Unconventional superconductivity in heavy fermion systems

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The research on heavy fermion superconductivity in our department focuses on materials in which superconductivity appears out of a normal state with strong electron-electron correlations. In such systems, multiple interactions with a small but similar energy scale are involved in determining the state of matter. Therefore, their physical properties can be easily changed by external perturbations such as strain, pressure or disorder. Studying the response of physical properties to external parameters provides a route to understand the underlying physics. With this motivation, our department has considerable expertise in characterizing materials at low temperatures and high magnetic fields while tuning these external perturbations. We also make consistent efforts to develop new materials which can serve as a platform for studying unconventional superconductivity. The main highlights of our recent research are (1) the systematic control of superconducting transition temperatures with local strain in $CeIrIn_5$, (2) the exploration of the phase diagram of CeFeAsO under hydrostatic pressure to reveal the relation between superconductivity and both Fe spin-density wave and Ce local magnetism, (3) the realization of intrinsic bulk superconductivity in YFe_2Ge_2 single crystals which is found to be highly sensitive to disorder, and (4) the discovery of a new heavy-fermion superconductor, $CeRh_2As_2$, which exhibits a field-driven phase transition between two distinct superconducting states, with evidencing for spin-triplet superconductivity at high fields.

Superconductivity in strongly correlated electron systems is widely believed to be unconventional with pairing mechanism differing from the conventional BCS (Bardeen–Cooper–Schrieffer) model. While in BCS superconductors the retarded attractive interactions between lattice ions and electrons act as the pairing glue, in strongly correlated superconductors repulsive interactions among electrons are believed to mediate the pairing, thus requiring strong modifications to the standard BCS picture. However, in most strongly correlated superconductors, both the pairing mechanism and the nature of the superconducting state are far from being settled.

Unconventional superconductivity usually appears in proximity to magnetism as widely seen in heavy-fermion Kondo-lattice systems, cuprates, and iron-based superconductors. In these systems, the spin, orbital, and lattice degrees of freedom are often intertwined to result in complex ordered states. The interplay between competing interactions with relatively low energy scales implies that properties of the materials can be easily changed by external perturbations such as pressure, strain, and disorder. Our research in the field of unconventional superconductivity exploits the possibility of measuring physical properties while tuning external control parameters in order to verify a suggested model or to explore new phases of matter.

We have studied the effect of strain as a control parameter in the tetragonal heavy-fermion metal $CeIrIn_5$. This is a strongly correlated electron system with a large Sommerfeld coefficient of 720 mJ/mol-K^2 corresponding to 30 times heavier effective mass than a bare electron. This results from the Kondo coupling between the localized Ce-4*f* moments and the spins of the itinerant electrons. Bulk superconductivity appears below the superconducting transition temperature T_c of 0.4 K, which is known to be highly sensitive to uniaxial strain: T_c increases under strain along the *a*-direction, and it decreases under compression along the *c*-direction. This implies that T_c can vary within a single crystal due to a non-uniform distribution of local strain caused by different thermal contractions of the sample and its substrate. A direct experimental observation of such spatial T_c distribution in an unconventional superconductor, however, has not been reported yet.

Our institute has expertise in focused ion beam (FIB) machining to carve crystals into a well-controlled shape in order to study anisotropic transport properties in a (sub-)micrometer length scale [1]. For a tailored shape of the $CeIrIn_5$ device, we simulated a local strain field induced by a boundary condition in which each corner of the square is pulled out through connected constrictions (the upper panels in Fig. 1). From the obtained strain field, we estimated a resultant T_c distribution. In a collaboration with a group at Cornell

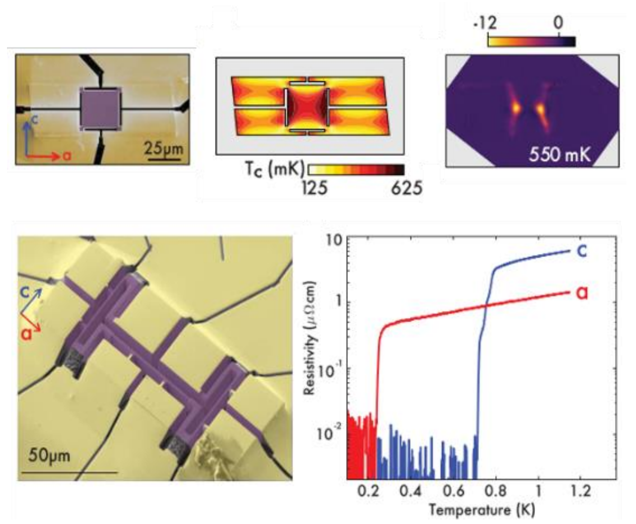

Fig. 1: (Upper panels) Scanning electron microscopy image of a $CeIrIn_5$ device, T_c map for the device from the finite element calculations, and local susceptibility image at 550 mK illustrating the premature superconductivity at the edges of the device. (Lower panels) SEM image of the device and the resistivity as a function of temperature along the a and c directions showing opposite evolution of T_c under local strain. (Figures taken from [1])

University, we adopted scanning superconducting quantum interference device (SQUID) microscopy (SSM) to image the diamagnetic response of the sample with micrometer-scale resolution. The results decisively revealed that the T_c distribution is indeed textured in accordance with the simulation results. The anisotropic transport studies confirm the SSM results and observe more than factor 4 modulation of T_c in different crystallographic directions (the lower panels in Fig. 1). This provides an answer to an open question about the origin of the commonly observed T_c discrepancy between thermodynamic and resistivity measurements. Moreover, quantum oscillation experiments, which are a probe of electronic structure at the Fermi level, were carried out on the device having the T_c distribution and provided similar results with a mesoscopic crystal. This indicates that a weak strain field which induces the significant change in T_c does not alter Fermi surface shape, suggesting that the Kondo hybridization of the 4*f* electrons varies without changes in the overall volume of the Fermi surface.

CeFeAsO is also an interesting and versatile system to study, as it combines the typical features of both iron-pnictide superconductors and Kondo-lattice systems. It exhibits a structural phase transition from a tetragonal to orthorhombic around 150 K. At a slightly lower temperature, itinerant iron moments form a commensurate spin-density wave (SDW). Below 3.7 K, the localized Ce-4*f* moments order antiferromagnetically. It has been known that upon substituting phosphorus for arsenic, the SDW transition is suppressed and superconductivity is induced. Furthermore, the phosphorous doping induces a switch from AFM to FM ordering of the Ce-moments at the same P-content where SC appears.

Similar modification of the system can be achieved by application of hydrostatic pressure without introducing additional chemical disorder. Therefore, we determined the phase diagram of CeFeAsO under hydrostatic pressure. The result is depicted in Fig. 2 [2]. Like the generic feature of iron-based superconductors, the SDW transition is suppressed and superconductivity emerges when the SDW transition disappears. On the other hand, the ordering of the Ce moments is gradually shifted to higher temperature by external pressure and suddenly disappears when superconductivity sets in. A further increase of pressure stabilizes a correlated metallic state with Kondo hybridization. This suggests that the emergence of superconductivity might also be connected with the suppression of 4*f* magnetic order and the onset of Kondo screening of the Ce-4*f* moments.

Over the last several years, we took part in optimizing the synthesis of a new type of iron-based superconductor: YFe_2Ge_2. In spite of having a similar type of crystalline structure as iron-based (oxy)pnictide and chalcogenide superconductors, the strongly three-dimensional electronic structures of YFe_2Ge_2 may suggest a different origin of the unconventional

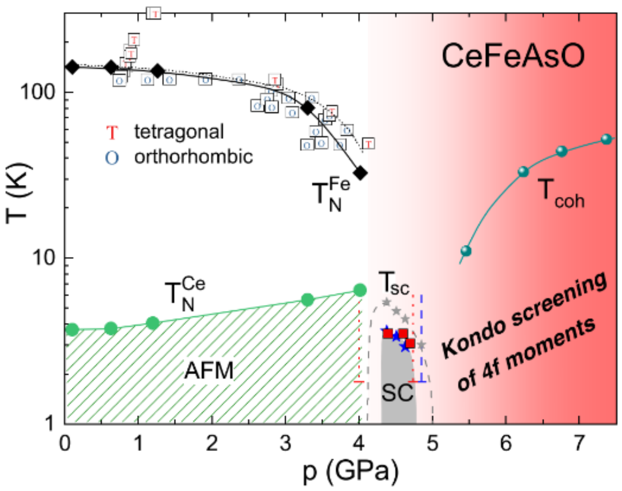

Fig. 2: Temperature-hydrostatic pressure phase diagram of CeFeAsO showing the SDW ordering temperature T_N^{FE}, the structural phase transition, the AFM ordering temperature of Ce moments T_N^{Ce}, and the SC transition temperature T_{SC}. T_{coh} is the Kondo-coherence temperature. The lines are guides to the eye. (Figure taken from [2])

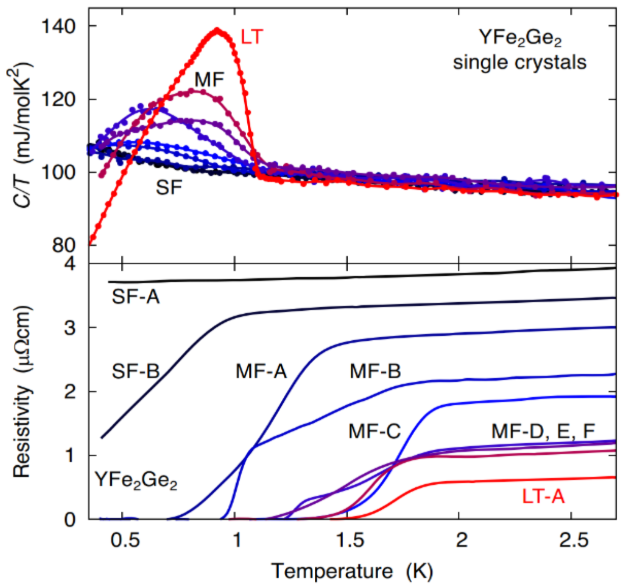

Fig. 3: The heat capacity C/T (upper panel) and electrical resistivity (lower panel) of YFe_2Ge_2 single crystals from different growth batches. SF - standard flux growth, MF - modified flux growth, LT - liquid transport growth. These samples show a wide variation in their heat capacity superconducting anomaly, resistive transition, and residual resistivity. Lower residual resistivities correlate with sharper superconducting heat capacity anomalies. (Figures taken from [3])

superconductivity. On the other hand, the enhanced Sommerfeld coefficient and the bad metal behavior at room temperature are reminiscent of heavily hole-doped iron-based superconductors AFe_2As_2 (A = K, Rb, and Cs), in which Hund's coupling within *d*-orbital electrons has been considered to be responsible for the unconventional behavior.

We contributed to this project by characterizing the low-temperature heat capacity of samples synthesized by a group of collaborators at Cambridge University. In earlier works, a specific-heat anomaly for the superconducting transition was absent or weak in polycrystalline and single crystals, leaving doubts about the bulk nature of superconductivity. After intense effort, the quality of single crystals as improved by introducing a tailored horizontal temperature gradient along the molten flux (liquid transport growth). The bulk superconductivity is revealed to be intrinsic in these higher quality samples. In addition, the process of the optimization enabled us to study the systematic change of physical properties with respect to the level of disorder, which can be considered here as our control parameter. We have characterized a series of crystals from different growth conditions. They were found to have different degrees of disorder parameterized by the absolute value of resistivity as shown in Fig. 3. We found that a sample with less disorder (lower resistivity) exhibits a higher T_c and a sharper transition in resistivity. And the corresponding specific-heat anomaly becomes more pronounced with a decrease of the residual specific-heat value within the superconducting phase. The sensitive response of the residual specific heat to disorder supports the proposal of a sign changing order parameter with impurity-induced states within the gap.

Finally, our continuous search for new unusual materials resulted in the discovery of a heavy-fermion superconductor with unique properties: $CeRh_2As_2$ [4]. This opens new opportunities for studying the combined effect of Kondo interaction and spin-orbit coupling, which is proposed to promote exotic superconducting states. While T_c is only 0.26 K, superconductivity is surprisingly robust against out-of-plane fields, for which we observe an upper critical field H_{c2} as high as 14 T. This large H_{c2} exceeds the Pauli limiting field (~ 1.84 T_c = 0.5 T) by more than one order of magnitude. In addition, we identified a phase transition line within the superconducting state, which is connected to an H_{c2} kink. For the in-plane field, the H_{c2} was determined to be 2 T, implying a highly anisotropic H_{c2}.

The large H_{c2} which exceeds the Pauli limiting field is reminiscent of the non-centrosymmetric heavy-fermion superconductors such as $CePt_3Si$. In this class of superconductors, the large H_{c2} is attributed to unusual pairing states from spin-textured electronic structures. Due to asymmetric spin-orbit couplings as a result of inversion symmetry breaking, spin states of the electrons are coupled to its crystal momentum. The Cooper pairs formed out of such electronic states were suggested to contain both even and odd-parity components. The robustness of superconductivity to the magnetic field is thus considered to be a signature of odd-parity superconductivity. The large H_{c2} and its anisotropic nature in $CeRh_2As_2$ can be also explained by similar arguments. The crystal structure of $CeRh_2As_2$ (space group P4/nmm) is globally centrosymmetric, but inversion symmetry is locally broken, especially at the relevant Ce-sites. Therefore, each Ce layer, which is at the core of heavy-fermion superconductivity, can be described as an effective non-centrosymmetric superconductor.

Furthermore, the unique crystal structure brings about even richer phenomena. As the unit cell contains an inversion pair of effective Ce layers, the superconducting order parameter can be arranged in

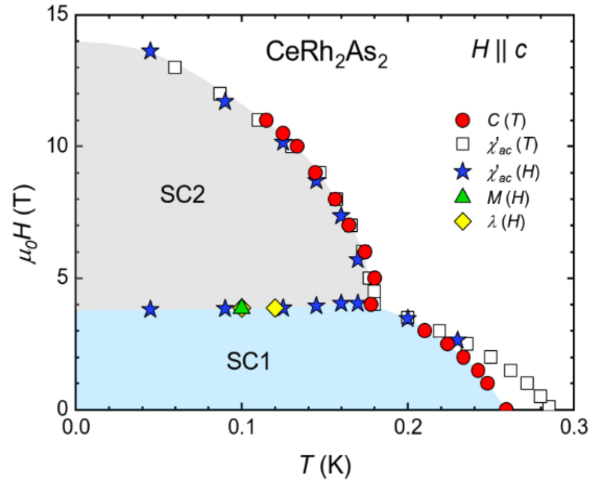

Fig. 4: Superconducting phase diagram of $CeRh_2As_2$ for field along the c-direction, determined by specific heat, ac-susceptibility, magnetization, and thermal expansion experiments. The clear phase boundary at $\mu_0 H$ = 4 T in the superconducting state, which is connected to a kink in H_{c2}, demonstrates a transition between two distinct superconducting states. We suggest it is a field-induced transition from a low field (SC1) even-parity state to a high field (SC2) odd-parity SC state. (Figure taken from [4])

two different ways; the even-parity state where the sign of the order parameter is the same in both sublayers, and the odd-parity state where the sign is opposite. This odd-parity state is equivalent to a spin-triplet pairing state. Under magnetic fields, the even-parity state gets suppressed because of the pair breaking in the spin channel. On the other hand, the odd-parity state is immune to the pair breaking due to the spin-triplet configuration and thus energetically favored in high fields. Thus, under appropriate conditions a field-induced transition from the even to odd-parity state is expected [4]. We indeed observe very clear anomalies e.g. in the ac-susceptibility, which demonstrate such a transition from one SC to another SC state at a field of 4 T along the *c*-direction (Fig. 4) (https://www1.cpfs.mpg.de:2443/MPRG_01). We could reproduce this phase diagram with two different SC states in a simplified model set up within a collaboration with a theory group at the University of Wisconsin. We suggest that $CeRh_2As_2$ is the first example of multiple superconducting phases driven by spin-orbit coupling.

Additional features remain to be clarified. We observed signatures of a phase transition above T_c, which is speculated to be connected with ordering of multipolar Ce-4*f* moments. As the multipolar moments are sensitively influenced by external fields, a complex magnetic field - temperature phase diagram could occur. At the same time, this system might be close to an unconventional quantum critical point, a possibility suggested by the observed power-law increase of specific heat at low temperatures.

In order to investigate this highly interesting superconducting state in depth, we have already established international collaborations with experts in nuclear magnetic resonance (NMR) spectroscopy, muon spin resonance spectroscopy, superconducting magnetic penetration depth, and scanning tunneling microscope techniques.

External Cooperation Partners

K. Ishida (Kyoto); T. Shibauchi (University of Tokyo, Japan); Z. Guguchia, R. Scheuermann (PSI, Swiss); G. Zwicknagl (TU Braunschweig, Germany); D. Vyalikh (TU Dresden, Germany); D. Agterberg (University of Wisconsin, USA); M. Grosch (University of Cambridge, UK); P. Wahl (St. Andrews, UK); K. C. Nowack (Cornell University, USA).

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