Nodeless superconductivity in Ca$_3$Ir$_4$Sn$_{13}$: 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

(Dated: February 24, 2012)

We report thermal conductivity measurements down to 50 mK on Ca$_3$Ir$_4$Sn$_{13}$ single crystals, in which superconductivity with $T_c \approx 7$ K was claimed to coexist with ferromagnetic spin-fluctuations. In zero magnetic field, no residual linear term $\kappa_0/T$ is found. In low magnetic fields, $\kappa_0(H)/T$ shows a slow field dependence. These results demonstrate that the superconducting gap of Ca$_3$Ir$_4$Sn$_{13}$ is nodeless, thus rule out an exotic nodal gap caused by ferromagnetic spin-fluctuations. The relatively fast increase of $\kappa_0(H)/T$ near the upper critical field $H_{c2}$ may result from gap anisotropy, or multiple isotropic gaps with different magnitudes.

PACS numbers: 74.25.fc, 74.70.Dd

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 for example, the antiferromagnetic (AF) spin-fluctuations are considered as the pairing glue in high-$T_c$ cuprates, iron-based superconductors, and many heavy-fermion superconductors. On another side, the ferromagnetic (FM) spin-fluctuations could be the origin of the superconductivity in Sr$_2$RuO$_4$, heavy-fermion superconductors UGe$_2$ and URhGe. These AF and FM spin-fluctuations usually result in superconducting gaps with nodes, such as the $d$-wave gap in cuprates and CeCoIn$_5$. and the $p$-wave gap in Sr$_2$RuO$_4$.

Ca$_3$Ir$_4$Sn$_{13}$ is a cubic transition metal compound, in which superconductivity with $T_c \approx 7$ K was found thirty years ago. 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 the FM spin-fluctuations in Ca$_3$Ir$_4$Sn$_{13}$. The non-Fermi-liquid behavior of resistivity in zero field has been attributed to such spin-fluctuations, and upon applying magnetic field, Fermi liquid behavior is recovered.

Since the FM spin-fluctuations may cause an exotic superconducting state in Ca$_3$Ir$_4$Sn$_{13}$, it will be interesting to probe its superconducting gap structure. Ultra-low-temperature thermal conductivity measurement is such a bulk technique. The existence of a finite residual linear term $\kappa_0/T$ in zero magnetic field is a clear evidence for gap nodes. The field dependence of $\kappa_0/T$ may further give support for a nodal superconducting state, and provide informations on the gap anisotropy, or multiple gaps.

In this Brief Report, we measure the low-temperature thermal conductivity of Ca$_3$Ir$_4$Sn$_{13}$ single crystals down to 50 mK. The absence of $\kappa_0/T$ in zero field and the slow field dependence of $\kappa_0(H)/T$ in low fields clearly demonstrate nodeless superconductivity in Ca$_3$Ir$_4$Sn$_{13}$.

The relatively fast increase of $\kappa_0(H)/T$ near the upper critical field $H_{c2}$ is discussed.

II. EXPERIMENT

Single crystals of Ca$_3$Ir$_4$Sn$_{13}$ were grown by flux method, as previously described in Ref. 5. The excessive Sn flux was etched in concentrated hydrochloric acid (HCl). The obtained single crystals have typical size of a few mm$^3$. We chose a single crystal with a large surface, which was determined as (110) plane by X-ray diffraction measurements. Then the single crystal was polished and cut to a rectangular shape of dimensions $2.5 \times 1.8$ mm$^2$ in the (110) plane, and 0.22 mm in thickness. The dc magnetic susceptibility was measured at $H = 20$ Oe, with zero-field cooled, using a SQUID (MPMS, Quantum Design). Four silver wires were attached on 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 mOhm at 2 K. The thermal conductivity was measured in a dilution refrigerator, using a standard four-wire steady-state method with two RuO$_2$ chip thermometers, calibrated in situ against a reference RuO$_2$ thermometer. Magnetic fields were applied perpendicular to the (110) plane. To ensure a homogeneous field distribution in the sample, all fields were applied at temperature above $T_c$.

III. RESULTS AND DISCUSSION

Figure 1(a) presents the normalized dc magnetization of Ca$_3$Ir$_4$Sn$_{13}$ single crystal, measured in $H = 20$ Oe with zero-field cooled condition. The transition temperature $T_c = 6.85$ K is determined from the onset of diamagnetic transition. Fig. 1(b) plots the low-temperature resistivity of Ca$_3$Ir$_4$Sn$_{13}$ single crystal in $H = 0$ T. The zero-resistivity $T_c = 6.95$ K is roughly the same as that obtained from the magnetization measurement in Fig.
The normal-state ρ(0)/T = 1.51 mW K⁻¹ cm⁻¹ was obtained from the fitting. This value meets the prediction of the Lorenz number 2.45. For example, ρ₀/Τ = 1.41 mW K⁻¹ cm⁻¹ for the overdoped cuprate Ti₂Ba₂CuO₆⁺δ (Tl-2201), a d-wave superconductor with Tc = 15 K. For the p-wave superconductor Sr₂RuO₄, κ₀/Τ = 17 mW K⁻² cm⁻¹. Therefore, the negligible residual linear term in Ca₃Ir₄Sn₁₃ strongly suggests that its superconducting gap is nodeless, thus rules out a nodal gap caused by FM spin-fluctuations.

In H = 7 T, κ₀/Τ = 1.51 ± 0.02 mW K⁻² cm⁻¹ was obtained from the fitting. This value meets the Wiedemann-Franz law expectation L₀/ρ₀(7T) = 1.49 mW K⁻² cm⁻¹ within experimental error bar, with L₀ the Lorenz number 2.45 × 10⁻⁸ WΩK⁻² and normal-state ρ₀(7T) = 16.4 µΩ cm. The verification of
exponentially with field (above wave superconductor with a single gap, $\kappa$ as a function of $\kappa$ increasing field. In Fig. 4, we plot the normalized superconducting alloy InBi, $s$ served in Nb.

liability of our thermal conductivity measurements.

the (110) plane. The solid lines are $\kappa/T = a + bT$ fit to all the curves, respectively. The dash line is the normal-state Wiedemann-Franz law expectation $L_0/\rho_0(7T)$, with $L_0$ the Lorenz number $2.45 \times 10^{-8}$ WΩK$^{-2}$ and normal-state $\rho_0(7T) = 16.4 \mu$Ω cm.

Wiedemann-Franz law in the normal state shows the reliability of our thermal conductivity measurements.

As seen in Fig. 3, $\kappa_0/T$ gradually increases with increasing field. In Fig. 4, we plot the normalized $\kappa_0(H)/T$ as a function of $H/H_c2$ for $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$, together with the clean $s$-wave superconductor Nb$^{24}$ the dirty $s$-wave superconducting alloy InBi$^{16}$ the multi-band $s$-wave superconductor NbSe$_2$ and an overdoped sample of the $d$-wave superconductor Ti-2201.$^{25}$ For a clean type-II $s$-wave superconductor with a single gap, $\kappa$ should grow exponentially with field (above $H_{c1}$), as is indeed observed in Nb.$^{24}$ 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.$^{19}$

The normalized $\kappa_0(H)/T$ of $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ clearly mimics that of the dirty $s$-wave superconductor InBi. However, previously Yang et al. estimated the superconducting coherence length $\xi_0 \sim 79 \text{ Å}$ and electronic mean free path $l \sim 811 \text{ Å}$, which implies that $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ is an intrinsic clean-limit superconductor $(\xi_0 \ll l)^{20}$ Since the $\rho_0$ of our single crystal is lower than that of Yang et al.’s, our sample is cleaner than theirs. Therefore, the relatively fast increase of $\kappa_0(H)/T$ near $H_{c2}$ in $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ should have different origin from the dirty $s$-wave superconductor InBi.

Band structure calculation shows that there are six bands in $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ which cross the Fermi level$^{23}$ Each sheet of the Fermi surface was found to be three dimensional, with rather complex shape.$^{23}$ In this context, we interpret the $\kappa_0(H)/T$ behavior of $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ may result from multiple gaps or gap anisotropy.

For the multi-band $s$-wave superconductor NbSe$_2$, $\kappa_0(H)/T$ increases rapidly in both low field and near $H_{c2}$. Similar behavior has been observed in $\text{LNi}_2\text{B}_2\text{C}$ ($L = \text{Y}, \text{Lu}$) with multiple and anisotropic gaps$^{20,21}$ In both NbSe$_2$ and $\text{LNi}_2\text{B}_2\text{C}$, 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 NbSe$_2$, the ration between larger and smaller gaps is approximately 3$^{22}$ and for $\text{YNi}_2\text{B}_2\text{C}$, the ratio is about 2.1$^{25}$ Recently, Bang has calculated the field dependence of $\kappa_0(H)/T$ for different gap ratios, to explain the thermal conductivity data of multi-gap iron-based superconductor $\text{Ba(Fe}_{1-x}\text{Co}_x\text{})_2\text{As}_2$. It is possible that in $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$, 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, the gap ratio in $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ should be around 1.4 or so. This interpretation needs to be checked by momentum dependent measurements of the superconducting gap, such as angle-resolved photoemission spectroscopy (ARPES) experiments.

**IV. SUMMARY**

In summary, we report the ultra-low-temperature thermal conductivity measurements of $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ single crystals. Despite that FM spin-fluctuations were claimed to exist in this superconductor, our thermal conductivity results clearly show that its superconducting gap is nodeless. This implies that the FM spin-fluctuations may be irrelevant to the superconductivity in $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$, 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 Ca$_3$Ir$_4$Sn$_{13}$ 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.

**ACKNOWLEDGEMENTS**

This work is supported by the Natural Science Foundation of China, the Ministry of Science and Technology of China (National Basic Research Program No: 2009CB929203 and 2012CB821402), Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

* E-mail: shiyan_li@fudan.edu.cn

---

1. M. R. Norman, Science **332**, 196 (2011), and references therein.
2. C. C. Tsuei and J. R. Kirtley, Rev. Mod. Phys. **72**, 969 (2000).
3. K. An, T. Sakakibara, R. Settai, Y. Onuki, M. Hiragi, M. Ichioka, and K. Machida, Phys. Rev. Lett. **104**, 037002 (2010).
4. A. P. Mackenzie and Y. Maeno, Rev. Mod. Phys. **75**, 657 (2003).
5. G. P. Espinosa, Mater. Res. Bull. **15**, 791 (1980). G. P. Espinosa, A. S. Copper, and H. Barz, Mater. Res. Bull. **17**, 963 (1982).
6. Jinhu Yang, Bin Chen, Chishiro Michioka, and Kazuyoshi Yoshimura, J. Phys. Soc. Jpn. **19**, 113705 (2010).
7. H. Shakiripur, C. Petrovic, and L. Taillefer, New J. Phys. **11**, 055065 (2009).
8. R. W. Hill, Shiyuan Li, M. B. Maple, and Louis Taillefer, Phys. Rev. Lett. **101**, 237005 (2008).
9. M. Sutherland, D. G. Hawthorn, R. W. Hill, F. Ronning, S. Wakimoto, H. Zhang, C. Proust, E. Boaknin, C. Lupien, and Louis Taillefer, Phys. Rev. B **67**, 174520 (2003).
10. S. Y. Li, J.-B. Bonnemaison, A. Payeur, P. Fournier, C. H. Wang, X. H. Chen, and L. Taillefer, Phys. Rev. B **77**, 134501 (2008).
11. S. Y. Li, G. Wu, X. H. Chen, and Louis Taillefer, Phys. Rev. Lett. **99**, 107001 (2007).
12. L. Ding, J. K. Dong, S. Y. Zhou, T. Y. Guan, X. Qiu, C. Zhang, L. J. Li, X. Lin, G. H. Cao, Z. A. Xu and S. Y. Li, New J. Phys. **11**, 093018 (2009).
13. J. K. Dong, S. Y. Zhou, T. Y. Guan, H. Zhang, Y. F. Dai, X. Qiu, X. F. Wang, Y. He, X. H. Chen, and S. Y. Li, Phys. Rev. Lett. **104**, 087005 (2010).
14. M. Suzuki, M. A. Tanatar, N. Kikugawa, Z. Q. Mao, Y. Maeno, and T. Ishiguro, Phys. Rev. Lett. **88**, 227004 (2002).
15. J. Lowell and J. B. Sousa, J. Low. Temp. Phys. **3**, 65 (1970).
16. J. O. Willis and D. M. Ginsberg, Phys. Rev. B **14**, 1916 (1976).
17. E. Boaknin, M. A. Tanatar, J. Paglione, D. Hawthorn, F. Ronning, R. W. Hill, M. Sutherland, Louis Taillefer, J. Sonier, S. M. Hayden, and J. W. Brill, Phys. Rev. Lett. **90**, 117003 (2003).
18. C. Proust, E. Boaknin, R. W. Hill, Louis Taillefer, and A. P. Mackenzie, Phys. Rev. Lett. **89**, 147003 (2002).
19. C. Caroli and M. Cyrot, Phys. Kondens. Mater. **4**, 285 (1965).
20. E. Boaknin, R. W. Hill, C. Proust, C. Lupien, Louis Taillefer, and P. C. Canfield, Phys. Rev. Lett. **87**, 237001 (2001).
21. T. Baba, T. Yokoya, S. Tsuda, T. Watanabe, M. Nohara, H. Takagi, T. Oguchi, and S. Shin, Phys. Rev. B **81**, 180509(R) (2010).
22. T. Yokoya, T. Kiss, A. Chainani, S. Shin, M. Nohara, H. Takagi, Science **294**, 2518 (2001).
23. S. K. Goh, L. E. Klintberg, P. L. Alireza, D. A. Tompsett, Jinhu Yang, Bin Chen, K. Yoshimura, and F. Malte Grosche, arXiv:1105.3941 (2011).
24. Yunkyu Bang, Phys. Rev. Lett. **104**, 217001 (2010).