Anisotropic superconducting order parameters in the iron pnictide superconductors

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Abstract. The symmetry and structure of the superconducting gap in the Fe-based superconductors are the central issues for understanding these novel materials. So far the experimental data and theoretical models have been highly controversial. Some experiments favor two or more isotropic gaps, others indicate strong anisotropy and even nodes. In this paper we present the experimental data of low temperature specific heat to illustrate that the superconducting gap is anisotropic. In the case of optimally doped 122, the gap minimum may appear as point nodes or small segment of nodal lines, while in the FeTe\textsubscript{0.55}Se\textsubscript{0.45} it may appear on the electron pockets with the gap minimum along the Γ-Z (Fe-Fe bond) direction.

1. Introduction

The discovery of superconductivity at 26 K in iron pnictides has trigged a great enthusiasm in the research on unconventional superconductivity.[1] One of the key issues here is about the superconducting pairing mechanism. Theoretically it was suggested that the pairing might be established via inter-pocket scattering of electrons between the hole pockets (around Γ point) and electron pockets (around M point), leading to the so-called S\textsuperscript{±} pairing manner.[2, 3, 4] Experimental results about the pairing symmetry remain highly controversial leaving the perspectives ranging from S\textsuperscript{++}-wave, to S\textsuperscript{±} and to d-wave.[5, 6, 7, 8, 9, 10, 11, 12, 13] The penetration depth measurements indicate power-law like temperature dependence Δλ \propto (T/T\textsubscript{c})\textsuperscript{n} (n ranges from below 2 to about 4).[10] And it becomes more linear like when the detecting current has a c-axis component, indicating the possibility of nodes along c-axis but nodeless along FeAs-plane.[14] This is further strengthened by the recent thermal conductivity measurements which suggest the possible existence of a horizontal nodal line.[15] In this paper, we present the data of low temperature specific heat (SH) in Ba(Fe\textsubscript{1-x}TM\textsubscript{x})\textsubscript{2}As\textsubscript{2} (TM = Co and Ni) single crystals. It is tempting to conclude the existence of small segments of nodal lines or point-like nodes. We also measured the angle resolved specific heat with an in-plane magnetic field in FeTe\textsubscript{0.55}Se\textsubscript{0.45}, and observed a clear four-fold oscillations of specific heat when the sample was rotated. These results suggest the gap anisotropy and are consistent with the recent five band tight binding calculations.[16, 17]
2. Results and Discussion

2.1. Low temperature specific heat of the optimally doped Ba(Fe\text{1-x}TM\text{x})\text{2}As\text{2} (TM = Co and Ni)

In Fig.1, we present the SH of the superconducting and heavily overdoped non-superconducting samples under zero field for each dopant. Sharp and clear SH anomalies near $T_e$ for the samples Ba(Fe\text{0.92}Co\text{0.08})\text{2}As\text{2} and Ba(Fe\text{0.95}Ni\text{0.05})\text{2}As\text{2} can be seen. For all samples investigated here, the Schottky anomalies are negligible. One can see that the SH in the normal state for the superconducting and non-superconducting samples share a very similar temperature dependence. This allows us to use the phonon part of SH of the non-superconducting sample as the reference, and subtract it safely for the superconducting one, a method suggested previously.[18, 19]

Suppose that the phonon contributions of the non-superconducting sample is $C_{ph}^N(T)$, which can be obtained by subtracting the linear electronic term from the total SH, and the phonon contribution of the superconducting sample is $C_{ph}^S(T)$, we naturally have $C_{ph}^S(T) = a \cdot C_{ph}^N(b \cdot T)$. Here $a$ and $b$ are fitting parameters which should be close to unity. Using a least-squares fit of our data and the rigid constraint of entropy conservation, we determined $a$ and $b$ to be 1.000, 1.013 for the Co-doped sample, and 0.98, 0.99 for the Ni-doped one, indicating that the phonon contributions of the superconducting sample and the overdoped non-superconducting one are indeed very close to each other. The electronic SH of the superconducting sample can then be obtained through $C_e^S(T) = C_{tot}^S(T) - C_{ph}^S(T) = C_{tot}^S(T) - a \cdot C_{ph}^N(b \cdot T)$ with $C_{tot}^S(T)$, $C_e^S(T)$ the total and the electronic SH of the superconducting samples, respectively. The obtained electronic SH for Co- and Ni-doped samples are shown in Fig.2. Surprisingly, we found a quadratic relation $\gamma_e = \gamma_0 + \alpha T^2$ in the low-T limit (see the insets of Fig.2). The parameters of $\gamma_0$ were determined from the fitting: 1.53 mJ/mol K$^2$ and 1.49 mJ/mol K$^2$, for the superconducting Co- and Ni-doped samples, respectively, which are rather small compared to the values reported in literatures. In order to get a comprehensive understanding, we used the BCS formula to fit our data

$$\gamma_e' = \frac{4N_F}{k_B T^3} \int_0^{+\infty} \int_0^{2\pi} \frac{e^{\xi/k_BT}}{(1 + e^{\xi/k_BT})^2} (\xi^2 +$$
presence of line nodes, we measured the magnetic field dependence of anisotropic gaps, possibly with nodes, may exist in these FeAs-based superconductors. 

\[ \Delta^2(\theta, T) = \frac{T}{2} \frac{d^2\Delta(\theta, T)}{dT^2} \]  

where \( \gamma_e' = \gamma_e - \gamma_0 \), \( \zeta = \sqrt{\epsilon^2 + \Delta^2(T, \theta)} \), \( N_F \) the DOS at the Fermi energy. We use four different gap structures to fit the data: single isotropic s-wave gap (\( S_{iso} \)), single anisotropic gap with a d-wave feature (\( S_d: \Delta = \Delta_0|\cos 2\theta| \)), mixture of two: \( S_{iso} + S_d \) and two isotropic gaps \( S_{iso1} + S_{iso2} \). In the latter two cases, the \( \gamma_e \) was calculated through a linear combination of the two components. The fitting curves are shown by the colored lines in Fig.3, and the fitting parameters and \( \chi^2 \) factors (\( = \sum (d_i - t_i)^2 / d_i^2 \) with \( d_i \) and \( t_i \) the experimental data and the theoretical value at the same temperature, respectively) are listed in Table I and Table II, respectively. The \( S_{iso} + S_d \) model seems to give the best fitting in the whole temperature region. The multigap scenario (\( S_{iso} + S_d \)) with a very small s-wave gap of about 2 meV, which accounts for less than 30% of the total quasiparticle DOS, seems possible. The global fitting with \( S_{iso} + S_d \), together with the relationship \( \gamma_e = \gamma_0 + \alpha T^2 \) in the low-T limit, suggest that anisotropic gaps, possibly with nodes, may exist in these FeAs-based superconductors.

To explore whether the quadratic temperature dependence \( \gamma_e = \gamma_0 + \alpha T^2 \) is due to the presence of line nodes, we measured the magnetic field dependence of \( \gamma_e \). By doing a linear extrapolation of the data to zero K, we get the field dependence of the electron SH coefficient \( \gamma_e(H) \), as shown in the left part of Fig.3. It is clear that \( \gamma_e(H) \) increases linearly with magnetic field for the two samples in both alignments. This excludes both the vertical (like a d-wave) or horizontal line nodes (right-hand side picture in Fig.3), since otherwise, as found in cuprate superconductors, a square root relation \( \gamma_e(H) \propto \sqrt{H} \) in the clean limit, or a curved feature \( \gamma_e(H) \propto H / H_c2 \log(BH_c2 / H) \) with impurity scattering[21] should be observed.

In order to reconcile the observations of a small \( \gamma_0 \), \( \gamma_e = \gamma_0 + \alpha T^2 \) and \( \gamma_e(H) - \gamma_0 \propto H \), we propose that nodes, in the form of point-like or small segments, may exist in our present samples. As indicated by the five-band tight-binding calculations[16] small segments of nodal lines (or

\[ \Delta^2(\theta, T) = \frac{T}{2} \frac{d^2\Delta(\theta, T)}{dT^2} \]
Table 1. Fitting parameters with different models for the Co-doped sample.

| model          | $\Delta_1$(meV) | fraction-1 | $\Delta_2$(meV) | fraction-2 | $\chi^2$ |
|----------------|-----------------|-------------|-----------------|-------------|-----------|
| $S_{iso}$      | 4.2             | 100%        | -               | -           | 11.21     |
| $S_d$          | 5.4             | 100%        | -               | -           | 0.52      |
| $S_{iso} + S_d$| 2.4             | 17%         | 5.9             | 83%         | 0.38      |
| $S_{iso1} + S_{iso2}$ | 1.0         | 25%         | 4.25            | 75%         | 0.94      |

Table 2. Fitting parameters with different models for the Ni-doped sample.

| model          | $\Delta_1$(meV) | fraction-1 | $\Delta_2$(meV) | fraction-2 | $\chi^2$ |
|----------------|-----------------|-------------|-----------------|-------------|-----------|
| $S_{iso}$      | 3.1             | 100%        | -               | -           | 10.95     |
| $S_d$          | 4.1             | 100%        | -               | -           | 5.07      |
| $S_{iso} + S_d$| 2.0             | 29%         | 4.7             | 71%         | 0.42      |
| $S_{iso1} + S_{iso2}$ | 1.15         | 29%         | 3.3             | 71%         | 0.70      |

Figure 3. Magnetic field dependence of the electronic specific heat for the samples Ba(Fe$_{0.92}$Co$_{0.08}$)$_2$As$_2$ and Ba(Fe$_{0.95}$Ni$_{0.05}$)$_2$As$_2$ when the field is aligned along FeAs-plane and c-axis. A rough linear feature was observed in all four cases. The cartoon picture illustrates the possible gap nodes on the $\Gamma$ Fermi surfaces: (left) horizontal nodal lines; (middle) small segments of nodal lines (shown by the red lines); (right) point nodes on the 3D Fermi pockets.

called as accidental nodes) may exist on the hole-pockets near $k_z = \pm \pi$, which is depicted by the middle cartoon picture of Fig.3. An alternative interpretation would assume the extreme case of point-like nodes with a closed 3D Fermi pocket. In a system with point nodes (or small segments of line nodes), it is anticipated that $N_F \propto E^2$, since the Doppler shift energy of $E_H \propto \sqrt{H}$, we have $N_F \propto H$. Meanwhile, the relation $\gamma_e = \gamma_0 + \alpha T^2$ is also anticipated by the point-like nodes.

2.2. Gap anisotropy in FeTe$_{0.55}$Se$_{0.45}$
In Figure 4a we present the angle resolved specific heat in FeTe$_{0.55}$Se$_{0.45}$ with an in-plane magnetic field of 9 T. The systematics about the data and analysis are presented in a recent publication.[22] The specific heat coefficient $= C/T$ shows clear fourfold oscillations. At low temperatures, $T = 2.6-2.7$ K, minima appear when the field is along the $\Gamma$-M direction. As discussed above, the observation of the oscillations of $SH$ can be interpreted as the gap anisotropy and that the minimum gap should be smaller than the Doppler shift energy. Taking the Fermi
Figure 4. (a) The angle dependence of the specific heat coefficient at 2.6, 2.65 and 2.7 K in the in-plane magnetic field of 9 T, where $\phi$ is the angle between the field and the Fe-Se-Fe bond direction. Fourfold oscillations are observed and the amplitude is about 0.12 mJ/mol-K$^2$ ($T = 2.6$ K). The maximum of $C/T$ is located at about zero degrees ($H \parallel$ Fe-Se-Fe). The red lines are theoretical simulations based on a nodal gap with four fold symmetry. (b) The sketch of the Fermi surfaces in the system. (c) The proposed gap form on the electron pocket tuned by the anisotropy factor $r$.

velocity of $2.5 \times 10^5$ and $2.6 \times 10^5$ m/s for the hole and outer electron FS sheets, and $4.0 \times 10^5$ m/s for the inner electron sheet and at 9 T, we estimate the Doppler shift energy, to be between 1 and 2 meV. Thus, these results present direct bulk evidence of a strong gap anisotropy with nodes or deep minima. In Fig.4b, we show a sketch of the Fermi surface. Our results can be briefly understood with a gap anisotropy on the electron pockets.

A canonical d-wave pairing on the hole-FS would readily explain our data. While this is clearly contradicted with the ARPES and thermal conductivity data on the similar system. Another alternative is that the nodal lines or the gap minimum form on the electron FSs with the gap minimum along the $\Gamma$-$M$ direction. Indeed a number of model calculations[16, 17, 4, 3] predict nodes at the electron FS in some parameter range. The gap structure in these calculations is set by the orbital composition of the electron bands in the unfolded Brillouin zone, and nodes appear roughly where the character changes from the $xy/(x^2-y^2)$ orbitals to the $xz/yz$ orbitals. In the theory of tight binding of the five bands scenario, it was shown that the accidental nodes or gap minimum can appear on the electron pockets. Phenomenologically our data was interpreted very well by assuming a gap anisotropy around the electron pocket, say $\Delta_e = \Delta_0 (1-r \sin 2\phi))$[23, 24]. As shown in Fig.4c, taking $\Delta_0 = 1.7$ meV, when the anisotropy is tuned by the variable $r$, nodes can appear when $r = 1$. Our data suggest that the $r$-value locates between 0.7 and 1 in the present system. Finally, since the oscillations can only be observed when the Doppler shift energy is larger than or comparable to the minimum value of the gap, the gap minima should be around 1 meV or less.

3. Conclusions
In summary, the electronic specific heat on the optimally Ni- and Co-doped 122 superconducting samples was derived by successfully removing the phonon contributions. A quadratic
temperature dependence of $\gamma_e = \gamma_0 + \alpha T^2$ in the low-T limit was discovered. The global temperature dependence of $\gamma_e$ can be fitted with a two-component model with possible nodes. However the linear field dependence $\gamma_e(H) \propto H$ observed with the magnetic field along FeAs-plane and c-axis excludes the existence of either vertical or horizontal line nodes. The results can be reconciled by the model of small segments of line nodes or point-like nodes. We have also observed a fourfold oscillations of the specific heat with a in-plane magnetic field in FeTe$_{0.55}$Se$_{0.45}$, which is explained by the strong fourfold anisotropy of the order parameter. A consistent interpretation can be provided in terms of an order parameter that has deep minima (the minimum gap is smaller than about 1 meV) on the electronic Fermi surfaces, located at the crossing point of the $\Gamma$-M direction (the Fe-Fe bond direction).

4. Acknowledgments
We appreciate the discussions with P. Hirschfeld, S. Graser, A. Chubukov, I. I. Mazin, Y. Matsuda, G. Stewart, and the help from I. I. Mazin, C. Ren and L. Shan. This work is supported by the NSF of China, the Ministry of Science and Technology of China (973 project: 2011CBA001002).

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