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

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The temperature dependencies of the lower critical field $H_{c1}(T)$ of several filled-skutterudite superconductors were investigated by local magnetization measurements. While $LaOs_4As_{12}$ and $PrRu_4As_{12}$ exhibit the $H_{c1}(T)$ dependencies consistent with the single-band BCS prediction, for $LaRu_4As_{12}$ (the superconducting temperature $T_c = 10.4$ K) with a similar three-dimensional Fermi surface, we observe a sudden increase in $H_{c1}(T)$ deep in a superconducting state below about $0.32T_c$. Remarkably, a rapid rise of $H_{c1}(T)$ at approximately the same reduced temperature $0.27T_c$ is also found for the heavy-fermion compound $PrOs_4Sb_{12}$ ($T_c \simeq 1.78$ K), in fair accord with the earlier macroscopic study. We attribute the unusual $H_{c1}(T)$ dependencies of $LaRu_4As_{12}$ and $PrOs_4Sb_{12}$ to a kink structure in their superfluid densities due to different contributions from two nearly decoupled bands. Whereas $LaRu_4As_{12}$ is established as a two-band isotropic *s*-wave superconductor, nonsaturating behavior of $H_{c1}(T)$ is observed for $PrOs_4Sb_{12}$, indicative of an anisotropic structure of a smaller gap. For this superconductor with broken time-reversal symmetry, our findings suggest a superconducting state with multiple symmetries of the order parameters.

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Recent experimental and theoretical studies have revealed a significance of multiband effects in the superconductivity of various exotic materials, such as iron-pnictides [1,2], heavy-fermion compounds [3–5], and topological insulators [6–8]. Moreover, multigap superconductivity is emerging as a complex phenomenon with physical consequences which are different from or cannot be found at all in single-band superconductors [9]. In this context, the heated debate on the nature of the pairing symmetry of the first heavy fermion superconductor $CeCu_2Si_2$ should be emphasized [10,11], since it has been stimulated by the surprising discovery of evidence for a fully gapped pairing state concomitant with multiband effects [5]. On the other hand, many properties of two-band superconductors do not strongly rely on the details but mainly on intra- and interband coupling strengths. For instance, as interband coupling increases, a two-band anomaly (usually associated with a smaller gap) is washed out, and thus symmetries of underlying order parameters are hard to be satisfactorily resolved. Furthermore, many properties were found to be similar in the two-band and anisotropic single-band models, making a distinction between these two scenarios difficult [12].

A rare opportunity to study multiband effects in the presence of a weak anisotropy arises in cubic superconductors from the family of the filled skutterudites, which have the formula MT_4Pn_{12} ($M =$ alkali metals, alkaline earth metals, lanthanides, or light actinides; $T =$ Fe, Os, or Ru; $Pn =$ P, As, or Sb) [13,14]. Of these, $PrOs_4Sb_{12}$ (a superconducting transition at around 1.85 K) has attracted considerable attention [15–21], also in the context of chiral superconductivity [22]. An unconventional pairing symmetry of this only known Pr-based heavy-fermion superconductor is suggested by a muon spin relaxation study and polar Kerr effect measurements which showed evidence of time-reversal symmetry breaking [23,24]. Furthermore, the weakly anisotropic antiferroquadrupole ordered state, that is induced by a magnetic field somewhat larger than the upper critical field $\mu_0 H_{c2}(0) = 2.3$ T, is in line with a nonphonon mediated Cooper pairing. In addition, the evidence for multiband order parameters was found in the field dependences of the thermal conductivity. However, while two *s*-wave gaps were proposed in Refs. [25,26], the observation of the residual electronic thermal conduction in the zero-temperature limit led to the suggestion of a superconducting state that is not only multiband, but also multisymmetric [4].

The vast majority of the LaT_4Pn_{12} filled skutterudites exhibit fully gapped superconductivity with T_c varying between 0.4 K to 10.4 K. The highest transition temperature accompanied by $\mu_0 H_{c2}(0) \simeq 10.2$ T exhibits $LaRu_4As_{12}$ [27], although this material does not show any distinct differences in both the conduction electron density of states at the Fermi level and the vibrational properties as compared to other La-filled skutterudite superconductors [28,29]. However, $LaRu_4As_{12}$ exhibits features suggestive of a nonsinglet superconducting order parameter [30]. This holds for (i) a non-BCS specific-heat temperature dependence, thought without a shoulder at intermediate temperatures, (ii) a nonlinear field dependence of the reduced Sommerfeld coefficient, and (iii) an upward curvature in $H_{c2}(T)$ close to T_c.

In this Letter, we present the temperature dependencies of the lower critical field $H_{c1}(T)$ for several filled-skutterudite superconductors. While $LaOs_4As_{12}$ and $PrRu_4As_{12}$ show a single-band BCS behavior, for $LaRu_4As_{12}$ and $PrOs_4Sb_{12}$ we observe sudden enhancements of $H_{c1}(T)$ at about $0.3T_c$. We find that the overall $H_{c1}(T)$ behavior of $LaRu_4As_{12}$ is consistent with a fully gapped two-band s-wave superconducting state in the limit of nearly decoupled bands. Exceptionally for the heavy-fermion superconductor $PrOs_4Sb_{12}$, we observe a quasilinear and nonsaturating $H_{c1}(T)$ dependence and this low-temperature finding suggests the sign-changing nature of a smaller gap.

Single crystals of the As-based filled skutterudites were grown by mineralization in a molten Cd:As flux [31]. Strong de Haas–van Alphen signals obtained from similarly prepared crystals attest to their high quality [32,33]. $PrOs_4Sb_{12}$ single crystals were grown from an Sb flux following the method described in Ref. [15]. The specific-heat data [Figs. 1(b) and S4] indicate the presence of a delicate A phase with $T_{c1} \simeq 1.78$ K (sample A) and a B phase with $T_{c2} \simeq 1.70$ K (sample A), and both T_c's are consistent with the literature data [19,21]. For a low-temperature magnetometry, we used micro-Hall sensors and a typical set of magnetization curves taken at different temperatures is shown in Fig. 1(a). In the mK temperature range, an electrical current as small as 0.1 μA was injected into both reference and sample sensors to minimize a resistive heating [cf. Fig. 1(c)]. (See the Supplemental Material for further details [34].)

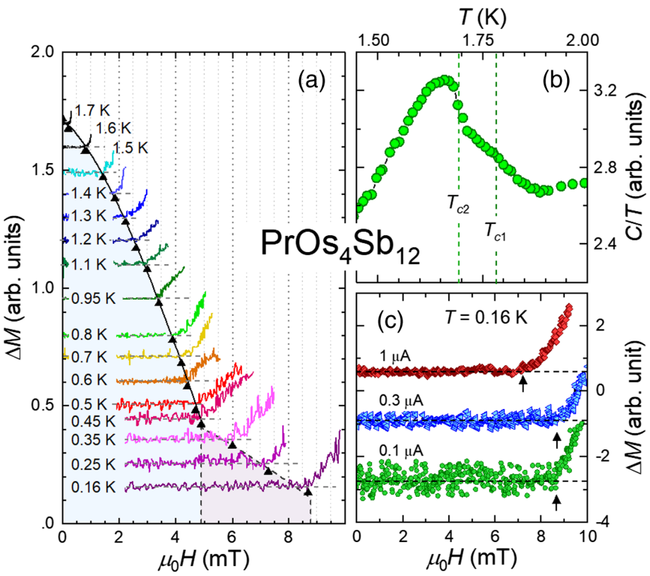

FIG. 1. Low-field magnetization measurements of the filled skutterudite superconductors, as illustrated for $PrOs_4Sb_{12}$ (sample A). (a) Local magnetization ΔM measured at different temperatures as a function of external field H. The triangles indicate the field of first flux penetration H_p. Each curve is vertically shifted for clarity. (b) Specific heat, as C/T vs T, measured around a double superconducting transition. (c) $\Delta M(H)$ curves taken at $T = 160$ mK for different injection currents. As indicated by the triangles, the same H_p's for $j = 0.1$ and 0.3 μA point at a negligible Joule heating.

Figure 2(a) shows the $H_{c1}(T)$ results for $LaRu_4As_{12}$ measured down to $\sim 0.03T_c$. As for other MT_4As_{12} samples, a magnetic field was aligned perpendicular to the (111) plane, the largest natural plane of our As-based crystals. Upon cooling down to about 4 K, the H_{c1} data show a conventional nearly parabolic increase. However, when the temperature decreases further, a pronounced anomaly emerges at around $0.32T_c$, resulting in a large enhancement of H_{c1}. At $T = 0.3$ K, the lower critical field amounts to 37.0 ± 0.3 mT and is $\sim 30\%$ larger than the anticipated zero-temperature value $\mu_0 H_{c1}(0) \simeq 26.5$ mT (dashed line). The upper inset of Fig. 2(a) additionally shows the $H_{c1}(T)$ data for two other $LaRu_4As_{12}$ samples used in both bulk and local magnetization studies as well as

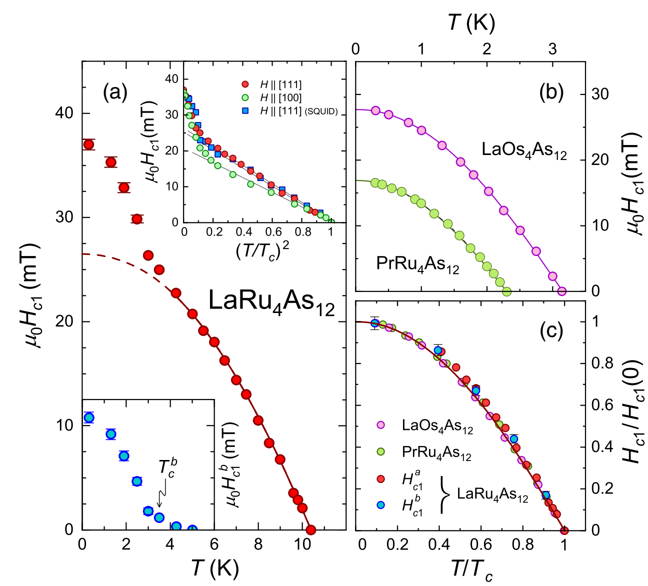

FIG. 2. (a) The temperature dependence of the lower critical field H_{c1} of $LaRu_4As_{12}$ measured for $H \| [111]$ showing a pronounced enhancement below $T/T_c \approx 0.32$. The solid red line represents a single-gap isotropic s-wave dependence fitted to the experimental data at $T > 4$ K. The dashed red line is a calculated low-T contribution to $H_{c1}(T)$ due to a larger gap. Lower inset: An estimated contribution to $H_{c1}(T)$ from a smaller energy gap, as described in the text. Upper inset: H_{c1} plotted vs $(T/T_c)^2$ for various samples used in different experiments. (b) The single-band BCS behavior of $H_{c1}(T)$ of $LaOs_4As_{12}$ and $PrRu_4As_{12}$. (c) Comparison of the normalized $H_{c1}(T)$ dependences for As-based filled-skutterudite superconductors. In the case of $LaRu_4As_{12}$, H_{c1}^a and H_{c1}^b denote the contributions due to larger and smaller gap, respectively. The red line delineates a single-gap BCS behavior.

measured in different configurations [see also Fig. S9(b)]. The fact that, in all these cases, we observe similar enhancements at essentially the same temperature is in consistence with a negligible lattice anisotropy of $LaRu_4As_{12}$ [30]. An irrelevance of anisotropy effects to the sudden enhancement in $H_{c1}(T)$ is additionally underlined by the fact that the isostructural compounds $PrRu_4As_{12}$ ($T_c = 2.3$ K) and $LaOs_4As_{12}$ ($T_c = 3.2$ K) with the similar Fermi-surface (FS) topologies [32,33] display no anomalies down to at least $0.12T_c$ and $0.17T_c$, respectively [Fig. 2(b)]. Although for both materials some signatures of multigap superconductivity were reported [49,50], a single-band BCS model accounts well for their $H_{c1}(T)$ data in the entire temperature range of study, as discussed below.

In the standard single-band Ginzburg-Landau theory, the lower critical field is given by

$$H_{c1} = \frac{\phi_0}{4\pi\mu_0\lambda^2}\left(\ln\frac{\lambda}{\xi} + 0.5\right) \quad (1)$$

where λ is the magnetic penetration depth and ξ is the coherence length. For a local-limit superconductor such as $LaRu_4As_{12}$ [51], the temperature dependence of the natural logarithm of the dimensionless Ginzburg-Landau parameter constructed from these two lengths $\kappa = \lambda/\xi$ is negligible, and thus H_{c1} relates to the normalized superfluid density as $\tilde{\rho}_s(T) = \lambda^2(0)/\lambda^2(T) \simeq H_{c1}(T)/H_{c1}(0)$, and $\tilde{\rho}_s(T)$ is given by

$$\tilde{\rho}_s(T) = 1 + 2\left\langle \int_0^\infty \frac{\partial f}{\partial E} \frac{E}{\sqrt{E^2 - \Delta_k^2(T)}} dE \right\rangle_{\rm FS} \quad (2)$$

where $f(E)$ is the Fermi function and $\langle\cdots\rangle_{\rm FS}$ denotes the average over the Fermi surface [52]. The gap function is given by $\Delta_k(T) = \Delta(0)\delta(T)g(\theta,\phi)$, where $\delta(T) = \tanh\{1.82[1.018(T_c/T - 1)]^{0.51}\}$ is the gap temperature dependence from the BCS theory, and $g(\theta,\phi)$ refers to the angular dependence on both azimuthal angle θ and polar angle ϕ. Note $g(\theta,\phi) = 1$ for an isotropic s-wave gap.

The superfluid density in a multiband superconductor has been theoretically investigated by several groups [47,53,54], and their results consistently point out that $\tilde{\rho}_s(T)$ in the limit of nearly decoupled bands could be well approximated by the straight sum of diverse bands as they would be in isolation. Specifically, a sharp kink in $\tilde{\rho}_s(T)$ is expected at around T_c^b, i.e., at the critical temperature associated with a smaller gap Δ_b, and essentially a single-gap behavior above T_c^b, reflecting properties of a larger gap Δ_a. In the following, we will analyze experimental data using this relatively simple but justifiable scheme. In Sec. V of the Supplemental Material [34], we also analyze our $H_{c1}^b(T)$ data using a two-band α model showing that this commonly used approach is inappropriate for multiband superconductors with a very small interband coupling [54].

For the clean-limit superconductor $LaRu_4As_{12}$ [51], the anomalous temperature dependence of the lower critical field provides solid evidence for two-band superconductivity. Most notably, the sudden increase of H_{c1} deep in the superconducting state signals the case of weak interband interactions. This is further supported by the fact that a single-band isotropic s-wave model accounts well for the H_{c1} data above $\sim 0.4T_c$ [solid line in Fig. 2(a)]. The fitted values are $\Delta_a(0) = 2.0k_BT_c$, $\mu_0H_{c1}^a(0) = 26.5 \pm 0.1$ mT, and the dashed line illustrates a calculated low-T dependence. Based on this, we applied the simplified weak-coupling two-band scheme of Ref. [54] to disclose the pairing symmetry of a smaller gap Δ_b. At the first step, we subtracted the $H_{c1}^a(T)$ contribution (red lines) from the experimental $H_{c1}(T)$ data. As a result, we obtained an $H_{c1}^b(T)$ term due to the attendance of the smaller gap Δ_b at $T_c^b \simeq 3.3$ K [cf. lower inset of Fig. 2(a)]. Then, we estimated a fraction for the smaller gap $x = [H_{c1}(0.3\ \text{K})\text{-}H_{c1}^a(0)]/H_{c1}(0.3\ \text{K}) \simeq 0.28$ at $0.03T_c$. Above $T_c^b \simeq 0.32T_c$, x is negligibly small. And lastly, we found that all singular curves, i.e., both $H_{c1}^a(T)$ and $H_{c1}^b(T)$ terms of $LaRu_4As_{12}$ as well as $H_{c1}(T)$ of $LaOs_4As_{12}$ and $PrRu_4As_{12}$ collapse into a single normalized BCS-like curve, as shown in Fig. 2(c). This establishes $LaRu_4As_{12}$ as a rare case of a two-band superconductor in the limit of nearly decoupled bands.

One can suppose that the greatly enhanced values of T_c and H_{c2} of $LaRu_4As_{12}$, as compared to other La-filled superconductors, are linked to multiband effects as well, since the electronic specific heat and the vibrational properties of $LaRu_4As_{12}$ fit well into smooth changes of both the electron density of states at the Fermi level and the Debye temperature of the series LaT_4Pn_{12} [28,29]. However, when comparing to other La-filled skutterudites, one notes a general similarity of their FSs and only slight differences reflect various electrostatic potentials and internal positions of the T and Pn atoms. In fact, a detailed Fermi-surface investigation of $LaRu_4As_{12}$ by means of de Haas–van Alphen measurements and density-functional-theory calculations also showed a nearly spherical sheet centered at the Γ point and a multiply connected three-dimensional FS sheet [33]. This indicates that multigap superconductivity in $LaRu_4As_{12}$ emerges for a different reason as in MgB_2 (different dimensionality of two bands) or iron-based superconductors (appearance of multiple Fermi-surface pockets). Certainly, the link between enhanced superconducting parameters and multiband effects in $LaRu_4As_{12}$ begs for further thorough experimental studies and theoretical investigations.

We now turn to the Meissner-Ochsenfeld state in the heavy fermion superconductor $PrOs_4Sb_{12}$ ($T_{c1} \simeq 1.78$ K), for which superconducting parameters are strongly enhanced as compared to the $LaOs_4Sb_{12}$ counterpart ($T_c = 0.74$ K) with almost the same FS topology [55]. First observation of the sudden increase of $H_{c1}(T)$ at $T \approx 0.6$ K was made using a SQUID magnetometer, but its origin was unexplained [48]. Although some other experiments on different $PrOs_4Sb_{12}$

crystals revealed a couple of signatures at around $0.3T_c$ [16–18], an intrinsic nature of the sudden change in $H_{c1}(T)$ was criticized because of the lack of associated anomalies in the specific heat and μSR measurements [56,57]. In the present work, three $PrOs_4Sb_{12}$ samples with a somewhat different double-jump structure in C/T were measured using micro-Hall magnetometry. As shown in Fig. S4 of the Supplemental Material [34], each sample exhibits an anomaly in the lower critical field. The fact that quite similar $H_{c1}(T)$ dependences are seen in both the local and bulk magnetization measurements preformed on different samples prepared separately (cf. Fig. S5) clearly rules out any conventional type of pinning and surface effects, suggested in Ref. [56].

Figure 3(a) illustrates a very large and sharp change of $H_{c1}(T)$ of $PrOs_4Sb_{12}$ (sample A with $T_c \simeq 1.78$ K) determined from the initial part of the measured isothermal magnetization curves shown in Fig. 1(a). We note that (i) a relative amplitude of this enhancement is similar to that reported previously (cf. Fig. S5), (ii) it occurs at clearly lower temperature $T \simeq 0.48$ K, and (iii) above $\sim 0.34T_c$, the H_{c1} data follow a single-band isotropic s-wave relation with the fitted values $\Delta_a(0) = 2.25k_BT_c$ and $\mu_0H^a_{c1}(0) = 11.1 \pm 0.1$ mT (solid line). Therefore, in order to extract

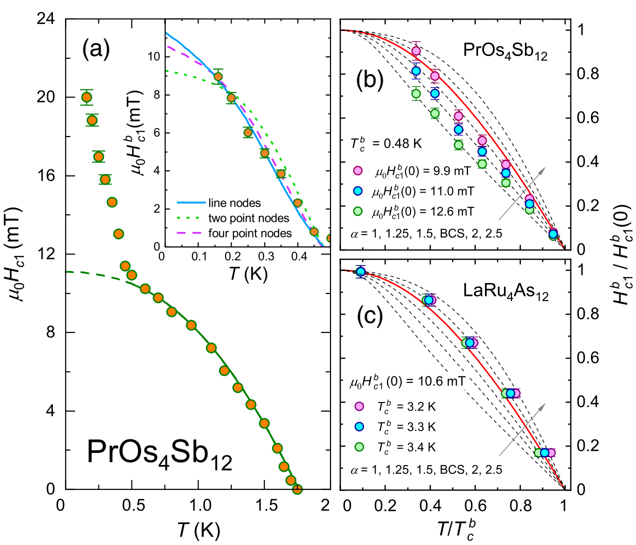

FIG. 3. (a) The temperature dependence of H_{c1} of $PrOs_4Sb_{12}$ measured for $H\|[100]$ showing a sharp anomaly at $T \simeq 0.48$ K. For $T/T_c \gtrsim 0.34$, the $H_{c1}(T)$ data follow the single-band isotropic s-wave dependence, as shown by the solid green line. Inset: The orange points mark a $H^b_{c1}(T)$ term due to a smaller gap. The lines are single-band fits with various nodal d-wave models. (b),(c) Comparison of experimentally determined $H^b_{c1}(T)$ contributions due to the attendance of a smaller gap in the heavy-fermion superconductor $PrOs_4Sb_{12}$ and the fully gapped s-wave superconductor $LaRu_4As_{12}$, respectively. The solid red line and the dashed lines are the normalized $H^b_{c1}(T)$ dependences using the α model with the BCS value and α as a varying parameter, respectively. Points with different colors correspond to different assumptions made for $H^b_{c1}(0)$ and T^b_c, as indicated.

the temperature dependence of H_{c1} due to a smaller gap Δ_b with $T^b_c \simeq 0.48$ K, we made an analysis similar to the case of $LaRu_4As_{12}$, supported by the fact that a visibly sharper enhancement indicates even weaker interband couplings in the Pr-based compound. The $H^b_{c1}(T)$ data for $PrOs_4Sb_{12}$ are shown in the inset of Fig. 3(a). First, we note that a fraction for the smaller gap is as large as $x \simeq 0.45$ at $T = 0.16$ K; i.e., it is larger than that of $LaRu_4As_{12}$ by a factor of nearly 2 at the corresponding temperature $0.1T_c$. Second, $H^b_{c1}(T)$ evidently deviates from the BCS relation [cf. solid red line in Fig. 3(b)]. Third and most importantly, the lower critical field associated with Δ_b increases nearly linearly and this increase continues down to the lowest temperature in our measurements, revealing a striking difference with $LaRu_4As_{12}$. The $H^b_{c1}(T)$ results for $PrOs_4Sb_{12}$ were fitted using sign-changing gap functions proposed for another filled-skutterudite superconductor $PrPt_4Ge_{12}$ [58]. As displayed by the solid blue line in the inset of Fig. 3(a), a single-band d-wave model with line nodes [$g(\theta,\phi) = \sin\theta \sin\phi$] shows good agreement with the experimental data. [The fitted values are $\Delta_b(0) = 4.0k_BT_c$ and $\mu_0H^b_{c1}(0) = 11.3 \pm 0.2$ mT with $R^2 = 0.953$]. The data were also analyzed using a d-wave model with four point nodes [dashed red line, $g(\theta,\phi) = 1\text{-}(\sin^4\phi + \cos^4\phi)\sin^4\theta$], but the agreement is poorer at around 0.25 K [$\Delta_b(0) = 3.2k_BT_c$, $\mu_0H^b_{c1}(0) = 10.6 \pm 0.4$ mT, $R^2 = 0.827$]. Finally, we note that the convex shape of a d-wave model with two point nodes [dotted green line, $g(\theta,\phi) = 1\text{-}\sin^4\theta\cos^4\theta$] is in marked contrast to the quasilinear behavior of $H^b_{c1}(T)$.

On the other hand, one can argue that the α model derived from the BCS theory [59,60] accounts for the $H^b_{c1}(T)$ data as well [cf. Fig. 3(b)] [61]. Indeed, if one assumes $\mu_0H^b_{c1}(0) \simeq 11.0$ mT then a quasilinear behavior of $H^b_{c1}(T)$ is expected for $\alpha = 1.25$ down to about $T = 0.1T^b_c$ (cyan points). However, it is difficult to reconcile a strongly anisotropic s-wave gap with the experimental observations of weakly anisotropic superconducting and normal-state properties of $PrOs_4Sb_{12}$ [19–21]. Furthermore, if there is no sign change of the gap function, $\alpha = 1.25$ is in obvious divergence with $\alpha \geq \alpha_{BCS} \approx 1.764$ for other filled-skutterudite superconductors with the similar FS topologies. We also note that the experimental uncertainty in estimation of $H^b_{c1}(T)$ for $LaRu_4As_{12}$ has a negligible effect on its isotropic behavior, as illustrated in Fig. 3(c). Furthermore, even the presence of noninteracting localized $4f$ electrons, as shown for $PrRu_4As_{12}$ which is considered to be a conventional paramagnetic metal [49], does not induce an anisotropy of phonon-mediated pairing. Studies at very low temperatures, i.e., at $T < 0.1T^b_c$ ($\simeq 0.05$ K) where the $\alpha = 1.25$ model is expected to saturate, could help to develop a detailed understanding of all these observations but this would require a highly elaborated approach.

A multigap and multisymmetry scenario of $PrOs_4Sb_{12}$ has been previously postulated to explain the field dependence of the low-temperature electronic thermal conductivity [4]. However, some other experiments have suggested the absence of a residual electronic conduction in zero field, which is inconsistent with nodes in the superconducting gap function [26]. Indeed, after almost two decades of intensive research on $PrOs_4Sb_{12}$, there is still no consensus on the underlying order parameter(s). On the other hand, indications of the breaking of time reversal symmetry, that emerged from a muon spin relaxation study [23] as well as recent polar Kerr effect measurements [24], provide strong support for the distinct symmetries allowed for a multigap superconducting state in this material. In addition to this, there have been reports of features in several physical properties of $PrOs_4Sb_{12}$ observed at around $0.3T_c$ together with different T dependencies below and above this temperature [16–18]. Specifically, the magnetic penetration depth has been found to follow a T^2 behavior below around 0.62 K, indicative of two point nodes in the energy gap [17]. Whereas this gap structure was concluded in the single-band model, none of nodal gap functions adequately describes the data over the entire temperature range. By contrast, the antimony nuclear quadrupole resonance measurements have yielded an inverse nuclear spin lattice relaxation time $1/T_1$ that displays an exponential dependence in the superconducting state down to $\sim 0.3T_c$, suggestive of an isotropic energy gap [16]. Below $\sim 0.3T_c$, the $1/T_1T$ behavior sharply changes and shows a tendency to saturation. Based on results from measurements of the lower critical field, we propose a resolution to these seemingly conflicting results. In fact, a multiband and multisymmetric scenario, with an isotropic s-wave order parameter and the emergence of an anisotropic gap above and below $\sim 0.3T_c$, respectively, seems to account for the above-mentioned observations.

In conclusion, we have studied the temperature dependencies of the lower critical field $H_{c1}(T)$ of several filled-skutterudite superconductors. For multiband superconductors $LaRu_4As_{12}$ and $PrOs_4Sb_{12}$, profound enhancements of $H_{c1}(T)$ are found deep in their superconducting states as well as the single-band behaviors at higher temperatures, indicative of rarely observed cases of almost decoupled bands. For $LaRu_4As_{12}$, the overall $H_{c1}(T)$ behavior agrees well with two-band isotropic s-wave superconductivity. For $PrOs_4Sb_{12}$, we provide evidence that the structure of a smaller gap is strongly anisotropic. Whereas an unsaturated lower critical field needs to be confirmed at very low temperatures to give the definitive determination of the sign-changing pairing state in $PrOs_4Sb_{12}$, the sharp kink in the superfluid density should be considered in future studies as well as calls for further analysis of some literature data for this heavy-fermion superconductor.

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