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Evidence for multiple superconducting gaps in the filled skutterudite compound $LaRu_4As_{12}$

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Superconducting properties of the filled skutterudite compound $LaRu_4As_{12}$ were investigated both as a function of temperature and magnetic field. At $T \ll T_c = 10.45$ K, the electronic contribution to the specific heat was found to be at variance with the predictions for an s-wave superconductor with one energy gap. In constant applied fields up to $H_{c2}(0) \approx 10.2$ T, multiple gaps have been further inferred from both a nonlinear magnetic-field dependence of the specific heat in the zero-temperature limit and a positive curvature of the upper critical field in the vicinity of T_c. Thus, $LaRu_4As_{12}$ appears to be a rare multiple-gap superconductor with cubic symmetry. Intriguing evidence for multiband effects is observed in the compound with enhanced superconducting properties as compared to other skutterudite superconductors.

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Shortly after the first announcement of the microscopic theory of superconductivity by Bardeen, Cooper, and Schrieffer (BCS),[1] it was pointed out that substantial interband scattering in systems with a complex electronic band structure can give rise to multiband superconductivity (MBSC).[2,3] It is noticeable that certain extensions of the multiband model predict an enhancement of the critical temperature T_c.[4] So far, the hexagonal MgB_2 with an unexpectedly high $T_c \approx 39$ K is the best experimentally characterized two-band superconductor with a large gap residing on the two-dimensional cylindrical sheets and a small gap on the three-dimensional tubular network.[5] Intriguingly, other convincing examples of MBSC were only found in layered materials with a strongly anisotropic Fermi surface (FS) such as, e.g., $NbSe_2$,[6] nonmagnetic borocarbides,[7,8] $Lu_2Fe_3Si_5$,[9] and iron pnictides and chalcogenides.[10,11]

In certain multiband superconductors with cubic symmetry, distinct superconducting gaps may reside on different sheets of a weakly anisotropic Fermi surface. Such a situation most likely coincides with an exotic pairing mechanism in the heavy-fermion superconductor $PrOs_4Sb_{12}$, as inferred from thermal-conductivity measurements in varying magnetic fields.[12,13] [While there are some claims for the observation of MBSC in its isostructural counterpart $PrRu_4Sb_{12}$,[13] more detailed studies are required on this fully gapped superconductor with an upper critical field $H_{c2}(0)$ that is as small as 0.2 T.] These observations indicate a rare opportunity to investigate multiband effects in superconductors with cubic symmetry. Indeed, the crystal structure of the filled skutterudite compounds MT_4X_{12} is composed of rigid covalently bonded cage-forming frameworks T_4X_{12} enclosing differently bonded guest atoms M, where M is an electropositive cation, T is a transition metal of the ninth group, and X is a pnictogen (P, As, or Sb). As a consequence, the large FS sheet occurs at the Γ point of the Brillouin zone. Whereas this slightly distorted cube is mainly formed by the X-p electrons, its details depend on an overlapping of X-p and T-d orbitals. It is noteworthy that, in some MT_4X_{12} compounds, T-d electrons were found to additionally contribute to the Fermi surface as a nearly spherical sheet.[14]

Here, we focus on the superconducting properties of the non-f-electron filled skutterudite compound $LaRu_4As_{12}$.[15,16] We take advantage of its high $T_c = 10.45$ K and $H_{c2}(0) \approx 10.2$ T, which enable investigations in a wide range of temperatures and magnetic fields. In particular, we found the nonlinear magnetic-field dependence of the specific heat in the limit $T \to 0$ K. Thus, for the cubic s-wave superconductor $LaRu_4As_{12}$, we observe a generic feature of layered multiband superconductors. Intriguingly, evidence for multiband order parameters is found in the material with enhanced superconducting properties as compared to other skutterudite superconductors.

High-purity single crystals of $LaRu_4As_{12}$ with dimensions up to 0.8 mm were grown by mineralization in a molten Cd:As flux utilizing a technique detailed elsewhere.[17] The electrical resistivity of a $LaRu_4As_{12}$ single crystal was investigated by a conventional four-point ac technique in zero and applied magnetic fields up to 14 T using a ^{4}He cryostat and a ^{3}H-^{4}He dilution refrigerator above and below 2 K, respectively. For the same specimen, thermoelectric power was measured in the whole temperature range. Specific heat for a collection of nine crystals with a total mass $m = 9.5(1)$ mg was determined with the aid of the thermal-relaxation method utilizing a commercial ^{3}He microcalorimeter (PPMS). Magnetic measurements for a different group of crystals were performed for $1.8 \leqslant T \leqslant 16$ K and $H = 30$ G s using a superconducting quantum interference device magnetometer (MPMS).

The temperature dependence of the thermoelectric power $S(T)$ for a $LaRu_4As_{12}$ single crystal is illustrated in Fig. 1. A positive and somewhat enhanced thermopower significantly deviates from a linear behavior, which is expected for a diffusive term in a one-band metal. In fact, a change of the slope of $S(T)$ at $T \approx 140$ K and a resultant convex T dependence resemble a multiband metal with substantial interband scattering. We emphasize that the interband scattering was recently concluded from a detailed analysis of the electrical resistivity $\rho(T)$ data (cf. Fig. 4 in Ref. 18 and the corresponding discussion therein), which are very similar to the previously reported results for polycrystalline samples.[16] This holds especially true for an impact of an interband $\propto T^3$ Mott term on $\rho(T)$ at $T \gtrsim 150$ K. On the other hand, the higher quality of our single-crystalline $LaRu_4As_{12}$ specimens is highlighted by (i) a smaller residual resistivity $\rho_0 = 1.54$ $\mu\Omega$ cm, which is consistent with a charge carrier mean free path $l \approx 250$ Å,[19]

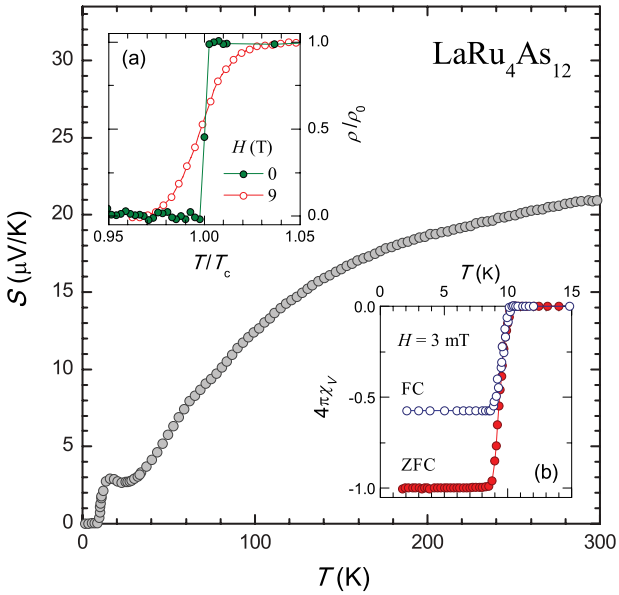

FIG. 1. (Color online) Temperature dependence of the thermoelectric power for a $LaRu_4As_{12}$ single crystal. (a) Normalized electrical resistivity in the vicinity of the superconducting transition in zero magnetic field and in $H = 9$ T. (b) Zero-field-cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature for a collection of $LaRu_4As_{12}$ single crystals.

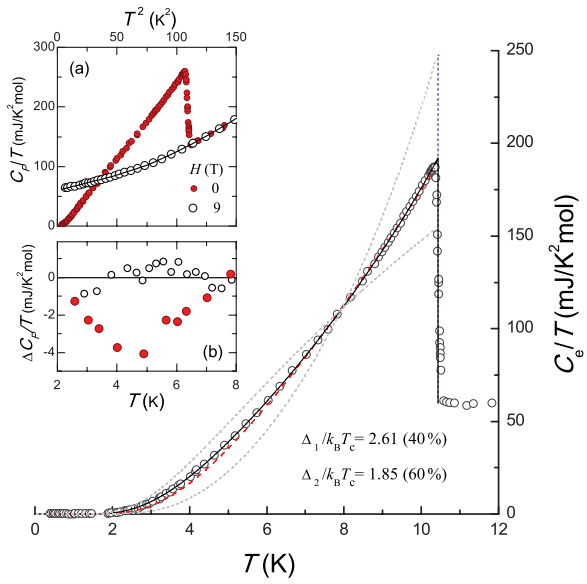

FIG. 2. (Color online) Low-temperature electronic specific heat of $LaRu_4As_{12}$. The dashed red curve is the result of the one-gap $\alpha = 2.18$ model. The solid line is a fit to the two-gap α model with the partial contribution represented by the two bands (dotted lines). (a) The low-T specific heat in zero magnetic field and in $H = 9$ T, as C_p/T vs T^2. The solid line represents a fit as described in the text. (b) Comparison of the residuals of the phonon fit (open circles) with the residuals of the single gap fit (solid circles) to the derived electronic specific heat.

(ii) a larger residual resistivity ratio $r_R = 198$, (iii) slightly enhanced values of $T_c = 10.45$ K and $H_{c2}(0) \approx 10.2$ T, and (iv) an extraordinarily narrow superconducting transition width $\Delta T_c = 0.03$ K estimated from the 10%–90% criterion. Also remarkable is the persistence of the sharp transition ($\Delta T_c/T_c = 0.043$) in large magnetic fields, as shown in Fig. 1(a) (inset).

In order to determine the Meissner volume in the $LaRu_4As_{12}$ samples investigated, magnetization experiments were performed. Figure 1(b) (inset) displays the zero-field-cooled (ZFC) and field-cooled (FC) magnetization data. When we assume the ZFC data to show the complete diamagnetic shielding below $T_c = 10.45$ K, we conclude from the FC results that about 57% volume of the sample was in the Meissner-Ochsenfeld state at these temperatures.

Careful microcalorimetric measurements additionally indicate a high purity of our $LaRu_4As_{12}$ single crystals. Indeed, an enormously sharp jump in the specific heat C_p was observed at $T_c = 10.42$ K, whose value (estimated from an equal-entropy construction) is found to be fully consistent with the value obtained from the $\rho(T)$ experiments. Additionally, the residual electronic specific heat as small as 0.1 mJ mol^{-1} K^{-1} at $T = 1$ K indicates that as little as 0.17% of conduction electrons do not form Cooper pairs in $LaRu_4As_{12}$.

Having established that impurity-induced pair-breaking effects are negligible in our specimens, we now analyze the nature of a superconducting state in $LaRu_4As_{12}$. Figure 2 shows the low-T electronic specific heat $C_e = C_p - C_{ph}$, where C_{ph} is the phonon contribution whose temperature dependence was estimated from the normal-state $H = 9$ T data (the inset of Fig. 2), yielding the Debye temperature $\Theta_D = 388(3)$ K and the Einstein temperature $\Theta_E = 98(2)$ K, in good agreement with previous estimates.[20] The γ_n coefficient was found to be 59.0 mJ mol^{-1} K^{-2}, i.e., slightly larger than that obtained for a polycrystalline sample.[16] A salient feature of $LaRu_4As_{12}$ is a large value of $\Delta C_e/\gamma_n T_c = 2.26$. This clearly shows an electron-phonon coupling that is significantly stronger than in the BCS theory (=1.426). Strong coupling is further corroborated by comparing the zero-field C_e data with the one-gap α model,[21] giving an energy gap ratio $\Delta/k_B T_c$ of 2.18 (1.764 in the BCS theory). Whereas the one-gap α model correctly describes $C_e(T)$ near T_c, its failure is evident at $T \lesssim 6$K (cf. dashed line in Fig. 2). Therefore, we have fitted the $C_e(T)$ data to the phenomenological two-gap α model. As shown by the solid line, $C_e(T)$ for $T \leqslant T_c$ is well reproduced by assuming two different gaps $\Delta_1/k_B T_c = 2.61$ and $\Delta_2/k_B T_c = 1.85$, with 40% and 60% in relative weight, respectively. Note that a similar analysis was previously applied to other multiband superconductors,[9,22] in particular to nonmagnetic borocarbides[8] and iron chalcogenides[11] whose two-gap corrections in the specific heat are of a similar size to this found for $LaRu_4As_{12}$.

The thermodynamic critical field $H_c(T)$ can be estimated from the free-energy difference between the normal and superconducting state $\Delta F(T) = \mu_0 V_m H_c^2(T)/2$, where $V_m = 1.86 \times 10^{-4}$ m^3 mol^{-1} is the molar volume. Since we obtained $H_c(0) \approx 0.1$ T, giving $H_{c2}(0)/H_c(0) \approx 100$, a magnetic-field dependence of the electronic specific-heat coefficient, i.e., $\gamma(H) \equiv \lim_{T\to 0} C_p(T,H)/T$, can be investigated in the wide range of a linear-in-H increase of the magnetic flux density. The normalized results are presented in Fig. 3 as γ/γ_n vs $H/H_{c2}(0)$. For $LaRu_4As_{12}$, we found a nonlinear $\gamma(H)$ behavior that strictly follows a $H^{0.65}$ dependence up to

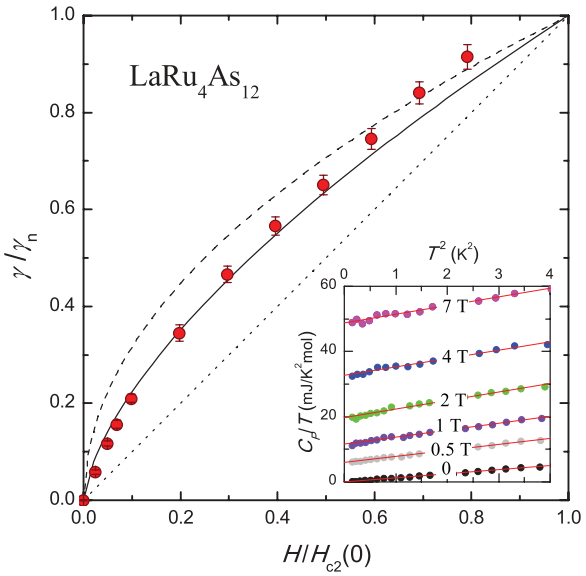

FIG. 3. (Color online) Normalized magnetic-field dependence of the electronic specific-heat coefficient for a strong coupling $LaRu_4As_{12}$ superconductor crystallizing in the bcc structure. The dashed and dotted lines represent the $\gamma(H)$ dependences predicted for the isotropic s-wave and nodal d-wave superconductors, respectively. The solid line is a fit to the nonlinear H^q dependence with $q = 0.65$. Inset: Specific heat of $LaRu_4As_{12}$ in selected magnetic fields, plotted as $C_p(T)/T$ vs T^2. For each applied field, $\gamma(H) \equiv \lim_{T\to 0} C_p(T,H)/T$ was determined from a linear extrapolation of the experimental data obtained in the temperature range 0.37–2 K.

$H \approx 5$ T. Upon approaching $H_{c2}(0)$, some deviations from the $H^{0.65}$ behavior were observed.

In a type-II s-wave superconductor, the number of vortices is directly proportional to the externally applied magnetic field. As a consequence, a linear increase of γ with $H \gtrsim H_c(0)$ is expected because each vortex consists of a region of a circulating supercurrent around a small central core that has essentially normal-state properties (dotted line in Fig. 3). In striking contrast to this conventional expectation are observations of $\gamma(H) \propto H^q$ with $0.5 \lesssim q < 1$ done for various superconductors with multiband order parameters. For compounds such as, e.g., MgB_2,[23] $NbSe_2$,[6] and YNi_2B_2C,[8] the nonlinear $\gamma(H)$ dependence was detected. For experimental reasons, similar investigations are usually limited to $H/H_{c2}(0) \lesssim 0.2$ for iron pnictides and iron chalcogenides.[10,11] On the other hand, a highly anisotropic gap may also cause the nonlinear behavior of $\gamma(H)$. For example, an exponent $q = 0.5$ and 0.7 is predicted for a d-wave paring and an anisotropic s-wave superconductor with the cylindrical Fermi surface, respectively.[24] Since fully gapped superconductivity in $LaRu_4As_{12}$ is inferred from the negligibly small residual electronic specific heat, the $\gamma(H) \propto H^{0.65}$ behavior points at either multiple superconducting gaps or a strong anisotropy of a single energy gap. Typically, the latter effect is related to a complexity of the entire Fermi surface which leads to a remarkable anisotropy of, e.g., the Fermi velocity or/and the electron phonon coupling. As stated below, a weakly anisotropic Fermi surface is anticipated for $LaRu_4As_{12}$ and hence its nonlinear $\gamma(H)$ dependence favors MBSC over a more generic scenario of the anisotropic gap.

For various LaT_4X_{12} skutterudites, oscillations of the magnetization reveal the large multiply connected FS sheet centered at the Γ point of the Brillouin zone and formed by the upper conduction band mainly consisting of the X-p electrons. Its shape is a slightly distorted cube whose details depend on an overlapping of X-p and T-d orbitals. However, a contribution of T-d electrons to the FS is dissimilar in different LaT_4X_{12} systems. For example, in superconducting $LaOs_4As_{12}$ with $T_c = 3.2$ K, the lower band crossing the Fermi level is formed by Os-d electrons and contributes as a nearly spherical sheet centered at the Γ point.[14] In contrast, theoretically predicted two small FS spheres formed by Ru-d electrons were not experimentally observed in a moderate-coupling and isotropic s-wave $LaRu_4P_{12}$ superconductor with $T_c = 7.3$ K.[25]

In Fig. 4 the H-T phase diagram of $LaRu_4As_{12}$ as determined from the $\rho(T)$ measurements is presented. This set of $H_{c2}(T)$ data, supplemented by the $C_p(T)$ results obtained on very different samples, clearly points at a minute anisotropy. Weak anisotropy is further corroborated from isothermal $\rho(H)$ measurements for H rotating in a transverse arrangement to the electrical current flowing along the [100] direction. Indeed, the angular dependence of H_{c2} observed deep in the superconducting state varies less than 4%, as shown in the inset of Fig. 4. More importantly, however, upon lowering temperature below around $0.85T_c \approx 9$ K and down to about 1.5 K, the upper critical field increases quasilinearly with the slope $(-dH_{c2}/dT) = 1.17$ T/K, i.e., significantly faster than in the vicinity of T_c where $(-dH_{c2}/dT)_{T_c} = 0.66$ T/K

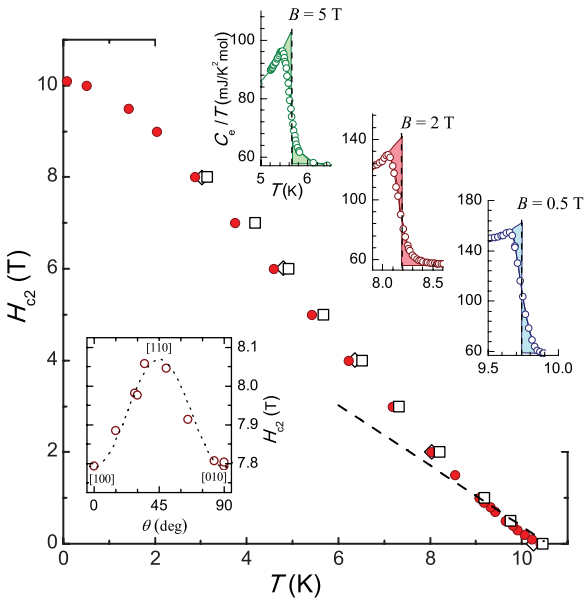

FIG. 4. (Color online) Magnetic field vs temperature phase diagram of $LaRu_4As_{12}$ as obtained from resistivity (solid circles) and specific-heat (open squares) measurements. The upper critical field was determined either from a midpoint of the resistivity drop adopting the 10%–90% criterion or an equal-entropy construction, as shown in the upper insets. Open diamonds are the H_{c2} data obtained from specific-heat experiments on the high-quality polycrystalline sample (Ref. 16). The dotted line marks the initial slope $(-dH_{c2}/dT)_{T_c} = 0.66$ T/K. Lower inset: Angular dependence of the upper critical field at $T = 3$ K.

was found.[26] As a consequence, a positive curvature emerges whose size is very similar to those observed for, e.g., borocarbides and MgB_2.[7,27] Those upper critical field peculiarities were successfully described within an effective two-band model based on the sizable coupling between two groups of electrons having different Fermi velocities,[7] although similar anomalies in $H_{c2}(T)$ were reported for anisotropic one-gap superconductors.[28]

The appearance of the spherical FS sheet along with a change of the T_4X_{12} framework emphasizes a general point. It suggests that the multiband s-wave superconductivity in $LaRu_4As_{12}$ manifests together with a FS sphere enclosing a small volume in the Brillouin zone and is strictly disconnected from the large FS sheet. To rough estimate of the ratio of Fermi velocities v_{F1}/v_{F2}, we follow a common belief for two-band superconductors that the $H_{c2}(T)$ dependence in the vicinity of T_c and in the limit $T \to 0$ K is mainly determined by a separate band with Δ_1 and Δ_2, respectively. From a comparison of $(dH_{c2}/dT)_{T_c}$ with the clean-limit Werthamer-Helfand-Hohenberg (WHH) model, one yields $H^1_{c2}(0) \approx 5.0$ T (dotted line in Fig. 4), while the experimental value of $H_{c2}(0) \approx 10.2$ T was taken for $H^2_{c2}(0)$. Thus, using an $H_{c2}(0) \propto (\Delta/v_F)^2$ relation for a zero-temperature value of the orbital critical field, we obtained $2(\Delta_1/\Delta_2)^2 \simeq (v_{F1}/v_{F2})^2$. Consequently, for $\Delta_1 = 23.4$ meV and $\Delta_2 = 16.7$ meV, we found $2v_{F1} \simeq v_{F2}$, whose relation is fairly similar to that one for the two different groups of conduction electrons in, e.g., MgB_2.[29]

As far as the enhanced superconducting parameters of $LaRu_4As_{12}$ are concerned, we note recent results of both experimental and theoretical studies of lattice dynamics in the La-filled skutterudite compounds.[30] In particular, a smooth change of vibrational properties with the average atomic mass was demonstrated without any exceptional difference between the Os_4As_{12}, Ru_4As_{12}, and Ru_4Sb_{12} frameworks. Additionally, no contribution to lattice dynamics from the off-center rattling was found in the ultrasonic measurements.[31] Since the phonon spectrum of $LaRu_4As_{12}$ does not show any evidence for unusual behavior with respect to other La-filled skutterudite superconductors, further work is needed to elucidate a puzzling observation of both enhanced superconductivity as well as multiband effects in this compound.

We have investigated superconducting properties of the filled skutterudite compound $LaRu_4As_{12}$ that displays substantial interband scattering. For this fully gapped superconductor, we have found compelling evidence for more than one superconducting energy gap. This holds for (i) a nonlinear H contribution to the specific heat in the zero-temperature limit, (ii) a positive curvature of the $H_{c2}(T)$ dependence in the vicinity of T_c, as well as (iii) a deviation of the electronic specific heat from the one-gap α model. Thus, $LaRu_4As_{12}$ with cubic symmetry appears to be a rare example of a multiband s-wave superconductor with a weakly anisotropic Fermi surface. We hope that our results for $LaRu_4As_{12}$ will have a significant impact on the subject of multiband superconductivity, given the fact that an enhancement of the superconducting transition temperature due to multiband order parameters is still a matter of exciting possibility.

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