$  are 100-200Å. They are strongly correlated electron systems that exhibit very large effective masses below certain temperature. It was found that the cooper-pairing in these materials arises from the magnetic interactions of the electron spins, rather than by lattice vibrations. In uranium-based heavy fermions containing a periodic array of uranium ions, the superconductivity co-exists with ferromagnetic or antiferromagnetic order. At quantum critical point (QCP) the magnetic ordering of atoms is destroyed by a small change in pressure. The quantum critical point provides an environment for superconductivity. Near quantum critical points, phase fluctuation with the material expands in both space and time, and these fluctuations help in cooper pair formation. The large value of specific heat ( $C_p/T$ ) near transition temperature ( $T_c$ ) indicates that quasi-particles of large masses play an important role in the superconducting pairing.

## II. RESEARCH METODOLOGY

$\approx 30$ K. Superconductivity in  $UGe_2$  was observed on the border of ferromagnetism [4]. Fig. 1 shows variation of P as a function of T for  $UGe_2$  in which the superconducting dome is completely inside the ferromagnetic phase. Here superconductivity coexists with strong ferromagnetism.

Revised Manuscript Received on February 05, 2020.

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## A. Uranium Based Superconductors

The uranium based superconducting materials exhibit the coexistence of superconductors with a magnetic long range order. In  $UPt_3$ ,  $UBe_{13}$ ,  $URu_2Si_2$ ,  $UPd_2Al_3$ ,  $UNi_2Al_3$ , and  $U_2PtC_2$ , a transition from to an antiferromagnetic state to a superconducting state takes place. In  $UGe_2$ ,  $URhGe$  and  $UCoGe$ , the superconductivity coexists with the ferromagnetism, resulting in the spin-triplet state of Cooper pairs [2]. In  $URhGe$  and  $UCoGe$  following changes occurs when magnetic field is applied

- $T_{curie}$  is overpowered.
- Ferromagnetic fluctuations are enhanced.
- Superconductivity behavior is enhanced.

In  $UPt_3$ , the anisotropic order parameter has unconventional symmetry. Superconductivity in hexagonal  $UPt_3$  has  $T_c \approx 0.53$ K and below  $T_c$  it exhibit more than one superconducting phase. Below Neel temperature ( $T_N$ ) = 5K,  $UPt_3$  is antiferromagnetic with size of magnetic moment ( $\mu = 0.02\mu_B$ ). The two superconducting transitions merge into one and antiferromagnetism is destroyed at the same pressure.  $UPt_3$  exhibit spin triplet pairing state supporting spin fluctuation mechanism.

$UBe_{13}$  is a non-fermi liquid (NFL) superconductor with a cubic crystal structure having superconducting transition temperature ( $T_c$ )  $\approx 0.97$ K. The large specific heat ( $1100$  mJ/mol-K<sup>2</sup>) and corresponding high effective mass ( $m^*/m \approx 260$ ) shows that the quasi-particles of large masses are involved in superconductivity. The superconducting symmetry has nodal superconducting gap structure due to its unconventional nature.

The body centered tetragonal crystal  $URu_2Si_2$  has transition temperature ( $T_c$ )  $\approx 1.5$ K.  $URu_2Si_2$  [3] is a multiband superconductor having semi-metallic compensated electronic structure. The hidden order transition takes place at 17.5K. The order parameter has even parity (spin singlet pairing).

$URhGe$  has  $T_{curie} \approx 9.5$ K and ferromagnetism appears at ambient pressure followed by superconductivity near 0.3K in fields lower than 2T. The involvement of the same 5f electrons in these materials shows that the ferromagnetic and superconducting behavior co-exists on the microscopic scale.  $UGe_2$  is an orthorhombic crystal having critical temperature  $T_c \approx 0.8$ K at 12kbar. When pressure is applied the ferromagnetism is overpowered at  $T_{curie}$



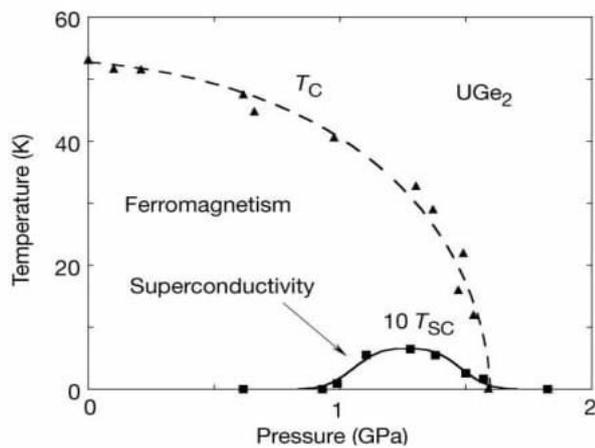


Fig. 1. P-T diagram of UGe<sub>2</sub> [5]

UTe<sub>2</sub> has superconducting transition temperature  $T_c \approx 1.6$  K at ambient pressure and zero magnetic fields [6]. The upper critical field  $H_{c2}(0) \approx 40$  tesla is very large. UTe<sub>2</sub> has body centered orthorhombic structure with lattice constants  $a=4.165\text{\AA}$ ,  $b=6.139\text{\AA}$  and  $c=13.979\text{\AA}$ . Transition temperature ( $T_c$ ), crystal structure and magnetism of some uranium based heavy fermion superconductors are given in table I.

Table I: Transition temperature ( $T_c$ ), crystal structure and magnetism of some uranium based heavy fermion superconductors

Material	$T_c$ K	Crystal Structure	Magnetism
UPt <sub>3</sub>	0.53	Hexagonal	Paramagnetic
UBe <sub>13</sub>	0.93	Cubic	Paramagnetic
URu <sub>2</sub> Si <sub>2</sub>	1.53	bc tetragonal	Antiferromagnetic ( $T_N=17.5$ K)
URhGe	0.25	orthorhombic	Ferromagnetic ( $T_{\text{curie}}=9.5$ K)
UPd <sub>2</sub> Al <sub>3</sub>	2.0	Hexagonal	Antiferromagnetic ( $T_N=14.5$ K)
UNi <sub>2</sub> Al <sub>3</sub>	1.6	Hexagonal	Antiferromagnetic ( $T_N=4.6$ K)
UGe <sub>2</sub>	0.8	orthorhombic	Ferromagnetic ( $T_{\text{curie}}=30$ K)
UTe <sub>2</sub>	1.6	orthorhombic	Nearly ferromagnetic

UPd<sub>2</sub>Al<sub>3</sub> has transition temperature  $T_c \approx 2.0$  K and having Neel temperature  $T_N \approx 14.5$  K. When pressure is increased up to 6.5GPa the Neel temperature  $T_N$  decreases while the onset of superconductivity remains unchanged but above 6.5GPa the critical temperature starts decreasing. Here pairing is mediated by spin fluctuation.

Hexagonal UNi<sub>2</sub>Al<sub>3</sub> has transition temperature  $T_c \approx 1.6$  K. At 4.5K, the co-existence of a small magnetic moment with

disproportionate spin density wave recommend spin triplet state.

Theoretically,  $H_{c1} \propto 1/\lambda^2$ , which may leads to anomalously small value of  $H_{c1}$  and  $H_{c2} \propto 1/\xi^2$  which may lead to large value of  $H_{c2}$  in heavy fermion superconductors. Superconducting parameters of uranium based superconductors are shown in table II.

Table II: Superconducting parameters of uranium based superconductors (Values are taken from the references quoted in the text)

Materials	$\lambda$ (Å)	$\xi$ (Å)	$H_{c1}(0)$ mT	$H_{c2}(0)$ T
UPt <sub>3</sub>	~7000	100-120	3.0	2.8
UBe <sub>13</sub>	~8000	100	4.6	10.1
UNi <sub>2</sub> Al <sub>3</sub>	~3000	240	1.5	1.5
UPd <sub>2</sub> Al <sub>3</sub>	~5000	85	1.0	3.6
URu <sub>2</sub> Si <sub>2</sub>	~15000	100-150	1.4	3.0

B. Cerium Based Superconductors

In these materials, there is interplay between two competing mechanisms. Due to strong RKKY interaction in CeCu<sub>6</sub> and CeRu<sub>2</sub>Si<sub>2</sub>, it shows collapse of long range magnetism [7]. When pressure is applied to CeIn<sub>3</sub>, CeCu<sub>2</sub>Si<sub>2</sub>, CeCu<sub>2</sub>Ge<sub>2</sub>, CeRh<sub>2</sub>Si<sub>2</sub> and CePd<sub>2</sub>Si<sub>2</sub>, the Neel temperature  $T_N$  decreases, and a quantum critical point is reached which makes the way for heavy fermion superconductivity to emerge. At quantum critical point a small change in pressure destroy the magnetic ordering of atoms.

In CeCu<sub>2</sub>Si<sub>2</sub> magnetism and superconductivity do not co-exist and has non-Fermi Liquid (NFL) behavior with critical temperature ( $T_c$ )  $\approx 0.7$ K [4]. The superconducting cooper pairs are particle having large effective masses.

The tetragonal crystal CeRhIn<sub>5</sub> has the layers of CeIn<sub>3</sub> separated by layers of RhIn<sub>2</sub>. At ambient pressure CeRhIn<sub>5</sub> show antiferromagnetism with a Neel temperature  $T_N \approx 3.8$  K. At around 2.3 – 2.5 GPa this antiferromagnetic state is replaced by a superconducting state having transition temperature ( $T_c$ )  $\approx 2.6$  K. Fig.2 show the T-P phase diagram of CeRhIn<sub>5</sub> in which the antiferromagnetic and superconducting phase co-exists at 2.4GPa.

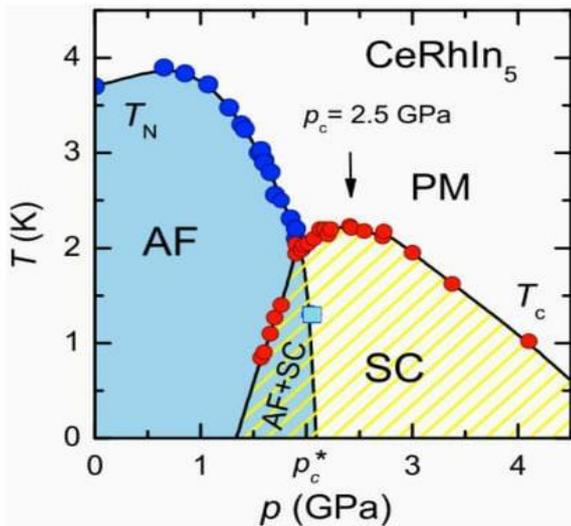


Fig.2. T-P phase diagram of CeRhIn<sub>5</sub> [8].

The tetragonal CeCoIn<sub>5</sub> has a quasi-2D structure with lattice constants  $a=b=4.612\text{\AA}$  and  $c=7.551\text{\AA}$ . CeCoIn<sub>5</sub> has the critical temperature  $T_c = 2.3\text{K}$ . A specific heat jump of  $290\text{mJ/mol}\cdot\text{K}^2$  at critical temperature ( $T_c$ ) has been observed at ambient condition. CeCoIn<sub>5</sub> has the layers of CeIn<sub>3</sub> separated by layers of CoIn<sub>2</sub>. The superconductivity in CeCoIn<sub>5</sub> arises from magnetic interactions and has line nodes in the order parameter. CeCoIn<sub>5</sub> has an unusual pairing symmetry and pairs up in a d-wave state. Under pressure, the fermi liquid behavior is broken in the non-fermi liquid state and superconductivity is realized in CeCoIn<sub>5</sub>.

Tetragonal CeRh<sub>2</sub>Si<sub>2</sub> show antiferromagnetism at  $T_N \approx 36\text{K}$ . Below  $T_N = 25\text{K}$ , the antiferromagnetism is replaced by superconducting state at critical pressure  $\approx 9\text{kbar}$ , superconductivity appears at critical temperature ( $T_c$ )  $\approx 0.4\text{K}$ . Cerium based heavy fermion superconductors with  $T_c$  and crystal structure are given in table III.

Table III: show cerium based heavy fermion superconductors with  $T_c$  and crystal structure.

Materials	$T_c(\text{K})$	Crystal Structure
CeCu <sub>2</sub> Si <sub>2</sub>	0.6	bc tetragonal
CeRhIn <sub>5</sub>	2.6	tetragonal
CeCoIn <sub>5</sub>	2.3	tetragonal
CeIn <sub>3</sub>	0.19	Cubic
CePd <sub>2</sub> Si <sub>2</sub>	0.43	bc tetragonal
CeRh <sub>2</sub> Si <sub>2</sub>	0.3	bc tetragonal
CePt <sub>3</sub> Si	0.75	tetragonal

At ambient pressure, CeIn<sub>3</sub> exhibit antiferromagnetism with temperature  $T_N = 10.2\text{K}$ . When pressure is applied at around  $0.19\text{K}$ ,  $T_N$  vanishes at a critical pressure of about  $26\text{kbar}$  and below this temperature antiferromagnetism is replaced by a superconducting state. The Pressure-Temperature phase diagram of CePd<sub>2</sub>Si<sub>2</sub> and CeIn<sub>3</sub> suggests that the superconductivity is magnetically mediated.

Tetragonal CePt<sub>3</sub>Si [9] undergoes a magnetic transition at  $T_N=2.2\text{K}$  and a superconductivity transition at  $T_c \approx 0.75\text{K}$  at ambient pressure. This material lacks a center of inversion symmetry which shows that it may not be favorable for superconductivity. Higher value of  $H_{c2}(0) \approx 5\text{T}$  indicates the possibility of spin triplet pairing state.

### C. Praseodymium Based Superconductors

PrOs<sub>4</sub>Sb<sub>12</sub> is filled skutterudites heavy fermion compound having superconducting critical temperature  $T_c \approx 1.85\text{K}$  with broken time reversal symmetry [10]. It consists of more than one superconducting phases. The field induced antiferroquadrupolar order phase just above the upper critical field indicates that electric quadrupole fluctuations play an important role in the superconducting mechanism.

PrV<sub>2</sub>Al<sub>20</sub> have the nonmagnetic cubic  $\Gamma_3$  doublet ground state. It exhibits superconductivity at transition temperature  $T_c \approx 50\text{mK}$  under ambient pressure. The large  $\gamma \approx 300\text{mJmol}^{-1}\text{K}^{-2}$  and corresponding large  $m^*/m \approx 140$  indicates the role of orbital fluctuation of the f electrons at ambient pressure. The gapless mode associated with quadrupolar ordering is indicated in cubic temperature dependence of specific heat capacity.

Cubic PrTi<sub>2</sub>Al<sub>20</sub> exhibits quadrupolar ordered state and has strong interaction between 4f and outer shell electrons. It has transition temperature  $T_c = 200\text{mK}$  in the non magnetic ferro-quadrupolar state. Praseodymium based heavy fermion superconductors with  $T_c$  and crystal structure is given in table IV.

Table IV: Superconducting transition temperature ( $T_c$ ) and crystal structure of praseodymium based heavy fermion superconductors.

Materials	$T_c(\text{K})$	Crystal Structure
PrOs <sub>4</sub> Sb <sub>12</sub>	1.85	Skutterudite
PrV <sub>2</sub> Al <sub>20</sub>	0.05	Cubic
PrTi <sub>2</sub> Al <sub>20</sub>	0.2	Cubic

### III. RESULT ANALYSIS

Heavy fermion superconductors are highly anisotropic and have close relationship with the possible pairing mechanism. Parity pairing state of heavy fermion materials are shown in Table V.

Table V: Parity pairing state of heavy fermion materials

Materials	Parity pairing state
CeCoIn <sub>5</sub>	Even
CeCu <sub>2</sub> Si <sub>2</sub>	Even
UPd <sub>2</sub> Al <sub>3</sub>	Even
URu <sub>2</sub> Si <sub>2</sub>	Even
UPt <sub>3</sub>	Odd
UNi <sub>2</sub> Al <sub>3</sub>	Odd

In CeCu<sub>2</sub>Si<sub>2</sub>, CeIn<sub>5</sub> [11], CeCoIn<sub>5</sub> and UPd<sub>2</sub>Al<sub>3</sub> the order parameter is of even parity and the NMR Knight Shift decreases below  $T_c$ . In UPt<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub>, odd parity pairing state is observed with no reduction in the NMR Knight Shift. Thus, NMR Knight Shift result classifies the heavy fermion superconductors into either even or odd parity pairing. The non-centrosymmetric crystals CePt<sub>3</sub>Si classify superconductivity with mixing of even and odd parity. The spin fluctuation model predicts that the ferromagnetic interactions should lead to odd parity pairing state while the antiferromagnetic spin fluctuations should lead to even parity pairing state.

As  $\gamma \propto m^*$ , cooper pair are particles consisting of large mass. Table VI show the Sommerfeld coefficient of specific heat and effective mass of uranium based superconductors.

**Table VI: Sommerfeld coefficient ( $\gamma$ ) and effective mass of uranium based heavy fermion superconductors.**

Materials	$\gamma$ [m Jmol <sup>-1</sup> K <sup>-2</sup> ]	$m^*/m$
URu <sub>2</sub> Si <sub>2</sub>	65	140
UPd <sub>2</sub> Al <sub>3</sub>	145-210	66
UNi <sub>2</sub> Al <sub>3</sub>	120	48
UPt <sub>3</sub>	450	180
UBe <sub>13</sub>	1100	260

In CeIn<sub>3</sub> and CePd<sub>2</sub>Si<sub>2</sub> antiferromagnetism is replaced by superconductivity at quantum critical point under applied pressure. In UPt<sub>3</sub>, URu<sub>2</sub>Si<sub>2</sub>, UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub> magnetism and superconductivity co-exist on microscopic scale. In UGe<sub>2</sub>, URhGe superconductivity appears inside a ferromagnetic phase near quantum critical point. The electron-electron interactions that lead to the Kondo effect dominating the RKKY interaction lead to a lot of quantum critical points and magnetic phase transitions. The presence of a superconducting dome near antiferromagnetic quantum critical point indicates that the quantum critical point (QCP) has its importance in pairing mechanism.

The presence of two superconducting transitions in PrOs<sub>4</sub>Sb<sub>12</sub> suggests for a homogeneous co-existence of two superconducting order parameters. Here quantum quadrupole fluctuations and the gap structure are vital for understanding the pairing mechanism of superconductors.

## IV. CONCLUSION

The complicated crystal structures, unusual magnetic and superconducting transition, co-existence of superconductivity and antiferromagnetism, multiple superconducting phases, appearance of superconductivity at quantum critical point and the gap structure indicate that pairing mechanism is still a difficult problem in heavy fermion superconductors.

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