The Superconductivity of $CeRh_2As_2$ and Related Materials

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Our department has been searching for new material systems that host peculiar emergent phenomena arising from strong electronic correlations. In this report, we present our recent discovery of a new unconventional superconductor $CeRh_2As_2$. Most intriguingly, the unique structural motif, an inversion pair of two Ce in the unit cell, gives rise to multiphase superconductivity characterized by a field-induced transition from an even-parity low-field state to an odd-parity high-field state. This is the first experimental realization of theoretical predictions that sublattice degrees of freedom and associated spin-orbit coupling can lead to the exotic superconducting pairing states. Furthermore, we show that this Kondo-lattice system demonstrates an unusual order of the Ce-4*f* moments, which is thought to be responsible for the strange metal behavior. Studies of local magnetism provide compelling evidence that this unusual order microscopically coexists with heavy-fermion superconductivity. Hence, $CeRh_2As_2$ is a versatile platform to study a complex interplay between unconventional superconductivity, higher-order Ce-4*f* moments, and quantum criticality together with strong spin-orbit coupling. This motivates us to further explore material systems in which local structural symmetry at the site of key elements is lower than global symmetry.

In conventional superconductors, electrons forming a Cooper pair are described as having opposite spins, namely as spin-singlet symmetry of the wave function in the spin part, and isotropic *s*-wave symmetry in the spatial part. Unconventional superconductivity, with a non-phononic pairing origin or a nontrivial topological nature, is signaled when the superconducting (SC) wave function has a significant spatial modulation or deviates from the spin-singlet symmetry. In particular, one possible way to realize an unconventional spin state is to build up superconductivity from spin-polarized electronic states involving magnetic interactions or strong spin-orbit coupling. The latter can be obtained by applying an external electric field or by breaking inversion symmetry, where an asymmetric electric potential introduces a relativistic magnetic field for the moving electron. This situation is mainly considered at the interface of different phases or in noncentrosymmetric material systems where inversion symmetry is broken globally. Hence, few-layer material devices, artificial heterostructures or noncentrosymmetric crystalline systems have been studied for elucidating the effect of spin-orbit coupling on superconductivity.

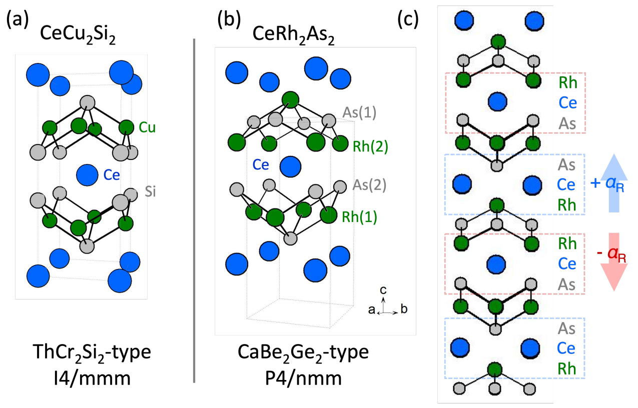

Fig. 1: Crystal structure of (a) $CeCu_2Si_2$ and (b) $CeRh_2As_2$ in the $ThCr_2Si_2$- and $CaBe_2Ge_2$-type structure, respectively. (c) The a-axis view of the $CeRh_2As_2$ structure depicts the two sublayers in the unit cell, which have an opposite electric field gradient (or resultant Rashba field α_R).

Local inversion symmetry breaking in a centrosymmetric crystal

Alternatively, we consider a material system that lacks local inversion symmetry while it remains globally centrosymmetric. The title compound $CeRh_2As_2$ crystallizes in the $CaBe_2Ge_2$-type crystal structure. This is an isomorph of the $ThCr_2Si_2$-type structure, which is well known for the first heavy-fermion superconductor $CeCu_2Si_2$ and the parent compound of iron-based superconductors $BaFe_2As_2$. Figure 1 compares the crystal structures of $CeCu_2Si_2$ and $CeRh_2As_2$. In $CeRh_2As_2$, there are two inequivalent Rh and As sites consisting of two different layers in the unit cell: the Rh and As sites are completely exchanged between two layers, breaking local inversion symmetry on the Ce site, whereas in $CeCu_2Si_2$ the two Cu-Si layers are identical. Since the inversion center is not on the Ce site, the unit cell can be described as containing two Ce sublayer blocks, which have an alternating local asymmetric electric potential while the electric potential is canceled out in the unit cell. If the electronic structure has a strongly localized character coupled to each block layer, we can expect Rashba-type spin-orbit coupling as in a noncentrosymmetric system, and its staggered nature could lead to richer properties. This motivated us to study $CeRh_2As_2$ whose low-temperature properties had not been determined until recently. We successfully synthesized single crystals of $CeRh_2As_2$ and our in-depth investigations reveal that superconductivity behaves in a highly unusual way under external fields. This indicates a manifestation of spin-orbit coupling due to local inversion symmetry breaking.

Heavy-fermion superconductivity near quantum critical point

We found that $CeRh_2As_2$ is a Kondo-lattice heavy-fermion superconductor with strong electronic correlations [1]. The bulk superconducting (SC) transition was identified in resistivity, magnetization, ultrasound, thermal expansion, and heat capacity measurements. As shown in Fig. 2a, the transition temperature T_c, defined by the onset of the heat capacity jump is 0.35 K. The enhanced heat capacity ($C/T \sim 1$ J/mol-K^2) clearly indicates that the itinerant electrons have Ce-4f-moment degrees of freedom through Kondo hybridization. A power-law increase of C/T with decreasing temperature between 2 K and 0.6 K clearly deviates from the Fermi-liquid behavior. This strange-metal character suggests strong electronic correlations near a quantum critical point associated with the unconventional nature of superconductivity. Furthermore, an additional anomaly at $T_0 \sim 0.55$ K is seen as an upturn in the resistivity and a hump in the heat capacity. The behavior of the T_0 transition is not consistent with conventional antiferromagnetic ordering, which will be explained later.

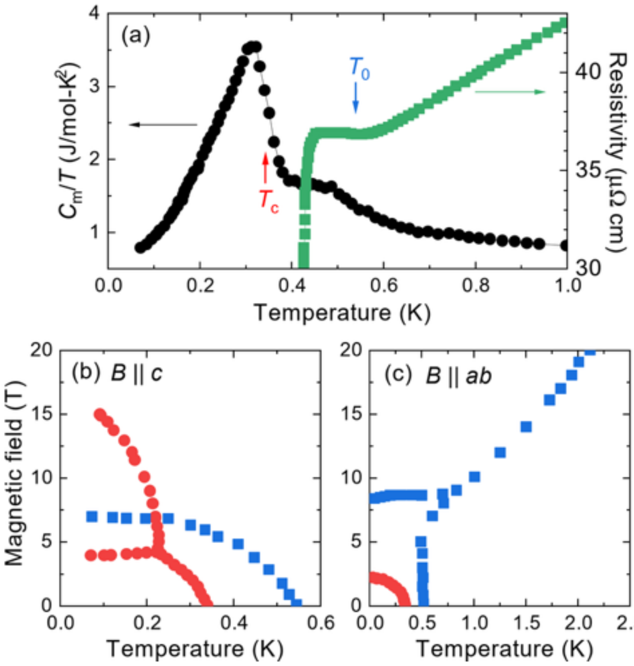

Fig. 2: (a) Temperature dependence of magnetic contribution of heat capacity (C_m/T) of $CeRh_2As_2$. Magnetic field (B) – temperature (T) phase diagrams for (b) the c-axis and (c) in-plane field, respectively. The SC phase diagrams are drawn by ac-magnetic susceptibility. The unknown low- and high-field states for the T_0 anomaly determined in thermal expansion (magnetostriction) measurements are labeled as UO1 and UO2, respectively.

Multiphase superconducting state driven by sublattice degrees of freedom

The response of the SC state to an external field is highly anisotropic. The SC state is completely suppressed at around 2 T for the in-plane field ($B \parallel ab$) (Fig. 2c). Pauli paramagnetic pair breaking, where the spin-polarized paramagnetic state is favored over the spin-singlet state, is the dominant mechanism determining the upper critical field H_{c2}. In contrast, for the c-axis field ($B \parallel c$), the SC state survives up to 16 T, violating the paramagnetic pair breaking (Fig. 2b). Furthermore, a phase transition within the zero-resistance SC state appears to be almost temperature independent at ~ 4 T, separating the SC state into two distinct phases. H_{c2} for $B \parallel c$ is rapidly suppressed in the low-field state (SC1) as for $B \parallel ab$, reflecting the spin-paramagnetic pair breaking of a spin-singlet state. The high-field state (SC2), on the other hand, is robust to the external field and H_{c2} is mainly determined by the orbital pair-breaking effect. The distinct behavior of H_{c2} reasonably suggests that each state is an even-parity and an odd-parity state, respectively. This type of multiphase superconductivity has been predicted in a multilayer superconductor, where inversion symmetry is locally broken at the interface. The crystal structure of $CeRh_2As_2$, in which the two sublayers in the unit cell, introduces an opposite direction of asymmetric potential and staggered Rashba spin-orbit coupling. This provides an additional sublattice degree of freedom for the SC order parameter, which should be purely an even- or an odd-parity state due to global inversion symmetry. Thus, the two-phase superconductivity consists of the SC1 state, where the SC order parameter has the same sign in the sublayers (even-parity state), while the SC2 state has an alternating sign of the SC order parameter (odd-parity state) that is energetically favored above 4 T. This scenario is also supported by careful angle-dependent measurements which examined the evolution of the phase diagram from the c-axis field to the in-plane field [3] (see also Status Report section 1.10).

Unknown Ce-4f moment order coexisting with superconductivity

The magnetic phase diagrams for the T_0 transition are also highly anisotropic, as shown in Fig. 2b and c [2, 4].

For $B \parallel c$, T_0 is monotonically decreased with increasing field and the corresponding anomalies could be detected even within the SC state, suggesting that this T_0 phase (UO1) still exists in the SC2 state. On the other hand, T_0 is enhanced for $B \parallel ab$ and a field-induced phase (UO2) appears above ~ 8 T. The T_0 phase diagram fo $B \parallel ab$ is clearly different from the conventional behavior of antiferromagnetic (AFM) ordering in Ce-based heavy-fermion systems where an AFM order is suppressed with field. This leads us to look for an alternative scenario for the T_0 state. The crystal electric field (CEF) level scheme of the localized Ce is determined to have two low-lying Kramers doublets that are closely located and their separation is comparable to the Kondo energy scale. This potentially allows for quadrupolar degrees of freedom, which is typically forbidden in the Ce-based tetragonal system. Accordingly, we have proposed a quadrupolar density wave (QDW) state in which the higher-order moments form itinerant order due to the Fermi surface nesting [2, 4]. This also implies that the strange metal behavior, which is considered to be originated from quantum fluctuations associated with a neighboring order, could be of an unusual nature. Further discussion of the QDW state for the T_0 order in conjunction with the unique CEF will be presented in report **PQM_05_Brando** and Status Report **section 1.10**.

Evidence of coexisting magnetic order with superconductivity

To clarify the nature of the superconducting phases and the T_0 order, we have studied local magnetism by means of nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) in a close collaboration with the group in Kyoto, Japan. [5, 6, 7]. Regarding the SC state, we observed a finite reduction of the Knight shift in both the SC1 and SC2 states, pointing to a spin-singlet pairing state [7]. While this result may be unexpected for the SC2 odd-parity state, it is still possible to realize an odd-parity state from a singlet pairing. For instance, superconductivity in each sublayer is mediated by a spin-singlet pairing while the SC order parameter is opposite to each other. This description is consistent with the theoretical prediction that the combination of sublattice degrees of freedom and spin-siglet pairing on each sublayer realizes a pseudo-spin triplet state. Furthermore, NQR measurements revealed a signature of magnetic order by observing line broadening selectively for the less symmetric As(2) site (Fig. 1b) [5]. Further NMR studies revealed that this signal is present only in the SC1 state, suggesting the phase diagram as shown in Fig. 3 [7]. Independently, our group has performed muon spin resonance (μSR) experiments and identified clear evidence of magnetic order in the T_0 phase, and this magnetic order microscopically coexists with superconductivity [8]. The discrepancy between two independent local magnetic probes may be related to the different probing timescale. In spite of that, both experimental works commonly identify a magnetic phase coexisting with superconductivity. This is in line with the phase diagram determined by thermodynamic probes as the T_0 continues within the SC state (Fig. 2b).

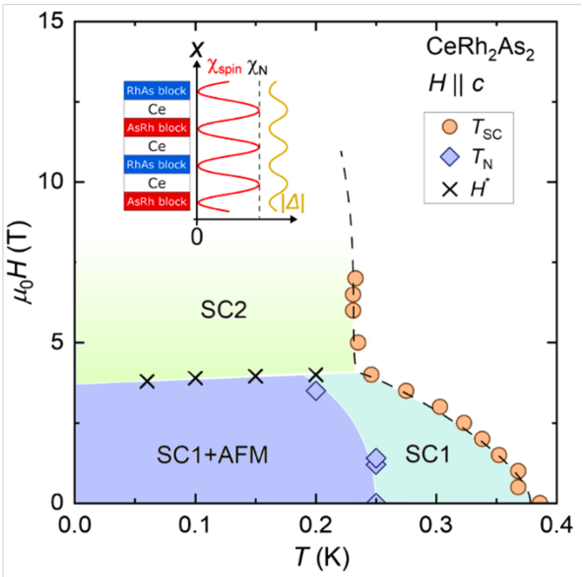

Fig. 3: Phase diagrams of CeRh$_2$As$_2$ for $B \parallel c$ determined by ^{75}As-NQR and NMR measurements [5, 7]. The signature of magnetic order presents only within the SC1 state. The inset exhibits a schematic picture that describes a modulating superconducting order parameter and concomitant SC spin susceptibility.

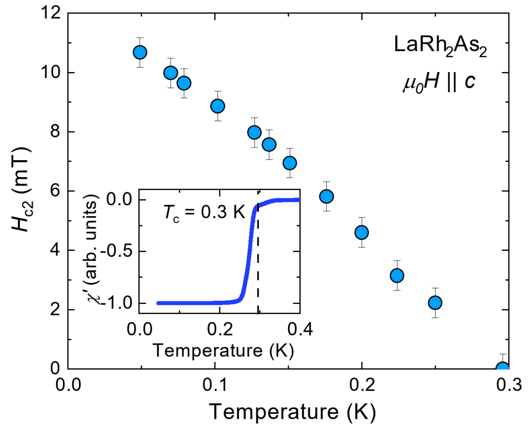

Fig. 4: H_{c2} of LaRh$_2$As$_2$ for $B \parallel c$ determined by ac susceptibilty (χ') measurements. The inset shows the temperature dependence of χ', which exhibits the onset of a diamagnetic signal below 0.3 K.

Exploring further related materials lacking local inversion symmetry

We have also investigated the nonmagnetic counterpart $LaRh_2As_2$ compound. This compound is a conventional superconductor and Tc of 0.3 K is similar to that of $CeRh_2As_2$ [9]. As shown in Fig. 4, the superconducting phase diagram demonstrates a conventional behavior with a low H_{c2} of ~ 10 mT. These results reflect that local inversion symmetry breaking is not a sufficient ingredient for the multiphase superconductivity and emphasize the important role of the Ce-4f heavy-fermion nature. Nevertheless, studies of material systems are not necessarily limited to the Ce compounds. Other 4f magnetic compounds in this structure could be a promising platform to investigate an impact of local inversion symmetry via the Dzyaloshinskii-Moriya (DM) interaction.

In addition to the $CaBe_2Ge_2$-type structure, we also explore other material systems that lack local inversion symmetry. Here we briefly introduce a new heavy-fermion compound $Ce_2Ir_3Ga_5$ in the centrosymmetric $U_2Co_3Si_5$-type structure (orthorhombic, space group Ibam) [10]. As shown in Fig. 5a, the Ce sites are surrounded by the Ir-Ga cage and are not located at the inversion center. A moderate heavy-fermion nature is identified by the clear Kondo coherence peak at ~ 40 K and the enhanced heat capacity of C/T ~ 150 mJ/mol-K^2 (Fig. 5b). We found a weak signature of a transition at 2.7 K, the origin of which remains to be investigated.

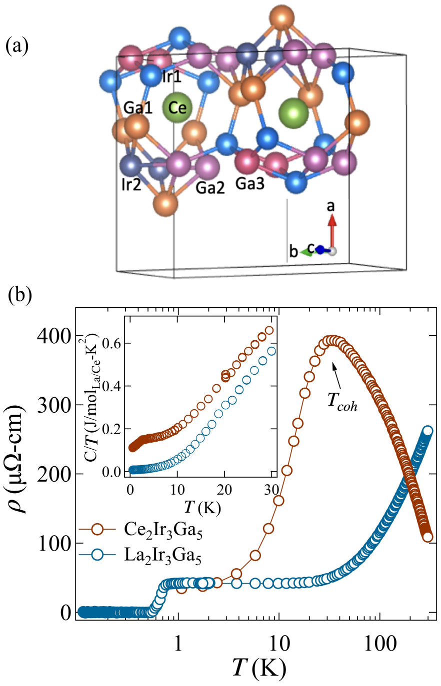

Fig. 5: (a) Crystal structure of $Ce_2Ir_3Ga_5$. (b) Temperature dependence of resistivity and heat capacity C/T (inset) of the Ce and La compounds.

External Cooperation Partners

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