Panorama of Nodal Superconductors

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Abstract

Since 1979, many new classes of superconductors have been discovered, including heavy-fermion compounds, organic conductors, high-$T_c$ cuprates, and Sr$_2$RuO$_4$. Most of these superconductors are unconventional and/or nodal. Therefore it is of central importance to determine the symmetry of the order parameter in each of these superconductors. In particular, the angular-controlled thermal conductivity in the vortex state provides a unique means of investigating the nodal structure of the superconducting energy gap when high-quality single crystals in the extremely clean limit are available. Using this method, Izawa et al have recently succeeded in identifying the energy gap symmetry of superconductivity in Sr$_2$RuO$_4$, CeCoIn$_5$, $\kappa$-(ET)$_2$Cu(NCS)$_2$, YNi$_2$B$_2$C, and PrOs$_4$Sb$_{12}$.

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1. Introduction

Since the appearance of anisotropic superconductors the determination of their gap symmetries has been one of the central issues.\cite{1,2} For the high-$T_c$ cuprate superconductors angular-resolved photoemission spectroscopy (ARPES)\cite{3,4} and Josephson interferometry\cite{5,6} provide a definitive signature of $d_{x^2-y^2}$-wave superconductivity. However, these methods have not yet been extended beyond the high-$T_c$ cuprates. In a remarkable paper Volovik\cite{7} showed that the quasiparticle density of states in nodal superconductors in a magnetic field is calculable within a semi-classical approximation. Here the Doppler shift due to the supercurrent circulating around vortices plays a crucial role. The resulting $\sqrt{H}$-dependence of the specific heat in the vortex state has been observed experimentally in YBCO\cite{9,10}, LSCO\cite{11}, $\kappa$-(ET)$_2$ salts\cite{12}, and Sr$_2$RuO$_4$\cite{13,14}. Here $H$ is the magnetic field strength.

This approach has been extended in many directions. Kübert and Hirschfeld\cite{15} considered the effect of non-zero temperature and established the scaling law, as formulated by Simon and Lee\cite{16}. In particular, Kübert and Hirschfeld found the scaling function within the semi-classical approximation. Won et al\cite{14} extended this approach for the superfluid density, the spin susceptibility, and the nuclear spin lattice relaxation rate. Measurements of the thermal conductivity tensor in the vortex state provide an advantage, since the heat current direction provides further directional information. Kübert and Hirschfeld\cite{15} and Vehkter et al\cite{17} have performed analyses in these directions. However, these authors did not take the spatial average over the vortex lattice at the same time as the average over the Fermi surface, but instead assumed a local thermal conductivity $\kappa_{ii}(r)$. It is known that the local quasiparticle density of states mostly consists of bound states around vortex cores. These bound states do not contribute to thermal conductivity when $H/H_{c2} \ll 1$. On the other hand, the nodal excitations which do contribute to the thermal conductivity run through many unit cells of the vortex lattice. Furthermore Vehkter et al chose a rather specific circular Fermi surface instead of the cylindrical Fermi surface commonly used in modeling the high-$T_c$ cuprates. These problems were addressed in references 18-21. In these works simple expressions for the thermal conductivity are found in the superclean limit $((\Gamma\Delta)_{1/2} \ll v\sqrt{\epsilon H} \ll \Delta(0)$, where $\Gamma$ is the quasiparticle scattering rate in the normal state and $v$ is the effective Fermi velocity).

Intuitively we understand that the Doppler shift generates quasiparticles in a plane per-
perpendicular to the vortex axis and the field direction. When this plane intersects the nodal
directions, there is enhancement of the available quasiparticles, which we call nodal excita-
tions. Therefore, by changing the field direction one can sweep the Fermi surface with the
plane associated with the Doppler shift. As this plane meets the nodal directions both the
specific heat and thermal conductivity are enhanced\[18, 19, 20\].

In particular when the Fermi surface is quasi-2D or cylindrical, rotating the magnetic
field within the conducting plane yields valuable information regarding the gap symmetry.
This was shown clearly in early experiments on YBCO\[23, 24, 25\] and more recent experi-
ments on Sr$_2$RuO$_4$\[26\], CeCoIn$_5$\[27\], and $\kappa$-(ET)$_2$Cu(NCS)$_2$\[28\]. Such experiments, probing
the angular dependence of the superconducting order parameter, indicate f-wave supercon-
ductivity for Sr$_2$RuO$_4$, $d_{x^2−y^2}$-wave superconductivity for CeCoIn$_5$ and $\kappa$-ET$_2$Cu(NCS)$_2$,
and $s+g$-wave superconductivity for YNi$_2$B$_2$C and PrOs$_4$Sb$_{12}$. These order parameters are
shown in Fig. 1. For $\Delta(k)$ of PrOs$_4$Sb$_{12}$ see Fig. 10.

![Diagram of 2D f-wave, d$\times^2$-y$^2$-wave, and s+g-wave symmetry.](image)

FIG. 1: 2D f-wave, $d_{x^2−y^2}$-wave, and $s+g$-wave symmetry.

In the following sections we focus on the salient features of superconductivity in high-$T_c$
cuprates, Sr$_2$RuO$_4$, $\kappa$-(ET)$_2$ salts, YNi$_2$B$_2$C, and PrOs$_4$Sb$_{12}$.

2. High-$T_c$ Cuprate Superconductivity in a Nutshell

The discovery of high-$T_c$ cuprate superconductivity in LBCO by Bednorz and Muller\[29\] in 1986 took the superconductivity community by surprise. The subsequent excitement and
confusion are well documented in a textbook by Enz\[30\]. In 1987 P.W. Anderson\[31\] proposed the 2-dimensional one-band Hubbard model and his famous dogma. His central theme
is to understand the superconductivity in the presence of the strong Coulomb repulsion. In the meantime $d_{x^2-y^2}$-wave symmetry of both the hole and the electron-doped high-$T_c$ cuprate superconductivity has been established\textsuperscript{3, 4, 5, 6}. Furthermore, the mean-field theory (i.e. the generalized BCS theory) for d-wave superconductivity works well\textsuperscript{32, 33, 34}. Also within the framework of the BCS theory of d-wave superconductivity, May Chiao et al\textsuperscript{35, 36} have derived the crucial parameter $\Delta(0)/E_F$ of optimally doped YBCO and Bi-2212 through the measurement of thermal conductivity at $T < 1K$. Here $\Delta(0)$ is the maximum value of the energy gap at $T = 0K$ and $E_F$ is the Fermi energy. They found $\Delta(0)/E_F \simeq 1/14$ and $1/10$ for YBCO and Bi-2212 respectively. Regrettably there are no experimental data available indicating the ratio $\Delta(0)/E_F$ in the underdoped and overdoped region of YBCO and Bi-2212, though we have no reason to worry that this ratio becomes substantially different.

First of all, these values tell us that high-$T_c$ cuprate superconductivity is very far away from the Bose-Einstein (BE) condensate, but is within the BCS regime. The BE condensate clearly requires $\Delta(0) \sim E_F$. Secondly, making use of Ginzburg’s criterion the fluctuation effect in high-$T_c$ cuprate superconductivity should be at most of the order of a few percent.

Thirdly, these $\Delta(0)/E_F$ values are incompatible with the assumption that $\Delta(0) \simeq E_F$, which was made in solving the Bogoliubov-de Gennes equation in the vortex state of d-wave superconductors\textsuperscript{37, 38, 39}. In particular the approximation $\Delta(0) \sim E_F$ appears to knock off all the bound states around a single vortex in d-wave superconductors. On the other hand, for $\Delta(0)/E_F = 1/10$, one finds hundreds of bound states around a single vortex\textsuperscript{40, 41}.

In fact, the local density of states around a single vortex looks very similar to the one found for s-wave superconductors\textsuperscript{42}. Second the approximation $\Delta(0) \sim E_F$ appears to increase the $\sqrt{H}$ term in the specific heat by a factor of 10 to 30\textsuperscript{39}. Therefore we stress that if we limit ourselves to the region $T \ll \langle |v \cdot q| \rangle \ll \Delta(0)$, the quasiclassical approach as discussed in Refs. 18 - 20 provides the most reliable result so far available.

Unfortunately the approximation $\Delta(0) \simeq E_F$ is very popular among the superconductivity community because it makes the calculation much simpler\textsuperscript{43, 44, 45}.

As to the observation of these bound states around vortices in YBCO and Bi2212, only a few bound states, if any, are observed\textsuperscript{46, 47}. But this appears to be due to the fact that the vortex core is filled with other order parameters like antiferromagnetism\textsuperscript{48, 49} or charge density wave.

In a popular paper Bob Laughlin\textsuperscript{50} proposed a very intuitive picture of superconduct-
tivity in the presence of the Mott insulator. We think that another interesting question is how the superconductivity can survive in the presence of d-wave density waves\cite{51, 52, 53}.

In section 4 we shall discuss a very similar conflict between two order parameters in the organic superconductor $\kappa$-(BEDT-TTF)$_2$X.

3. Superconductivity in Sr$_2$RuO$_4$

Superconductivity in Sr$_2$RuO$_4$ was discovered in 1994\cite{54}. The surprising prediction of triplet p-wave pairing and related chiral symmetry breaking\cite{55} was verified by muon spin rotation experiments\cite{56} and a flat Knight shift as seen by NMR measurements\cite{57}. Also, the triplet superconductivity implies clapping collective modes\cite{58} and half-quantum vortices\cite{59} as topological defects. Since sample quality has improved and single crystal Sr$_2$RuO$_4$ with $T_c \simeq 1.5$ K have become available, experiments have found clearly nodal structures\cite{13, 60}. This is inconsistent with the initially proposed fully gapped p-wave model. Consequently, several f-wave models were proposed\cite{61, 62, 63}.

As shown in Ref. 19, most of these models are consistent with the specific heat data\cite{13} and the magnetic penetration depth data\cite{60}. The p-wave model cannot account for these measurements. Furthermore, ultrasonic attenuation data by Lupien et al\cite{64} eliminates models with vertical nodal lines parallel to $k_z$. This leaves only the 2D f-wave model with energy gap

$$\Delta(k) = \Delta e^{\pm i\phi} \cos(ck_z)$$  \hspace{1cm} (1)

where $e^{\pm i\phi} = k_x \pm ik_y$\cite{22}.

Zhitomirsky and Rice\cite{65, 66} have proposed a multi-gap model where one of the superconducting order parameters associated to the $\alpha$ and $\beta$ band has horizontal nodes at the Brillouin points\cite{67}. However, this multi-gap model gives a two-fold-symmetric angular dependence ($\sim \cos(2\phi)$, where $\phi$ is the angle between the heat current and the magnetic field) ten times larger than observed experimentally\cite{26}. Moreover, the two-gap model cannot give universal heat conduction as observed in $\kappa$-\text{$_{\text{Cu}}$}\cite{68}. More recently, further tests of the 2D f-wave model for Sr$_2$RuO$_4$ were proposed\cite{69, 70, 71}. If the f-wave model is established for Sr$_2$RuO$_4$, it implies that the 2D model used in the high-$T_c$ cuprates is inapplicable to Sr$_2$RuO$_4$. From the point of view of the electronic interaction Sr$_2$RuO$_4$ should be a 3D system\cite{72}. Also it is possible that p-wave pairing is forbidden in the electronic systems. It appears we now have 3 f-wave superconductors: UPt$_3$\cite{73}, Sr$_2$RuO$_4$, and UNi$_2$Al$_3$\cite{74}. Finally, it is important to
identify the gap symmetry of the organic superconductor \((\text{TMTSF})_2\text{PF}_6\) for which triplet pairing has already been established\[75\].

Very recently Deguchi et al\[76\] have reported specific heat data for \(0.12 \leq T \leq 0.51\) K and for magnetic field \(0.05 \leq B \leq 1.7\) T and rotating within the a-b plane. One of the most surprising data is the fourfold term with cusps at \(\phi = 0, \pi/2\), etc., which appears only for \(B = 0.30T\), \(0.60T\) and \(0.90T\) at \(T = 0.12K\). For data at \(T = 0.31K\) the cusp feature becomes less clear.

Perhaps the most interesting question is 1) Does this include 2 energy gaps?, and if so, 2) What is the gap symmetry of this new gap?

If we compare their Fig. 3 for \(T = 0.12K\), the angular dependence is very similar to what one expects in s+g-wave superconductivity in the presence of impurities\[77\]. In s+g-wave superconductors the impurity scattering induces a small energy gap. Therefore, the most natural interpretation of the above data is that the specific heat has picked up four point-like mini-gaps located at \(\theta = \pi/2\) and \(\phi = 0, \pi/2\), etc. The size of the minigap would be around 0.3 K. Then it is rather difficult to accommodate this with the Miyake-Narikiyo model\[79\]. Also this quasi-nodal structure is difficult to accommodate with the f-wave order parameter above. Perhaps this experiment indicates the presence of the second energy gap? The gap function \(\Delta(k)\) with minigap is shown in Fig. 2. Here we take

\[
|\Delta(k)| \sim |\cos(\chi)|(1 - 1.8 \cos(4\phi) \cos^2(\chi) + 0.81 \cos^4(\chi))^{1/2}.
\]

FIG. 2: Proposed Gap Function for \(\text{Sr}_2\text{RuO}_4\)
4. Gossamer Superconductivity in $\kappa$-(BEDT-TTF)$_2$X?

The organic superconductors $\kappa$-(BEDT-TTF)$_2$X with $X = \text{Cu[N(CN)$_2$} \text{Br, Cu[N(CN)$_2$} \text{Cl}$ and Cu(NCS)$_2$ have the highest superconducting transition temperature $T_c = 10$-$13$ K among organic conductors. There are many parallels between high-$T_c$ cuprates and $\kappa$-(BEDT-TTF)$_2$X; the quasi-two dimensionality of the Fermi surface, and the proximity to the antiferromagnetic state. More recently angular dependent STM and angular dependent thermal conductivity measurements in the vortex state indicate $d_{x^2-y^2}$ superconductivity. The nodal lines run in the diagonal direction of the b-c (i.e. the conducting) plane. Although d-wave superconductivity has been speculated theoretically, the diagonal lines come as a surprise. This indicates that perhaps the exchange of an antiparamagnon is not adequate to generate d-wave superconductivity.

Indeed from the thermal conductivity data from $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_4$, we can deduce that $\Delta(k) = \Delta(\cos(2\phi)-0.067)$. This $d+s$-wave symmetry is somewhat similar to that of YBCO.

Perhaps more surprising is the sensitivity of the superconductivity to the cooling rate, which has been studied by Pinteric et al in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. To make the story simple we consider two extreme cases only. We define the relaxed sample as the one cooled very slowly down to 10 K. For example this sample is left for 3 days in liquid $N_2$ and then cooled down for a fraction of a degree K per hour down to 10 K. The other extreme is the quenched sample, wherein the sample is dropped in liquid $N_2$, then cooled down to 10 K within a few hours.

Of interest, the superconducting transition temperature $T_c$ shows little dependence on the cooling procedure, with $T_c$ varying by only a few percent. More surprising is the sensitivity to the cooling rate of the superfluid density as measured by magnetic penetration depth. The superfluid density of the quenched sample is only 1-2 percent of the relaxed sample. Also the temperature dependence of the relaxed sample exhibits a $T$-linear dependence typical of d-wave superconductors. On the other hand, the superfluid density of the quenched sample is very flat for $T \leq 0.2 T_c$, which may be interpreted as a sign of $s$-wave superconductivity. Until recently there were debates on the symmetry of superconductivity in $\kappa$-(BEDT-TTF)$_2$ salts: d-wave versus s-wave. We therefore wonder if this controversy originates from the difference in the cooling rate. For example, Elsinguer et al did not describe how their samples were cooled down.
Recently the effect of the cooling rate on the normal state of the three $\kappa$-(BEDT-TTF)$_2$ salts has been reported\cite{90}. These organic conductors go through a glassy phase when they are cooled down from room temperature to liquid $\text{N}_2$ temperature (70 - 90 K).

The BEDT-TTF molecules have ethylene groups attached to each end. For $T > 100K$ these ethylenes are rotating freely. As the temperature decreases below 70 K these ethylenes cannot move freely but are settled in their equilibrium configurations. Therefore it is very likely that in the relaxed samples these ethylene groups are relatively well ordered while in the quenched samples they are oriented randomly.

But it is not known at present how the randomness of the ethylene groups interferes with the quality of the superconductivity. From the insensitivity of $T_c$ to the cooling procedure we infer that this cannot be the simple effect of disorder. Also Pinteric et al have shown the superconductivity to be homogeneous. More likely is that the disorder controls the appearance of another order parameter, a “hidden order parameter”, like unconventional density wave (UDW). This forces the superconductivity to coexist with UDW.

As we have discussed in section 2 we call this type of superconductivity “gossamer superconductivity”\cite{91}. Unfortunately at present we do not know what kind of order parameter is appropriate to characterize the glassy phase, although we suspect it should be UCDW or USDW. We believe that this is the most fascinating question in $\kappa$-(BEDT-TTF)$_2$ salts.

5. Superconductivity in $\text{YNi}_2\text{B}_2\text{C}$

Superconductivity in $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$ was discovered in 1994\cite{92}. Recent interest has focused on these materials because of their relatively high superconducting transition temperatures of 15.5 K and 16.5 K, respectively. There is a substantial $s$-wave component in the order parameter of these compounds. This was shown by substituting Ni with a small amount of Pt and observing the subsequent opening of the quasiparticle energy gap as observed in specific heat measurements\cite{93}. Nevertheless, recent experiments clearly indicate the presence of nodal excitations\cite{94, 95}.

Furthermore, the upper critical field within the $a$-$b$ plane exhibits a clear four-fold symmetry\cite{96, 97}. The simplest model to describe the superconductivity in $\text{YNi}_2\text{B}_2\text{C}$ appears to be\cite{98, 99, 100}

$$\Delta(k) = \frac{1}{2} \Delta(1 - \sin^4 \theta \cos(4\phi))$$ (2)
or s+g-wave superconductivity. Here $\theta$ and $\phi$ are the polar and azimuthal angles, respectively, describing the direction of $\mathbf{k}$. The corresponding $\Delta(\mathbf{k})$ is shown in Fig. 1(c). The quasiparticle density of states is given by

$$ G(E) \equiv N(E)/N_0 = |E|Re\left(\frac{1}{(E^2 - \Delta^2(\mathbf{k}))^{1/2}}\right) $$

where $\langle - - \rangle$ means $(1/4\pi) \int d\Omega - - -$. This is shown in Fig. 3. In particular, for $|E|/\Delta \ll 1$, we obtain

$$ G(E) = \frac{\pi|E|}{4\Delta} + \frac{9}{16}(E/\Delta)^2 + \ldots $$

This gives rise to power laws in the specific heat and other quantities as follows\cite{101}:

$$ \frac{C_s}{\gamma_N T} = \frac{27\zeta(3)}{4\pi}(T/\Delta) + \frac{63}{50}(T/\Delta)^2 + \ldots $$

$$ \frac{\chi_s(T)}{\chi_N} = \frac{\pi \ln(2)}{2}(T/\Delta) + \frac{3\pi^2}{16}(T/\Delta)^2 + \ldots $$

$$ \frac{\rho_{ab}(T)}{\rho_{ab}(0)} = 1 - \frac{3\pi \ln 2}{4}(T/\Delta) - \frac{5\pi^2}{32}(T/\Delta)^2 + \ldots $$

$$ \frac{\rho_{sc}(T)}{\rho_{sc}(0)} = 1 - \frac{\pi^2}{4}(T/\Delta)^2 - \frac{783\pi}{256}(T/\Delta)^3 + \ldots $$

$$ T_1^{-1}/T_{1N}^{-1} \simeq \frac{\pi^4}{48}(T/\Delta)^2 + \frac{81\pi \zeta(3)}{32}(T/\Delta)^3 + \ldots $$

**FIG. 3:** Quasiparticle density of states of an s+g-wave superconductor.

This gives rise to power laws in the specific heat and other quantities as follows:
where $\gamma_N$ is the Sommerfeld coefficient, and $\zeta(3) \simeq 1.202$ is the Riemann zeta function. We note that the presence of point nodes in the a-b plane creates an anisotropic temperature dependence in the superfluid density.

These specific heats, spin susceptibility and anisotropic superfluid densities are compared with those of a d-wave superconductor in Figs. 4, 5, and 6(a) and 6(b).

**FIG. 4:** Specific heats normalized by normal state specific heat are shown for s+g-wave, s-wave and d-wave superconductors. $\gamma_N$ is the Sommerfeld constant.

**FIG. 5:** The spin susceptibility normalized by that of the normal state are shown for s+g-wave, s-wave and d-wave superconductors.
In the vortex state and in the superclean limit ($\Gamma \ll \tilde{v}\sqrt{eH}$, where $\tilde{v} = \sqrt{v_a v_b}$ and $\Gamma$ is the scattering rate in the normal state) the specific heat and other quantities are given by

$$\frac{C_s}{\gamma_N T} = \frac{\tilde{v}\sqrt{eH}}{2\Delta} I(\theta, \phi)$$  \hspace{1cm} (10)

$$\frac{\chi_s(T)}{\chi_N} = \frac{\tilde{v}\sqrt{eH}}{2\Delta} I(\theta, \phi)$$  \hspace{1cm} (11)

$$\frac{\rho_{sab}(T)}{\rho_{sab}(0)} = 1 - \frac{3\tilde{v}\sqrt{eH}}{4\Delta} I(\theta, \phi)$$  \hspace{1cm} (12)

$$\kappa_{zz}/\kappa_n = \frac{x}{4\ln(2/x)}$$  \hspace{1cm} (13)

where

$$x = \frac{2\tilde{v}\sqrt{eHI(\theta, \phi)}}{\pi\Delta}$$  \hspace{1cm} (14)

and

$$I(\theta, \phi) = \frac{1}{2}((1 - \sin^2 \theta \sin^2 \phi)^{1/2} + (1 - \sin^2 \theta \cos^2 \phi)^{1/2})$$  \hspace{1cm} (15)

Here $\theta$ and $\phi$ are the polar and azimuthal angles describing the direction of the magnetic field.

Recent thermal conductivity\[99\] and specific heat data \[102\] establish experimentally this striking angular dependence. In Fig. 7 we show the experimental data together with the
theoretical expression. The cusps at $\phi = 0, \pi/2$, etc. for $\theta = \pi/2$ clearly indicate the presence of point nodes. In the presence of line nodes the angular dependence of $\kappa_{zz}$ is well approximated by $\cos(4\phi)$. As is seen from the denominator of Eq. 13, the effect of impurity scattering is very unusual.$^{103, 104}$.

FIG. 7: Experimental and theoretical angular dependence of $I(\theta, \phi)$

Regarding Raman scattering, we present here results from a concurrent work$^{101}$ wherein theoretical calculations, based on the s+g symmetry, for the modes $A_{1g}$, $B_{1g}$ and $B_{2g}$ are performed. The comparison between theory and experiment$^{105}$ is shown in Figure 8, with the theoretical results on the left and the experimental results, taken at 6 K, on the right. Strong agreement is seen for the whole energy range in the $A_{1g}$ mode, with fair agreement for the other two modes. Notably absent from the $B_{2g}$ data is the secondary cusp feature found at $\omega = 2\Delta$; we believe that this may be a temperature-related effect and eagerly await the results of lower-temperature experiments.

From the experimental data$^{105}$ we can extract $\Delta(0) = 50.4$ K and 64.7 K for YNi$_2$B$_2$C and LuNi$_2$B$_2$C respectively. On the other hand, the weak coupling theory gives $\Delta(0) = 42.2$ K and 43.3 K respectively, where we need $\Delta(0)/T_c = 2.72$. Therefore we may conclude that YNi$_2$B$_2$C is close to the weak coupling limit whereas LuNi$_2$B$_2$C is in the moderately strong coupling limit.

In the absence of a magnetic field the quasiparticle spectrum in the presence of impurities
is determined by

\[ \tilde{\omega} = \omega + \Gamma \tilde{\omega} \frac{1}{\sqrt{(\tilde{\Delta} - \Delta f/2)^2 - (\tilde{\omega})^2}} \]  

and

\[ \tilde{\Delta} = \Delta/2 + \Gamma \frac{\tilde{\Delta} - \Delta f/2}{\sqrt{(\tilde{\Delta} - \Delta f/2)^2 - (\tilde{\omega})^2}} \]  

where \( \tilde{\omega} \) and \( \tilde{\Delta} \) are the renormalized Matsubara frequencies and order parameter, respectively, and \( \langle -- -- \rangle \) means \( 1/(4\pi) \int d\Omega \ -- -- \).

Then the quasiparticle density of states is given by

\[ G(E) = N(E)/N_0 = |E| \left( \text{Re} \left( \frac{1}{\sqrt{\tilde{\omega}^2 - (\tilde{\Delta} - \Delta f/2)^2}} \right) \right) \]  

where \( G(E) \) is evaluated at \( \omega = E \). The DOS for a few \( \Gamma \) are shown in Fig. 8. Here we have used the so-called Born limit due to the presence of a substantial s-wave component in \( \Delta(k) \). The unitary limit gives virtually the same result as the Born limit. The most unusual
feature one notices is the immediate appearance of an energy gap when $\Gamma \neq 0$. This is in contrast to the usual nodal superconductors with line nodes. In particular, the energy gap is given by $\omega_g = \Gamma(1 + 2\Gamma/\Delta)^{-1}$. This has a number of consequences. First of all, in the absence of a magnetic field both the specific heat and the thermal conductivity vanish exponentially.

$$C_s/T, \kappa_{ii}/T \sim (\omega_g/T)^{3/2} e^{-\beta \omega_g}$$

There is no universal heat conduction unlike other nodal superconductors. This remarkable effect of impurity scattering on nodal excitation is clearly shown by Kamata. In Fig. 9 we show the thermal conductivity data of Y(Ni$_{1-x}$Pt$_x$)$_2$B$_2$C with x=0.05. As is readily seen the fourfold term typical of the pure YNi$_2$B$_2$C has vanished completely. For example, the quasiparticle density of states in the presence of both a magnetic field and impurities is given by

$$G(H, \Gamma) = x \cos^{-1}(y) \theta(1 - y)$$

where $x$ is defined in Eq.(14) and $y = \frac{\Gamma}{\Delta x}$.

Further we obtain

$$\frac{\kappa_{zz}}{\kappa_n} = \frac{x}{2 \cosh^{-1}(1/x)} ((1 - y^2)^{3/2} - \frac{3y}{2}(\cos^{-1}(y) - y \sqrt{1 - y^2})) \theta(1 - y)$$

$$\frac{\kappa_{xx}}{\kappa_n} = \frac{3}{2 \cosh^{-1}(1/x)} \left( \frac{x'}{x} \right)^2 (\cos^{-1}(y') - y' \sqrt{1 - y'^2}) \theta(1 - y')$$
where
\[ x' = \frac{1}{\pi} \frac{\tilde{v} \sqrt{eH}}{\Delta} (1 - \sin^2 \theta \cos^2 \phi)^{1/2}, \quad y' = \frac{\Gamma}{\Delta x'}. \tag{23} \]

These expressions indicate clearly that the nodal excitations are eliminated when \( y > \sqrt{2} \).

6. Puzzle of Superconductivity in PrOs\(_4\)Sb\(_{12}\)

New heavy-fermion superconductivity in the skutterudite PrOs\(_4\)Sb\(_{12}\) with \( T_c = 1.8 \) K was discovered quite recently [110]. The existence of two distinct superconducting phases and the presence of point nodes in \( \Delta(k) \) are of great interest [111, 112]. Indeed, recent angular-dependent magnetothermal conductivity data [113, 114] indicate the presence of two phases, with 4 point nodes in the ab-plane in phase A and 2 point nodes parallel to the b axis in phase B (see Fig. 10).

In order to accommodate the observed nodal structure within the cubic symmetric crystal, the following order parameters are proposed:
\[ \Delta_A(k) = \Delta(1 - k_x^4 - k_y^4) \tag{24} \]
\[ \Delta_B(k) = \Delta(1 - k_y^4) \tag{25} \]

for the A and B phases, respectively.

From an experimental point of view, it must be acknowledged that whether the superconductivity is the spin singlet or the spin triplet is unclear. Here we have assumed the spin singlet symmetry. However, a muon spin rotation experiment indicates the presence
of remanent magnetization which may be indicative of the spin triplet symmetry\cite{115}. Indeed alternative models have been proposed\cite{116, 117, 118}, although these models cannot describe the observed angular dependence of the thermal conductivity.

The models given in Eq.\((24)\) and \((25)\) have the \(T^2\)-specific heat

\[
\frac{C_s}{\gamma N T} = \begin{cases} 
27(\zeta(3)(T/\Delta))/4\pi & \text{for A phase} \\
27(\zeta(3)(T/\Delta))/8\pi & \text{for B phase}
\end{cases}
\]  

Of more interest is the anisotropic superfluid density\cite{114}. In particular, in the B-phase

\[
\frac{\rho_s(0)}{\rho_s(0)} = 1 - \frac{\pi^2}{4} \left(\frac{T}{\Delta}\right) - \frac{\pi^2}{16} \left(\frac{T}{\Delta}\right)^2 + \ldots 
\]  

\[
\frac{\rho_s(0)}{\rho_s(0)} = 1 - \frac{\pi^2}{16} \left(\frac{T}{\Delta}\right) - \frac{21\pi(3)}{128} \left(\frac{T}{\Delta}\right)^3 + \ldots 
\]  

where the suffixes \(\parallel\) and \(\perp\) indicate directions parallel and perpendicular to the nodal directions.

Very recently surprising superfluid density measurements of \(\text{PrOs}_4\text{Sb}_{12}\) were reported\cite{118}. Chia et al measured the superfluid density parallel to each of the three crystal axes and found that the superfluid densities are isotropic and decrease like \(T^2\) at
low temperatures. Both the isotropy and the $T^2$ dependence are incompatible with all models for PrOs$_4$Sb$_{12}$ proposed to date. However, if one assumes that the nodal points in the B-phase are always aligned parallel to $\mathbf{H}$ when the samples are cooled in a fixed magnetic field, our model for the B-phase fits the experimental data precisely. This is plausible, since the magnetic field is the only symmetry-breaking parameter in the present model. Also, a simple analysis of the effect of the magnetic field on the superconducting order parameter tells us that the effect of the magnetic field is minimized when the field is parallel to the nodal directions.

In the presence of a magnetic field the specific heat and the thermal conductivity in the superclean limit are given by

\[
\frac{C_s}{\gamma_N T} = \pi x_i/4 \quad (30)
\]

\[
\frac{\kappa_{zz}^A}{\kappa_n} = \frac{x_A}{2\ln(2/x_A)} \frac{1 + \pi x_A/2 + 31x_A^2/40}{1 + 31x_A^2/64} \quad (31)
\]

\[
\frac{\kappa_{zz}^B}{\kappa_n} = \frac{x_B}{2\ln(2/x_B)} \frac{1 + \pi x_B/12 + 31x_B^2/40}{1 + 31x_B^2/64} \quad (32)
\]

where

\[
x_A = \frac{v\sqrt{eH}}{\pi \Delta} ((1 - \sin^2(\theta) \cos^2(\phi))^{1/2} + (1 - \sin^2(\theta) \sin^2(\phi))^{1/2}) \quad (33)
\]

and

\[
x_B = \frac{v\sqrt{eH}}{2\pi \Delta} (1 - \sin^2(\theta) \sin^2(\phi))^{1/2} \quad (34)
\]

Here we assumed that $\Delta(\mathbf{k})$ is given by equations (24) and (25) for the A-phase and B-phase, respectively. The above expressions are consistent with the thermal conductivity data [113], although experimental data at lower temperatures would help to further clarify this point.

Therefore the model proposed in Refs. 112 and 113 appears to be the most consistent with the available data. On the other hand we have assumed the spin singlet pairing, while some experiments appear to indicate spin triplet pairing[115]. Further clarification on this question is highly desirable.

7. Outlook

In the past decade we have witnessed the identification of the gap symmetry of the high-$T_c$ cuprates through ARPES [3, 4] and phase sensitive Josephson interferometry [5, 6]. However,
these techniques do not appear to be practical to use on heavy-fermion superconductors or organic superconductors.

In recent years measurements of the angular dependent magnetothermal conductivity have provided a unique alternative means to explore the gap symmetry of superconductors with $T_c \sim 1$-2 K. In this way the gap symmetries of Sr$_2$RuO$_4$, CeCoIn$_5$, $\kappa-(ET)_2Cu(NCS)_2$, YNi$_2$B$_2$C and PrOs$_4$Sb$_{12}$ have been identified. The next step will be to interpret these gap symmetries in terms of available interaction terms in these systems.

In this journey we have discovered that superconductivity with mixed representations play a crucial role in both YNi$_2$B$_2$C and PrOs$_4$Sb$_{12}$. This is very surprising, but it appears that one must accept this new development. Clearly this will open up a new vista in the rich field of nodal superconductors.

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