INTRODUCTION TO UNCONVENTIONAL SUPERCONDUCTIVITY

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Dedicated to Professor Boran Leontić on the occasion of his 70th birthday

Received 2 December 1999; Accepted 3 April 2000

The dawn of the 21st century may be characterized as the era of unconventional superconductivity. First we shall classify unconventional superconductors so far identified. Then we survey some of remarkable properties of f-wave superconductivity in UPt$_3$. We suggest also that the superconductivity in URu$_2$Si$_2$ is most likely of f-wave.

PACS numbers: 74.70.-b UDC 538.945

Keywords: new superconductors, f-wave superconductivity, UPt$_3$, URu$_2$Si$_2$

1. Introduction

Since the discovery of the hole-doped high $T_c$ cuprate superconductors by Bednorz and Müller [1], the most heroic moment in high $T_c$ cuprates is the identification of d-wave symmetry in the superconductivity [2,3]. Within this legacy, the unconventional superconductivity will take central stage in the world of superconductivity [4,5].

Of course the notion of unconventional superconductivity is around us [6,7] even before the discovery of superfluid $^3$He in 1972 [8,9]. Also the unconventional superconductivity has been suggested almost immediately after the discovery of heavy fermion superconductors [10,11] and organic superconductors [12,13]. But all these changed more dramatically after the discovery of d-wave superconductivity in the hole-doped high $T_c$ cuprates.

First of all, we can now rely on the mean-field theory as embodied in the BCS theory of superconductivity [14] and the Fermi liquid theory of Landau [15]. Of course Landau considered the fermions with spherical Fermi surface, while the electrons we are considering have the Fermi surface quite different from a sphere, in particular in hole-doped high $T_c$ cuprates. Therefore, obvious modification is necessary. This often called in the literature “non-Fermi liquid behaviour”. But we
believe it is sheer exaggeration. More proper wording should be “unconventional Fermi liquid”.

As to the model, the Coulomb dominance in contrast to the electron-phonon dominance is perhaps the most crucial. Of course the electron-phonon interaction is the key element for classic s-wave superconductors [7]. But there is ample evidence that the Coulomb dominance and the related spin fluctuation (antiparamagnon) exchange are crucial for unconventional superconductors. For example, the antiparamagnon model for hole-doped high $T_c$ cuprates has predicted correctly the d-wave superconductivity [16–18].

Also working on d-wave superconductivity within the framework of BCS theory, we are continuously surprised by the fact that the weak-coupling theory of d-wave superconductivity [19] works so well.

More recently, we find that a similar approach is very useful for recently discovered p-wave superconductivity in Sr$_2$RuO$_4$ [20].

In the following, we shall first classify some of the identified unconventional superconductors. Then we shall review our recent work on f-wave superconductivity in UPt$_3$ [21].

2. Classification

Here we shall present unconventional superconductors with known symmetry.

a) Planar d-wave superconductors are characterized by

$$\Delta(\hat{k}) \propto \cos(2\phi) \text{ or } \Delta(\hat{k}) \propto \sin(2\phi),$$

where $\phi$ is the angle $\vec{k}$ the planar quasi-particle wave vector makes from the a-axis. Since around 1993, overwhelming evidence indicates superconductivity in the hole-dopped cuprates is $d_{x^2-y^2}$ wave, though most of experiments are concentrated on YBCO and BSCCO (Bi$_2$2212). In this context, it is very puzzling why the superconductivity in the electron-doped high $T_c$ cuprates is of s-wave [22–24]. There are perhaps three distinct ways to test the d-wave superconductivity. The first one is to look for the sign of the nodal structure in $\Delta(\hat{k})$. As is seen from Fig. 1, the quasi-particle along the diagonal directions are gapless. This can be seen by ARPES [25,26], the $T$-linear dependence of the magnetic penetration depth [27], the $T^2$ dependence of the electronic specific heat [28,29], the Raman scattering [30] and the thermal conductivity tensor in a planar magnetic field [31–33].

Second, the phase-sensitive experiment [34] which tests the sign changes in the order parameter is performed either by the Josephson junction between YBCO and s-wave superconductors like Pb [35] or Nb [36], or the detection of a half-flux in the tri-crystal geometry [[37–39]. The latter method appears to be not only elegant but also versatile. In this way, Tsuei, Kirtley et al. identified d-wave superconductivity in YBCO, Bi2212, GdBBCO and Tl2201.
Third, the Zn-substitution of Cu in the CuO$_2$ plane gives extremely useful diagnostic means. A small amount of impurities not only suppresses the superconducting transition temperature, but also introduces a lot of low-energy excitations [40,41].

The Zn impurity is treated as the scatterer in the unitarity limit [42]. The change in the residual density of states [43], the superfluid density [44] and the thermal conductivity [45] can be tested experimentally. From these analyses, we have learned that the weak-coupling theory works extremely well. For example, in d-wave superconductors we have [19] $\Delta_0/T_c = 2.14$ where $\Delta_0$ is the order parameter at $T = 0$ K. This ratio may be contrasted with the well-known BCS relation for s-wave superconductors $\Delta_0/T_c = 1.76$.

So for example for LSCO, $\Delta_0/T_c = 2.14$ appears to be obeyed within the 5% error. For the optimally doped YBCO, we deduce [19] $\Delta_0/T_c = 2.77$. However in Bi2212, this ratio becomes 5 – 6. Both YBCO and Bi2212 have almost the same superconducting transition temperature $T_c \approx 82$ K. On the other hand, $\Delta_0$ for Bi2212 appears to be at least twice of the one in YBCO. So there is a qualitative difference between YBCO and Bi2212. This will be one of puzzles the strong coupling theory has to address.

Also in the thermal conductivity the universality proposed by Patrick Lee is one of the central themes [46,47].

It is known that Ni as impurity is a weaker scatterer. Though there is still no systematic study, it is very tempting to assume that Ni is the scatterer in the Born limit [48]. In this limit, for example, the residual density of states remains exponentially small until $\Gamma/\Gamma_c \approx 0.5$. This feature is consistent with the density of states observed from Ni-substituted Bi2212 [49].

Recently a number of studies on superconductivity in $\kappa$-(ET)$_2$ salts indicate $d_{xy}$-superconductivity. First of all, $\kappa$-(ET)$_2$ salts have the layered structure similar to the high $T_c$ cuprates [13]. Further, the superconductivity resides in the vicinity of the antiferromagnetic state. We believe that this is a clear sign of the Coulomb dominance.

Further, some microscopic models predict $d_{xy}$-wave superconductivity [50,51]. The absence of the Hebel-Slichter peak and the $T^3$ dependence of the low-temperature $T_1^{-1}$ indicate the nodal structure in $\Delta(\hat{k})$ [52]. Similarly, the $T^2$-dependence
of specific heat [53] as well as the $T$-linear thermal conductivity [54] support this idea. Until recently, the temperature dependence of the magnetic penetration depth, which should be most crucial, has been rather controversial [13]. However, a recent susceptibility data shows clearly the $T$-linear dependence of the in-plane penetration depth and $T^2$-dependence of the out of plane penetration depth [55]. Also, the latter behaviour implies that the out of plane transport is different from the one expected from the usual tight-binding model [55]. Indeed, the similar $T^2$-dependence is observed also in high $T_c$ cuprates YBCO [56] and Tl2201 [57]. Actually, this behaviour is consistent with the absence of the Drude tail in the out-of-plane optical conductivity in these systems [58,59].

In spite of all these facts, we don’t know yet the nodal direction in $\Delta(\hat{k})$ of $\kappa$-$(ET)_2$ salts. A recent experiment [60] suggests the nodal directions parallel to the b- and the c-axis. Though this result is very attractive, we are not convinced with their theoretical interpretation. Clearly more work is desirable on superconductivity in the $\kappa$-$(ET)_2$ salts and related organic superconductors.

a') $A_{1g}$ or $Y_{20}$ state

Both the anisotropy of the upper critical field [61] and the c-axis tunnelling data [62] from UPd$_2$Al$_3$ are consistent with the d-wave superconductor. Clearly, further work on this system is highly desirable.

b) p-wave superconductivity

$$\Delta(\hat{k}) = \Delta d(\hat{k}_1 \pm i\hat{k}_2) = \Delta d e^{\pm i\phi}$$

p-wave superconductivity is the simplest triplet superconductor. Also the one in Sr$_2$RuO$_4$ [20] appears to be described by the above order parameters [63]. $^{17}$O-Knight shift measurement tells that the triplet pair is involved [64]. Also the spontaneous spin polarization observed by muon spin rotation supports the triplet pairing [65]. Further, the extreme sensitivity of the superconducting transition temperature to disorder implies the unconventional superconductivity [66].

Although the energy gap $\Delta$ is independent of $\hat{k}$, we find that impurity scattering introduces low-energy excitations which are perhaps accessible to both thermodynamic and transport measurement [67]. Also, the upper critical field in a magnetic field $\vec{H} \parallel \hat{c}$ is studied theoretically [68]. Recently, the upper critical fields in Sr$_2$RuO$_4$ crystals have been observed [69]. The theory describes the observed upper critical field except for the purest sample with $T_c \geq 1.4$ K [68–70].

Further, p-wave superconductivity is of great interest, since it possesses the collective modes and topological defects as in superfluid $^3$He, which should be accessible experimentally [71–73]. More recently, both the specific heat measurement and NMR disclosed the presence of the nodal structure in $\Delta(\hat{k})$ in the purest crystal, which is inconsistent with the model we have so far described [74].

It is well known, there are three electron bands in Sr$_2$RuO$_4$, $\alpha$, $\beta$ and $\gamma$ [75]. Earlier, it has been assumed that the superconductivity resides mostly in the $\gamma$ band. Then the new experiment shows 1) the electrons in both $\alpha$ and $\beta$ bands are superconducting and 2) though most likely they belong to the p-wave, $\Delta(\hat{k})$
in these bands has the nodal structure. This is a rather exciting possibility and it warrants further study.

Also, there is indication that the superconductivity in Bechgaard salt, (TMTSF)$_2$X with X = ClO$_4$. PF$_6$ etc. is of p-wave [5]. First of all, the upper critical field of (TMTSF)$_2$ClO$_4$ and (TMTSF)$_2$PF$_6$ under pressure for $\vec{B} \parallel \vec{a}$ and $\vec{B} \parallel \vec{b}'$ exceeds by far the Pauli limiting field $H_p = \Delta_0/(\sqrt{2}\mu_B) \simeq 2$ T [76,77], where $\mu_B$ is the Bohr magneton. Since these samples are extremely pure, the only escape from the Pauli limiting is the triplet pairing. Secondly, in the absence of the magnetic field, the full energy gap is observed by tunnelling spectroscopy [78] and more recently by thermal conductivity [79].

Since the superconductivity in Bechgaard salts is most likely realized within the a-b plane, it is very likely that exactly the same order parameter as Sr$_2$RuO$_4$ with $\hat{d} \parallel c^*$ describes the superconductivity in Bechgaard salts. Then the spin susceptibility measured from the Knight shift for both $\vec{B} \parallel \vec{b}'$ and $\vec{B} \parallel \vec{a}$ should be constant across the superconducting transition temperature $T_c$. Indeed, very recently $^{77}$Se Knight shift in (TMTSF)$_2$PF$_6$ under pressure and for $\vec{B} \parallel \vec{b}'$ is reported, which exhibits no change at $T = T_c$ [80]. We believe it is a rather definitive signature for p-wave superconductivity.

We have proposed that the thermal conductivity tensor in a planar magnetic field will provide another test of p-wave superconductivity [70,81].

c) f-wave superconductivity

$$\Delta(\hat{k}) = \frac{3\sqrt{3}}{2} \Delta \hat{d}\hat{k}^2(\hat{k}_1 \pm i\hat{k}_2)^2$$

At this moment, the only well established case for f-wave superconductor (or $E_{2u}$) is UPt$_3$. However, we believe some of other heavy-fermion superconductors will be of f-wave. In the following section, we describe some of salient properties of f-wave superconductors.

3. f-wave superconductivity

After a long controversy, the f-wave superconductivity (i.e. $E_{2u}$-state) in UPt$_3$ has been established in 1996 [11]. First of all, the thermal conductivities in the superconducting state of UPt$_3$ with the heat current parallel to the c-axis and in the basal plane are shown to decrease linearly with $T$ at low temperature [82]. This behaviour is inconsistent with d-wave superconductor (or $E_{1g}$) but consistent with f-wave superconductor [83,84]. Second, $^{195}$Pt Knight-shift measurement found the spin triplet pairing in UPt$_3$ [85]. In the second measurement, it was discovered that among three phases A, B and C, only the B phase is non-unitary [85]. Therefore, these two sets of experiment are fully consistent with the f-wave superconductivity in UPt$_3$. However, very little has been done theoretically on f-wave superconductivity except for the thermal conductivity [83,84]. Very recently, we have shown that the f-wave superconductivity describes the observed upper critical field (of the C phase) very well [21,86,87].
Here we shall report the effect of impurity scattering in f-wave superconductor [88]. Following the standard method, the effect of impurity scattering is incorporated by replacing $\omega$ in the quasi-particle Green function by the renormalized one

$$G^{-1}(\omega, \vec{p}) = \tilde{\omega} - \xi \rho_3 - \Delta' \rho_1 k_3 (k_1 \pm ik_2 \rho_3)^2 \sigma_1,$$

where $\rho_i$ are the Pauli matrices in the Nambu space, $\Delta' = \frac{3\sqrt{3}}{2}\Delta$, and

$$\tilde{\omega} = \omega + i\Gamma \left( \sqrt{\omega^2 - \Delta^2 f^2} \right)^{-1},$$

where $f = \frac{\sqrt{3}}{2} \sin \theta \cos^2 \theta$ and $\Gamma = n_i (\pi N_0)^{-1}$ is the scattering rate. $\langle \cdots \rangle$ means the average over the Fermi surface.

Solving the gap equation

$$\lambda^{-1} = 2\pi T \frac{1}{<|f|^2>} \sum_n \left( \frac{|f|^2}{\sqrt{\omega^2_n + \Delta^2 |f|^2}} \right),$$

we find a) for $\Delta \to 0$

$$-\ln \left( \frac{T_c}{T_{c0}} \right) = \psi \left( \frac{1}{2} \right) + \frac{\Gamma}{2\pi \Gamma_c} - \psi \left( \frac{1}{2} \right),$$

the Abrikosov-Gor’kov-relation for $T_c$ [89], and b) for $T \to 0$, we find $\Delta_0/\Delta_{00}$ where $\Delta_{00}$ is the order parameter at $T = 0$ and in the pure system.

Also, the residual density of states is given by

$$\frac{N(0)}{N_0} = \frac{C_0}{\sqrt{C_0^2 + f^2}} = \frac{\Gamma}{\Delta C_0},$$

where $C_0$ is determined from

$$C_0^2 = \frac{\Gamma}{\Delta} \left( \frac{1}{\sqrt{C_0^2 + f^2}} \right)^{-1}.$$

In Fig. 2 we show $T_c/T_{c0}$, $\Delta_0/\Delta_{00}$ and $N(0)/N_0$ as functions of $\Gamma/\Gamma_c$, where $\Gamma_c = \frac{\pi}{2} T_{c0}$. This figure is remarkably similar to the one we had not only for d-wave superconductors [42] but also for p-wave superconductors [67]. In the presence of impurities, the quasi-particle density of states is given by

$$\frac{N(E)}{N_0} = \text{Re} \left( \frac{u}{\sqrt{u^2 - f^2}} \right),$$

where $u = \tilde{\omega}/\sqrt{\tilde{\omega}^2 - \Delta^2 f^2}$.
where \( u = \frac{\omega}{\Delta} \). In Fig. 3a and b, we compare the quasi-particle density of states for f-wave and d-wave superconductors for a few values of \( \Gamma/\Delta \).

![Graph showing \( \Gamma/\Gamma_c \) versus \( \Delta/\Delta_0 \) and \( N(0)/N_0 \) versus \( T_c/T_{c0} \).]

**Fig. 2.** \( T/T_{c0}, \Delta(\Gamma,0)/\Delta_{00} \) and \( N(0)/N_0 \) versus \( \Gamma/\Gamma_c \).

![Graph showing \( \Delta/\Delta_0 \) versus \( E/\Delta \) for different values of \( \Gamma/\Delta \).]

**Fig. 3.** The quasi-particle density states \( N(E)/N_0 \) versus \( E/\Delta \) for several \( \Gamma/\Delta \): a) for f-wave, b) for d-wave superconductor.

Again, they are remarkably similar to each other except perhaps for \( \Gamma/\Delta > 1 \). It appears that f-wave superconductor is a little more affected by impurities. Of course the quasi-particle density of states for p-wave superconductor is quite different [67].

Another interesting theme is isotropy. If you normalize away the anisotropy in the Fermi velocity, both \( \rho_s(T)/\rho_s(0) \) and \( \kappa_s(T)/\kappa_s(0) \) are completely isotropic, which is somewhat surprising since \( \Delta(\vec{k}) \) is anisotropic. In Figs. 4 and 5, we show \( \rho_s(T)/\rho_s(0) \) and \( \kappa_s(T)/\kappa_s(0) \) for a few impurity concentrations.
Fig. 4. $\rho_s(T)/\rho_s(0)$ versus $T/T_{c0}$ for several values of $g(=\Gamma/\Gamma_c)$.

Fig. 5 (right). $\kappa_s(T)/\kappa_n(T)$ versus $T/T_{c0}$ for several values of $g$. Here $\kappa_n(T) = \pi^2 n/(3m\Gamma)T$, and $n$ is the electron density.

Fig. 6. $\kappa/\kappa_0 = \lim_{T \to 0} \kappa_s(T)/T \kappa_0$ versus $\Gamma/\Gamma_c$. Here $\kappa_0 = \lim_{\Gamma \to 0} \kappa_s(T)/T$, $\kappa/\kappa_0 > 1$ implies the deviation for the universality.

The universality is an important question in the thermal conductivity [42, 46]. The deviation from the universality is seen from $\kappa/\kappa_0$ shown in Fig. 6, where

$$\frac{\kappa}{\kappa_0} = \frac{\sqrt{3}\Delta_{00}}{\Delta(1,0)} \left\langle \frac{C_0^2}{(C_0^2 + f^2)^{3/2}} \right\rangle. \quad (8)$$

Here $\kappa$ is the $T$ linear coefficient of the thermal conductivity. This coefficient increases with $\Gamma/\Gamma_c$ as in d-wave superconductors [42]. Such a deviation from the
universality is verified quantitatively in YBCO [45]. Indeed, a clear deviation from the universality is reported for UPt$_3$ irradiated by electrons [90].

The further study of f-wave superconductor is of great interest. A causal comparison of the specific heat measured for URu$_2$Si$_2$ indicates that it is very close to the one for f-wave. Also, a recent $^{29}$Si Knight shift in URu$_2$Si$_2$ exhibits no change in the spin susceptibility at $T = T_c$, which indicates again the triplet pairing [91].

4. Summary

We have seen that most of the novel superconductors are unconventional (i.e. non-s-wave). In addition to the well established d-wave superconductors in hole-doped cuprates, there are p-wave superconductors and f-wave superconductors. Therefore, it is extremely important to identify their symmetry and clarify their individual nature. At this moment, we are not sure what new things these new systems will bring us. For example, the nature of vortex state is still very poorly understood, in spite of the fact these new superconductors are all type II superconductors. For us the exploration in this new world of unconventional superconductivity will bring new challenge, surprise and excitement. We are very happy to dedicate our paper to Professor Boran Leontić for the occasion of his 70th anniversary.

Acknowledgements

We thank M. Kato, H-Y. Kee, Y. B. Kim, M. Kohmoto, Y. Morita, M. Pinterić, E. Puchkaryov, J. Shiraishi, Y. Sun, S. Tomić, A. Virosztek, G. F. Wang and H. Won for continued collaboration on related subjects.

We would also like to thank H. Adrian, K. Behnia, J. P. Brison, J. Flouquet, T. Ishiguro, Y. Kitaoka, Y. Maeno and M. Sigrist for useful discussions. One of us (K. M.) thanks the continual support of Max-Planck Institut für Physik Komplexer Systeme at Dresden and Yukawa Institute for Theoretical Physics in Kyoto.

Note added proof. Recently d-wave superconductivity has been established in the electron-doped high $T_c$ cuprates NCCO and PCCO as well [92]. This development is very satisfying from the point view of universality and generality of d-wave superconductivity in high $T_c$ cuprates.

Also the superconductivity in Sr$_2$RuO$_4$ seems to be non-p-wave. Both the specific heat data [74] and the magnetic penetration depth data [93] appear to be more consistent with f-wave superconductor described here.

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