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Symmetry of Order Parameters in Multiband Superconductors $LaRu_4As_{12}$ and $PrOs_4Sb_{12}$ Probed by Local Magnetization Measurements

Abstract of doctoral dissertation

Nowadays, due to the extraordinary achievements in solid-state physics throughout the 20th century, we are witnessing a remarkable surge in the development of the information civilization. Cyberspace, ubiquitous digitization, global supply chains, and artificial intelligence are some of the aspects of these civilizational changes that require the processing of ever-increasing volumes of information. Looking ahead optimistically, it must be noted that the technological revolution not only contributes to improving the quality of life but also presents a range of new challenges, such as cybersecurity and the increasing global energy consumption. A solution to the exponential growth in computational power can be found in quantum computing. Topological superconductivity represents one of the main directions for realizing zero-energy Majorana modes, which hold enormous potential as units of information in quantum computers. Special attention is given to potential chiral superconductors − bulk topological materials with finite angular momentum Cooper pairs circulating around a unique chiral axis, thereby spontaneously breaking time-reversal symmetry.

One of the fundamentally important characteristics of a superconductor is the superfluid density ρ_s which temperature dependence $\rho_s(T)$ can be experimentally evaluated from the London penetration depth $\lambda(T)$. Alternatively, $\rho_s(T)$ can be obtained from measurements of the lower critical field $H_{c1}(T)$, because these quantities are mutually related with normalized temperature dependence of the superfluid density $\tilde{\rho}_s(T) = \rho_s(T)/\rho_s(0) = \lambda^2(0)/\lambda^2(T) \simeq H_{c1}(T)/H_{c1}(0)$. This means that precise measurements of $H_{c1}(T)$ can be a useful tool in determining the symmetry of the energy gap. In this doctoral dissertation, a method of measuring local magnetization based on Hall microsensors was used for determining the symmetry of the energy gaps in selected superconductors. For this purpose, Hall sensors with an active area of $40 \times 40\ \mu m^2$ and magnetic field sensitivity $0.86\ \Omega/mT$ were utilized. This minimizes the difficulties corresponding to distortion of the magnetic field at sample boundaries and allows for accurate measurements of the magnetic field in which the first vortex enters the sample [1]. Measurements of $H_{c1}(T)$ were carried out at the Laboratory of Low Temperature Physics in the ILTSR PAS in Wrocław. The miniaturized Hall sensors were implemented in the ^3He cryostat (T_{base} = 300 mK) [2] and in the dilution refrigerator ^3He–^4He (T_{base} = 160 mK) [3].

The focus of this thesis is to determine the symmetry of the energy gaps in two-band superconductors $PrOs_4Sb_{12}$ ($T_c \simeq 1.85$ K) [4] and $LaRu_4As_{12}$ ($T_c = 10.4$ K) [5]. These compounds belong to the family of filled skutterudites MT_4Pn_{12} (M = alkali metals, alkaline earth metals, lanthanides or light actinides, T = Fe, Ru or Os, Pn = P, As or Sb) which crystallize in the $LaFe_4P_{12}$-type structure with the space group $Im\overline{3}$ (No. 204). Superconductivity in MT_4Pn_{12} compounds has attracted considerable attention due to the observation of multiband effects and possible unconventional superconductivity, understood as a sign change in the energy gap. Multiband superconductivity is studied in the context of superconductivity with two *s*-wave gaps, as well as the case of two gaps with different symmetries. The most interesting of all filled skutterudites is the heavy-fermion superconductor $PrOs_4Sb_{12}$, which has been proposed as a promising candidate for a chiral superconductor [6]. An unconventional pairing symmetry of this first Pr-based heavy-fermion superconductor is suggested by a muon spin relaxation study and polar Kerr effect measurements which showed evidence for time-reversal symmetry breaking [7, 8]. Moreover, the evidence for multiband order parameters was found in the field dependences of the thermal conductivity, but conflicting results were obtained in the zero-temperature limit [9, 10]. Thus, after almost two decades of intensive research on $PrOs_4Sb_{12}$, the symmetry of the order parameter is still under debate. Evidence for two-band *s*-wave superconductivity was observed in the isostructural homologue $LaRu_4As_{12}$ with higher $T_c = 10.4$ K [5]. The close related compounds such as $PrRu_4As_{12}$ (T_c = 2.3 K) and $LaOs_4As_{12}$ (T_c = 3.2 K) has been recognized as conventional single-band superconductors. In the case of the latter compound, the literature data do not report the specific heat analysis, which was carried out in this dissertation. The obtained results were compared to previous data for a two-band superconductor $LaRu_4As_{12}$ [5]. A detailed analysis of the temperature dependence of the electronic specific heat showed a slight deviation from the single-band model, suggesting multiband superconductivity [11]. However, this discrepancy was resolved by the local magnetization studies, which unambiguously demonstrated $H_{c1}(T)$ single-band behavior predicted by the BCS theory [3].

All measurements of $H_{c1}(T)$ were performed on single crystals grown at the ILTSR PAS in Wrocław. The author synthetized single crystals of $PrOs_4Sb_{12}$, while As-based filled skutterudites, were obtained earlier by Professor Zygmunt Henkie. Following his original method, the author synthetized himself single crystals of novel compound $ThOs_4As_{12}$ [12]. The interest in this compound was related to the fact, that filling the $[Os_4As_{12}]^{4-}$ framework with a thorium atom could result in superconductivity, as it is reached for the related compound $ThPt_4Ge_{12}$ with $T_c \simeq 4.7$ K [13, 14]. Unfortunately, no signature of superconductivity in $ThOs_4As_{12}$ was found in ac magnetic susceptibility down to 0.08 K [12].

The results of local magnetization studies show anomalous temperature dependences of the lower critical field of $PrOs_4Sb_{12}$ and $LaRu_4As_{12}$, which were determined down to $\sim 0.03T_c$ and $\sim 0.08T_c$, respectively. The typical parabolic dependence of $H_{c1}(T)$, consistent with an isotropic *s*-wave single band behavior has been observed in sister compounds $PrRu_4As_{12}$ ($\sim 0.13T_c$) and $LaOs_4As_{12}$ ($\sim 0.09T_c$). Interestingly, the same $H_{c1}(T)$ characteristic was observed for $PrOs_4Sb_{12}$ and $LaRu_4As_{12}$ only at temperature above $0.3T_c$. When the temperatures decreases, $H_{c1}(T)$ data show a pronounced enhancement. The sudden enhancement of $H_{c1}(T)$ deep in the superconducting state indicate that $PrOs_4Sb_{12}$ and $LaRu_4As_{12}$ represent a rare case of a two-band superconductors with nearly decoupled bands. Remarkable that at $T < 0.3T_c$, these superconductors exhibit a qualitatively different $H_{c1}(T)$ behavior associated with different symmetries of smaller energy gap. While the $H_{c1}(T)$ behavior for $LaRu_4As_{12}$ is consistent with a fully gapped two-band *s*-wave superconducting state, for $PrOs_4Sb_{12}$ only the larger energy gap exhibits a conventional character, and the difference between the large and small gaps is in striking contrast. Indeed, for the heavy-fermion superconductor $PrOs_4Sb_{12}$, a quasilinear $H_{c1}(T)$ dependence was observed below 0.5 K, with no tendency to saturation even at the lowest temperature measured of T = 0.16 K. The $H_{c1}(T)$ characteristic obtained for $PrOs_4Sb_{12}$ provides strong evidence for a sign-changing nature of the smaller energy gap. In other words, on the example of the potential chiral superconductor $PrOs_4Sb_{12}$, it is shown that multi-band effects can result in the presence of non-trivial topological properties deep in the superconducting state.

References

1. K. R. Joshi, N.M. Nusran, M.A. Tanatar, Kyuil Cho, W.R. Meier, S.L. Bud'ko, P.C. Canfield, and R. Prozorov. Measuring the Lower Critical Field of Superconductors Using Nitrogen-Vacancy Centers in Diamond Optical Magnetometry. *Phys. Rev. Applied* 11, 014035 (2019).
2. **J. Juraszek**, R. Wawryk, Z. Henkie, M. Konczykowski, and T. Cichorek. Anomalous enhancement of the lower critical field deep in the superconducting state of $LaRu_4As_{12}$. *Phys. B: Condens. Matter* 536, 813 (2018).
3. **J. Juraszek**, R. Wawryk, Z. Henkie, M. Konczykowski, and T. Cichorek. Symmetry of Order Parameters in Multiband Superconductors $LaRu_4As_{12}$and $PrOs_4Sb_{12}$ Probed by Local Magnetization Measurements. *Phys. Rev. Lett.* 124, 027001 (2020).
4. E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple. Superconductivity and heavy fermion behavior in $PrOs_4Sb_{12}$. *Phys. Rev. B* 65, 100506(R) (2002).
5. L. Bochenek, R. Wawryk, Z. Henkie, and T. Cichorek. Evidence for multiple superconducting gaps in the filled skutterudite compound $LaRu_4As_{12}$. *Phys. Rev. B* 86, 060511(R) (2012).
6. E. M. Levenson-Falk, E. R. Schemm, Y. Aoki, M. B. Maple, and A. Kapitulnik. Polar Kerr Effect from Time-Reversal Symmetry Breaking in the Heavy-Fermion Superconductor $PrOs_4Sb_{12}$. *Phys. Rev. Lett. 120*, 187004 (2018).
7. Y. Aoki, A. Tsuchiya, T. Kanayama, S. R. Saha, H. Sugawara, H. Sato, W. Higemoto, A. Koda, K. Ohishi, K. Nishiyama, and R. Kadono. Time-Reversal Symmetry-Breaking Superconductivity in Heavy-Fermion $PrOs_4Sb_{12}$ Detected by Muon-Spin Relaxation. *Phys. Rev. Lett.* 91, 067003 (2003).
8. V. Kozii, J. W. F. Venderbos, and L. Fu. Three-dimensional Majorana fermions in chiral superconductors, *Sci. Adv*. 2, e1601835 (2016).

9. R. W. Hill, S. Li, M. B. Maple, and L. Taillefer. Multiband Order Parameters for the $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ Skutterudite Superconductors from Thermal Conductivity Measurements. *Phys. Rev. Lett.* 101, 237005 (2008).
10. G. Seyfarth, J. P. Brison, M.-A. Méasson, J. Flouquet, K. Izawa, Y. Matsuda, H. Sugawara, and H. Sato. Multiband Superconductivity in the Heavy Fermion Compound $PrOs_4Sb_{12}$. *Phys. Rev. Lett.* 95, 107004 (2005).
11. **J. Juraszek**, Z Henkie, and T. Cichorek. Specific heat of the filled skutterudite superconductor $LaOs_4As_{12}$. *Acta Phys. Pol. A* 130, 597 (2016).
12. **J. Juraszek**, K. Rola, M. Daszkiewicz, M. Samsel-Czekała, T. Cichorek, Z. Henkie. Crystal growth, low-temperature specific heat, and electronic structure of the filled skutterudite compound $ThOs_4As_{12}$. *Phil. Mag.* 100, 1355 (2020).
13. D. Kaczorowski and V. H. Tran, Superconductivity in the actinoid-bearing filled skutterudite $ThPt_4Ge_{12}$, *Phys. Rev. B* 77, 180504 (2008).
14. E. Bauer, X.-Q. Chen, P. Rogl, G. Hilscher, H. Michor, E. Royanian, R. Podloucky, G. Giester, O. Sologub, and A. P. Gonçalves. Superconductivity and spin fluctuations in Th,UPt_4Ge_{12} skutterudites, *Phys. Rev. B* 78, 064516 (2008).

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