Nodeless superconductivity in Ca₃Ir₄Sn₁₃: Evidence from quasiparticle heat transport

S. Y. Zhou, H. Zhang, X. C. Hong, B. Y. Pan, X. Qiu, W. N. Dong, X. L. Li, and S. Y. Li*

State Key Laboratory of Surface Physics, Department of Physics, and Laboratory of Advanced Materials,

Fudan University, Shanghai 200433, P. R. China

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We report resistivity ρ and thermal conductivity κ measurements on Ca₃Ir₄Sn₁₃ single crystals, in which superconductivity with $T_c \approx 7$ K was claimed to coexist with ferromagnetic spin fluctuations. Among three crystals, only one crystal shows a small hump in resistivity near 20 K, which was previously attributed to the ferromagnetic spin fluctuations. The other two crystals show the $\rho \sim T^2$ Fermi-liquid behavior at low temperature. For both single crystals with and without the resistivity anomaly, the residual linear term κ_0/T is negligible in zero magnetic field. In low fields, $\kappa_0(H)/T$ shows a slow field dependence. These results demonstrate that the superconducting gap of Ca₃Ir₄Sn₁₃ is nodeless and thus rule out a nodal gap caused by ferromagnetic spin fluctuations.

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I. INTRODUCTION

The interplay between magnetism and superconductivity has been a central issue in unconventional superconductors. While the static magnetism is generally believed to compete with superconductivity, the dynamic magnetism could be the source of electron pairing.¹ For example, the antiferromagnetic (AF) spin fluctuations are considered the pairing glue in high- T_c cuprates, iron-based superconductors, and many heavyfermion superconductors.¹ However, the ferromagnetic (FM) spin fluctuations could be the origin of the superconductivity in Sr₂RuO₄, and in the heavy-fermion superconductors UGe₂ and URhGe.¹ These AF and FM spin fluctuations usually result in superconducting gaps with nodes, such as the d-wave gap in cuprates and CeCoIn₅,^{2,3} and the *p*-wave gap in Sr₂RuO₄,⁴ but in some cases, such as in multiband iron-based superconductors, the AF spin fluctuations may give an s_+ -wave gap without nodes.5

Ca₃Ir₄Sn₁₃ is a cubic transition-metal compound in which superconductivity with $T_c \approx 7$ K was found 30 years ago.⁶ Very few studies have been done on this compound since its discovery. Until recently, detailed resistivity, susceptibility, and specific heat measurements suggested that the superconductivity coexists with FM spin fluctuations in Ca₃Ir₄Sn₁₃.⁷ A peaklike anomaly near 30 K in resistivity was observed. Below the anomaly, the non-Fermi-liquid behavior of resistivity in zero field has been attributed to the FM spin fluctuations, and, upon applying magnetic field, Fermi liquid behavior is recovered.⁷

Since the FM spin fluctuations may cause a nodal superconducting state in Ca₃Ir₄Sn₁₃, it is interesting to probe its superconducting gap structure. Ultralow-temperature thermal conductivity measurement is such a bulk technique.⁸ The existence of a finite residual linear term κ_0/T in zero magnetic field is evidence for gap nodes. The field dependence of κ_0/T may further give support for a nodal superconducting state and provide information on the gap anisotropy, or multiple gaps.⁹

In this paper, we measure the resistivity and thermal conductivity of Ca₃Ir₄Sn₁₃ single crystals. We find that while one crystal shows a small hump in resistivity near 20 K, the other two crystals show $\rho \sim T^2$ Fermi-liquid behavior in zero field. For both single crystals with and without the resistivity anomaly, the absence of κ_0/T in zero field and the slow field

dependence of $\kappa_0(H)/T$ in low fields clearly demonstrate nodeless superconductivity in Ca₃Ir₄Sn₁₃.

II. EXPERIMENT

Single crystals of $Ca_3Ir_4Sn_{13}$ were grown by the flux method, as previously described in Ref. 6. The excessive Sn flux was etched in concentrated hydrochloric acid (HCl). The obtained single crystals have typical size of a few cubic millimeters. We chose three single crystals with a large flat surface, which was identified as the (110) plane by x-ray diffraction measurements. Then the single crystals were polished and cut to a rectangular shape of typical dimensions $2.5 \times 1.0 \text{ mm}^2$ in the (110) plane, and 0.2 mm in thickness. The dc magnetic susceptibility was measured at H = 20 Oe both parallel and perpendicular to the (110) plane, using a superconducting quantum interference device (MPMS, Quantum Design). Four silver wires were attached to the sample with silver paint, which were used for both resistivity and thermal conductivity measurements, with electrical and heat currents in the (110) plane. The contacts are metallic with typical resistance 50 m Ω at 2 K. The thermal conductivity was measured in a dilution refrigerator, using a standard fourwire steady-state method with two RuO₂ chip thermometers, calibrated in situ against a reference RuO₂ thermometer. Magnetic fields were applied perpendicular to the (110) plane. To ensure a homogeneous field distribution in the sample, all fields were applied at temperatures above T_c .

III. RESULTS AND DISCUSSION

Figure 1(a) presents the typical dc magnetic susceptibility of Ca₃Ir₄Sn₁₃ single crystals, measured in H = 20 Oe parallel and perpendicular to the (110) plane, with zero field cooled. The transition temperature $T_c \approx 6.9$ K is determined from the onset of diamagnetic transition. In the field perpendicular to the (110) plane, the shielding volume fractions exceed -1 at 2 K, indicating bulk superconductivity of the sample. Figure 1(b) plots the resistivities of samples S1, S2, and S3 in zero magnetic field. For all three samples, the zero resistivity $T_c \approx 7.25$ K is slightly higher than that obtained from the



FIG. 1. (Color online) (a) The typical dc magnetic susceptibility of Ca₃Ir₄Sn₁₃ single crystals measured in H = 20 Oe both parallel and perpendicular to the (110) plane, with zero field cooled. (b) Resistivity of three samples in zero magnetic field. (c) Low-temperature data of the resistivities in (b). The data sets are offset for clarity. Samples S2 and S3 both show $\rho \sim T^2$ Fermi-liquid behavior at low temperature, as indicated by the solid lines.

magnetization measurements in Fig. 1(a), and the 10–90% resistive transition widths are less than 0.2 K.

From Fig. 1(b), only the resistivity of S1 shows an anomaly at low temperature, while S2 and S3 show good metallic behavior. Figure 1(c) plots the resistivity data below 50 K. All data sets are offset for clarity. One can see that the small hump near 20 K of S1 is much less pronounced than the peak near 30 K in Ref. 7. Interestingly, for S2 and S3, the



FIG. 2. (Color online) (a) Resistivity of Ca₃Ir₄Sn₁₃ single crystal S1 in H = 0, 1, 2, 3, 4, 5, 6, and 7 T. The normal-state $\rho(7 \text{ T})$ curve is quite flat, extrapolating to residual resistivity $\rho_0(7 \text{ T}) \approx 114 \,\mu\Omega$ cm. (b) Temperature dependence of the upper critical field H_{c2} , defined by $\rho = 0$. The dashed line is a guide to the eye, which points to $H_{c2}(0) \approx 7$ T.

low-temperature data obey the Fermi-liquid behavior $\rho \sim T^2$, as indicated by the solid lines. We note that the residual resistivity ρ_0 of S1 is the highest among all three samples. If lower ρ_0 indicates higher sample quality, the resistivity anomaly may be not an intrinsic property of Ca₃Ir₄Sn₁₃. However, we are not sure about this at the current stage.

Nevertheless, it is necessary to check the superconducting gap structure of both Ca₃Ir₄Sn₁₃ samples with and without the resistivity anomaly. The upper critical field H_{c2} needs to be determined first. Figure 2(a) shows the resistivity of the Ca₃Ir₄Sn₁₃ single crystal S1 in a magnetic field up to H = 7 T. For H = 7 T, no superconducting transition is observed down to 2 K. The normal-state $\rho(7 \text{ T})$ curve is quite flat, extrapolating to a residual resistivity $\rho_0(7 \text{ T}) = 114.0 \ \mu\Omega$ cm. In Fig. 2(b), we plot the temperature dependence of the upper critical field H_{c2} , defined by $\rho = 0$ from the curves in Fig. 2(a). A rough estimation gives $H_{c2}(0) \approx 7$ T. Similar measurements on S2 give the same $H_{c2}(0)$, and $\rho_0(7 \text{ T}) = 79.6 \ \mu\Omega$ cm.

Figure 3(a) shows the temperature dependence of the thermal conductivity for samples S1 and S2 in zero magnetic fields, plotted as κ/T vs *T*. The measured thermal conductivity is the sum of two contributions, from electrons and phonons, respectively, so that $\kappa = \kappa_e + \kappa_p$. In order to obtain the residual linear term κ_0/T contributed by electrons, we extrapolate κ/T to T = 0. Usually, this can be done by fitting the data to



FIG. 3. (Color online) (a) Low-temperature thermal conductivity of Ca₃Ir₄Sn₁₃ single crystals S1 and S2 in zero magnetic field. The solid lines are $\kappa/T = a + bT^{\alpha-1}$ fits below 250 mK, respectively. (b) Thermal conductivity of S1 in magnetic fields. The dashed line is the normal-state Wiedemann-Franz law expectation $L_0/\rho_0(7 \text{ T})$, with L_0 the Lorenz number $2.45 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}$ and $\rho_0(7 \text{ T}) =$ 114.0 $\mu\Omega$ cm.

 $\kappa/T = a + bT^{\alpha-1}$ at low temperature, where $a \equiv \kappa_0/T$.^{10,11} The power α of the second term contributed by phonons is typically between 2 and 3, due to specular reflections of phonons at the boundary.^{10,11} From Fig. 3(a), the curves below 250 mK can be well fitted by $\kappa/T = a + bT^{\alpha-1}$ with $\alpha = 2.41$ and 2.27 for S1 and S2, respectively. Previously $\alpha \approx 2.2$ has been observed in the *s*-wave superconductor Cu_{0.06}TiSe₂,¹² and recently $\alpha \approx 2$ was found in some iron-based superconductors such as BaFe_{1.9}Ni_{0.1}As₂ and KFe₂As₂.^{13,14} Below we only focus on κ_0/T .

In zero field, the fittings give $\kappa_0/T = -3 \pm 3$ and $8 \pm 5 \ \mu W K^{-2} cm^{-1}$ for S1 and S2, respectively. Note that our experimental error bar is about $5 \ \mu W K^{-2} cm^{-1}$. For *s*-wave nodeless superconductors, there are no fermionic quasiparticles to conduct heat as $T \rightarrow 0$, since all electrons become Cooper pairs. Therefore, there is no residual linear term of κ_0/T , as seen in V₃Si.¹⁰ However, for unconventional superconductors with nodes in the superconducting gap, the nodal quasiparticles will contribute a finite κ_0/T in zero field.⁸ For example, $\kappa_0/T = 1.41 \text{ mW K}^{-2} cm^{-1}$ for the overdoped cuprate Tl₂Ba₂CuO_{6+ $\delta}$} (Tl-2201), a *d*-wave superconductor with $T_c = 15 \text{ K.}^{15}$ For the *p*-wave superconductor Sr₂RuO₄,



FIG. 4. (Color online) Normalized residual linear term κ_0/T of Ca₃Ir₄Sn₁₃ plotted as a function of H/H_{c2} . For comparison, similar data are shown for the clean *s*-wave superconductor Nb,¹⁷ the dirty *s*-wave superconducting alloy InBi,¹⁸ the multiband *s*-wave superconductor NbSe₂,¹⁹ and an overdoped sample of the *d*-wave superconductor Tl-2201.¹⁵

 $\kappa_0/T = 17 \text{ mW K}^{-2} \text{ cm}^{-1}.^{16}$ Therefore, the negligible κ_0/T of both S1 and S2 samples strongly suggests that the superconducting gap of Ca₃Ir₄Sn₁₃ is nodeless.

Figure 3(b) plots the thermal conductivity of S1 in magnetic fields. All the curves are also fitted by $\kappa/T = a + bT^{\alpha-1}$. In $H_{c2} = 7$ T, $\kappa_0/T = 0.216 \pm 0.003$ mW K⁻² cm⁻¹ was obtained from the fitting. This value meets the Wiedemann-Franz law expectation $L_0/\rho_0(7 \text{ T}) = 0.215$ mW K⁻² cm⁻¹ nicely, with L_0 the Lorenz number 2.45×10^{-8} W Ω K⁻² and $\rho_0(7 \text{ T}) = 114.0 \ \mu\Omega$ cm. The verification of the Wiedemann-Franz law in the normal state shows the reliability of our thermal conductivity measurements.

As seen in Fig. 3(b), κ_0/T of S1 gradually increases with increasing field. In Fig. 4, we plot the normalized $\kappa_0(H)/T$ as a function of H/H_{c2} for S1. The κ_0/T of S2 shows similar field dependence, which is not shown here. For comparison, the data of the clean *s*-wave superconductor Nb,¹⁷ the dirty *s*-wave superconducting alloy InBi,¹⁸ the multiband *s*-wave superconductor NbSe₂,¹⁹ and an overdoped sample of the *d*-wave superconductor TI-2201¹⁵ are also plotted. For a clean type II *s*-wave superconductor with a single gap, κ should grow exponentially with field (above H_{c1}), as is indeed observed in Nb.¹⁷ For InBi, the curve is exponential at low *H*, crossing over to a roughly linear behavior closer to H_{c2} as expected for *s*-wave superconductors in the dirty limit.²⁰

The normalized $\kappa_0(H)/T$ of Ca₃Ir₄Sn₁₃ clearly mimics that of the dirty *s*-wave superconductor InBi. However, previously Yang *et al.* estimated the superconducting coherence length $\xi_0 \sim 79$ Å and the electronic mean free path $l \sim 811$ Å, which implies that Ca₃Ir₄Sn₁₃ is an intrinsic clean-limit superconductor ($\xi_0 \ll l$).⁷ Since the ρ_0 of our sample S1 is about twice that of Yang *et al.*, we estimate the mean free path $l \sim 400$ Å for S1. The $H_{c2}(0)$ of S1 is the same as in Ref. 7, which gives the same $\xi_0 \sim 79$ Å through the relation $H_{c2}(0) = \Phi_0/2\pi\xi_0^2$. Therefore, sample S1 is still a clean superconductor, and the relatively fast increase of $\kappa_0(H)/T$ near H_{c2} should have a different origin from the dirty *s*-wave superconductor InBi.

Band structure calculation shows that there are six bands in Ca₃Ir₄Sn₁₃ which cross the Fermi level.²¹ Each sheet of the Fermi surface was found to be three-dimensional, with rather complex shape.²¹ In this context, we interpret that the $\kappa_0(H)/T$ behavior of Ca₃Ir₄Sn₁₃ may result from multiple gaps or gap anisotropy.

For the multiband s-wave superconductor NbSe₂, $\kappa_0(H)/T$ increases rapidly in both low field and near H_{c2} .¹⁹ Similar behavior has been observed in LNi_2B_2C (L = Y, Lu) with multiple and anisotropic gaps.^{22,23} In both NbSe₂ and LNi₂B₂C, applying a field rapidly delocalizes quasiparticle states confined within the vortices associated with the smaller gap band, while those states associated with the larger gap band delocalize more slowly. For NbSe₂, the ratio between larger and smaller gaps is approximately 3^{24} and for YNi₂B₂C, the ratio is about 2.1.²³ Recently, Bang has calculated the field dependence of $\kappa_0(H)/T$ for different gap ratios to explain the thermal conductivity data of the multigap iron-based superconductor $Ba(Fe_{1-x}Co_x)_2As_2$.²⁵ It is possible that in Ca₃Ir₄Sn₁₃ the gaps in the six Fermi surfaces may have different magnitudes, or in some Fermi surface the gap is anisotropic. If this is the case, according to Bang's calculation,²⁵ the gap ratio in Ca₃Ir₄Sn₁₃ should be around 1.4 or so. This interpretation needs to be checked by momentum-dependent measurements of the superconducting gap, such as angleresolved photoemission spectroscopy (ARPES) experiments.

IV. SUMMARY

In summary, we report the resistivity and thermal conductivity measurements of Ca₃Ir₄Sn₁₃ single crystals. Among three crystals, only one sample shows a resistivity anomaly near 20 K, and the other two samples display Fermi-liquid behavior $\rho \sim T^2$ at low temperature. This suggests that the resistivity anomaly may be not intrinsic in Ca₃Ir₄Sn₁₃. Thermal conductivity results clearly demonstrate that the superconducting gap is nodeless in both crystals with and without the resistivity anomaly. This implies that the FM spin fluctuations, if they exist, may be irrelevant to the superconductivity in $Ca_3Ir_4Sn_{13}$, and the conventional electron-phonon interaction should be responsible for the electron pairing. The $\kappa_0(H)/T$ shows a relatively fast increase near H_{c2} . Since Ca₃Ir₄Sn₁₃ is not in the dirty limit, but rather has multiple Fermi surfaces with complex shape, we interpret that the behavior of $\kappa_0(H)/T$ may result from gap anisotropy, or multiple isotropic gaps with different magnitudes.

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- *shiyan_li@fudan.edu.cn
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