Microscopic Studies of the Normal and Superconducting State of Ca$_3$Ir$_4$Sn$_{13}$

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We report on muon spin rotation ($\mu$SR) studies of the superconducting and magnetic properties of the ternary intermetallic stannide Ca$_3$Ir$_4$Sn$_{13}$. This material has recently been at the focus of intense research activity due to a proposed interplay of ferromagnetic spin-fluctuations and superconductivity. In the temperature range $T = 1.6 - 200$ K, we find that the zero field muon relaxation rate is very small and does not provide evidence for spin-fluctuations. The field-induced magnetization cannot be attributed to localized magnetic moments. In particular, our $\mu$SR data reveal that the anomaly observed in thermal and transport properties at $T^* \approx 38$ K is not of magnetic origin. Results for the transverse field muon relaxation rate at $T = 0.02 - 12$ K, suggest that superconductivity emerges out of a normal state that is not of a Fermi liquid type. This is unusual for an electronic system lacking partially filled $f$-electron shells. The superconducting state is dominated by a nodeless order parameter with a London penetration length of $\lambda_L = 416(1)$ nm and the electron-phonon pairing interaction is in the strong-coupling limit.

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I. INTRODUCTION

Interactions between charge, spin, orbital and lattice degrees of freedom lead to emergent symmetry-breaking ground states in correlated electron systems, such as charge or spin order, superconductivity and structural transitions. The correlations between the different degrees of freedom can lead to coexistence and even a coupling of the different constituents, such as superconductivity close to charge order and magnetically-mediated superconducting states.

Ca$_3$Ir$_4$Sn$_{13}$ is a member of the material class of superconducting and/or magnetic ternary intermetallic stannides. The compound was first synthesized more than 30 years ago, but has recently regained interest in the condensed matter community. Only a few of the physical properties, such as the superconducting transition at $T_c \approx 7$ K and the quasi-skutterudite crystal structure, were reported in early studies.

Recently an anomaly at $T^* \approx 38$ K, well above the superconducting transition, was detected by macroscopic probes, such as magnetization $M(T)$, electrical resistivity $\rho(T)$, Seebeck coefficient and Hall resistivity. Yang et al have proposed that the anomaly is the result of ferromagnetic spin-fluctuations, coupled to superconductivity. Non-Fermi liquid behavior was claimed from $\rho(T, B)$ at low applied magnetic fields with a crossover to a Fermi liquid ground state as superconductivity is suppressed at high fields. Results for the electronic specific heat capacity $C_p(T)$ suggest a nodeless, strong-coupling superconducting order parameter.

In the temperature-pressure phase diagram, a dome-shaped superconducting phase was found, along with a monotonous decrease of $T^*$ with increasing pressure $p$. A scenario, where $T_c$ and $T^*$ are linked by a $p$-induced superlattice quantum critical point, is supported by X-ray diffraction on the isovalent compound Sr$_3$Ir$_4$Sn$_{13}$. A structural transition is observed at $T^*$, involving a doubling of the unit cell ($Pm\overline{3}a \rightarrow I\overline{4}3d$). The case of (Sr,Ca)$_3$Ir$_4$Sn$_{13}$ is reminiscent of Cu$_3$TiSe$_2$, where superconductivity emerges as charge-density wave (CDW) order is suppressed with increasing pressure.

We have carried out muon spin rotation ($\mu$SR) experiments of Ca$_3$Ir$_4$Sn$_{13}$ to obtain additional insights into the role of ferromagnetic spin-fluctuations in this material, especially in connection with the anomaly at $T^* \approx 38$ K. The zero field (ZF) muon relaxation rate is marginal in the temperature range $T = 1.6 - 200$ K. We do not find an increase of the rate near $T^*$ that can be attributed to localized magnetic moments. This microscopic finding supports structural and/or CDW scenarios as the origin of the $T^*$-anomaly in ternary intermetallic stannides. We find no coupling of magnetic fluctuations and superconductivity. The nature of superconductivity, which emerges out of a normal state that is not of a Fermi liquid type, was studied with low temperature transverse field (TF) measurements. Our results point to a nodeless strong-coupling superconductor with a London penetration length of $\lambda_L = 416(1)$ nm.

II. SAMPLE CHARACTERIZATION

Gram-sized high-quality Ca$_3$Ir$_4$Sn$_{13}$ single crystals were synthesized using the Sn self flux technique and concentrated HCl acid was used to remove excess Sn. A melting point of 1150$^\circ$ C was found using thermogravimetry. X-ray fluorescence reveals a homogeneous composition without segregations on a 20 $\mu$m length scale.

The crystal structure was investigated using neutron
powder diffraction. Crushed Ca₃Ir₄Sn₁₃ single crystals were measured using the high-resolution powder diffractometer (HRPT) at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institute, Villigen, Switzerland. The neutron diffraction pattern (λn = 1.494 Å) measured at T = 300 K indicates that the crystals are single phase and free of impurities (see Fig. 1). The data at T = 300 K can be satisfactorily fitted using the cubic Pm₃n structure, reported earlier, and a refined lattice parameter of a = 9.71922(8) Å.

A physical properties measurements system (PPMS, Quantum Design) was used for an accurate characterization of macroscopic properties, such as M(T, B) and ρ(T). Figure 2a shows the field dependence of the magnetization M(B) at T = 1.9 K, where B is the effective field of the bulk sample, taking into account demagnetization effects. For low fields B < 200 G we find a diamagnetic Meissner state (χ = -1/4π) with a crossover to the mixed state for B greater than the lower critical field Bc₁ = 530 G. Superconductivity is type-II with a large value of Bc₂/Bc₁ ≈ 100.

Figure 2b shows the magnetic susceptibility χ(T) (DC measurement, Bext = 20 G) with Tc ≈ 6.6 K and a superconducting volume fraction of 94 % at T = 3 K after zero field cooling (ZFC). Field cooling (FC) reduces χ(3 K) to -0.1/4π, indicative of vortex pinning—most likely predominantly at the surface of the sample.

Our Ca₃Ir₄Sn₁₃ single crystals show a clear anomaly at T* ≈ 38 K in ρ(T) (see Fig. 2c). This anomaly was found in all measured samples and is thought to be intrinsic. Assuming a scenario, where a pinned CDW emerges at T*, one would expect nonlinear current-voltage IV curves. This is the result of expected depinning of the CDW for applied currents above a certain critical current density Jc, which strongly depends on the actual pinning potential landscape. Thereby, the resistivity anomaly would be suppressed for sufficiently high applied currents, as it was observed for NbSe₃. Our setup allowed the application of up to J = 1.6 A/cm². However, with these current densities no change of the T*-anomaly is observed.

III. EXPERIMENTAL SETUP

μSR experiments were carried out at the πM3 beamline of the Swiss Muon Source SμS, Paul Scherrer Institute, Villigen, Switzerland. Magnetic fields were applied along a cubic main crystal axis in all measurements.

High temperature data (T = 1.6 – 200 K) in ZF and weak longitudinal field (wLF) were measured on the general purpose surface (GPS) muon spectrometer in the longitudinal muon polarization mode. A flow cryostat was used to control the temperature of one large Ca₃Ir₄Sn₁₃ single crystal (m = 900 mg) and a Helmholtz coil to apply BwLF = 30.5 G.

Transverse field (TF) data were taken on the low temperature facility (LTF) instrument in the transverse muon polarization mode. A dilution refrigerator and a superconducting magnet allowed to access the temperature range T = 0.02 – 12 K with a longitudinal magnetic field of B = 622 G. A mosaic of co-aligned single crystals, glued onto an Ag sample plate, was measured on LTF.
IV. RESULTS AND DISCUSSION

A. Search for Ferromagnetic Spin-Fluctuation

We carried out measurements of the ZF and wLF muon spin relaxation of longitudinally polarized muons to search for previously proposed ferromagnetic spin-fluctuations. Figure 3 shows the time-dependence of the muon spin polarization $P(t)$ in the asymmetry function

$$A(t) = A_0 \cdot P(t) = \frac{N_b(t) - N_f(t)}{N_b(t) + N_f(t)},$$

(1)

where $N_b(t)$ and $N_f(t)$ are the normalized histogram values of the backward and forward positron detector, respectively. ZF data are shown in red and wLF data with $B_{wLF} = 30.5$ G in blue. Open and filled data points were measured above and below $T^*$, respectively. The wLF quenches the randomly oriented, static (on muon time scales) nuclear dipole moments. The data in the time window $t = 0 \rightarrow 8 \mu s$ was fitted in different manners and shows only a marginal relaxation. In particular, the data is well described by a static Gaussian Kubo-Toyabe relaxation function

$$P(t) = \frac{1}{3} + \frac{2}{3} (1 - (\sigma t)^2) \exp \left( -\frac{(\sigma t)^2}{2} \right),$$

(2)

where $\sigma$ is the muon relaxation rate due to quasi-static magnetic fields (see Fig. B).

The main panel of Fig. 3 shows the extracted muon relaxation rate $\sigma(T)$ of ZF and wLF measurements up to $T = 100$ K. The full measured range $T = 1.6 \rightarrow 200$ K is shown in the inset. We find low $\sigma$ values of less than $0.06 \mu s^{-1}$. $\sigma_{ZF}$ is slightly enhanced for temperatures $T < T_{diff} \approx 120$ K. We attribute this effect to muon diffusion above $T_{diff}$, leading to a decrease of the effective line width of the nuclear field distribution. Application of a weak longitudinal field $B_{wLF} = 30.5$ G suppresses to a large extend, the already very small, relaxation rate. $\sigma_{wLF} = 0.013(10) \mu s^{-1}$ is constant over the entire temperature range $T = 1.6 \rightarrow 200$ K and also $\sigma_{ZF} = 0.054(2) \mu s^{-1}$ is constant for $T < 100$ K. The error/shaded areas in Fig. 3 correspond to one standard deviation.

The muon relaxation rate does not change across the $T^* \approx 38$ K anomaly, and also not at $T_c = 6.6$ K, as it would be expected in a scenario involving fluctuating or quasi-static magnetism. We, therefore, conclude that our data do not support a scenario, where spin-fluctuations are present in Ca$_3$Ir$_4$Si$_{13}$.

A Fermi surface reconstruction was conjectured from the $T$-dependence of the Scebeck coefficient. Our $\mu$SR result is the first microscopic confirmation of a non-magnetic structural and/or CDW scenario as the origin of the $T^*$-anomaly in the ternary intermetallic stannides without the proposed coupling of magnetic fluctuations and superconductivity.
B. Nature of the Superconducting State

We carried out TF measurements with transverse muon polarization and a FC applied magnetic field of $B_{\text{TF}} = 622 \, G > B_{c1}$ to study the mixed/vortex state of superconducting Ca$_2$I$_3$Sn$_3$. The precession of the muon spin caused by $B_{\text{TF}}$ is visible as an oscillation of $A(t)$ with a frequency $\gamma_\mu B_{\text{int}}/2\pi$ (see Fig. 5). $B_{\text{int}}$ is the internal field of the bulk sample and $\gamma_\mu/2\pi = 13.55 \, \text{kHz/G}$, with $\gamma_\mu$ the muon gyromagnetic ratio. The left and right positron detectors were used for the analysis of the LTF data to minimize absorption effects from the sample. The normal state data ($T = 10 \, K > T_c$) show only a marginal relaxation, as expected from the ZF and wLF results. However, deep inside the superconducting state ($T = 0.02 \, K < T_c$) the relaxation increases strongly. This is the result of the field distribution arising from the ordered vortex lattice in the mixed state. The TF data can be well fitted for $T = 0.02 - 12 \, \text{K}$ with a sinusoidally oscillating Gaussian relaxation function:

$$P(t) = \exp \left( -\frac{(\sigma t)^2}{2} \right) \cos (\gamma_\mu B_{\text{int}} + \theta) ,$$

where $\theta$ is the phase of the muon spin polarization with respect to the positron detectors at $t = 0$. No background term for the Ag sample plate was needed for fitting, since the mosaic of co-aligned single crystals covered practically the entire area of incoming muons and the sample thickness ensured that all muons were absorbed before reaching the sample plate.

Figure 6a shows the TF muon relaxation rate $\sigma(T) = \sigma_{sc}(T) + \sigma_{bg}$, consisting of a constant nuclear background $\sigma_{bg} = 0.096 \, \mu s^{-1}$ and a finite superconducting component $\sigma_{sc}(T)$ for $T < T_c$. The $T$-dependence of the diamagnetic shift $\Delta B(T) = B_{\text{int}}(T) - B_{\text{eff}}$, with respect to the effective field $B_{\text{eff}}$ of the bulk sample (averaged normal state $B_{\text{int}}$) is shown in the inset of Fig. 6a. Both $\Delta B(T)$ and $\sigma(T)$ are rather flat at very low temperatures, $T < T_c$. This occurs when the superconducting gap function does not contain nodes, as it is the case for $s$-wave pairing. The penetration depth $\lambda$ in the mixed state, assuming an ideal Ginzburg-Landau vortex lattice, can be derived from $\sigma_{sc}$ by

$$\frac{1}{\lambda^2} = \frac{2\pi\sigma_{sc}}{0.172\phi_0\gamma_\mu(1-b)[1 + 1.21(1 - \sqrt{b})^3]} ,$$

where $\phi_0 = 2.07 \cdot 10^{-11} \, \text{G m}^2$ is the magnetic flux quantum and $b(T) = B_{\text{TF}}/B_{c2}(T)$. Experimental values of $B_{c2}(T)$ were taken from Yang et al.

The penetration depth as derived from Eq. (4) is shown in Fig. 6b, in the form of $1/\lambda(T)^2 \propto n_s(T)$, proportional to the superfluid density. In the limit of zero temperature, we obtain a London penetration depth of $\lambda_L = \lambda = 2 \times 10^{-4} \, \mu m$.
$\lambda(0) = 416(1)$ nm. The blue curve shows the numerical solution of the weak-coupling BCS gap equation. In general, not only for weak-coupling, the $T$-dependence of the isotropic superconducting gap function can be approximated by

$$\Delta(T) = \Delta_0 \tanh \left( \frac{\pi}{\alpha} \sqrt{\frac{2 \Delta C_p}{3 \gamma T_c} \left( \frac{T_c}{T} - 1 \right)} \right),$$

with $\alpha = \Delta_0/k_B T_c$, $\Delta C_p$ the jump of the specific heat capacity at $T_c$ and $\gamma$ the Sommerfeld coefficient. The weak-coupling BCS superfluid density does clearly not account for the measured data. However, if the experimental value $\Delta C_p/\gamma T_c = 2.4$ is used in Eq. 5 and the coupling strength $\alpha$ is as a free parameter, we find a lower bound of $\alpha \approx 5$ (red curve in Fig. 6b). From our microscopic data, we find an even stronger coupled non-relaxing superconducting order parameter than inferred from macroscopic measurements. The derived $\alpha$ is larger than the corresponding values for Hg and Pb, typical strong-coupling electron-phonon superconductors.

The slight deviations between the experimental data and the approximation Eq. 5, could in principle be accounted for by assuming a small admixture of a second superconducting gap. Such a scenario has been previously suggested. However, our data rules out admixture of a large nodal gap, since low-energetic nodal excitations would lead to a non-zero slope of $n_n(T)$ at lowest temperatures—in contrast to our experimental results. Our data also rules out a high degree of admixture.

C. $\mu$SR in the Normal State

We searched for the muon stopping sites by calculating the lattice sum of the electrostatic potential $\Phi$ at all ion positions (within a radius of 120 \AA) in the cubic unit cell. For all oxidation states Ca $^{2+}$, Ir $^{2+},^{3+},^{4+}$ and Sn $^{2+},^{4+}$ we find minima of $\Phi$ at the $(1/2, 0, 0)$, $(1/2, 1/2, 0)$ and $(h, h, h)$, with $h = 0.19(2)$ and 0.43(1), positions and the crystallographically equivalent sites (see Fig. 7a). $\Phi_0$ in Fig. 7a is a constant background to reduce the potential, as for example caused by the conduction electron’s negative contribution.

For the four candidates of muon sites, we calculated the nuclear dipolar sum to extract the expected r.m.s. $\mu$SR line width $\sigma_{dip}$. Table I shows that the muon site $(0.43, 0.43, 0.43)$ is closest to the experimentally determined nuclear line width $\sigma_{nuc} = \sigma_{ZF} - \sigma_{wLF} = 3.0(8)$ G, obtained from the data shown in Fig. 4. The discrepancy between the experimental and calculated value may be understood because of the simple model for the ideal crystal structure. In any case, the match of the experimental results and the estimates seems to be reasonable (30% error). The calculation of $\Phi$ supports our interpretation that $(0.43, 0.43, 0.43)$ is the muon site, since we also find that this is the lowest of the four minima.

**TABLE I. Minima of the electrostatic potential along high symmetry directions**

| direction | $h$ (r.l.u.) | $\sigma_{dip}$ (G) |
|-----------|-------------|------------------|
| $(h, 0, 0)$ | 1/2 | 1.2 |
| $(h, h, h)$ | 0.19(2) | 0.9 |
| 0.43(1) | 2.1 |

**Figure 7.** (Color online) a) Electrostatic potential along the $(h, 0, 0)$ (red), $(h, h, 0)$ (blue) and $(h, h, h)$ (green) high symmetry directions. Four candidates of muon sites are found at $(1/2, 0, 0)$ (red arrow), $(1/2, 1/2, 0)$ (blue arrow) and $(h, h, h)$ with $h = 0.19(2)$ and 0.43(1) (green arrows). Ca $^{2+}$, Ir $^{4+}$ and Sn $^{4+}$ was assumed for the depicted calculation. b) A $T$-dependent diamagnetic shift in the normal state is not expected for a Fermi liquid ground state.

Finally, we return to the question of localized magnetic moments. A moment of 0.6 $\mu_B$/Ir was derived by Yang et al., but this would result in a internal magnetic field $B_{\mu} = 2.4$ kG at the $(0.43, 0.43, 0.43)$ muon site. Our calculation assumes an induced ferromagnetic alignment of the moments along an external field parallel to a main cubic crystal axis. Even a much smaller induced moment, for instance of 0.06 $\mu_B$/Ir results in $B_{\mu} = 240$ G at $(0.43, 0.43, 0.43)$, clearly in conflict with the experimental observations. We note that demagnetization effects of our mosaic of roughly spherical single crystals cannot account for the large discrepancy. Therefore, we conclude
that there are no localized magnetic moments at the Ir sites and we attribute the observed diamagnetic shift in the normal state to extended magnetic moments of the conduction electrons.

V. CONCLUSIONS

We have investigated the ternary intermetallic stannide Ca$_3$Ir$_4$Sn$_3$ using muon spin rotation. Over the entire range $T = 1.6 - 200$ K we find no support for a scenario involving fluctuating or quasi-static localized magnetism. Therefore, our results favor a non-magnetic scenario, where a structural transition and/or charge-density wave formation occurs at $T^*$ in ternary intermetallic stannides. We have also studied the microscopic nature of the superconducting state of Ca$_3$Ir$_4$Sn$_3$, which emerges at out of a normal state that is not of a Fermi liquid type. We find a nodeless strong-coupling superconducting order parameter with a London penetration depth $\lambda_L = 416(1)$ nm. Our study may allow for admixture of a small second superconducting order parameter, but rules out large nodal gaps.

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