Superfluid Density and Energy Gap Function of Superconducting $PrPt_4Ge_{12}$

A. Maisuradze,[1,*] M. Nicklas,[2] R. Gumeniuk,[2] C. Baines,[1] W. Schnelle,[2] H. Rosner,[2] A. Leithe-Jasper,[2] Yu. Grin,[2] and R. Khasanov[1,†]

[1]*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*
[2]*Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany*
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The filled skutterudite superconductor $PrPt_4Ge_{12}$ was studied in muon-spin rotation (μSR), specific heat, and electrical resistivity experiments. The continuous increase of the superfluid density with decreasing temperature and the dependence of the magnetic penetration depth λ on the magnetic field obtained by means of μSR, as well as the observation of a T^3 dependence of the electronic specific heat indicate the presence of pointlike nodes in the superconducting energy gap. The gap and the specific heat are found to be well described by two models with point nodes, similar to results obtained for the unconventional heavy fermion skutterudite superconductor $PrOs_4Sb_{12}$.

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The filled skutterudite compounds MT_4Pn_{12} (M = rare-earth or alkaline-earth metals, T = Fe, Ru, Os, and Pn = P, As, Sb) have attracted much attention in recent years [1]. One of the most interesting representatives is $PrOs_4Sb_{12}$ which exhibits heavy fermion superconductivity below 1.85 K with a complex phase diagram [2,3]. Despite of numerous studies the symmetry of the superconducting order parameter and even the existence of nodes in the gap function is still discussed and controversial. While some probes indicate a nodal order parameter [3–5], other measurements suggest a gap without nodes [3,6,7]. Moreover, the presence of multiband superconductivity is discussed [7]. Superconductivity with a similarly low T_c is found in $PrRu_4As_{12}$ ($T_c = 2.4$ K) and $PrRu_4Sb_{12}$ ($T_c = 1.1$ K) [8] which are however conventional weakly-correlated BCS superconductors [3].

Recently, a new Pr-containing skutterudite superconductor, $PrPt_4Ge_{12}$ with a Pt-Ge framework, was discovered [9]. Specific heat and other experiments reveal strongly coupled superconductivity with $T_c \approx 7.9$ K, a factor of 4 higher than that in $PrOs_4Sb_{12}$ [2]. The small coefficient γ_N of the electronic specific heat indicates that $PrPt_4Ge_{12}$ is not a heavy fermion superconductor as $PrOs_4Sb_{12}$, but more similar to the two ruthenium skutterudites [8]. While the crystal field ground states in all here discussed Pr superconductors are singlets, the splitting to the first exited state differs greatly: $\Delta_{CEF} \approx 7$ K for $PrOs_4Sb_{12}$ [3] and ≈ 130 K in $PrPt_4Ge_{12}$ [9,10]. Thus, comparing the superconducting properties of $PrPt_4Ge_{12}$ with that of $PrOs_4Sb_{12}$ and other skutterudites allows us to gain insight into the mechanisms of superconductivity in these materials. The isostructural $LaPt_4Ge_{12}$ ($T_c = 8.29$ K [9]) has been suggested to be an s-wave superconductor [10] like $LaOs_4Sb_{12}$ [3].

Here, we report on a study of the superconducting state of $PrPt_4Ge_{12}$ by means of specific heat, muon-spin rotation (μSR), and electrical resistivity measurements down to very low temperatures. The observation of a T^3 dependence of the electronic specific heat, the continuous increase of the superfluid density (ρ_s) with decreasing temperature, as well as its dependence on the magnetic field suggests [11] the presence of pointlike nodes in a single superconducting energy gap. The temperature dependence of ρ_s was analyzed with various gap models and is found to be well described by two functions with pointlike nodes.

The preparation procedures of the $PrPt_4Ge_{12}$ samples are identical to that described in [9]. The transverse field μSR experiments were performed at the $\pi M3$ beam line at the Paul Scherrer Institute (Villigen, Switzerland). The sample was field cooled from above T_c down to 1.5 K and measured as function of temperature in series of fields ranging from 35 mT to 640 mT. Additional experiments down to $T \simeq 0.03$ K were performed at 75 mT. Typical counting statistics were 7×10^6 positron events per each particular data point. Electrical resistivity $R(T, H)$ and specific heat $C(T)$ down to 0.4 K were measured in a commercial system (PPMS, Quantum Design) using an ac resistance bridge (LR-700, Linear Research) and the HC option of the PPMS, respectively.

Figure 1 shows the electronic specific heat C_{el}/T vs T^2. The phonon contribution $\propto T^3$ was subtracted using a Debye temperature $\Theta_D = 189$ K. The normal-state electronic term γ_N of the current sample is 63 mJ mol^{-1} K^{-2} and the jump Δ_{Cp}/T_c at T_c is 130 mJ mol^{-1} K^{-2}. At the lowest temperatures an upturn from a nuclear Schottky contribution of Pr [12] becomes visible ($C_{nucl} \propto T^{-2}$). After its subtraction we find $C_{el}(T) = \gamma' T + \eta T^3$ with $\gamma' \approx 1.31$ mJ mol^{-1} K^{-2} originating from a minor metallic impurity phase. For $0.05 < T/T_c < 0.2$ the clear T^3 dependence of the superconducting state electronic term ($\eta = 2.88(2)$ mJ mol^{-1} K^{-4}) already demonstrates that the gap function of $PrPt_4Ge_{12}$ has pointlike nodes [13]. Further investigation of the energy gap and the order parameter symmetry was performed in the transverse field μSR experiments.

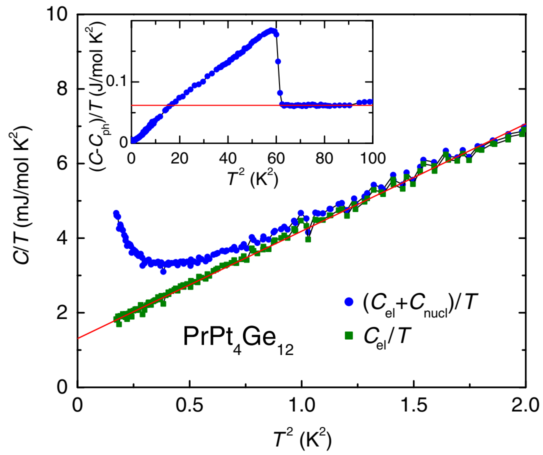

FIG. 1 (color online). Inset: specific heat $C - C_{\mathrm{ph}}$ of $PrPt_4Ge_{12}$ (corrected for the phonon term) and normal-state electronic γ_N (horizontal line). Main panel: data ($C_{\mathrm{el}} + C_{\mathrm{nucl}}$) below 1.4 K and data C_{el} corrected for the nuclear Schottky contribution C_{nucl} of Pr (see text).

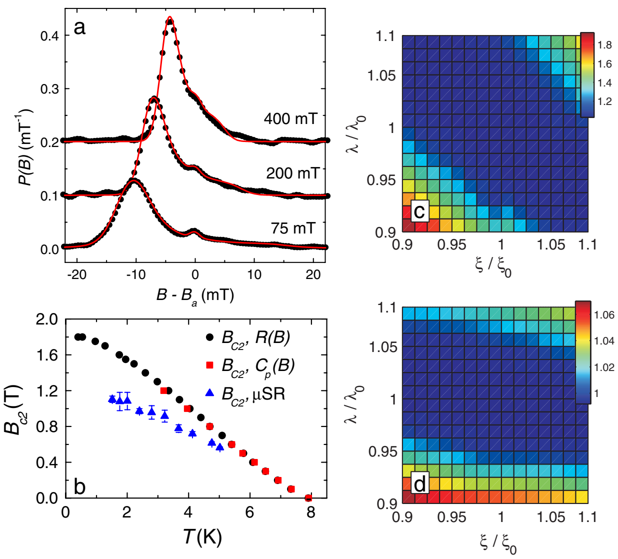

FIG. 2 (color online). (a) The magnetic field distribution $P(B)$ at $T = 1.55$ K and applied fields $B_a = 75$, 200, and 400 mT obtained by means of fast Fourier transform. The solid lines are fits to the data (see text for details). (b) Temperature dependence of the upper critical field B_{c2} obtained in specific heat (squares) and resistivity (dots) experiments compared with fit results of μSR time spectra (see text). Panels (c) and (d) show correlation plots $\chi^2(\lambda, \xi)$ for $B_a = 400$ mT and 50 mT, respectively.

The μSR time spectra were fit to a theoretical polarization function $\tilde{P}(t)$ by assuming the internal field distribution $P_{\mathrm{id}}(B)$ calculated for the hexagonal flux line lattice (FLL) within the Ginzburg-Landau model and accounting for the FLL disorder by multiplying $P_{\mathrm{id}}(B)$ with a Gaussian function:

$$\tilde{P}(t) = Ae^{i\phi} \int e^{-(\sigma_g^2 + \sigma_{\mathrm{nm}}^2)t^2/2} P_{\mathrm{id}}(B) e^{i\gamma_\mu B t} dB. \quad (1)$$

Here A and ϕ are the initial asymmetry and the phase of the muon-spin ensemble, σ_g is a parameter related to FLL disorder and σ_{nm} the nuclear moment contribution measured at $T > T_c$. For a detailed description of the analysis we refer to Ref. [14] and references therein.

Figure 2(a) shows representative internal field distributions $P(B)$ obtained from the measured μSR time spectra by performing the fast Fourier transform. $P(B)$'s have asymmetric shape as expected for a field distribution within a well arranged FLL. The small peak in the vicinity of the applied field is due to muons stopped outside of the sample ($\approx$ 2–3%). Above T_c an additional magnetic depolarization is observed, which increases with increasing field. The measurements at zero field, below (1.5 K) and above T_c (10 K) reveal negligibly small change of this magnetic depolarization.

Magnetic penetration depth is defined in the London limit of low fields as a measure of superfluid density $\rho_s \propto 1/\lambda^2$. The λ obtained in the vortex state is often called an effective magnetic penetration depth λ_{eff} [15,16], since it might be field dependent. For a classical BCS superconductor with isotropic s-wave gap $\lambda_{\mathrm{eff}} = \lambda$ [16]. The fit of Eq. (1) to the single μSR time spectra does not allow us to obtain independently λ and ξ, since they are strongly correlated [14]. In order to get rid of this correlation one needs to perform a *simultaneous* fit of several spectra, measured at the same temperature but different magnetic fields, with λ and ξ as common parameters [14,17]. $B_{c2} = \Phi_0/2\pi\xi^2$ as a function of temperature, obtained after such fit, is presented in Fig. 2(b). The fit was performed on combined data measured at $B_a = 35$ and 400 mT. Figures 2(c) and 2(d) show the corresponding correlation plots [$\chi^2(\lambda, \xi)$]. The normalized χ^2 was obtained for λ and ξ varied within 10% around their optimal fit values [$\lambda_0 = 114(4)$ nm and $\xi_0 = 18.1(8)$ nm]. Strong correlations between λ and ξ as well as a field dependent slope of the correlation curves are obvious.

Figure 2(b) implies, however, that $B_{c2}(T)$ obtained in simultaneous fit is $\approx 40\%$ smaller than that measured directly in specific heat [9] and resistivity experiments (the upper critical field $B_{c2}(T = 0)$ determined for the polycrystalline μSR sample is 1.82(2) T and $T_c(B = 0) = 7.90$ K). This suggests that the assumption of a field-independent λ may not be valid for $PrPt_4Ge_{12}$. Field dependence of λ (Fig. 3 inset) is actually expected for a nodal superconductor since a field induces excitations at the gap nodes due to nonlocal and nonlinear effects, thus reducing the superconducting carrier concentration $n_s \propto 1/\lambda^2$ [15]. We believe however that the Ginzburg-Landau (GL) theory developed for superconductors with isotropic s-wave gap is a valid approximation in the present case. In order to avoid the correlation between λ and ξ we fixed the values of $\xi(T) = \sqrt{\Phi_0/2\pi B_{c2}(T)}$ by using the $B_{c2}(T)$ curve obtained in resistivity measurements down to $0.05T_c(0)$ ($T_c(B) = T(\rho = 0)$; data not shown).

The GL theory allows to extend the London definition of superfluid density for a finite applied field [18]:

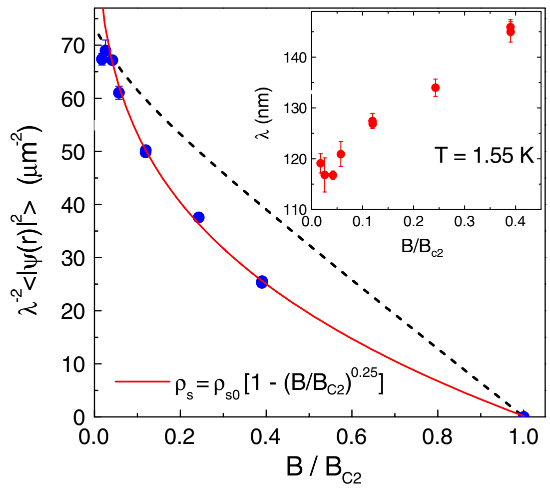

FIG. 3 (color online). Field dependence of the superfluid density $\rho_s \propto \langle|\psi|^2\rangle/\lambda^2$. The solid line is the power law fit $\rho_s(T)/\rho_s(T=0) = 1 - (B/B_{c2})^{\alpha}$ with $\alpha = 0.26(2)$. The dashed line represents the case when λ does not depend on the magnetic field. The inset shows $\lambda(B/B_{c2})$ at $T = 1.55$ K.

$$\rho_s \propto \langle|\psi(\mathbf{r})|^2\rangle/\lambda^2 \simeq (1 - B/B_{c2})/\lambda^2. \tag{2}$$

Here, $\psi(\mathbf{r})$ is the GL order parameter and $\langle\cdots\rangle$ means averaging over the unit cell of the FLL. Equation (2) implies that in isotropic s-wave superconductors the mean superfluid density decreases with increasing field as $\langle|\psi(\mathbf{r})|^2\rangle$ (the dashed line in Fig. 3). Obviously, the experimental ρ_s decreases much stronger with increasing magnetic field than for a field-independent λ, thus confirming the presence of nodes in the gap. A power law fit $\rho_s(T)/\rho_s(T=0) = 1 - (B/B_{c2})^{\alpha}$ results in $\alpha = 0.26(2)$ (solid line in Fig. 3).

Figure 4(a) shows ρ_s, normalized to its value at $T = 30$ mK, as a function of T/T_c. Surprisingly, $\rho_s(T/T_c)/\rho_s(0)$ is identical for all applied fields. Only the data measured at 35 mT deviate slightly, which may be due to larger vortex disorder and, consequently, larger inaccuracies at such a low field. The inset of Fig. 4(a) shows ρ_s measured at 75 mT for $0.004 \le T/T_c \le 0.3$. As expected for a nodal superconductor, ρ_s does not saturate but increases continuously with decreasing temperature. This is consistent with the conclusion already drawn from the analysis of $\rho_s(B/B_{c2})$.

Symmetries of the order parameter for superconductors with $LaFeP_{12}$ type crystal (space group $Im\bar{3}$) with tetrahedral point group symmetry (T_h) are in detail investigated in Ref. [19]. Possible gap functions $\Delta(\theta, \phi)$ (the quasiparticle energy spectrum gaps), among them some discussed for $PrOs_4Sb_{12}$, are collected in Table I. For comparison we first list the nodeless s-wave gap (A) $\Delta(\theta, \phi) = \Delta_0$ and a model with a line node in the gap (B). As motivated by our specific heat and μSR results above, the only suitable gap functions should be those with point nodes in the gap, models C–F.

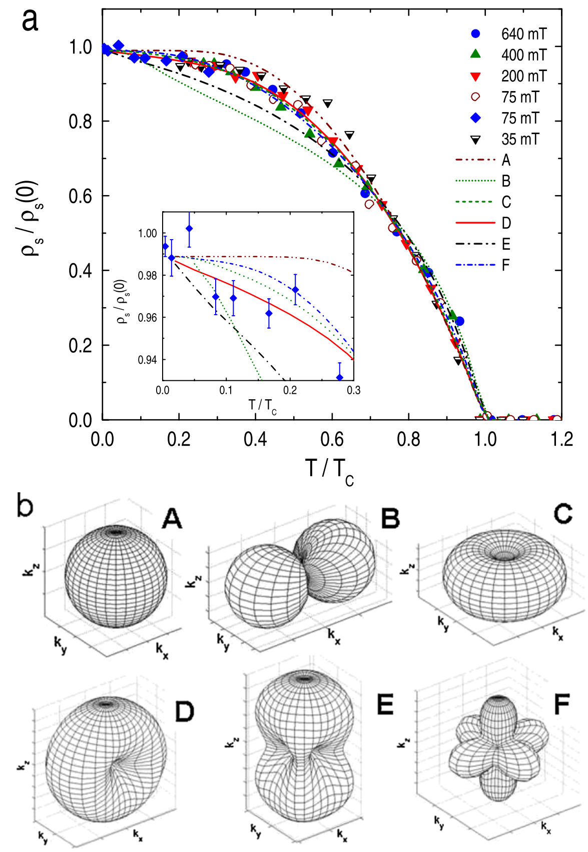

FIG. 4 (color online). (a) Temperature dependence of $\rho_s \propto \langle|\psi(\mathbf{r})|^2\rangle/\lambda^2$ normalized to its value $\rho_s(0)$ at $T = 30$ mK. The lines represent the fits by using six different gap models as illustrated in panel (b). The inset shows the low-temperature region between $T = 0$ and $T = 0.3T_c$. The panel (b) illustrates the gap functions listed in Table I.

The temperature dependence of the gap $\Delta(\theta, \phi, T/T_c) = \Delta(\theta, \phi)\delta(T/T_c)$ was assumed to follow $\delta(T/T_c) = \tanh\{1.82[1.018(T/T_c - 1)^{0.51}]\}$ according to the weak-coupling BCS theory [20]. Note that the function $\delta(T/T_c)$ is practically independent of the gap model [21].

TABLE I. Summary of the analysis of $\rho_s(T)$ data for $PrPt_4Ge_{12}$. The character of the nodes, line (l) or point (p), of the gap function models A-F is given. Δ_0 is the maximum value of the gap at $T = 0$, and θ and ϕ are the angular coordinates in k-space. $\hat{k}_x = \sin\theta\cos\phi$, $\hat{k}_y = \sin\theta\sin\phi$, $\hat{k}_z = \cos\theta$. The least-squares deviation χ^2 of the fits with these models to $\rho_s(T)$ are compared to the χ^2 of model F.

	Nodes	Superconducting gap function $\Delta(\phi, \theta)$	$\frac{\Delta_0}{k_B T_c}$	$\frac{\chi^2}{\chi^2(F)}$
A	$\cdots$	Δ_0	1.95(5)	3.99
B	l	$\Delta_0\lvert\hat{k}_y\rvert$	4.88(30)	9.32
C	p	$\Delta_0\lvert\hat{k}_x \pm i\hat{k}_y\rvert$	2.68(5)	1.05
D	p	$\Delta_0(1 - \hat{k}_y^4)$	2.29(5)	1.17
E	p	$\Delta_0(1 - \hat{k}_x^4 - \hat{k}_y^4)$	3.84(14)	3.46
F	p	$\Delta_0[1 - 3(k_x^2k_y^2 + k_x^2k_z^2 + k_y^2k_z^2)]^{1/2}$	3.56(7)	1

The temperature dependence of the superfluid density was calculated within the local (London) approximation by using the equations [21]:

$$\rho_{(aa/bb/cc)} = 1 - \frac{3}{4\pi T}\int d\epsilon d\phi d\theta \begin{pmatrix} \sin^2\theta\cos^2\phi \\ \sin^2\theta\sin^2\phi \\ 2\cos^2\theta\cos^2\phi \end{pmatrix} \times \cosh^{-2}\left(\frac{\epsilon^2 + \Delta^2}{2T}\right) \quad (3)$$

Here, $\rho_{ii} \propto \langle|\psi|^2\rangle/\lambda_i\lambda_i$ ($i = a$, b, or c) is the component of the superfluid density along ith principal axis. Since our experiments were performed on a polycrystalline sample, we used the powder average of ρ_s [4]:

$$\rho_s = (\sqrt{\rho_{aa}\rho_{bb}} + \sqrt{\rho_{aa}\rho_{cc}} + \sqrt{\rho_{cc}\rho_{bb}})/3. \quad (4)$$

The fits of the six model gap functions to the ρ_s data were made for the only free parameter Δ_0. The results of the fits are presented in Fig. 4(a) and in Table I. The goodness of a fit can be assessed by the χ^2 value given in the last column of Table I. It is obvious that the gap functions A (isotropic s wave), B (line nodes), and also E fit the data poorly. The data are best described by gap function F, but also models C and D result in only 5% and 17% larger χ^2 values, respectively. Thus, from our present analysis these three gap functions—all with point nodes—can be considered as candidates for the gap symmetry.

The resulting gap-to-T_c ratios Δ_0/k_BT_c of model C, D, and F are 2.68(5), 2.29(5), and 3.56(7), respectively. All three ratios are higher than the weak-coupling BCS limit 1.76. The ratio of the specific heat jump Δc_p to $\gamma_N T_c$ for the present $PrPt_4Ge_{12}$ sample is 2.06 (BCS weak-coupling value 1.43). This observation and the previous estimate of Δ_0/k_BT_c of 2.35 from the electronic specific heat in the superconducting state at $T_c/2$ [9] suggest that function C or D may represent the symmetry of the superconducting gap in $PrPt_4Ge_{12}$. The high gap-to-T_c ratio of model F would correspond to a significantly larger $\Delta c_p/\gamma_N T_c$ than observed. Thus, our combined results from thermodynamics and μSR give evidence that $PrPt_4Ge_{12}$ is a strong coupled superconductor with point nodes in the gap.

To conclude, the $PrPt_4Ge_{12}$ skutterudite superconductor was studied in μSR, specific heat, and electrical resistivity experiments. A clear T^3 dependence of the electronic specific heat and the μSR data give evidence that the gap function of $PrPt_4Ge_{12}$ has point nodes. A detailed analysis of the μSR data was performed by exact minimization of the Ginzburg-Landau free energy. The temperature dependence of ρ_s is well described by three models with point-like nodes in the gap. One of these models can be excluded due to its very strong coupling. Thus, possible superconducting gap functions for $PrPt_4Ge_{12}$ are $\Delta_0|\hat{k}_x \pm i\hat{k}_y|$ and $\Delta_0(1 - \hat{k}_y^4)$ [22]. The maximum gap-to-T_c ratios Δ_0/k_BT_c for these models are 2.68(5) and 2.29(5), respectively. Note, the former gap with identical gap-to-T_c ratio was suggested for the isostructural *unconventional* superconductor $PrOs_4Sb_{12}$ [4], the latter of our "best" gap functions $\Delta_0(1 - \hat{k}_y^4)$ was suggested for the low-field B phase of $PrOs_4Sb_{12}$ [23] and is in better agreement with our specific heat data. Further investigations are desirable to clarify the reason for such remarkable resemblance of order parameters to address the questions of gap symmetry and pairing mechanism.

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*alexander.maisuradze@psi.ch
†rustem.khasanov@psi.ch

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