Multiphase Superconductivity in Skutterudite PrOs$_4$Sb$_{12}$

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PACS. 74.20.Rp –.
PACS. 74.25.Fy –.
PACS. 74.70.Tx –.

Abstract. – We propose a model of nodal order parameters for the superconducting A and B-phase of skutterudite PrOs$_4$Sb$_{12}$ and discuss the associated angular dependent magnetothermal conductivity at low temperatures. The model for the hybrid gap functions $\Delta(k)$ containing an s- and g-wave parts is consistent with recent thermal conductivity experiments in PrOs$_4$Sb$_{12}$. In particular the model accounts for the data on polar and azimuthal field angle dependence of $\kappa_{zz}(\theta, \phi)$. The low temperature behaviour of thermodynamic properties in zero field is also presented. We show that the effect of impurity scattering on a nodal hybrid gap function immediately leads the opening of a gap and related exponential behaviour of low temperature specific heat and thermal conductivity which is very different from d-wave superconductors.

Introduction. – Superconductivity in the cubic ($T_h$ symmetry) Heavy Fermion (HF) skutterudite PrOs$_4$Sb$_{12}$ with $T_c=1.8$ K has provoked great interest since it exhibits a number of characteristics that suggest the presence of nodes. However there is also a proposal that it is a conventional s-wave superconductor. The specific heat results indicate that firstly a low temperature power law behaviour and secondly the presence of two superconducting (sc) phases with two consecutive specific heat jumps at $T_{c1}=1.82$ K and $T_{c2}=1.75$ K somewhat similar to the observations in UPt$_3$. More recent low temperature thermal conductivity results in the vortex state confirm i) the presence of two superconducting A ($T < T_{c1}$) and B ($T < T_{c2}$) phases with different nodal structure, ii) the presence of point nodes in both A ($H > 0.75$T, $T < T_c$) and B ($H < 0.75$T, $T < T_c$) phase. More specifically the thermal conductivity indicates the presence of four point nodes at $k=(1,0,0)$, $(0,1,0)$, $(-1,0,0)$ and $(0,-1,0)$ (in units of $k_F$) in $\Delta(k)$ in the A-phase while in the B-phase the two point nodes are located at $k=(0,1,0)$ and $(0,-1,0)$. Present investigation also excludes a fully symmetric A-phase order parameter with additional point nodes along [001] direction.

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Symmetry classification of SC order parameter. – The presence of two SC phases is possibly connected with the vicinity of a field induced antiferroquadrupolar ordered phase above 4T which is likely due to a level crossing of the tetrahedral CEF states \( \Gamma_1 \) where one of the excited triplet \( \Gamma_5 \) states crosses the singlet ground state \( \Gamma_1 \). In U-based unconventional HF superconductors an exchange of (dipolar) spin fluctuations in the itinerant 5f-electrons is frequently implied as the mechanism for unconventional SC pair formation. In the present case a new interesting possibility for pair formation is the exchange of inelastic quadrupolar \( \Gamma_1 - \Gamma_5 \) fluctuations of the essentially localized 4f electrons of Pr. Since the AFQ critical field is of the same order of magnitude as the SC upper critical field of \( H_{c2}(0) = 2T \), impeding CEF level crossing as function of applied magnetic field will strongly affect the pair potential and may lead to a change of the SC gap symmetry. This does however not explain the origin of the zero field \( T_c \) splitting. Details of this microscopic mechanism and its preferred gap symmetries are not clear, hence we have to consider possible order parameters compatible with the above node structure on a phenomenological basis. The gap function may be expanded in terms of basis functions \( \psi_i^\Gamma(k) \) which transform like representations \( \Gamma \) of the crystal symmetry group \((i=1-d \text{ is the degeneracy index, the index } l \text{ denoting the degree of } \Gamma \text{ is suppressed})\). So far there is no information from NMR Knight shift or \( H_{c2} - \text{Pauli limiting} \) whether PrOs\(_4\)Sb\(_{12}\) has spin singlet or triplet pairing, although recent \( \mu^S\text{SR} \) measurements \([7]\) seem to suggest the presence of condensate magnetic moments. Only the singlet case will be considered here. The gap function should then be given by

\[
\Delta(k) = \sum_{\Gamma,i} \eta_i^\Gamma \psi_i^\Gamma(k) \equiv \Delta f(k) \tag{1}
\]

where the form factor \( f(k) \) is normalized to one and \( \Delta \) is the temperature dependent maximum gap value. In the spirit of the Landau theory only a single representation with the highest \( T_c \) should be realized and for \( T \geq T_c \), the free energy may then be expanded in terms of possible invariants of the order parameter components \([5] \eta_i^\Gamma \) which are determined by Landau parameters \( \alpha_i^\Gamma(T) \) and \( \beta_i^\Gamma \). The node structure is then fixed by the specific symmetry class of \( \Delta(k) \) defined by the set of \( \eta_i^\Gamma \). However we are interested in the complementary temperature range \( T \ll T_c \) relevant for magnetothermal conductivity experiments. In this regime Landau expansion is unreliable. Especially it is unjustified to assume that only a single representation \( \Gamma \) will have appreciable amplitude in Eq. (1), one should expect that at low temperatures \( \Delta(k) \) will be a hybrid gap function, i.e. a superposition of basis functions belonging to a few favorable representations which have approximately equal \( T_h^\Gamma \). A striking realization of such a hybrid gap function has recently been found in the nonmagnetic borocarbide superconductor YNi\(_2\)B\(_2\)C \([9]\) and possibly also in LuNi\(_2\)B\(_2\)C. There \( \Delta(k) = \Delta f(k) \) is a sum of two fully symmetric (for \( D_{4h} \)) gap functions of different degree (‘s+g-wave’) given by

\[
f(k) = \frac{1}{2} \left[ 1 - \left( k_x^4 + k_y^4 - 6k_x^2k_y^2 \right) \right] \tag{2}
\]

For hybrid gap functions nodes occur only for special ‘fine tuning’ of amplitudes, they are not enforced by the gap symmetry. \([10,11]\). Microscopic model calculations \([12]\) show that this is possible for a wide variety of plausible pairing potentials. The case of a nodal hybrid order parameter is realized in YNi\(_2\)B\(_2\)C to an astonishing accuracy. This is not yet clear for PrOs\(_4\)Sb\(_{12}\) but the nodal structure referred above cannot be realized with gap functions corresponding only to a single \( T_h \)-representation. Experimental evidence from the field angle
dependence of $\kappa_{zz}(\theta, \phi)$ leads us to the following simple proposals for hybrid gap functions $\Delta(k) = \Delta f(k)$ for PrOs$_4$Sb$_{12}$ with four and two nodal points respectively:

$$f_A(k) = 1 - k_x^4 - k_y^4,$$

$$f_B(k) = 1 - k_y^4.$$  \hspace{1cm} (3)

Both A-phase and B-phase are described by hybrid gap functions which are superpositions of three $T_h$ representations. The B-phase gap function has lower symmetry and both are threefold degenerate. An alternative gap function for the A-phase of PrOs$_4$Sb$_{12}$ would be the same model of eq. (2) as used already for the borocarbides.

**Quasiparticle DOS and thermodynamics.** – In the normal state the estimated linear specific heat coefficient is $\gamma \geq 350$ mJ/mole K$^2$, considerably larger than the value obtained from the effective dHvA masses ($m^* \sim 2.4 - 7.6$ m). However in comparison with other Pr-compounds both experiments support the HF character of PrOs$_4$Sb$_{12}$. We have calculated the quasiparticle DOS $N(E)$ for the gap functions of A and B phase which determines the low temperature thermodynamics. The DOS functions are shown in Fig. 1. For $E/\Delta \ll 1$ the lowest linear term $N(E)/N_0 = \alpha(E/\Delta)$ has $\alpha = \frac{\pi}{4}$ for A phase and $\frac{\pi}{8}$ for B phase. Here $N_0$ is the normal state DOS. Correspondingly, the low $T$ specific heat, spin susceptibility and superfluid density are given by, respectively,

$$\frac{C_s}{\gamma_n T} = \frac{\alpha 27}{\pi^2} \zeta(3) \left( \frac{T}{\Delta} \right), \quad \frac{X_s}{X_n} = \alpha \left( 2 \ln 2 \right) \frac{T}{\Delta},$$

A-phase: $\hat{\rho}_s(T) = 1 - \frac{3}{2} \frac{X_s}{X_n}$, $\hat{\rho}_s^c(T) = 1 - c_A \left( \frac{T}{\Delta} \right)^2$

B-phase: $\hat{\rho}_s^b(T) = 1 - \frac{3}{2} \frac{X_s}{X_n}$, $\hat{\rho}_s^c(T) = 1 - c_B \left( \frac{T}{\Delta} \right)^2$ \hspace{1cm} (4)

Here $\hat{\rho}_s(T) \equiv \rho_s^i(T)/\rho_s^i(0)$ for the axis directions $i=a,b,c$ and $c_{A,B}$ are numerical constants. Furthermore the specific heat in the whole temperature region is calculated and given by Fig. 2 where we have assumed phenomenologically the pairing interaction $V_{kk'}$ to be of the
separable form $V f(k)f(k')$. The $C_s/(\gamma_n T)$ vs. $T/T_c$ is found to be nearly independent of $V$ for each gap model. However for fixed $V$ the obtained $T_c$ values for A and B phase are quite different. We consider now thermodynamics in the vortex state and in the low temperature limit with $\Gamma \ll T \ll v\sqrt{eH} \ll \Delta(0)$ where $v$ is the (isotropic) Fermi velocity and $\Gamma$ the quasiparticle scattering rate and $v\sqrt{eH}$ is the typical magnetic energy. The field $H$ is applied in an arbitrary direction defined by polar and azimuthal angles $\theta$ and $\phi$ respectively referred to a cubic [001] axis. In \[14, 15\] it has been established that the dominant effect of the magnetic field in nodal superconductors is the Doppler shift in the quasiparticle spectrum introduced by the supercurrent around each vortex. A short derivation is also sketched in Ref. \[10\]. In the low $T$ limit the quasiparticle DOS for $E=0$ in the two phases ($i=A,B$) is given by

$$\frac{N(0)}{N_0} = \frac{\pi}{4} \langle |x| \rangle = g(H, \theta, \phi), \quad \langle |x| \rangle_i = \frac{2}{\pi} \frac{v\sqrt{eH}}{\Delta} I_i(\theta, \phi).$$

Here $x = v \cdot q/\Delta$ is the normalized Doppler shift energy and the averaging over the Fermi surface and vortex lattice has to be performed. For brevity we use $x_A \equiv \langle |x| \rangle_A$ and $x_B \equiv \langle |x| \rangle_B$. The angular dependent functions $I_{A,B}(\theta, \phi)$ are given by

$$I_A(\theta, \phi) = \frac{1}{2} \left[ (1 - \sin^2 \theta \sin^2 \phi)^{\frac{1}{2}} + (1 - \sin^2 \theta \cos^2 \phi)^{\frac{1}{2}} \right],$$
$$I_B(\theta, \phi) = \frac{1}{4} \left( 1 - \sin^2 \theta \sin^2 \phi \right)^{\frac{1}{2}}. \quad (6)$$

This leads to a field angle dependent specific heat for the A and B phase which is given by

$$C_s/\gamma_n T = \frac{v\sqrt{eH}}{2\Delta} I_i(\theta, \phi). \quad (7)$$

Similar angular dependences governed by $I_{A,B}(\theta, \phi)$ may be obtained for the spin susceptibility $\chi_s(T)$ and superfluid density $\rho_s(T)$. In principle the angular dependent specific heat is adequate to identify the point nodes in $\Delta(k)$. Recently a related experiment is reported for YNi$_2$B$_2$C. \[16\] The observed cusps in the angular dependence of $C_s$ clearly indicate the presence of point nodes along the tetragonal plane axes at (1,0,0), (0,1,0) etc., which is fully consistent with thermal conductivity data. \[9\].

**Impurity scattering and magnetothermal conductivity.** – In order to compute the thermal conductivity, it is imperative to consider the effect of impurity scattering. As already discussed elsewhere the impurity scattering in “s+g”-wave superconductors is completely different from other nodal superconductors without s-wave component \[14, 18\]. Since the unitary limit gives practically the same result as Born limit, we can follow Abrikosov and Gor’kov \[19\] and we have

$$\tilde{\omega}_n = \omega_n + \Gamma \langle \frac{\tilde{\omega}_n}{\sqrt{\omega_n^2 + (\Delta + \Delta f')^2}} \rangle$$
$$\tilde{\Delta} = a\Delta + \Gamma \langle \frac{(\tilde{\Delta} + \Delta f')}{\sqrt{\omega_n^2 + (\Delta + \Delta f')^2}} \rangle. \quad (8)$$
where $\tilde{\omega}_n$ and $\Delta$ are renormalized Matsubara frequency and superconducting order parameter respectively. Here $a = \frac{3}{5}$ and $\Gamma' = \frac{3}{5}k^2f$ for A phase while $a = \frac{4}{5}$ and $\Gamma' = \frac{1}{5}k^2f$ for the B phase. First we consider $H=0$. In the limit of small $\Gamma$ it is shown that $\tilde{\Delta} \approx a\Delta + \Gamma$ which implies that a quasiparticle energy gap opens up immediately. These energy gaps are well approximated by $\omega \approx 0$ for $\Gamma \ll 1$. This leads to $C_s/\gamma_n T$ and $\kappa_{ii}/T \sim (\tilde{\omega}_n)^2 e^{-\omega_n/T}$. Therefore unlike d-wave superconductors there will be no universal heat conduction [20, 21]. The thermal conductivity vanishes exponentially when $T/\omega_g \ll 1$.

In the presence of a magnetic field $\tilde{\omega}_n$ in r.h.s of eq. (5) have to be replaced by $\tilde{\omega}_n - i\mathbf{v} \cdot \mathbf{q}$ where $\mathbf{v} \cdot \mathbf{q}$ is the Doppler shift. Then for $\mathbf{q} \ll 1$ the quasiparticle damping $C_0 = \lim_{\omega \to 0} \frac{\omega}{4\pi}$ in A and B phase is given by

$$C_0 = \frac{3}{b_i \Delta} x_i \ln \left( \frac{2}{x_i} \right) \left( 1 + \frac{31}{64} x_i^2 \right)$$

(9)

where $x_i (i=A,B)$ are defined below eq. (6) and $b_A = 2, b_B = 4$. A similar expansion in terms of $x_i$ up to second order is used to obtain the thermal conductivity tensor:

$$\frac{\kappa_{zz}^A}{\kappa_n} = \frac{x_A}{\ln \left( \frac{2}{x_A} \right)} \left( 1 + \frac{31}{64} x_A^2 \right)$$

$$\frac{\kappa_{xx}^A}{\kappa_n} = \frac{x_A}{2 \ln \left( \frac{2}{x_A} \right)} \left( \frac{x'}{x_A} \right) \left( 1 + \frac{31}{64} x_A^2 \right)$$

(10)

where we have defined $x' \equiv \frac{2\sqrt{\omega_n}}{x_A}(1 - \sin^2 \theta \cos^2 \phi)$. The component $\kappa_{yy}^A$ may be obtained by replacing $x' \to x_B$ in $\kappa_{xx}^A$. Similarly for the B-phase we obtain

$$\frac{\kappa_{zz}^B}{\kappa_n} = \frac{x_B}{\ln \left( \frac{2}{x_B} \right)} \left( 1 + \frac{31}{64} x_B^2 \right)$$

$$\frac{\kappa_{xx}^B}{\kappa_n} = \frac{x_B}{2 \ln \left( \frac{2}{x_B} \right)} \left( \frac{x'}{x_B} \right) \left( 1 + \frac{31}{64} x_B^2 \right)$$

$$\frac{\kappa_{yy}^B}{\kappa_n} = \frac{3}{2 \ln \left( \frac{2}{x_B} \right)} \left( \frac{x'}{x_B} \right) \left( 1 + \frac{31}{64} x_B^2 \right)$$

(11)

Note that in $\kappa_{xx}^A$ and $\kappa_{yy}^B$ have no linear term in $x_i$ and therefore don’t exhibit a $\sqrt{H}$ behaviour. Indeed eqs. (10,11) reproduce the $\phi$ dependence of $\kappa_{zz}^A$ observed in [5]. For $\phi = \pi/2$ cusps at $\phi = 0, \pi/2$ (A phase) and $\phi = \pi/2$ (B phase) are predicted in accordance with experiment. On the other hand the present theory predicts the $\sqrt{H}$ dependence of $\kappa_{zz}$ while the data appear to be approximately linear in $H$. Also when the heat current is parallel to a pair of nodal directions the dominant term is almost independent of $H$ except for $\ln \left( \frac{2}{x} \right)$ term. Also we have neglected the $\Gamma$ dependent terms completely due to $T \gg \Gamma$. However, in a more realistic situation the inclusion of the scattering term is necessary.

In Fig. 5 we show $I_{A,B}(\theta, \phi)$ which determines the $\theta, \phi$ dependence of specific heat and $\phi$- dependence of thermal conductivity $\kappa_{zz}$ for various fixed $\theta$. For planar field ($\theta=90^\circ$) cusps appear when the field points along the node directions which are equivalent to the [100] and [010] axis directions ($\phi=0, \pm 90^\circ$) for the A-phase. In the B-phase only twofold oscillations with cusps for field direction along [010] ($\phi=\pm 90^\circ$) occur.

Very recently from the $\mu$SR experiment a possibility for triplet sc in PrOs$_4$Sb$_{12}$ is suggested [7]. If this is indeed the case, we can still reproduce the angular dependence of thermal
Concluding remarks. – We present here a simple nodal hybrid gap function model for $\Delta(k)$ which appears to describe many features of the angular dependent magnetothermal conductivity in the multiphase superconductor PrOs$_4$Sb$_{12}$. From the thermal conductivity we infer the presence of point nodes at $k=(1,0,0)$, $(0,1,0)$, $(0,-1,0)$ and $(1,0,0), (0,1,0), (0,-1,0)$ in A-phase and at $k=(0,1,0)$ and $(0,-1,0)$ in B-phase. We have shown that the hybrid nature of the order parameter leads to a very unusual effect of impurities. Already for arbitrary small scattering $\Gamma$ an energy gap opens immediately with related low temperature exponential behaviour of specific heat and thermal conductivity. This implies the extreme sensitivity of $s+g$-wave superconductivity to the presence of impurities. We hope that the present work will stimulate further experimental investigations in the multiphase superconductivity of skutterudite PrOs$_4$Sb$_{12}$.

The authors thank J. Goryo for useful discussions. K. Maki thanks the hospitality and support of Max-Planck-Institute for the Physics of Complex Systems where part of this work was performed. Q. Yuan acknowledges the partial support by the National Natural Science Foundation of China (Grant No. 19904007).
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