Nodeless superconductivity in the cage-type superconductor Sc$_5$Ru$_6$Sn$_{18}$ with preserved time-reversal symmetry

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Abstract
We report the single-crystal synthesis and detailed investigations of the cage-type superconductor Sc$_5$Ru$_6$Sn$_{18}$, using powder x-ray diffraction (XRD), magnetization, specific-heat and muon-spin relaxation ($\mu$SR) measurements. Sc$_5$Ru$_6$Sn$_{18}$ crystallizes in a tetragonal structure (space group $I4_1/acd$) with lattice parameters $a = 1.387(3)$ nm and $c = 2.641(5)$ nm. Both DC and AC magnetization measurements prove the type-II superconductivity in Sc$_5$Ru$_6$Sn$_{18}$ with $T_c \approx 3.5(1)$ K, a lower critical field $H_{c1}(0) = 157(9)$ Oe and an upper critical field, $H_{c2}(0) = 26(1)$ kOe. The zero-field electronic specific-heat data are well fitted using a single-gap BCS model, with $\Delta(0) = 0.64(1)$ meV. The Sommerfeld constant $\gamma$ varies linearly with the applied magnetic field, indicating $s$-wave superconductivity in Sc$_5$Ru$_6$Sn$_{18}$. Specific-heat and transverse-field (TF) $\mu$SR measurements reveal that Sc$_5$Ru$_6$Sn$_{18}$ is a superconductor with strong electron–phonon coupling, with TF-$\mu$SR also suggesting a single-gap $s$-wave character of the superconductivity. Furthermore, zero-field $\mu$SR measurements do not detect spontaneous magnetic fields below $T_c$, hence implying that time-reversal symmetry is preserved in Sc$_5$Ru$_6$Sn$_{18}$.

Keywords: superconductivity, muon-spin relaxation, time reversal symmetry

(Some figures may appear in colour only in the online journal)

1. Introduction

In 1957, Bardeen, Cooper, and Schrieffer (BCS) explained superconductivity by using the concept of Cooper pairs [1], implying electrons with equal and opposite spins and crystal momenta, which pair together. Understanding the pairing mechanism in unconventional superconductors is a challenging task. In conventional $s$-wave superconductors, only the gauge symmetry is broken. However, in the case of unconventional pairing, besides the global gauge symmetry
(responsible for the Meissner and Josephson effects [2]) other symmetries of the Hamiltonian might be broken in the superconducting state, including spin-rotation, lattice-point and translation-group symmetries. Studying such broken symmetries in superconductors is crucial and it can be achieved by investigating the symmetry properties of the order parameter, $\psi(k)$. Depending on the parity of superconducting order parameter [3], superconductors with an inversion center may be classified in either even parity spin-singlet ($S = 0$) or in odd parity spin-triplet pairing states ($S = 1$). For instance, a few compounds, such as the 4$d$-electron system Sr$_2$RuO$_4$ [4, 5] or the 5$f$-electron system UGe$_2$ [6] have been reported to be spin-triplet superconductors.

Besides modifying the properties of the system, broken symmetry may lead to some interesting unconventional behavior. Superconductivity itself is one of the best examples of a symmetry-breaking phenomenon. Time-reversal symmetry (TRS) breaking is another interesting example. TRS breaking is a rare phenomenon and has been observed only in a few unconventional superconductors, such as Sr$_2$RuO$_4$ [4], LaNiC$_2$ [7], Re$_2$Zr [8], Re$_5$Ir$_3$ [9]. TRS breaking can be probed with the help of zero-field muon spin-relaxation (ZF-$\mu$SR) technique, by detecting the occurrence of tiny spontaneous magnetic fields, below the onset of superconductivity. The presence of such spontaneous fields restricts the pairing symmetry of the superconducting states. TRS breaking is associated with a special kind of superconducting states having a degenerate representation. The two or more degenerate superconducting phases lead to a spatially inhomogeneous order parameter near the resulting domain walls, which, in turn, create spontaneous supercurrents and hence, spontaneous magnetic field in those regions [3]. TRS breaking fields may also originate from the intrinsic magnetic moments due to spin-polarization (in case of spin-triplet pairing) and the relative spin-angular momentum associated with the Cooper pairs [10]. Recently, some of the noncentrosymmetric superconductors, such as Re$_2$Zr [8] and La$_5$Ir$_3$ [11], with a mixed singlet-triplet pairing, were found to exhibit TRS breaking. However, it has been established theoretically [12] and experimentally [13] that the presence of singlet-triplet mixing not necessarily implies a broken TRS.

Compounds with cage-like structures have attracted remarkable attention due to their peculiar features. There are three major classes of cage-type compounds which are being studied extensively, i.e., skutterudites (RT$_4$X$_{12}$), $\beta$-pyrochlore oxides (AO$_5$O$_8$) and Ge/Si clathrates [14]. Exotic phenomena such as heavy-fermion superconductivity or exciton-mediated superconductivity were discovered in these materials. These compounds consist of 3D skeletons which surround large atomic cages, in which small atoms are situated. Because of a strong electron-phonon coupling and weak structural couplings, the small atoms can ‘rattle’ with large atomic excursions, ultimately leading to a rattling vibration. Such rattling of small atoms might result in interesting phenomena, such as strong-coupling superconductivity in AO$_5$O$_8$ [15]. A specific case of cage-type compounds is given by R$_2$Rh$_6$Sn$_{18}$ ($R =$ Sc, Y, Lu). These crystallize in a tetragonal structure with space group $I4_1/acd$ and $Z = 8$, where $Z$ represents the number of formula units per unit cell ($R$ occupies sites of different symmetry [16]). R$_2$Rh$_6$Sn$_{18}$ exhibit superconductivity at 5 K (Sc), 3 K (Y) and 4 K (Lu) [17], respectively. The superconducting properties of Lu$_2$Rh$_6$Sn$_{18}$ and Y$_2$Rh$_6$Sn$_{18}$ compounds have been studied [2, 18]. Unconventional superconductivity has been observed in both Lu$_2$Rh$_6$Sn$_{18}$ and Y$_2$Rh$_6$Sn$_{18}$, where the former has an isotropic superconducting gap, while the latter shows anisotropic gap. In addition, ZF-$\mu$SR studies reveal the presence of spontaneous magnetic fields, hinting at TRS breaking. However, the superconductivity of ruthenate stan- nides R$_2$Ru$_6$Sn$_{18}$ is largely unexplored. This motivated us to study the superconducting properties of Sc$_2$Ru$_6$Sn$_{18}$ and to search for possible TRS breaking in this compound.

In this paper, we report on the superconducting properties of the cage-type superconductor Sc$_2$Ru$_6$Sn$_{18}$ investigated via magnetization, specific-heat, and $\mu$SR measurements. The symmetry of the superconducting gap was studied using TF-$\mu$SR, whereas ZF-$\mu$SR measurements could not detect the spontaneous magnetic fields below $T_c$, hence indicating that the TRS is preserved in Sc$_2$Ru$_6$Sn$_{18}$. We also report on the calculated critical current density ($J_c$) as obtained from the isothermal hysteresis loops in Sc$_2$Ru$_6$Sn$_{18}$.

2. Experimental methods

Single crystals of Sc$_2$Ru$_6$Sn$_{18}$ were grown using a Sn-flux method with Sc-powder (99.99%), Ru-powder (99.99%) and Sn-shot (99.99%) as the starting materials. The typical dimensions of the crystals used in our investigations were $2.5 \times 2.8 \times 2.5$ mm$^3$ as shown in the inset of figure 1. The smaller crystals were crushed into powder for x-ray diffraction (XRD) measurements (using a Bruker AXS GmbH D2 Phaser desktop x-ray diffractometer) with Cu-K$_\alpha$ radiation. The quality of the single crystal was verified using a 2D XRD technique with omega scan without crystal rotation. Well-defined spots on the 2D image indicated a good crystalline quality. The magnetization was measured using a

![Figure 1. Powder XRD pattern of Sc$_2$Ru$_6$Sn$_{18}$. All the peaks were indexed successfully to a tetragonal R$_2$M$_6$Sn$_{18}$ (R = rare earth, M = transition metal) phase. The inset shows the single crystal used in our study. The hexagonal-shaped plane was identified with the (112) plane by means of x-ray reflection.](image-url)
superconducting quantum interference device (SQUID) magnetometer (Quantum Design) at temperatures down to 1.8 K and magnetic fields up to 20 kOe. The specific-heat measurements were performed in various magnetic fields (up to 30 kOe) in the temperature range 1.8–10 K, using the heat-capacity option of a physical property measurement system (PPMS) (Quantum Design). The temperature dependence of AC susceptibility was again studied with PPMS, using a small ac-driving field with frequencies up to 10 kHz.

The ZF-$\mu$SR measurements were carried out at the pulsed muon beam of the RIKEN-RAL Muon Facility at ISIS (United Kingdom). In this case the sample temperature was varied from about 30 K ($> T_c$) down to 1.5 K ($< T_c$) with cooling being performed in a helium-flow type cryostat (Janis Co.). Helium exchange gas was used to achieve good temperature homogeneity. The asymmetry parameter is defined as $A(t) = [F(t) - \alpha B(t)]/[F(t) + \alpha B(t)]$, where $F(t)$ and $B(t)$ represent the muon events recorded in the forward and backward counters, respectively. $\alpha$ is a geometrical factor, which accounts for the different solid angles and efficiencies of the two detectors, as viewed from the sample position. The time dependence of $A(t)$, also known as the $\mu$SR time spectrum, was measured. The TF-$\mu$SR measurements were carried out in the superconducting mixed state in an applied field of 300 Oe, using the general-purpose surface (GPS) muon instrument located at the m3 beamline of the Swiss Muon Source of the Paul Scherrer Institute in Villigen, Switzerland.

3. Results and discussion

3.1. Crystal structure

Figure 1 shows the room temperature powder XRD pattern for Sc$_5$Ru$_6$Sn$_{18}$ with the scattering angle $2 \theta$ varying between $20^\circ$–$80^\circ$. All the peaks in the pattern can be well indexed using a tetragonal structure with lattice constants $a = 1.387(3)$ nm and $c = 2.641(5)$ nm, which give a unit cell volume $= 5.080(5)$ nm$^3$ and a density $\rho = 7.8(3) \ g \ cm^{-3}$ (space group $P4_{1}/nmc$).

$$c_1(0) = 157(9) \ Oe.$$ (1)

where $H_{c1}(0)$ is the lower critical field at zero-temperature. The fit gives $H_{c1}(0) = 157(9) \ Oe$.

The upper critical field is defined as the point where the magnetization curve touches the zero magnetic moment line (see inset in figure 4). The main panel in figure 4 shows the temperature variation of $H_{c2}$, which can be fitted using the Ginzburg–Landau equation given by [25]:

$$H_{c1}(T) = H_{c1}(0) \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

$$H_{c2}(T) = \frac{H_{c2}(0)}{1 + (T/T_c)^2}$$

$H_{c1}(0)$ is the lower critical field at zero-temperature.

$H_{c2}(0)$ is the upper critical field at zero-temperature.

The lower critical field, $H_{c1}$, is defined as the point where the field-dependent magnetization starts to deviates from linearity (see inset in figure 3) [22]. Since the actual magnetic field around the sample is larger than the applied magnetic field due to the demagnetizing effects by a factor of $1/(1 - N)$, where $N$ is the demagnetizing factor, we have to correct the $H_{c1}$ values for such an effect [23]. We have estimated the value of $N$ from the dimensions of the crystal [24] and we get $N = 0.39$. The main panel of figure 3 shows the temperature variation of corrected values of $H_{c1}$, which can be fitted by the relation [25]:

3.2. Magnetization

Figure 2 shows the hysteresis curves of Sc$_5$Ru$_6$Sn$_{18}$ recorded at various temperatures below $T_c$, characterized by symmetric $M-H$ loops. The $M(H)$ curves exhibit a butterfly shape, typical of type-II superconductors. The symmetry of the hysteresis loop (or the lack of it) allows one to distinguish between pinning- and surface- (or geometrical barrier) induced hysteresis, with flux pinning known to produce symmetric hysteresis loops [21], as in our case. The lower-$H_{c1}$ and upper-$H_{c2}$ field values were determined from the magnetization data. The lower critical field, $H_{c1}$, is defined as the point where the field-dependent magnetization starts to deviates from linearity (see inset in figure 3) [22]. Since the actual magnetic field around the sample is larger than the applied magnetic field due to the demagnetizing effects by a factor of $1/(1 - N)$, where $N$ is the demagnetizing factor, we have to correct the $H_{c1}$ values for such an effect [23]. We have estimated the value of $N$ from the dimensions of the crystal [24] and we get $N = 0.39$. The main panel of figure 3 shows the temperature variation of corrected values of $H_{c1}$, which can be fitted by the relation [25]:

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The upper critical field is defined as the point where the magnetization curve touches the zero magnetic moment line (see inset in figure 4). The main panel in figure 4 shows the temperature variation of $H_{c2}$, which can be fitted using the Ginzburg–Landau equation given by [25]:

$$H_{c2}(T) = \frac{H_{c2}(0)}{1 + (T/T_c)^2}$$
\[ H_{c2}(T) = H_{c2}(0) \left( \frac{1 - q^2}{1 + q^2} \right) \]  

(2)

where \( q = \frac{T}{T_\text{c}} \) and \( H_{c2}(0) \) is the upper critical field at zero-temperature. The fit gives \( H_{c2}(0) = 26(1) \text{ kOe} \). From this, we estimate a Ginzburg–Landau coherence length, \( \xi(0) \approx 11.26(3) \text{ nm} \), by using the relation [25]:

\[ \xi(0) = \frac{\phi_0}{2\pi\lambda^2(0)} \]  

(3)

Figure 4. Temperature dependence of \( H_{c2} \) for Sc\(_3\)Ru\(_6\)Sn\(_{18} \) (squares) and a fit to equation (2) (solid line). Inset: magnetization curves for Sc\(_3\)Ru\(_6\)Sn\(_{18} \) for temperatures in the 1.8–3.5 K range. \( H_{c2} \) is defined as the field at which the magnetization becomes zero.

By using the previously obtained values of \( \phi_0 = 2.07 \times 10^{-15} \text{ Tm}^2 \), the quantum of the magnetic flux, in addition, we can estimate the Ginzburg–Landau penetration depth using the relation [25]:

\[ H_{c2}(0) = \frac{\phi_0}{2\pi\lambda^2(0)} \left[ \ln \frac{\lambda(0)}{\xi(0)} + 0.12 \right] \]  

(4)

By using \( H_{c2}(0) = 157(9) \text{ Oe} \) and \( \xi(0) \approx 11.26(3) \text{ nm} \), we obtain \( \lambda(0) = 260(7) \text{ nm} \).

Finally, the Ginzburg–Landau parameter (\( \kappa \)) is obtained from the relation \( \kappa = \frac{\lambda(0)}{\xi(0)} \). By using the values for \( \lambda(0) \) and \( \xi(0) \), we find \( \kappa \approx 23(2) > \frac{1}{\sqrt{2}} \), the latter indicating that Sc\(_3\)Ru\(_6\)Sn\(_{18} \) is indeed a strong type-II superconductor. The zero-temperature thermodynamic critical field was estimated by using the relation [25],

\[ H_{c2}(0) = \sqrt{2\kappa}H_c(0). \]  

(5)

By using the values for \( H_{c2}(0) = 26(1) \text{ kOe} \) and \( \kappa \approx 23(2) \), we get \( H_c(0) = 799(6) \text{ Oe} \).

The field dependence of the critical current density \( J_c \) was derived from the width \( \Delta M \) of the magnetization curve, by using the Bean model [26, 27]:

\[ J_c = 20\Delta M/[d(1 - d/3b)] \]  

(6)

where \( d \) (mm) and \( b \) (mm) are the sample dimensions (\( d < b \)). In our case \( d = 1.25 \text{ mm} \) and \( b = 1.40 \text{ mm} \). The critical current density \( J_c \) is expected to have a maximum at the lower critical field, whereas above this threshold it decreases rapidly with the increasing field. Figure 5(a) shows \( J_c \) as a function of the magnetic field at various temperatures. Above the threshold field, for each isothermal measurement, initially \( J_c \) shows an exponential decrease followed by a power-law variation, in good agreement with the previous reports [28, 29]. We obtain \( J_c(1.8 \text{ K}) \sim 6(3) \times 10^8 \text{ A m}^{-2} \). The de-pairing current is given by the relation:

\[ J_d = \frac{\phi_0}{3\sqrt{2}\mu_0\pi\lambda^2\xi}. \]  

(7)

By using the previously obtained values of \( \xi(0) = 11.26(3) \text{ nm} \) and \( \lambda(0) = 260(7) \text{ nm} \), we find \( J_d = 3.07(5) \times 10^{10} \text{ A m}^{-2} \). The long coherence length implies a high pinning energy and flux-lines that do not move easily [30]. The material might have a large concentration of weak pinning centers, which ultimately leads to collective pinning. In the scenario of collective pinning, the critical current density depends strongly on the magnetic field and is typically small. This behavior has been observed, e.g., in case of layered inhomogeneous superconductors [31]. The irreversibility field \( (H_{irr}) \), at which the magnetic hysteresis disappears, is determined by the criterion \( J_c = 2 \times 10^7 \text{ A m}^{-2} \) [28]. The variation of the \( H_{irr} \) and \( H_{c2} \) with temperature is shown in figure 5(b). We note that the irreversibility field is comparable to the upper critical field \( (H_{c2}) \), a rather plausible result considering that the material has a low \( T_c \) and a high coherence length [30].

3.3. AC susceptibility

To further confirm the superconducting transition temperature we measured the ac magnetic susceptibility in the temperature range 1.8–10 K, with \( H_{ac} = 5 \text{ Oe} \) and \( H_{dc} = 0 \text{ Oe} \). Figure 6(a) shows the imaginary part of the ac susceptibility, while figure 6(b) shows the real part, corresponding to the out-of-phase and in-phase components, respectively (with respect to the ac field). The real part of the ac susceptibility versus temperature, represents the transition from the Meissner state (perfect shielding) to the complete penetration of the ac magnetic field inside the sample. On the other hand, the imaginary part of the ac susceptibility represents the ac losses occurring when the ac field penetrates the sample. As shown in figure 6(a), \( \chi'' \) has a sharp transition near \( T_c = 3.6 \text{ K} \). The transition in \( \chi'' \) is independent of the frequency of the driving ac field. The appearance of a peak in \( \chi'' \) is commonly associated with the superconducting transition. When the temperature is far below the critical temperature and the magnetic field is smaller than the lower critical field \( H_{c1} \), the screening current generated by the ac field is confined to regions near the sample surface. Hence, no magnetic flux enters the sample and the ac losses are minimal; consequently \( \chi'' \) is almost zero. As the temperature is raised, the magnetic field starts penetrating the sample and ac losses start increasing. The maximum in \( \chi'' \) occurs when the ac field fully penetrates the sample.

3.4. Specific heat

The specific heat in the superconducting state is one of the key parameters to reflect closely the superconducting gap and
Figure 5. (a) Variation of the critical current density ($J_c$) with the applied magnetic field for different temperatures for a single crystal of Sc$_5$Ru$_6$Sn$_{18}$. The critical current density shows a peak near the lower critical field ($H_{c1}$) and an ensuing exponential decrease followed by a power-law ($H^a$) variation versus applied field. The $J_c(1.8 \, \text{K}) \approx 6 \times 10^8 \, \text{A m}^{-2}$ is obtained at a low field of 150 Oe. (b) Phase diagram showing the variation of the irreversibility ($H_{irr}$) and upper critical ($H_{c2}$) fields for Sc$_5$Ru$_6$Sn$_{18}$.

Figure 6. (a) Temperature dependence of the imaginary part of ac susceptibility for $H_{dc} = 0$ Oe and $H_{ac} = 5$ Oe and different frequencies for Sc$_5$Ru$_6$Sn$_{18}$. (b) Temperature dependence of the real part of ac susceptibility measured in identical conditions.

Figure 7. Temperature dependence of the zero-field electronic specific heat of Sc$_5$Ru$_6$Sn$_{18}$. The solid line refers to a fit using a fully-gapped $s$-wave model. Inset: raw $C/T$ data versus $T^5$. The solid line shows the fit to $\frac{C}{T} = \gamma + \beta T^3 + \delta T^4$, which is used to calculate the phonon contribution to the specific heat.
its symmetry. Therefore, we measured and analyzed in detail the zero-field specific heat of Sc$_5$Ru$_6$Sn$_{18}$. The electronic specific heat ($C_e/T$) of the sample was obtained after subtracting the phonon contribution from the raw experimental data. As shown in the inset of figure 7, the normal-state specific heat was fitted using the relation $C_e/T = \gamma + \beta T^2 + \delta T^4$ for $14 K^2 \lesssim T^2 \lesssim 42 K^2$ to obtain $\gamma = 36.93(6) \text{ mJ mol}^{-1} \text{ K}^{-2}$, $\beta = 2.5(5) \text{ mJ mol}^{-1} \text{ K}^{-4}$ and $\delta = 1.2(9) \text{ mJ mol}^{-1} \text{ K}^{-6}$. The Debye temperature $\theta_D$ = 205(1) K was calculated using the relation:

$$\beta = \rho(\frac{12}{5})\pi^4 R\theta_D^{-3}$$

where $\rho = 29$ is the number of atoms in one formula unit and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. The density of states at the Fermi level $N(E_F)$ was estimated from [32]:

$$\gamma = \frac{\pi k_B^2}{3} N(E_F)$$

where $k_B$ is the Boltzmann constant. By using the previously obtained $\gamma$ value, we obtain $N(E_F) = 15.24(6) \text{ states/eV per formula unit.}$

The calculated density of states $N(E_F)$ and the effective mass of quasiparticles $m^*$, depend on the many-body electron-phonon interactions. These quantities are related to the bare band-structure of density of states $N_{\text{band}}(E_F)$ and $m_{\text{band}}^*$ by the following relations [34]:

$$N(E_F) = N_{\text{band}}(E_F)(1 + \lambda_{\text{el-ph}})$$

$$m^* = m_{\text{band}}^*(1 + \lambda_{\text{el-ph}})$$

By using the values of $N(E_F)$ and $\lambda_{\text{el-ph}}$ in equation (11), we get $N_{\text{band}}(E_F) = 9.270(6) \text{ states eV}^{-1} \text{ fm}^{-1}$. By using $m_{\text{band}}^* = m_e$ (the free electron mass), in equation (12), we obtain $1.644 m_e$ for the mass of the quasiparticles.

The density of states can be used to estimate the Fermi velocity, $v_F$, which is related to $N(E_F)$ by [35],

$$v_F = (\pi^2\hbar^3/m^*v_{\text{FN}})N(E_F).$$

Where $\hbar = \text{Planck’s constant}/2\pi$, $v_{\text{FN}} = V_{\text{cell}}/2$ is the volume per formula unit. Using the values of $m^*$, $V_{\text{cell}}$ and $N(E_F)$, we get $v_F = 1.94(7) \times 10^6 \text{ cm s}^{-1}$ for Sc$_5$Ru$_6$Sn$_{18}$. We can further estimate the mean free path ($l$) of the superconducting carriers by using the relation $l = \frac{\gamma}{v_F \tau}$, where $\tau$ is the mean free scattering time, given by $\tau = m^*/n_e e^2 \rho_0$, where $\rho_0$ is the residual resistivity and $n_e$ is the superconducting carrier density. The latter is given by $n_e = m^* \frac{\sqrt{2}}{\pi^2} \hbar^3$, assuming a spherical Fermi surface [35]. Using the value of $v_F$, we get $n_e = 7.05(2) \times 10^{26} \text{ carriers m}^{-3}$. By combining these expressions we get [35],

![Figure 8. Sommerfeld constant $\gamma$ versus normalized field $H/H_{c2(0)}$ for Sc$_5$Ru$_6$Sn$_{18}$. The solid line shows the linear relation between $\gamma$ and field, which indicates the $s$-wave nature of superconductivity in Sc$_5$Ru$_6$Sn$_{18}$.](image)

$$l = 3\pi^2 \left( \frac{\hbar}{e^2 \rho_0} \right) \left( \frac{\hbar}{m^* v_F} \right)^2.$$ (14)

Putting $\rho_0 = 200 \mu\Omega \text{ cm}$ (resistivity data not shown here) and the above estimated values of $m^*$ and $v_F$, we get $l = 8.14(5)$ nm.

The normalized electronic specific heat $C_e/\gamma T$ is plotted versus the normalized temperature $TT_c$ as shown in figure 7. The normalized specific heat jump at $T_c = \frac{\Delta(0)}{k_B} = 1.6$ for $\gamma = 36.93(6) \text{ mJ mol}^{-1} \text{ K}^{-2}$. Since such a value is higher than the BCS value of 1.43 (for a weakly coupled superconductor), it again indicates a strong electron-phonon coupling in Sc$_5$Ru$_6$Sn$_{18}$.

The temperature dependence of specific heat in the superconducting state is best modelled by an $s$-wave single-gap BCS expression of the normalized entropy $S$ [34]:

$$\frac{S}{\gamma T_c} = -\frac{6}{\pi^2} \left( \frac{\Delta(0)}{k_B T_c} \right) \int_0^\infty \left[ f \ln (f) + (1 - f) \ln (1 - f) \right] df$$

where $f(\xi) = \left[ \frac{\exp (\frac{\xi(1/\sqrt{2})}{\Delta(0)}) + 1}{\exp (\frac{\xi(1/\sqrt{2})}{\Delta(0)}) - 1} \right]^{-1}$ is the Fermi function, $E(\xi) = \sqrt{\xi^2 + \Delta^2(\xi)}$, where $\xi$ is the energy of electrons in the normal state, measured with respect to the Fermi energy, $x = \xi/\Delta(0)$, $q = T/T_c$ and $\Delta(\xi) = \Delta(0) \tan \left[ 1.82 \left( 1.018 \left( \frac{1}{3} - 1 \right) \right)^{0.51} \right]$ is the temperature dependence of the superconducting gap. The normalized electronic specific heat is given by the expression [34]:

$$\frac{C_e}{\gamma T_c} = q \frac{d}{dq} \left( \frac{S}{\gamma T_c} \right).$$ (16)

The electronic specific heat ($C_e$) in the superconducting state is described by equation (16), while it is equal to $\gamma T_c$ in the normal state. The specific heat data were fitted to equation (16) as shown in the figure 7. The fit gives a superconducting gap, $\Delta(0) = 0.64(1) \text{ meV}$. 

![Figure 8. Sommerfeld constant $\gamma$ versus normalized field $H/H_{c2(0)}$ for Sc$_5$Ru$_6$Sn$_{18}$. The solid line shows the linear relation between $\gamma$ and field, which indicates the $s$-wave nature of superconductivity in Sc$_5$Ru$_6$Sn$_{18}$.](image)
The Sommerfeld constant ($\gamma$) is calculated by fitting the $C_e/T$ versus $T$ data for various fields using the relation [36]:

$$\frac{C_e}{T} = \gamma + \frac{A_1}{T} \exp \left( -\frac{A_2 T_c}{T} \right)$$

where $A_1$ and $A_2$ are constants.

The single gap $s$-wave superconductivity in Sc$_5$Ru$_6$Sn$_{18}$ is also confirmed by the magnetic-field dependence of the electronic specific-heat coefficient (Sommerfeld constant), $\gamma(H)$. In a single-gap type-II superconductor, the Sommerfeld constant is proportional to the vortex density. When the applied magnetic field is increased, the density of vortices increases too, which, in turn, result in an increase of the quasiparticle density of states. Consequently, $\gamma$ turns out to be proportional to the applied magnetic field in case of a nodeless and isotropic $s$-wave superconductor [34, 36, 37]. On the other hand, in case of nodes in the superconducting gap, Volovik predicted a nonlinear relation given by $\gamma \propto H^{1.5}$ [38]. The field dependence of $\gamma$ is shown in figure 8. The linear relation between $\gamma$ and $H$ confirms the single-gap $s$-wave superconductivity in Sc$_5$Ru$_6$Sn$_{18}$.

The condensation energy $U(0)$ can be estimated from the relation:

$$U(0) = \frac{1}{2}\Delta^2(0) N_{\text{band}}(E_F) = \frac{3\gamma \Delta^2(0)}{4\pi^2 k_B^2}.$$  \hspace{1cm} (17)

Using the previously obtained values of $\gamma = 36.93(6)$ mJ mol$^{-1}$ K$^{-2}$ and $\Delta(0) = 0.641(1)$ meV, we get $U(0) = 156.8(9)$ mJ mol$^{-1}$.

To further confirm the characteristics of the superconducting gap function, we analyzed $C_e(T)$ by fitting the data by means of different functional forms, i.e., $e^{-bT/T}$, $T^2$ and $T^3$, corresponding to the expected temperature dependence of a superconducting gap which is isotropic, has line nodes or linear point nodes, respectively. As can be seen in figure 9, well below $T/T_c = 0.8$, data are best modelled by the exponential function, $C_e/T = ae^{-bT_c/T}$. The quadratic and cubic fits instead are rather poor. Similar exponential fits have been used to model the superconducting gap of other superconductors with comparable transition temperatures [9, 39, 40]. Thus, the above analysis confirms that Sc$_5$Ru$_6$Sn$_{18}$ has an isotropic gap and $s$-wave pairing.

We can estimate the London penetration depth at $T = 0$ K, $\lambda_L(0)$, using the relation [25]:

$$\lambda_L^2(0) = \frac{m^* e^2}{4\pi \kappa e} = \frac{3\pi c^2 \hbar^3}{4m^* e^2 \nu_F},$$

where $c$ is the speed of light in vacuum. Putting the values of all parameters, we get $\lambda_L(0) = 245(6)$ nm. The BCS coherence length $\xi_0$ can be estimated from $\nu_F$ and the superconducting energy gap $\Delta(0)$ using the relation [41]:

$$\xi_0 = \frac{\hbar \nu_F}{\pi \Delta(0)}.$$  \hspace{1cm} (19)

Putting the values of $\nu_F = 1.94(7) \times 10^7$ cm s$^{-1}$ and $\Delta(0) = 0.641(1)$ meV, we get $\xi_0 = 63.72(9)$ nm. We find that BCS coherence length ($\xi_0$) is much larger than the mean free path.
Using \( G \) non-magnetic, \( \sigma \) is the Gaussian relaxation rate. Since the sample holder is magnetic moments (superconductivity in Sc\(_5\)Ru\(_6\)Sn\(_{18}\) is in the moderate dirty limit. Figure 11. (a) ZF-\( \mu \)SR time spectra of Sc\(_5\)Ru\(_6\)Sn\(_{18}\) measured at various temperatures. The solid lines are the best-fit results by using the function \( A(T) = A_0 G_{\text{TF}}(t) \exp(-\lambda_1 t) \). (b) Temperature dependence of the muon-spin relaxation rate (see text for details). The temperature independent behavior below 10\( K \) suggests the absence of spontaneous internal magnetic fields at the muon site, indicating that time reversal symmetry is unlikely to be broken in Sc\(_5\)Ru\(_6\)Sn\(_{18}\).

\[ l = 8.14(5) \text{ nm, } \frac{1}{\xi_0} = 0.12 \ll 1, \text{ which indicates that the } \text{superconductivity in Sc}_5\text{Ru}_6\text{Sn}_{18} \text{ is in the moderate dirty limit.} \]

3.5. \( \mu \)SR

Figure 10(a) shows the TF-\( \mu \)SR spectra collected above (5 K) and below (1.5 K) the superconducting transition temperature, \( T_c \). The fast decay of muon-spin polarization below \( T_c \) indicates an inhomogeneous field distribution due to the flux line lattice (FLL) in the vortex state. The time-domain spectra were fit by using the following model [9]:

\[ G(t) = A_1 \cos(\gamma\mu H_0 t + \Phi) e^{-\sigma_1 t} + A_2 \cos(\gamma\mu H_0 t + \Phi). \]  

(21)

Here \( A_1 \) and \( A_2 \) are the initial muon-spin asymmetries, whereas \( B_1 \) and \( B_2 \) are the local fields sensed by muons implanted in the sample and the sample holder. \( \gamma_\mu = 2\pi \times 135.53 \text{ MHz} \cdot \text{T}^{-1} \) is the muon gyromagnetic ratio, \( \Phi \) is the phase factor and \( \sigma \) is the Gaussian relaxation rate. Since the sample holder is non-magnetic, \( B_2 \) coincides with the applied magnetic field.

In the superconducting state, the Gaussian relaxation rate \( \sigma \) contains contributions from both the FLL (\( \sigma_{sc} \)) and the nuclear magnetic moments (\( \sigma_n \)), such that:

\[ \sigma = \sigma_{sc} + \sigma_n. \]

(22)

By using equation (22), one can estimate the FLL-related relaxation rate \( \sigma_{sc} = \sqrt{\sigma^2 - \sigma_n^2} \), since \( \sigma_n \) is expected to be temperature independent in the measured temperature range and is determined from the measurements made above \( T_c \). Considering that \( \sigma_{sc} \) is directly related to the superfluid density, the temperature dependence of \( \sigma_{sc} \) provides hints on the superconducting gap and its symmetry. Further, \( \sigma_{sc} \) can be modeled by [42–44]:

\[ \frac{\sigma_{sc}(T)}{\sigma_{sc}(0)} = 1 + 2 \left( \int_{\Delta_1}^\infty \frac{E dE}{\sqrt{E^2 - \Delta_0^2}} \frac{\partial f}{\partial E} \right)_{FS} \]  

(23)

where \( f \) and \( E \) are the same as defined in equation (15). The curved brackets represent an average over the Fermi surface (FS). The superconducting gap is defined by \( \Delta_1(q) = \Delta(q) g_k \), \( q = T/T_c \), which contains an angular dependent part \( g_k \) and a temperature dependent part \( \Delta(q) \), which can be approximated as \( \Delta(q) = \Delta(0) \tanh\left[ 1.82 \left( 0.51 \left( \frac{q}{q_0} \right) - 1 \right) \right] \)

As shown in figure 10(b), the temperature dependence of the normalized FLL-related relaxation rate \( \sigma_{sc}(T)/\sigma_{sc}(0) \) can be fitted by a single-gap isotropic \( s \)-wave using equation (23) (for single gap \( s \)-wave model, \( g_k = 1 \), with \( \Delta(0) = 0.64(1) \text{ meV} \) and \( \sigma_{sc}(0) = 0.178 \mu s^{-1} \). This implies a ratio \( 2\Delta(0)/k_B T_c = 4.25(4) \), i.e., higher than 3.53 expected for a weakly coupled BCS superconductor. This further confirms the strong electron–phonon coupling in Sc\(_5\)Ru\(_6\)Sn\(_{18}\) and is consistent with the results obtained from specific-heat data.

The effective penetration depth (\( \lambda_{eff} \)) for small applied fields, such that \( H_{applied}/H_{c2} = 0.0115 \ll 1 \), is given by the relation [9, 45]:

\[ \frac{\sigma_{sc}(0)}{\lambda_{sc}(0)} = 0.00371 \frac{\phi_0^2}{\lambda_{eff}}. \]

(24)

Using \( \sigma_{sc}(0) = 0.178 \mu s^{-1} \), we get \( \lambda_{eff} = 774 \text{ nm} \). The effective penetration depth (\( \lambda_{eff} \)) and London penetration depth \( \lambda_L(0) \) are related by \( \lambda_{eff} = \lambda_L(0) \sqrt{1 + \frac{\rho}{\rho_f}} \) [25]. Using \( \lambda_{eff} = 774 \text{ nm, } \xi_0 = 63.72(9) \text{ nm and } l = 8.14(5) \text{ nm, we get, } \lambda_L(0) = 258(7) \text{ nm, which is comparable to the value estimated using } m^* \text{ and } v_F \text{ and the magnetization measurements. This confirms the validity of our fitting model.}

To probe the occurrence (or absence) of TRS breaking in Sc\(_5\)Ru\(_6\)Sn\(_{18}\), we performed ZF-\( \mu \)SR experiments. The availability of 100% spin-polarized muon beams, along with the large muon gyromagnetic ratio, make ZF-\( \mu \)SR a very useful technique to detect the spontaneous internal fields, as has been shown in previous studies of Y\(_3\)Rh\(_6\)Sn\(_{18}\) [18] and Sc\(_2\)RuO\(_4\) [4]. In general, in absence of an external magnetic field, the onset
of the superconducting phase does not induce any changes in the ZF-muon spin-relaxation rate. However, in the case of TRS breaking, the presence of tiny spontaneous currents leads to the associated weak magnetic fields, which are detected by ZF-µSR as an increase in the muon spin-relaxation rate. Since no precession signals were observed in the entire temperature range, we rule out the possibility of some unpaired electronic spins still remain, thus causing the observed muon-spin depolarization behavior.

A key result of the ZF-µSR data is the almost temperature independent $\lambda_1$ below ~10 K, especially when crossing $T_c$ i.e. upon entering the superconducting phase. In conventional BCS type $s$-wave superconductors, no effects are expected in the ZF-µSR data in the superconducting state. On the other hand, when TRS is broken, ZF-µSR time spectra are modified due to the appearance of spontaneous magnetic fields below $T_c$. This is typically the case for the Cooper pairs with a $p$-wave symmetry, as, e.g. in Sr$_2$RuO$_4$ [4]. As shown in figure 11(b), since the time spectra do not show any relevant changes (within statistical errors), we must conclude that a TRS breaking is unlikely in the superconducting state of Sc$_5$Ru$_6$Sn$_{18}$.

Table 1. Superconducting parameters of Sc$_5$Ru$_6$Sn$_{18}$, Y$_5$Rh$_6$Sn$_{18}$ [18] and Lu$_5$Rh$_6$Sn$_{18}$ [2].

| Parameter | Unit | Sc$_5$Ru$_6$Sn$_{18}$ | Y$_5$Rh$_6$Sn$_{18}$ | Lu$_5$Rh$_6$Sn$_{18}$ |
|-----------|------|----------------------|----------------------|----------------------|
| $T_c$ | K | 3.5(1) | 3 | 4(1) |
| $H_{c2}(0)$ | kOe | 26(1) | 43 | 72.4 |
| $\gamma$ | mJ mol$^{-1}$ K$^{-2}$ | 36.93(6) | 38.13(3) | 48.1(5) |
| $\Delta C_p/T_c$ | 1.6 | 1.95 | 2.06 |
| $2\Delta(0)/k_B T_c$ | 4.25(4) | 4.26(4) | 4.26(4) |
| $\theta_d$ | K | 205(1) | 183(2) | 157(2) |
| $m^*$ | 1.64(4) $m_e$ | 1.21$m_e$ | 1.32$m_e$ |
| $n_s$ | carriers m$^{-3}$ | 7.05(2) $\times$ 10$^{26}$ | 2.3 $\times$ 10$^{28}$ | 2.6 $\times$ 10$^{26}$ |
| $H_{c1}(0)$ | Oe | 157(9) | |
| $H_{c2}(0)$ | Oe | 799(6) | |
| $J_c(1.8$ K) | A m$^{-2}$ | 6(3) $\times$ 10$^3$ | |
| $J_d$ | A m$^{-2}$ | 3.07(5) $\times$ 10$^{10}$ | |
| $\lambda(0)$ | nm | 260(7) | |
| $\xi(0)$ | nm | 11.26(3) | |
| $\kappa_{GL}$ | 23(2) | |
| $\lambda_{ef}(0)$ | nm | 774(8) | |
| $N(E_f)$ | states/eV f.u. | 15.24(6) | |
| $l$ | nm | 8.14(5) | |

A key result of the ZF-µSR data is the almost temperature independent $\lambda_1$ below ~10 K, especially when crossing $T_c$ i.e. upon entering the superconducting phase. In conventional BCS type $s$-wave superconductors, no effects are expected in the ZF-µSR data in the superconducting state. On the other hand, when TRS is broken, ZF-µSR time spectra are modified due to the appearance of spontaneous magnetic fields below $T_c$. This is typically the case for the Cooper pairs with a $p$-wave symmetry, as, e.g. in Sr$_2$RuO$_4$ [4]. As shown in figure 11(b), since the time spectra do not show any relevant changes (within statistical errors), we must conclude that a TRS breaking is unlikely in the superconducting state of Sc$_5$Ru$_6$Sn$_{18}$.

Note that the TRS breaking depends on the pairing symmetry of the electrons in the superconducting state. The TRS can be broken if the superconducting state has degenerate representations, as is the case of triplet superconducting states [4]. However, in the case of singlet-superconducting states, where the superconducting state has non-degenerate representations, the TRS may not be broken. While TRS breaking is possible in systems with strong spin–orbit coupling such as Y$_5$Rh$_6$Sn$_{18}$ [18], it might still be conserved in systems with weak spin–orbit coupling, such as Sc$_5$Ru$_6$Sn$_{18}$.
effect, it is energetically favorable for electron spins to point in the direction of the applied magnetic field, thus decoupling from their partner, which results in the splitting of the Cooper pair [34]. For a BCS superconductor the orbital limit of the upper (i.e. orbital) critical field is given by the Werthamer–Helfand–Hohenberg (WHH) expression [47, 48]:

$$H_{c2}^{\text{orbital}}(0) = -0.693T_c \left( \frac{dH_{c2}(T)}{dT} \right)_{T=T_c}.$$  

The slope \( \left. \frac{dH_{c2}(T)}{dT} \right|_{T=T_c} \) is estimated from the \( H_{c2} - T \) phase diagram (see figure 4) and is equal to 8.1(1) kOe K\(^{-1}\) in our case, which gives an orbital upper limiting field, \( H_{c2}^{\text{orbital}}(0) \approx 19.18 \) kOe. The Pauli limiting field, \( H_{c2}^{\text{P}}(0) \), within the BCS theory is given by [49, 50]:

$$H_{c2}^{\text{P}}(0) = 1.86 T_c.$$  

For \( T_c = 3.5 \) K, \( H_{c2}^{\text{P}}(0) \approx 65.1 \) kOe. The Maki parameter [51], \( \alpha_M \), is used to measure the relative strength of the orbital and Pauli limiting field values and is given by the expression:

$$\alpha_M = \sqrt{\frac{H_{c2}^{\text{P}}(0)}{H_{c2}^{\text{orbital}}(0)}}.$$  

From this relation, we get \( \alpha_M \approx 0.29 \), which means that in our case, \( H_{c2}^{\text{P}}(0) \) is much larger than \( H_{c2}^{\text{orbital}}(0) \), hence implying that the upper critical field is limited by the orbital effects and the Pauli paramagnetic effect is negligible as indicated by a small value of Maki parameter. For Sc\(_5\)Ru\(_6\)Sn\(_{18}\), the calculated \( H_{c2}(0) \) is close to the orbital limiting field and is much smaller than the Pauli limiting field.

4. Summary

After successfully growing single crystals of Sc\(_5\)Ru\(_6\)Sn\(_{18}\), their superconducting properties were investigated by means of powder XRD, DC and AC magnetization, specific heat and \( \mu \)SR measurements. The powder XRD pattern was indexed as a tetragonal structure with lattice constants, \( a = 1.387(3) \) nm, \( c = 2.641(5) \) nm, which imply a density of 7.8(3) g cm\(^{-3}\). We find that Sc\(_3\)Ru\(_6\)Sn\(_{18}\) is a type-II superconductor with \( T_c \approx 3.5(1) \) K, a lower critical field \( H_{c1}(0) \), which zero-temperature thermodynamic critical field is estimated to be \( H_{c1}(0) = 157(9) \) Oe and an upper critical field \( H_{c2}(0) = 26(1) \) kOe. The zero-temperature thermodynamic critical field is estimated to be \( H_c(0) = 799(6) \) Oe. With a coherence length, \( \xi(0) = 11.26(3) \) nm and a penetration depth, \( \lambda(0) = 260(7) \) nm, Sc\(_3\)Ru\(_6\)Sn\(_{18}\) has a Ginzburg Landau parameter, \( \kappa \approx 23(2) \). The Bean model was used to calculate the critical current density, \( J_c(1.8 \) K) \approx 6 \times 10^8 \) A m\(^{-2}\) at 150 Oe. The de-pairing current \( J_D \) is estimated to be \( 3.07 \times 10^{10} \) A m\(^{-2}\).

Our analysis of the normal-state specific heat yields a Sommerfeld coefficient, \( \gamma = 36.93(6) \) mJ mol\(^{-1}\) K\(^{-2}\), corresponding to a density of states at the Fermi level, \( N(E_F) = 15.24(6) \) states/eV f.u. The superconducting transition is revealed by a sharp jump at \( T_c = 3.5(1) \) K, with \( \Delta T_c \approx 1.6 \) for \( \gamma = 36.93(6) \) mJ mol\(^{-1}\) K\(^{-2}\), which is higher than the BCS value of 1.43 for a weakly coupled superconductor, which indicates strong electron–phonon coupling in Sc\(_3\)Ru\(_6\)Sn\(_{18}\).

The electronic specific heat can be fitted with a single-gap BCS model with \( \Delta(0) = 0.64(1) \) meV. The Sommerfeld constant \( \gamma \) exhibits a linear variation with the applied magnetic field, indicating an s-wave superconducting pairing in Sc\(_3\)Ru\(_6\)Sn\(_{18}\). TF-\( \mu \)SR measurements reveal that Sc\(_3\)Ru\(_6\)Sn\(_{18}\) is a strongly coupled superconductor. TF-\( \mu \)SR measurements also suggest an s-wave character of the superconducting gap. ZF-\( \mu \)SR measurements do not show the presence of spontaneous internal magnetic fields and hence, indicate a preserved TRS in Sc\(_3\)Ru\(_6\)Sn\(_{18}\). In table 1, we have summarized the experimentally estimated parameters of Sc\(_3\)Ru\(_6\)Sn\(_{18}\), along with those of Y\(_3\)Rh\(_6\)Sn\(_{18}\) [18] and Lu\(_3\)Rh\(_6\)Sn\(_{18}\) [2]. It is clear that most of the parameters of Sc\(_3\)Ru\(_6\)Sn\(_{18}\) are comparable with the corresponding parameters of Y\(_3\)Rh\(_6\)Sn\(_{18}\) and Lu\(_3\)Rh\(_6\)Sn\(_{18}\), except for \( H_{c2}(0) \). Other compounds of the Ru\(_5\)M\(_6\)Sn\(_{18}\) family are currently being investigated to clarify the nature of the TRS breaking mechanism in this class of caged-type superconducting compounds.

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