

## Evidence for time-reversal symmetry breaking in superconducting PrPt<sub>4</sub>Ge<sub>12</sub>

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Zero- and longitudinal-field muon-spin-rotation ( $\mu$ SR) experiments were performed on the superconductors PrPt<sub>4</sub>Ge<sub>12</sub> and LaPt<sub>4</sub>Ge<sub>12</sub>. In PrPt<sub>4</sub>Ge<sub>12</sub> below  $T_c$  a spontaneous magnetization with a temperature variation resembling that of the superfluid density appears. This observation implies time-reversal symmetry (TRS) breaking in PrPt<sub>4</sub>Ge<sub>12</sub> below  $T_c=7.9$  K. This remarkably high  $T_c$  for an anomalous superconductor and the weak and gradual change in  $T_c$  and of the related specific-heat anomaly upon La substitution in La<sub>1-x</sub>Pr<sub>x</sub>Pt<sub>4</sub>Ge<sub>12</sub> suggests that the TRS breaking is due to orbital degrees of freedom of the Cooper pairs.

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### I. INTRODUCTION

The large family of filled skutterudite compounds  $RT_4X_{12}$  ( $R$ =rare-earth, actinides, alkaline-earth, and alkali metals;  $T$ =Fe, Ru, Os;  $X$ =P, As, Sb) displays an astonishing diversity of physical properties among which superconductivity represents a particularly complex one. Within more than 20 isostructural skutterudites known up to now a perplexing multitude of conventional and unconventional superconducting phases has been observed.<sup>1-5</sup> In large part, the filler cations  $R$  which are embedded in the polyanionic  $[T_4X_{12}]$  host structure have a significant influence on these properties. Superconducting members of this family containing Pr have attracted considerable interest with PrOs<sub>4</sub>Sb<sub>12</sub> being the most prominent one. While LaOs<sub>4</sub>Sb<sub>12</sub> (critical temperature  $T_c=0.74$  K) is found to obey the classical BCS theory, PrOs<sub>4</sub>Sb<sub>12</sub> ( $T_c=1.85$  K) exhibits heavy-fermion behavior and unconventional superconductivity<sup>6-8</sup> with time-reversal symmetry (TRS) breaking.<sup>9,10</sup> Moreover, multiple superconducting phases and order parameters with nodes have been detected.<sup>8</sup> Recent research efforts show that these phenomena depend on a subtle interplay of the crystal electric field (CEF) acting on the Pr<sup>3+</sup> ion together with the hybridization of the  $f$  shell with the conduction electrons of the host. This is also found, e.g., for the RFe<sub>4</sub>P<sub>12</sub> system, where LaFe<sub>4</sub>P<sub>12</sub> and YFe<sub>4</sub>P<sub>12</sub> are conventional superconductors and isovalent substitution by Pr leads to an antiferroquadrupolar ground state with heavy electron masses.<sup>6,11,12</sup>

Recently, we investigated the properties of a different family of compounds with a filled skutterudite structure based on platinum and germanium,  $RPt_4Ge_{12}$  ( $R$ =Sr, Ba, La, Ce, Pr, Nd, Eu).<sup>13</sup> The compounds with Sr and Ba,<sup>13,14</sup> Th,<sup>15</sup> and with La and Pr (Refs. 13 and 16) are superconductors. These latter compounds have the highest  $T_c$  among the  $[Pr_4Ge_{12}]$  skutterudites of 8.3 K and 7.8 K, respectively. In addition to the surprisingly high  $T_c$  of PrPt<sub>4</sub>Ge<sub>12</sub> its superconducting energy gap has point nodes, as has been demonstrated by specific-heat as well as muon-spin-rotation ( $\mu$ SR) measurements down to very low reduced temperatures ( $T/T_c \leq 0.005$ ).<sup>16</sup>

An analysis of the temperature variation in the superfluid density has shown that the data can be well described by

three selected gap functions, of which two are compatible with the thermodynamic data.<sup>16</sup> One of the remaining functions,  $|\Delta|=\Delta_0|\hat{k}_x-i\hat{k}_y|$ , has been favored to describe the *unconventional* superconducting low-field ( $B$ ) phase of PrOs<sub>4</sub>Sb<sub>12</sub>, for which TRS breaking<sup>8-10,17</sup> is observed and has been discussed in connection with spin-triplet pairing.<sup>18</sup> Moreover, the gap-to- $T_c$  ratios  $\Delta_0/k_B T_c$  of the two Pr superconductors are similar. While these aspects of the superconducting states of PrPt<sub>4</sub>Ge<sub>12</sub> and PrOs<sub>4</sub>Sb<sub>12</sub> are similar, the CEF splitting distinguishes the compounds. Having the same nonmagnetic singlet ground state  $\Gamma_1$ , in PrOs<sub>4</sub>Sb<sub>12</sub> the first excited triplet  $\Gamma_4^{(2)}$  ( $E/k_B \approx 7-10$  K) (Ref. 8) strongly hybridizes with the ground state and the conduction electrons, generating the heavy-fermion state. In PrPt<sub>4</sub>Ge<sub>12</sub> the first excited CEF state is a different triplet ( $\Gamma_4^{(1)}$  in  $T_h$  notation). The  $\Gamma_1$ - $\Gamma_4^{(1)}$  splitting is huge (120–130 K),<sup>13,19,20</sup> allowing for a  $T_c$  only little less than for LaPt<sub>4</sub>Ge<sub>12</sub>. No heavy-electron states are present at the Fermi surface of PrPt<sub>4</sub>Ge<sub>12</sub>, as can be concluded from thermodynamic data.<sup>13</sup>

TRS breaking can lead to the appearance of a small magnetic moment of the superconducting condensate due to spin or orbital degrees of freedom of the Cooper pairs.<sup>21</sup>  $\mu$ SR successfully detected this field in a number of *unconventional* and *spin-triplet* superconductors.<sup>9,18,22-24</sup> Here, we report on detailed zero magnetic field (ZF)  $\mu$ SR experiments in PrPt<sub>4</sub>Ge<sub>12</sub> and LaPt<sub>4</sub>Ge<sub>12</sub>. The absolute value and the mechanism of ZF muon depolarization above  $T_c$  in PrPt<sub>4</sub>Ge<sub>12</sub> are similar to that reported for PrOs<sub>4</sub>Sb<sub>12</sub>. Below  $T_c=7.8$  K a spontaneous magnetization resembling the temperature dependence of the superfluid density was observed for PrPt<sub>4</sub>Ge<sub>12</sub>. No such anomaly is detected for LaPt<sub>4</sub>Ge<sub>12</sub>. The magnitude of this magnetization is of the same order as that reported for PrOs<sub>4</sub>Sb<sub>12</sub> and other superconductors with TRS breaking.<sup>9,22,23</sup> Due to the contrasting behaviors of the La and Pr compound and in order to elucidate the origin of the TRS breaking we synthesized samples of the solid solution La<sub>1-x</sub>Pr<sub>x</sub>Pt<sub>4</sub>Ge<sub>12</sub> and studied the variation in  $T_c$  and of the specific-heat anomaly.

### II. EXPERIMENTAL

The preparation procedures of the La<sub>1-x</sub>Pr<sub>x</sub>Pt<sub>4</sub>Ge<sub>12</sub> samples are similar to that described previously.<sup>13</sup> The end

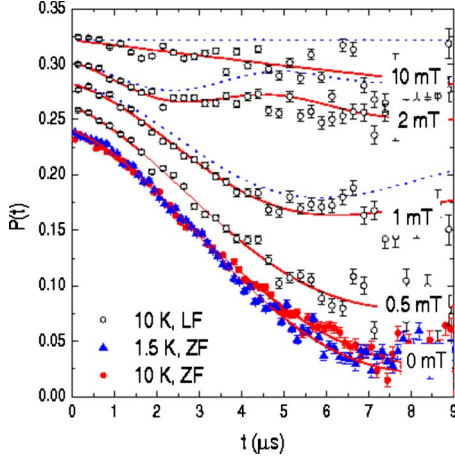


FIG. 1. (Color online) Zero-field  $\mu$ SR time spectra at 1.5 K ( $\blacktriangle$ ) and 10 K ( $\bullet$ ) for  $\text{PrPt}_4\text{Ge}_{12}$ . The corresponding solid (red) lines are fits to the data according to Eq. (5). ( $\circ$ ) Spectra measured with LFs of 0.5, 1, 2, and 10 mT at 10 K and corresponding fit with Eq. (5) [the solid (red) lines]. The dashed (blue) lines are simulation of the spectra assuming only the static field distribution (i.e.,  $\lambda_d=0$ ). For better visualization each LF spectrum is shifted by 0.02 units.

member samples have residual resistance ratios  $\rho_{300\text{ K}}/\rho_0 \geq 30$  and the  $\text{PrPt}_4\text{Ge}_{12}$  sample showed crystallites up to 2 mm size. The ZF and longitudinal-field (ZF and LF)  $\mu$ SR experiments were performed on the DOLLY spectrometer at the  $\pi$ E1 beam line at the Paul Scherrer Institute (Villigen, Switzerland). In addition, a powdered sample of  $\text{PrPt}_4\text{Ge}_{12}$  was measured in ZF on the GPS spectrometer at the  $\pi$ M3 beam line. The samples were cooled in ZF or LF down to 1.5 K and  $\mu$ SR spectra were taken as a function of temperature. During ZF measurements, an active magnetic field compensation with three orthogonal couples of Helmholtz coils was used in order to reduce the field at the sample to values lower than  $3 \times 10^{-6}$  T. Typical counting statistics were  $12 \times 10^6$  positron events per each particular data point. Magnetization was measured in a commercial superconducting quantum interference device magnetometer.

### III. RESULTS AND DISCUSSION

Figure 1 shows ZF and LF  $\mu$ SR time spectra for  $\text{PrPt}_4\text{Ge}_{12}$  at 1.5 and 10 K. The spectra of several histograms were fitted simultaneously. Each histogram is described by the function

$$N(t) = N_0 \exp(-t/\tau)[1 + AP(t)] + B, \quad (1)$$

where  $\tau=2.197019 \mu\text{s}$  is the muon lifetime,  $N_0$  a proportionality coefficient,  $B$  the background,  $A$  the asymmetry, and  $P(t)$  the muon depolarization function. Preliminary fits showed that the ZF muon depolarization is well described by a Kubo-Toyabe depolarization function reflecting a static Voigt field distribution, i.e., describing two mechanisms for the profile, one producing a Gaussian distribution and one producing a Lorentzian distribution.

The zero- and longitudinal-field  $\mu$ SR depolarization functions for the static Voigt field distribution were calculated

using the general formula derived by Kubo, [Eq. 21 of Ref. 25]. For Voigt-type functions this equation can be reformulated as follows:

$$P_G(t) = 1 - \frac{2Q'(t)}{\omega_0^2 t} [\cos \omega_0 t - j_0(\omega_0 t)] - 2 \int_0^t \frac{Q'(s) j_0'(\omega_0 s)}{s \omega_0} ds. \quad (2)$$

Here,  $j_0(x) = \sin(x)/x$ ,  $\omega_0 = \gamma_\mu B$  is the Larmor frequency corresponding to the applied longitudinal field  $B$ . For the Voigt function  $Q(t) = \exp(-\frac{1}{2}\sigma^2 t^2 - \lambda t)$ , where  $\sigma^2/\gamma_\mu^2$  is the second moment of the Gaussian distribution and  $\lambda/\gamma_\mu$  is the half width at half maximum of the Lorentzian distribution, and finally the prime denotes the derivative.<sup>25</sup> In the limit of  $\omega_0 \rightarrow 0$  (i.e., in the ZF situation), Eq. (2) converges to the ‘‘golden formula’’ of Kubo,<sup>26</sup>

$$P_{G,ZF}(t) = \frac{1}{3} + \frac{2}{3}[Q(t) + Q'(t)t] \quad (3)$$

and for the case of  $Q(t) = \exp(-\frac{1}{2}\sigma^2 t^2 - \lambda t)$  one finally gets the equation,

$$P_{G,ZF,V}(t) = \frac{1}{3} + \frac{2}{3}(1 - \sigma^2 t^2 - \lambda t) \exp\left(-\frac{1}{2}\sigma^2 t^2 - \lambda t\right). \quad (4)$$

Actually, a closer look at the data indicates that the ZF and LF data are best fitted using the depolarization function,

$$P(t) = P_G(t) \exp(-\lambda_d t), \quad (5)$$

where  $\lambda_d \approx 0.020 \mu\text{s}^{-1}$  (which is practically temperature independent) is a dynamical muon depolarization which does not decouple up to fields of 20 mT. Such dynamical depolarization is best seen in LF experiments. In Fig. 1, the fits obtained with Eq. (5) are shown with the solid (red) curves. The best fit to the data is obtained with field independent parameters  $\sigma=0.173 \mu\text{s}^{-1}$ ,  $\lambda=0.029 \mu\text{s}^{-1}$ , and  $\lambda_d=0.020 \mu\text{s}^{-1}$ . The total asymmetry  $A=0.242$  was fixed during the fitting procedure. The small dynamic contribution  $\lambda_d$  to the relaxation is obvious only when comparing the LF spectra with the depolarization curves calculated for the case of a static only field distribution [see the dashed (blue) curves in Fig. 1]. Note that for such small values of  $\lambda$  and  $\lambda_d$ , as in the present case, these parameters are strongly correlated in the ZF spectra. However, LF experiments allow us to disentangle this correlation. Zero- and longitudinal-field experiments suggest the presence of static muon depolarization predominantly from nuclear moments of the Pr, Pt, or Ge isotopes. Note that usually for a depolarization due to nuclear moments, one assumes a Gaussian field distribution (i.e., a situation with  $\lambda=0$ ). However, a pure Gaussian field distribution is an approximation and does not take into account, for example, the presence of different isotopes with different nuclear moments (as for Pt and Ge). It is therefore likely that the field distribution due to nuclear moments is not purely Gaussian in our case. Note also that the main conclusions concerning the temperature dependence of the muon depolarization (see below) do not depend on the exact static field distribution assumed. Decoupling of this static field is well described with the general expression given in

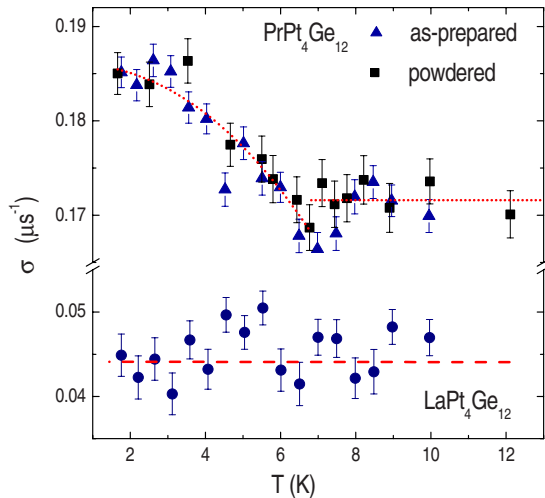


FIG. 2. (Color online) Temperature dependence of the muon depolarization rate  $\sigma$  in as-prepared ( $\blacktriangle$ ) and powdered ( $\blacksquare$ ) samples of  $\text{PrPt}_4\text{Ge}_{12}$  and in as-prepared  $\text{LaPt}_4\text{Ge}_{12}$  ( $\bullet$ ) as obtained by Eq. (5). The lines are guides to the eye (see text).

Eq. (5).<sup>25</sup> The small dynamic contribution  $\lambda_d$  which does not decouple up to fields of 20 mT is presumably due to some additional spin-lattice relaxation mechanisms.

When studying the temperature dependence of the parameters  $\sigma$  and  $\lambda$ , we first noticed that  $\lambda$  is practically independent of temperature. In a second step,  $\lambda$  was fixed to its average value  $0.029 \mu\text{s}^{-1}$  and solely  $\sigma$  was kept free. Figure 2 presents  $\sigma(T)$  recorded in ZF for  $\text{PrPt}_4\text{Ge}_{12}$  and  $\text{LaPt}_4\text{Ge}_{12}$ , measured on two different spectrometers. For the Pr compound, above  $T_c=7.8$  K  $\sigma$  is independent of temperature, as expected for depolarization due to nuclear moments.

However below  $T_c$  one can observe a clear increase in the muon relaxation rate with decreasing temperature. Just below  $T_c$  the data systematically decrease below the normal-state level showing a small dip. The rise of  $\sigma$  starts only below  $\approx 6.5$  K. There is no indication for a phase transition at this temperature from other measurements as, e.g., specific heat or the superfluid density.<sup>13,16</sup>

The corresponding ZF depolarization rates  $\sigma(T)$  for  $\text{LaPt}_4\text{Ge}_{12}$  with  $T_c=8.3$  K [obtained via Eq. (5) with  $\lambda=\lambda_d=0$  and free parameter  $\sigma$ ] are small and temperature independent (see Fig. 2).<sup>27</sup> No anomaly is resolved at  $T_c=8.3$  K.  $\sigma$  for  $\text{LaPt}_4\text{Ge}_{12}$  is substantially smaller than in  $\text{PrPt}_4\text{Ge}_{12}$ , indicating that in  $\text{PrPt}_4\text{Ge}_{12}$  the dominant part of the relaxation is due to the presence of  $^{141}\text{Pr}$  nuclei.

A similarly strong (nearly the same value of  $\sigma$ ) hyperfine-enhanced nuclear muon depolarization was observed in the isostructural  $\text{PrOs}_{4-x}\text{Ru}_x\text{Sb}_{12}$  compounds.<sup>28</sup> The authors explain the relaxation by a Van Vleck-type admixture of magnetic excited CEF states into the nonmagnetic  $\Gamma_1$  ground state of  $\text{Pr}^{3+}$  by the nuclear hyperfine coupling. This hybridization strongly increases the strength of the interactions between the  $^{141}\text{Pr}$  nuclear spins and the muon spins as well as within the  $^{141}\text{Pr}$  nuclear spin system.<sup>29</sup> Shu *et al.* observe that this relaxation is *dynamic* due to the relatively low energy ( $E/k_B \approx 7-10$  K for  $x=0$ ) of the first excited CEF level  $\Gamma_4^{(2)}$  of  $\text{Pr}^{3+}$  with a spin-spin correlation time  $\tau_c \approx 0.2-0.6 \mu\text{s}^{-1}$ . For  $\text{PrPt}_4\text{Ge}_{12}$ , the first excited CEF level  $\Gamma_4^{(1)}$  is found at

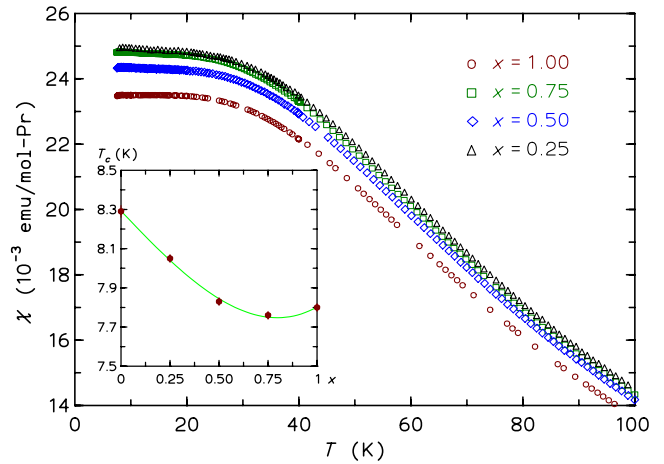


FIG. 3. (Color online) Magnetic susceptibility of  $\text{Pr}_x\text{La}_{1-x}\text{Pt}_4\text{Ge}_{12}$  samples in  $\mu_0H=0.1$  T. The inset shows the superconducting  $T_c$  ( $\mu_0H=2$  mT) vs the nominal Pr-content  $x$ .

$E/k_B \approx 120-130$  K,<sup>13,19,20</sup> in agreement with our observation of a quasistatic nuclear magnetism of Pr. The very small population of all excited CEF states at  $T \approx T_c = 7.8$  K is the reason for this behavior and the negligible Cooper-pair breaking in  $\text{PrPt}_4\text{Ge}_{12}$ . The origin of the additional dynamic relaxation  $\lambda_d$  in the present case is unknown. To reduce the magnitude of  $\lambda_d$  in LF the LF Larmor precession frequency should exceed the characteristic fluctuations of magnetic field probed in the sample.<sup>30</sup> Since it does not decouple up to 20 mT one estimates the characteristic fluctuation frequency larger than  $\nu > 2\pi\gamma_\mu \times 0.02 = 17$  MHz.

Figure 3 shows the susceptibility measurements for the series of  $\text{La}_{1-x}\text{Pr}_x\text{Pt}_4\text{Ge}_{12}$  samples. The magnetic susceptibility  $\chi(T)$  of the  $\text{La}_{1-x}\text{Pr}_x\text{Pt}_4\text{Ge}_{12}$  samples becomes temperature independent below  $\sim 20$  K (see Fig. 3) and the amplitude simply scales with the Pr content  $x$ , as expected for a single-ion CEF effect. No detectable Curie-type contributions indicating localized magnetic impurities (e.g.,  $\text{Pr}^{3+}$  ions on different crystallographic sites or in secondary phases) are observed. The inset of Fig. 3 displays the dependence of  $T_c$  on  $x$  in  $\text{La}_{1-x}\text{Pr}_x\text{Pt}_4\text{Ge}_{12}$ . This dependence is weak and the small sagging of the curve below the linear relationship may be due to the weak crystallographic disorder introduced by the statistical occupation of the  $2a$  site. Specific-heat data (not shown) reveal that also the size of the specific-heat jump  $\delta c_p/T_c$  at  $T_c$  varies linearly with the Pr content  $x$ . This is in contrast to the observations in the series  $\text{La}_{1-x}\text{Pr}_x\text{Os}_4\text{Sb}_{12}$  where  $\delta c_p/T_c$  shows a strongly nonlinear variation with  $x$ .<sup>8</sup> For the substitution series  $\text{PrOs}_{4-x}\text{Ru}_x\text{Sb}_{12}$  even a strong depression of  $T_c$  well below that of both end members is observed.<sup>8,28,31</sup>

In the ZF  $\mu\text{SR}$  data (Fig. 2) it can be seen that for  $\text{PrPt}_4\text{Ge}_{12}$  the data show the presence of an additional depolarization below  $T_c$ . In addition, our data seem to reveal a small dip of  $\sigma(T)$  just below  $T_c$ . At the moment we do not have an explanation for this dip. Most plausible would be the presence of diluted magnetic centers separated on distances of order of the magnetic penetration depth  $\Lambda \approx 120$  nm. In such a case, a reduction in  $\sigma$  is expected due to screening of the magnetic field by the superfluid condensate. The required

concentration of such impurities would be of the order of  $\sim 0.01\text{--}0.1\%$  [from  $\sigma(T > T_c)$ ]. Clearly, such impurities are not present in our samples as can be concluded from the absence of an upturn in the magnetic susceptibilities toward low temperatures (see Fig. 3). Another possibility for this dip could be a coupling of Pr nuclei with free carriers. Below  $T_c$  the density of states at the Fermi level  $N_F$  drops. Hence, in case of a Korringa-type coupling it is expected that the muon relaxation will drop  $\propto N_F^2$ . However, the observation of quasistatic magnetism of the Pr nuclei contradicts this assumption.

Beyond the possible observation of this small dip, the main observation is the *increase* in  $\sigma$  upon lowering the temperature below  $T_c$ . Such an increase cannot be explained by a Pr-Pr RKKY coupling, since it would reduce the muon depolarization below  $T_c$  ( $\propto N_F^2$ ), in contrast to our observation. The influence of external fields can be excluded, since true zero field was controlled with high precision and, moreover, the Meissner effect automatically shields any fields in the superconducting state. Note, only for the heavy-fermion superconductor  $\text{PrOs}_4\text{Sb}_{12}$  a similar spontaneous magnetization was detected to appear below  $T_c$  (Ref. 9) whereas there is no change in  $\sigma$  in  $\text{PrRu}_4\text{Sb}_{12}$  at  $T_c$ .<sup>32</sup> In both of these samples a nearly similar muon depolarization was observed above  $T_c$ . The electronic specific-heat coefficient  $\gamma$  and  $N_F$  are small for  $\text{PrPt}_4\text{Ge}_{12}$ .<sup>13,16</sup> In addition, our measurements of two different samples of  $\text{PrPt}_4\text{Ge}_{12}$  (“as-prepared” and powdered) on two different spectrometers with the same result and no anomaly at  $T_c$  for  $\text{LaPt}_4\text{Ge}_{12}$  strongly supports that the enhanced depolarization below  $T_c$  is an intrinsic property of the superconducting state of  $\text{PrPt}_4\text{Ge}_{12}$ .

The enhanced muon depolarization below  $T_c$  gives evidence of TRS breaking in  $\text{PrPt}_4\text{Ge}_{12}$ . TRS breaking can be realized for *spin* or *orbital* multicomponent (vector-) order parameters that may have an internal phase degree of freedom between the components.<sup>21</sup> An example is the chiral  $p$ -wave triplet state proposed for  $\text{Sr}_2\text{RuO}_4$  (Ref. 23) and the  $E_{2u}$  triplet state for  $\text{UPt}_3$ .<sup>33,34</sup> Triplet pairing has been proposed—and heavily debated—for  $\text{PrOs}_4\text{Sb}_{12}$ .<sup>17,18,35</sup> For  $\text{PrPt}_4\text{Ge}_{12}$  we recently reported<sup>16</sup> that the superfluid density fits well to the expectations of a chiral  $p$ -wave form of the gap function  $|\Delta| = \Delta_0 |k_x \pm ik_y|$  with a gap-to- $T_c$  ratio  $\Delta_0/T_c = 2.6$  similar to that of  $\text{PrOs}_4\text{Sb}_{12}$ .<sup>8,16</sup> Most interestingly, the  $T_c$  of  $\text{PrPt}_4\text{Ge}_{12}$  is larger than that of other proposed spin-triplet superconductors which have  $T_c$  values  $< 2.7$  K.<sup>9,22–24</sup>

For  $\text{LaPt}_4\text{Ge}_{12}$  we observe no indications for (or an unresolvably small) TRS breaking. Unfortunately, our investigations of the gap symmetry are inconclusive at the moment, however a nodeless gap and spin-singlet pairing has been concluded from NMR relaxation data for  $\text{LaPt}_4\text{Ge}_{12}$ .<sup>19</sup> The weak variation in  $T_c$  and in  $\delta c_p/T_c$  with the Pr-content  $x$  in

$\text{La}_{1-x}\text{Pr}_x\text{Pt}_4\text{Ge}_{12}$  indicates that the order parameters of the end members are compatible and not separated by a first-order phase transition. Thus, it is plausible that  $\text{PrPt}_4\text{Ge}_{12}$  is also a *spin-singlet* superconductor. In this case, the observation of TRS breaking in the condensate requires that the gap function belongs to a complex *orbitally* degenerate representation leading to an internal orbital moment of the Cooper pairs. In such a state supercurrents are induced around non-magnetic impurities which in turn generate a condensate magnetic-moment density with a spatial extension on the order of the coherence length  $\xi$ .<sup>36</sup> Such a complex spin-singlet state of  $T_g$  symmetry with point nodes along the cubic axes has actually been proposed in Ref. 37 to explain the TRS breaking in  $\text{PrOs}_4\text{Sb}_{12}$  and as an alternative to the spin-triplet model. The orbital moment of the Cooper pairs may vary and in this way the seemingly conflicting observations of a TRS broken state for  $\text{PrPt}_4\text{Ge}_{12}$  and of no visible TRS breaking for the La compound as well as a continuous changeover in  $\text{La}_{1-x}\text{Pr}_x\text{Pt}_4\text{Ge}_{12}$  may appear.

#### IV. CONCLUSIONS

To conclude, zero-field  $\mu\text{SR}$  measurements on  $\text{PrPt}_4\text{Ge}_{12}$  and  $\text{LaPt}_4\text{Ge}_{12}$  showed that the dominant contribution for the muon relaxation comes from the Pr nuclei. Below  $T_c$  in  $\text{PrPt}_4\text{Ge}_{12}$  we observe an additional muon depolarization with a temperature variation resembling that of the superfluid density while no anomalous effect was seen for  $\text{LaPt}_4\text{Ge}_{12}$ . This observation indicates TRS breaking in the superconducting state of  $\text{PrPt}_4\text{Ge}_{12}$  with an extraordinary high  $T_c$ .<sup>21</sup> We have argued that the origin of the TRS breaking is the unconventional multicomponent nature of the order parameter. From the present experiments no definite conclusion can be made whether this is due to the spin or orbital degeneracy of the Cooper pairs. The  $T_c$  of 7.8 K for  $\text{PrPt}_4\text{Ge}_{12}$  seems to be rather high for spin-triplet pairing. In the series  $\text{La}_{1-x}\text{Pr}_x\text{Pt}_4\text{Ge}_{12}$  the  $T_c$  as well as the size of the related specific-heat anomaly vary almost linearly with the Pr content  $x$ . Together with the absence of TRS breaking for  $\text{LaPt}_4\text{Ge}_{12}$  this renders a spin-triplet Cooper pairing for these compounds, including  $\text{PrPt}_4\text{Ge}_{12}$ , unlikely, since one would expect strong effects for incompatible superconducting order parameters. Due to the high tetrahedral symmetry, orbital degeneracies are present which allow for a complex spin-singlet gap function with an internal phase. Such a kind of pairing with orbital degeneracy also breaks TRS and may lead to a condensate with a magnetic-moment density.

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