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# Time reversal symmetry breaking in superconducting(Pr, La)$Os_4Sb_{12}$ and Pr(Os, Ru)$_4Sb_{12}$

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**Abstract**

Zero-field muon spin relaxation (μSR) experiments have been carried out in the Pr$(Os_{1-x}Ru_x)_4Sb_{12}$ and $Pr_{1-y}La_yOs_4Sb_{12}$ alloy systems to investigate the time-reversal symmetry (TRS) breaking found in an earlier ZF-μSR study of the end compound $PrOs_4Sb_{12}$. Our results suggest that Ru doping is considerably more efficient than La doping in suppressing TRS-breaking superconducting pairing in $PrOs_4Sb_{12}$.



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The filled skutterudite compound $PrOs_4Sb_{12}$ has attracted an enormous amount of interest since it was discovered as the first Pr-based heavy-fermion (HF) superconductor a few years ago [1,2]. It has proved to be an intriguing material due to unusual properties of its HF ($\gamma \sim 500\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$) and superconducting ($T_c = 1.85\,\mathrm{K}$) states. A recent zero-field muon-spin relaxation (ZF-μSR) experiment [3] revealed the spontaneous appearance of static internal magnetic fields below $T_c$, providing evidence that the superconducting state breaks time reversal symmetry (TRS). Magnetic penetration depth [4] and flux-line lattice distortion studies [5] suggest nodes of the superconducting energy gap. However, transverse-field muon-spin relaxation (TF-μSR) [6] and antimony nuclear quadrupole resonance measurements [7] indicate an isotropic nodeless energy gap.

The isostructural compounds $PrRu_4Sb_{12}$ ($T_c = 1.1\,\mathrm{K}$) and $LaOs_4Sb_{12}$ ($T_c = 0.74\,\mathrm{K}$) are both conventional BCS-like superconductors [8,9]. The alloy series Pr$(Os_{1-x}Ru_x)_4Sb_{12}$ [10] and $Pr_{1-y}La_yOs_4Sb_{12}$ [11] both exhibit superconductivity for all values of Ru or La concentration, with relatively slow changes of $T_c$ with composition. This is quite different from the behavior of the majority of heavy-fermion superconductors, where chemical substitution rapidly suppresses $T_c$. In Pr$(Os_{1-x}Ru_x)_4Sb_{12}$, $T_c$ decreases smoothly from 1.85 K at $x = 0$ to a minimum of $\sim$0.75 K at $x \approx 0.6$, and then increases to 1.04 K at $x = 1$ [10]. In $Pr_{1-y}La_yOs_4Sb_{12}$, $T_c$ varies monotonically with $y$ to 0.74 K

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at $y = 1$. These properties immediately raise the question of how the TRS-breaking superconductivity of $PrOs_4Sb_{12}$ evolves with Ru and La substitution.

We report the results of ZF-μSR experiments in $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, $x = 0.1$, 0.2, and 1.0, and in $Pr_{1-y}La_yOs_4Sb_{12}$, $y = 0.2$, 0.4, and 1.0. The ZF-μSR data suggest that Ru doping is more efficient than La doping in suppressing TRS breaking superconductivity in $PrOs_4Sb_{12}$.

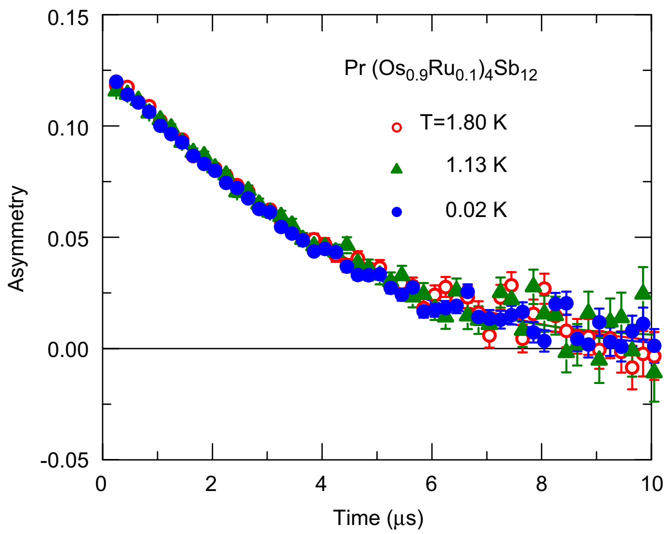


Fig. 1. ZF-μSR spectra in $Pr(Os_{0.1}Ru_{0.9})_4Sb_{12}$ measured across the superconducting transition temperature $T_c$. The corrected asymmetry was obtained by subtracting the contribution from silver holder.

ZF-μSR experiments were carried out on powdered samples at the Meson Science Laboratory, KEK, Tsukuba, Japan, using a dilution refrigerator to obtain temperatures down to 20 mK. Standard time-differential μSR asymmetry data were taken for temperatures in the range 0.02–2.0 K.

Representative time evolution of the ZF muon-spin polarization is shown in Fig. 1 for $Pr(Os_{0.1}Ru_{0.9})_4Sb_{12}$ at $T = 0.02$, 1.13, and 1.80 K. The relaxation is essentially the same at all the temperatures. Similar behavior of the relaxation function is found for $Pr(Os_{0.2}Ru_{0.8})_4Sb_{12}$. In $Pr_{1-y}La_yOs_4Sb_{12}$, however, a small increase of relaxation rate below $T_c$ can be seen for $y = 0.2$ and 0.4, as was first observed in undoped $PrOs_4Sb_{12}$ [3]. This indicates the onset of a spontaneous local field $H_{loc}$ below $T_c$. The present results suggest that $H_{loc}$ is rapidly suppressed by Ru doping, but is less affected by La substitution.

The commonly used damped Gaussian Kubo–Toyabe (K–T) function

$$P_\mu = \exp(-\Lambda t) G_z^{KT}(\Delta, t) \quad (1)$$

was fit to the data, where

$$G_z^{KT}(\Delta, t) = \tfrac{1}{3} + \tfrac{2}{3}(1 - \Delta^2 t^2) \exp(-\tfrac{1}{2}\Delta^2 t^2) \quad (2)$$

is the K–T functional form expected [12] from a static Gaussian. Here $\Delta/\gamma_\mu$ is the rms width of the static field distribution ($\gamma_\mu$ is the muon gyromagnetic ratio), and $\Lambda$ is

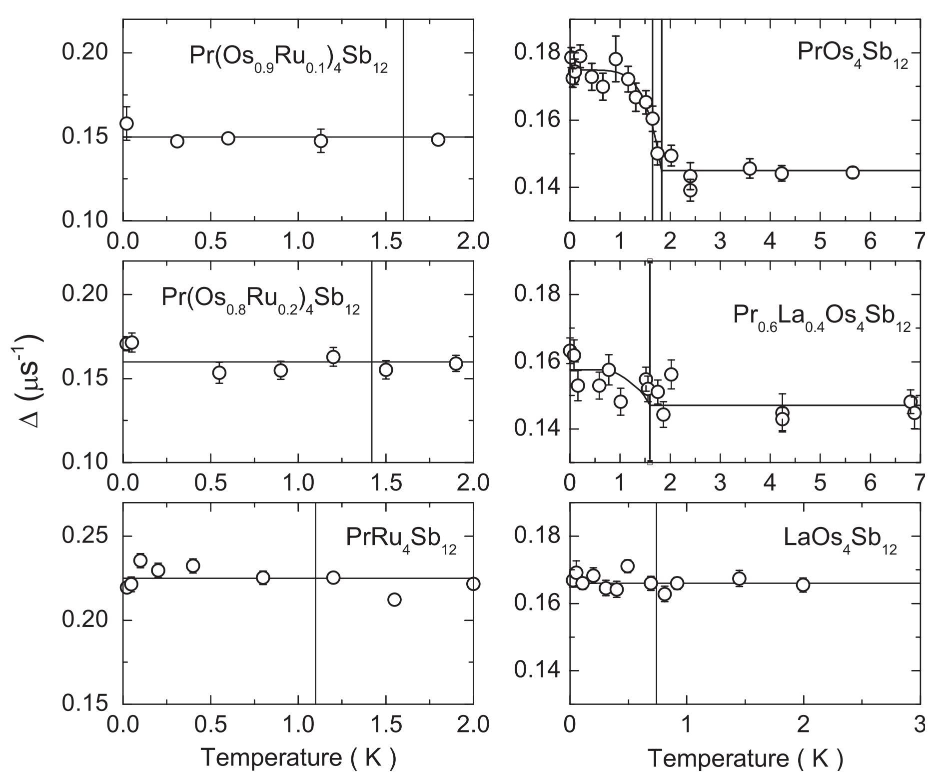


Fig. 2. Temperature dependence of ZF Kubo–Toyabe relaxation rate $\Delta$ in $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, $x = 0.1$, 0.2, and 1.0, and $Pr_{1-y}La_yOs_4Sb_{12}$, $y = 0$ (data from Ref. [3]), 0.4, and 1.0. The vertical lines indicate the position of $T_c$.

the rate associated with an additional contribution to the muon relaxation process.

Fig. 2 shows the temperature dependence of $\Delta(T)$ in $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, $x = 0.1$, 0.2, and 1.0, and $Pr_{1-y}La_yOs_4Sb_{12}$, $y = 0$, 0.4, and 1.0. For Ru doping, $\Delta(T)$ is temperature-independent to within experimental uncertainties for $x \geqslant 0.1$. No extra spontaneous field is observed to set in below $T_c$. In contrast, for La doping the increased relaxation below $T_c$ seen for $y = 0$ is also observed with reduced amplitude for $y = 0.4$, indicating the onset of a spontaneous field correlated with the superconductivity. No spontaneous field is observed in the end compounds $PrRu_4Sb_{12}$ [13] and $LaOs_4Sb_{12}$ [14]. For all alloys, $\Lambda$ is essentially independent of temperature.

Ru doping is more effective than La doping in (a) distorting the Sb cage that surrounds each Pr ion, which modifies the $Pr^{3+}$ crystalline electric field splitting and restricts the "rattling" motion of the Pr ions; and (b) in changing the character and density of states of band electrons on the Fermi surface. One or more of these effects may be involved in quenching the TRS-breaking.

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