Superconducting (SC) mechanism is the central issue in the study of unconventional superconductors. Since the discovery of Fe-based superconductors (FeSCs) [1], many efforts have been made on this problem [2]. Gap structure can supply very important information for this issue, because typically different SC mechanism will predict distinct gap symmetry and structure. For example, the Fermi surfaces with a better nesting condition tend to have a stronger pairing amplitude and larger SC gap in the itinerant mechanism [3, 4], while according to the local scenario, a larger SC gap should open on the smaller Fermi surface [5].

For the 1111 system with the ZrCuSiAs-type structure, the SC gap structure has been investigated by diverse methods and the conclusions are, however, rather controversial. Most of the early studies based on the polycrystalline samples claimed a nodal gap structure [6–8]. Later on, the nodeless scenarios were also reported by other groups, some of which were measured on single-crystalline samples [9–11]. Overall, however, the investigations on this issue are still lacking. Especially, an in-depth specific heat study based on high-quality single crystals is almost blank, mainly because the SH measurements usually require a considerable sample mass. Specific heat is one of the powerful tools to measure the quasiparticle density of states (DOS) at the Fermi level to detect the information about the gap structure [12–17]. The feature of the gap structure can be essentially determined by measuring the variation in the electronic SH versus temperature and magnetic field [18, 19].

Multiple gaps revealed by low temperature specific heat in the 1111-type CaFe$_{0.88}$Co$_{0.12}$AsF single crystals

Jianan Chu$^{1,2,3}$, Teng Wang$^{1,2,4}$, Yonghui Ma$^{1,2,3}$, Jiaxin Feng$^{1,2,3}$, Lingling Wang$^1$, Xuguang Xu$^4$, Wei Li$^{5,6}$, Gang Mu$^{1,2,*}$ and Xiaoming Xie$^{1,2,3}$

1 State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, People’s Republic of China
2 CAS Center for Excellence in Superconducting Electronics (CENSE), Shanghai 200050, People’s Republic of China
3 University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
4 School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, People’s Republic of China
5 State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, People’s Republic of China
6 Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, People’s Republic of China

E-mail: mugang@mail.sim.ac.cn

Received 13 May 2019, revised 17 July 2019
Accepted for publication 24 July 2019
Published 19 August 2019

Abstract

Low-temperature specific heat (SH) is measured on the 1111-type CaFe$_{0.88}$Co$_{0.12}$AsF single crystals under different magnetic fields. A clear SH jump with the height $\Delta C/T\vert_{T_c} = 10.4$ mJ mol$^{-1}$ K$^{-2}$ is observed at the superconducting transition temperature $T_c$. The electronic SH coefficient $\Delta \gamma(B)$ increases linearly with the field below 5 T and a kink is observed around 5 T, indicating a multi-gap feature in the present system. Such a sign is also reflected in the $T_c - B$ data. A detailed analysis shows that this behavior can be interpreted in terms of a two-gap scenario with the ratio $\Delta_L/\Delta_S = 2.8$–4.5.

Keywords: superconducting gap, specific heat, 1111 type Fe-based superconductors

(Some figures may appear in colour only in the online journal)
more efforts are urgently required to obtain the intrinsic thermodynamic property of the 1111 system.

Recently, due to the progresses on the single-crystal growth of the fluorine-based 1111 system Ca(Fe,Co)AsF [20, 21], systematic investigations have been carried out on this system [22–31]. In our previous works, a two-gap feature is revealed by the temperature dependence of lower critical field $H_{c1}(T)$ and point-contact spectroscopy measurements on the single-crystalline samples [30, 31]. However, the ratio of the two gaps ($\frac{\Delta_L}{\Delta_S}$) is not very consistent between different measuring means. According to the data of $H_{c1}(T)$, $\frac{\Delta_L}{\Delta_S} \approx 5.2$ [30]. While from point-contact spectroscopy measurement, the ratio $\frac{\Delta_L}{\Delta_S} \approx 2.6$ [31] is obtained. Thus more experiments are required to further clarify this issue. In this paper, low temperature specific heat is measured on the 1111-type single crystals of CaFe$_{0.88}$Co$_{0.12}$AsF. A linear field dependence of the electronic SH coefficient $\Delta \gamma (B)$ is discovered in the field region below 5 T, which turns to another linear evolution with a smaller slope under the even higher field. This is very like the behavior of MgB$_2$ [32] and implies a clear two-gap picture. The ratio of the two gaps is estimated to be $\frac{\Delta_L}{\Delta_S} = 2.8 \pm 4.5$.

The CaFe$_{0.88}$Co$_{0.12}$AsF single crystals were grown by the self-flux method. The detailed growth conditions and sample characterizations has been reported in our previous work [20, 21]. In order to ensure a sufficient mass for the SH measurement, three high-quality single crystals with very similar magnetization transitions (see the inset of figure 1) were chosen. The total mass of the three samples is 1.4 mg. The dc magnetization measurements were done with a superconducting quantum interference device (Quantum Design, MPMS 3). The specific heat were measured on the physical property measurement system (Quantum Design, PPMS). We employed the thermal relaxation technique to perform the specific heat measurements. The external field was applied along the $c$ axis of all the three single crystals during the SH measurements.

The superconducting transition of the single crystals was checked by the dc magnetization measurements down to 1.8 K. In the inset of figure 1, we show the temperature dependence of the normalized magnetization data for three CaFe$_{0.88}$Co$_{0.12}$AsF samples. The data were collected using a zero-field-cooling mode under a field of 5 Oe. The SC transitions for three samples are basically the same with the onset transition temperature $T_c = 21$ K. The main frame of figure 1, we show the temperature dependence of total dc magnetization for three CaFe$_{0.88}$Co$_{0.12}$AsF single crystals. The data is measured using the zero-field-cooling mode. The magnetic field of 5 Oe is applied along the $ab$ plane. The inset shows the data of the three samples, respectively, which is normalized to the absolute value at 2 K to have a clear comparison.
times of formula units, [CaFe0.88Co0.12AsF]2. An unobvious SH anomaly can be seen from the raw SH data under zero field near \(T_c\). The inset of figure 2(a) shows an enlarged view of this anomaly near the SC transition. Under 9 T, the SH anomaly was suppressed markedly due to the field-induced pair-breaking effect and could not be distinguished from the raw data which include a large contribution from phonon. In order to highlight the SH anomaly under 0 T, we subtracted the data under 9 T from the zero field data to eliminate influences of the phonon contribution and the results is shown in figure 2(b). The SH anomaly at zero field was determined to be about \(\Delta C/T\mid_{T,0} = 7.5 \text{ mJ mol}^{-1} \text{ K}^{-2}\), as indicated by the red arrowed line in figure 2(b). Considering the non-SC fraction of about 28%, the actual magnitude of the SH anomaly should be \(\Delta C/T\mid_{T,\text{actual}} = 10.4 \text{ mJ mol}^{-1} \text{ K}^{-2}\). We found that this magnitude is clearly smaller than that observed in the 122 system with similar \(T_c\) [16] and markedly deviates from the plot based on the Bud’ko, Ni and Canfield (BNC) law [33], \(\Delta C \propto T^2\) (see figure 2(c)). To have a meaningful comparison, the SH data for all the samples in this figure has been normalized to per [FeAs]2. Assuming a weak-coupling BCS picture where the ratio \(\Delta C/\gamma_n T\mid_{T_c} \approx 1.43\), we can estimated the normal state electronic SH coefficient \(\gamma_n \approx 7.3 \text{ mJ mol}^{-1} \text{ K}^{-2}\). We note here that this value may be an upper limit of \(\gamma_n\) since typically the coupling strength is larger than the BCS prediction of 1.43.

We next focus our attention on the SH data in the low temperature range to study the low-energy quasiparticle (QP) excitations. Typically important information about the QP excitations can be obtained by monitoring the temperature and field dependence of the electronic SH data. To study the temperature dependent behavior, it is essential to isolate the electronic term by removing the phonon contribution \(C_{\text{ph}}\) from the total SH data. One reliable way to handle this issue is to achieve the normal state by applying a magnetic field above the upper critical field [15]. The normal state SH only includes simply the phonon contribution and the normal state electronic \(\gamma_n T\), which is convenient to be removed. Another method is to simulate the phonon SH using the Debye model [13], which has a simple formula \(C_{\text{ph}} \propto T^3\) in the low temperature region. However, in the present material, it is very difficult to adopt these two methods because the upper critical field is far above our experimental condition and the simple Debye relation is not applicable in the temperature range around \(T_c\). Moreover, the rather small magnitude of the electronic term in the present system, as compared with the hole-doped 122 system for example, further increases the difficulty in this issue. This seems to be a common challenge in the field of unconventional high-\(T_c\) superconductors. Thus here we focus on the field induced QP excitations. The raw data of the SH in various magnetic fields in the low-temperature region below 3.5 K is shown as \(C/|T|\) versus \(T^2\) in figure 3. The curves display a clear linear tendency in this low temperature region. No Schottky anomaly can be observed, which facilitates the following analysis of our data. The SH data generally shows a monotonous upward shift with the increase of the magnetic field, implying the QP excitation induced by the magnetic field. By extrapolating this linear tendency to zero temperature (as shown by the dashed lines in (figure 3), we can obtain the field dependence of the electronic SH coefficient \(\gamma(B)\) because the phonon contribution vanishes as the temperature is reduced to 0 K. As shown in the inset of figure 3, a residual term \(\gamma_0 \equiv \gamma(0) \approx 2.0 \text{ mJ mol}^{-1} \text{ K}^{-2}\) was revealed. Considering the rather small values of \(\Delta C/T\mid_{T_c}\) and \(\gamma_n\), the magnitude of \(\gamma_0\) should not be ignored. Typically this term was attributed to the non-superconducting fraction of the sample and/or the residual quasiparticle DOS in the SC material with d-wave or S^5 gap symmetry [12, 16, 39]. Since the SC volume fraction was determined to be above 72% by the magnetization measurement (see figure 1), \(\gamma_0 (\gamma_0/\gamma_n \approx 27\%)\) can mainly be attributed to the non-superconducting fraction of the sample.

The field-induced term \(\Delta \gamma(B) = (\gamma(B) - \gamma_0)/72\%\) is shown in figure 4(a). The data is divided by 72% to deduce the intrinsic SC property of this material. \(\Delta \gamma(B)\) increases linearly as the magnetic field increases from 0 T to 5 T and shows a kink feature around 5 T, above which another linear evolution can be seen with a smaller slope. This behavior is very similar to that observed in the famous multi-band superconductor MgB2, where a two-gap picture is proposed [32]. Obviously such an observation is consistent qualitatively with the reported of the lower critical field and point-contact spectroscopy measurements [30, 31]. In order to give a more precise understanding, we attempted to obtain the normal state values of \(\gamma_n\) and the out-of-plane upper critical field \(B_{c2}\) (\(\equiv B_{c2}(0)\)). The value of \(\gamma_n = 7.3 \text{ mJ mol}^{-1} \text{ K}^{-2}\) has been derived from the height of SH jump. As for the estimation of \(B_{c2}\), experiments under high magnetic fields reveal that the \(B_{c2} - T\) curve shows a roughly linear behavior at low temperature [40, 41] and does not display a flattening tendency near 0 K as predicted by the Wertheramer–Helfand–Hohenberg (WHH) relation [42]. From the data of our previous work [25], we can obtain the \(B_{c2} - T\) data of the present system near \(T_c\) and replot it as \(T_c\) versus \(B\), as shown in figure 4(a) (right). Assuming a
The position of the normal state \( B_c \) have two characteristic fields: \( \gamma_n \) and \( B_{c2} \) respectively. As shown by the vertical dashed lines in figure 4(a), now we replotted the \( \Delta \gamma(B) \) data in logarithmic scale with both coordinate axes normalized and showed the results in figure 4(b). All the experimental data locate in between the magenta and orange lines, which represent the square root and linear relations between \( \Delta \gamma/\gamma_n \) and \( B/B_{c2} \) respectively. The square root behavior \( \Delta \gamma/\gamma_n \propto \sqrt{B/B_{c2}} \) is a characteristic of the SC gap with line nodes [46, 47] and the linear relation is a consequence of the isotropic gap structure [44]. Thus the degree of the gap anisotropy in the present system is lower than the line nodal case.

In summary, we studied the low-temperature specific heat of the 1111-type \( \text{CaFe}_{0.88}\text{Co}_{0.12}\text{AsF} \) single crystals. We found an SH jump with the height of 10.4 mJ mol\(^{-1}\) K\(^{-2}\), which diverges from the BNC scaling. The electronic SH coefficient \( \Delta \gamma \) shows a linear increase with field in the field region below 5 T and changes the slope with further increasing the field, indicating a multi-gap behavior. The degree of the anisotropy was estimated to be \( \Delta L/\Delta S = 2.8 \pm 4.5 \).

**Acknowledgments**

This work is supported by the Youth Innovation Promotion Association of the Chinese Academy of Sciences (No. 2015187), the Natural Science Foundation of China (No. 11204338), and the ‘Strategic Priority Research Program (B)’ of the Chinese Academy of Sciences (No. XDB04040300). W L also acknowledges the start-up funding from Fudan University.

**ORCID iDs**

Gang Mu  [https://orcid.org/0000-0001-5676-4702](https://orcid.org/0000-0001-5676-4702)

**References**

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008  *J. Am. Chem. Soc.* **130** 3296
[2] Hirschfeld P J, Korshunov M M and Mazin I I 2011  *Rep. Prog. Phys.* **74** 1245080
[3] Mazin I and Schmalian J 2009  *Physica C* **469** 614
[4] Graser S, Maier T A, Hirschfeld P J and Scalapino D J 2009  *New J. Phys.* **11** 025016
[5] Seo K, Bernevig B A and Hu J 2008  *Phys. Rev. Lett.* **101** 206404
[6] Mu G, Zhu X Y, Fang L, Shan L, Ren C and Wen H H 2008  *Chin. Phys. Lett.* **25** 2221
[7] Matano K, Ren Z A, Dong X L, Sun L L, Zhao Z X and Zheng G Q 2008  *Europhys. Lett.* **83** 57001
[8] Shan L, Wang Y, Zhu X, Mu G, Fang L, Ren C and Wen H H 2008  *Europhys. Lett.* **83** 57004
[9] Chen T Y, Tesanovic Z, Liu R H, Chen X H and Chien C L 2008  *Nature* **453** 1224
[10] Hashimoto K et al 2009  *Phys. Rev. Lett.* **102** 017002
[11] Malone L, Fletcher J D, Serafin A, Carrington A, Zhigadlo N D, Bukowski Z, Katrych S and Karpinski J 2009  *Phys. Rev. B* **79** 140501
[12] Wen H H, Liu Z Y, Zhou F, Xiong J, Ti W, Xiang T, Komiya S, Sun X and Ando Y 2004  *Phys. Rev. B* **70** 214505
[13] Mu G, Wang Y, Shan L and Wen H H 2007  *Phys. Rev. B* **76** 064527

---

**Figure 4.** (a) Field dependence of the of the electronic SH coefficient \( \Delta \gamma \) (left) and \( T_c \) (right). The solid and dashed lines are guides for eyes. (b) The same data as (a) plotted in logarithmic scale. \( \Delta \gamma/\gamma_n \) at \( B/B_{c2} \) can be observed around \( B_1 = 5 \) T in the \( T_c = B \) curve. Such an accordance supplies a good example that the multi-gap feature can be reflected in the temperature dependent \( B_{c2}(T) \) data. As shown by the vertical dashed lines in figure 4(a), now we have two characteristic fields: \( B_1 \) and \( B_{c2} \). Within the multiple-gap picture, these two fields corresponds to two gaps in different Fermi surfaces (FSs) [32, 45]. \( B_1 \) is a virtual upper critical field for the band with a smaller gap while \( B_{c2} \) is the upper critical field for that with a larger gap. In this case, we have \( B_{c2} = (\Delta/\nu_F)^2 \) and \( \Delta L/\Delta S = (\nu_{FL}/\nu_{FS})(B_{c2}/B_1)^{1/2} \), where \( \nu_{FL} \) and \( \nu_{FS} \) are the Fermi velocities in the Fermi surface with the larger and smaller gap respectively. According our previous estimation [30], we have \( \nu_{FL}/\nu_{FS} = 1.25 \). Considering the fact that \( B_{c2}/B_1 = 5 \), we can give an estimation \( \Delta L/\Delta S = 2.8 \pm 4.5 \). To have a vivid impression, we
[14] Mu G, Luo H, Wang Z, Shan L, Ren C and Wen H H 2009
Phys. Rev. B 79 174501
[15] Wen H H, Mu G, Luo H, Yang H, Shan L, Ren C and Fang I 2009
Phys. Rev. Lett. 103 067002
[16] Mu G, Zeng B, Cheng P, Wang Z S, Fang L, Shen B, Shan L, Ren C and Wen H H 2010
Chin. Phys. Lett. 27 037402
[17] Mu G, Tang J, Tanabe Y, Xu J, Heguri S and Fang L 2009
Phys. Rev. Lett. 103 067002
[18] Mu G, Zeng B, Cheng P, Wang Z S, Fang L, Shen B, Shan L, Ren C and Wen H H 2010
Chin. Phys. Lett. 27 037402
[19] Sigrist M and Ueda K 1991
Rev. Mod. Phys. 63 239
[20] Hussey N E 2002
Adv. Phys. 51 1685
[21] Ma Y H, Mu G, Zhang H, Gao B, Li W, Mu G, Huang F Q and Xie X M 2015
Supercond. Sci. Technol. 28 085008
[22] Ma Y H, Luo H, Yang H, Shan L, Ren C and Wen H H 2009
Phys. Rev. B 79 014501
[23] Wang T et al 2019
Acta Phys. Sin. 67 177401
[24] Wang T et al 2019
NPJ Quantum Mater. 4 33
[25] Yu A, Lei L, Wu Y, Wang T, Ma Y, Mu G, Xiao H and Hu T 2019
in preparation
[26] Bouquet F, Wang Y, Sheikin I, Plackowski T, Junod A, Lee S and Tajima S 2002
Phys. Rev. Lett. 89 257001
[27] Bud’ko S L, Ni N and Canfield P C 2009
Phys. Rev. B 79 014506
[28] Chu J H, Analytis J G, Kucharzyk C and Fisher I R 2009
Phys. Rev. B 79 014506
[29] Ni N, Thaler A, Kracher A, Yan J Q, Bud’ko S L and Canfield P C 2009
Phys. Rev. B 80 024511
[30] Ni N, Bud’ko S L, Kreyssig A, Nandi S, Rustan G E, Goldman A I, Gupta S, Corbett J D, Kracher A and Canfield P C 2008
Phys. Rev. B 78 014507
[31] Welp U, Xie R, Koshelev A E, Kwok W K, Luo H Q, Wang Z S, Mu G and Wen H H 2009
Phys. Rev. B 79 094505
[32] Bud’ko S L, Sturza M, Chu J H, Kanatzidis M G and Canfield P C 2013
Phys. Rev. B 87 100509
[33] Bang Y 2010
Phys. Rev. Lett. 104 217001
[34] Fang M, Yang J, Balakirev F F, Kohama Y, Singleton J, Qian B, Mao Z Q, Wang H and Yuan H Q 2010
Phys. Rev. B 81 020509
[35] Khim S, Lee B, Kim J W, Stewart G R and Kim K H 2011
Phys. Rev. B 84 104502
[36] Werthamer N R, Helfand E and Hohenberg P C 1966
Phys. Rev. 147 295
[37] Clogston A M 1962
Phys. Rev. Lett. 9 266
[38] Nakai N, Miranovi P, Ichioka M and Machida K 2004
Phys. Rev. B 70 100503
[39] Bourgeois-Hope P, Chi S, Bonn D A, Liang R, Hardy W N, Wolf T, Meingast C, Doiron-Leyraud N and Toulouse L 2016
Phys. Rev. Lett. 117 097003
[40] Volovik G E 1993
JETP Lett. 58 469
[41] Volovik G E 1997
JETP Lett. 65 491