Impurity Scattering Effect on Superconductivity and the Violation of Anderson Theorem in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ Single Crystals

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Low-temperature specific heat (SH) and resistivity were measured on Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals in wide doping region. A sizeable residual specific heat coefficient $\gamma_0$ was observed in the low temperature limit of all samples. The specific heat jump near $T_c$, i.e. $\Delta C/T|_{T_c}$ and the upper critical field $H_{c2}$ ($H||c$) were also determined. It is found that $-\gamma_0$, $\Delta C/T|_{T_c}$, $\sqrt{H_{c2}}$ and $T_c$ all shared a similar evolution with doping. All these can be well understood within the model of $S^\pm$ pairing symmetry when accounting the Co-dopants as unitary scattering centers in the FeAs planes. Our results give a direct evidence for the violation of the Anderson theorem in FeAs-based superconductors.

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The discovery of superconductivity in iron pnictides has generated enormous interests in the community of condensed matter physics.$^1$ One of the key issues here is about the superconductivity mechanism. Phenomenologically it has been found that in many, if not all, structures of the iron-pnictide materials, the parent phase has a long range antiferromagnetic (AF) ordered state,$^2$ and the superconductivity is induced by suppressing this AF order.$^3$ An important issue concerning the superconductivity mechanism is about the pairing symmetry. Up to date, experimental results gave rather contradicting conclusions about the pairing symmetry in the iron pnictide superconductors.$^7$ Another important issue concerning the superconductivity mechanism is the so-called $S^\pm$ pairing symmetry. Theoretically it was suggested that the superconducting pairing may be established via exchanging spin fluctuations between the electrons in the hole pockets (around $\Gamma$ point) and the electron pockets (around M point), thus a model concerning $s$-wave symmetry with opposite sign between different bands (the so-called $S^\pm$) was proposed.$^{11, 12}$ A direct evidence to prove this unique pairing manner is still lacking although some indirect evidence does indicate that the superconductivity vanishes gradually when the condition for this inter-pocket scattering deteriorates.$^{16, 17}$

In a conventional superconductor, the non-magnetic impurity will not lead to apparent pair-breaking effect, therefore no quasiparticle density of states (DOS) can be generated at the Fermi energy $E_F$. This was called as the Anderson theorem.$^{18}$ In sharp contrast, in a $d$-wave superconductor, non-magnetic impurities can induce a high DOS due to the existence of nodes. Thus it is not strange when a large residual specific heat coefficient $\gamma_0$ (which measures actually the DOS at $E_F$) was observed in the cuprate superconductors.$^{19}$ As for the case with the pairing symmetry of $S^\pm$, it has been pointed out that non-magnetic impurity disorder could severely suppress $T_c$ and the gap.$^{20}$ Recently, the effect of impurity scattering in the case of $S^\pm$ pairing symmetry was considered and it was found that the DOS spectrum $\rho(\omega)$ can be significantly modified leading to a finite DOS at $E_F$. Conclusions about the residual DOS from thermal transport measurement are controversial with each other.$^{23, 24}$ To verify this theoretical hypothesis, specific heat (SH) measurement may be a good choice because it is straightforward to get the information of DOS at the Fermi level. In this Letter, we report the low-temperature SH under different magnetic fields on the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals from underdoped to overdoped region. We found a sizeable value of $\gamma_0$ for all samples in the low temperature limit. The doping dependence of $\gamma_0$ anti-correlates with that of $T_c$, $\Delta C/T|_{T_c}$ and $\sqrt{H_{c2}}$. These behaviors were well interpreted within the model of $S^\pm$ pairing symmetry.

The Co-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals were grown by the self-flux method.$^{17}$ The samples for the SH measurement have typical dimensions of 2.5 × 1.5 × 0.2 mm$^3$. The dc magnetization measurements were done with a superconducting quantum interference device (Quantum Design, SQUID, MPMST). The resistivity and the specific heat were measured with a Quantum Design instrument physical property measurement system (PPMS) with the temperature down to 1.8 K and the magnetic field up to 9 T. We employed the thermal relaxation technique to perform the specific heat measurements. To improve the resolution, we used a latest developed SH measuring frame from Quantum Design, which has negligible field dependence of the sensor of the thermometer on the chip as well as the thermal conductance of the thermal linking wires.

In Fig. 1(a), we show the temperature dependence of resistivity under zero field for five samples with nominal doping compositions of $x = 0.06$, 0.07, 0.08, 0.12, and 0.15, respectively. The sample with $x = 0.08$ was found to be optimally doped with the highest onset transition temperature $T_{c\text{onset}} \approx 24.5$ K. In the underdoped region ($x < 0.08$), an upturn in the resistivity curve above $T_c$ can be easily seen, which was supposed to be related with the structural and antiferromagnetic (AF) transition.$^{17}$
FIG. 1: (color online) (a) Temperature dependence of resistivity for the Ba(Fe_{1-x}Co_x)As_2 single crystals in wide doping range under zero field. (b) The enlarged view of the resistivity data near the superconducting transition. (c) The dc magnetization data measured with $H = 20$ Oe for the zero field cooling (ZFC) process. The curves were normalized by the magnetization data obtained at 2 K.

An enlarged view of the $\rho(T)$ curves near $T_c$ was shown in Fig. 1(b). We also measured the dc magnetization of the samples, which was displayed in Fig. 1(c). The rather sharp transitions suggest the high quality of our samples.

We show the raw data of SH for the sample $x =$ 0.08 in the main frame of Fig. 2. The red solid line displays roughly the tendency of the normal state SH, $C_{\text{norm}}/T = \gamma_n + C_{\text{ph}}/T$, where $\gamma_n$ is the electronic contribution and $C_{\text{ph}}/T$ is the phonon contribution obtained based on a simple polynomial fit in the normal state. This will not be relied on to analyze our data. A clear anomaly due to the superconducting transition can be observed at about 23 K in the zero-field data. A magnetic field of 9 T suppresses the anomaly remarkably and also moves the transition to lower temperatures. We also show the enlarged view of the data in the low-T region in Fig. 2(a). One can see the roughly linear behavior in the $C/T$ vs $T^2$ plot in low-T region. Surprisingly, no clear Schottky anomaly was detected in all the samples, which may suggest that the Co-doping here induces no local magnetic moment which would on the other hand give a large contribution to SH as the Schottky anomaly. It is clear that the magnetic field enhances the low-T SH continuously, indicating the increase of quasiparticle DOS at $E_F$ induced by magnetic field. We will discuss this issue later.

In order to have a comprehensive understanding, we also measured the temperature and field dependence of SH on samples in wide doping region. We extracted the SH difference between 0 T and 9 T and showed the results in Fig. 3(a). From the main frame of Fig. 2, we can see that a magnetic field of 9 T can not suppress the superconductivity completely, but it shifts the superconducting transition to a distinguishable lower temperature. As a result, we can evaluate the height of the SH anomaly $\Delta C/T|_{T_c}$ near $T_c$ from the difference of $C/T$ at 0 T and 9 T. It is clear that the optimal doped sample with highest $T_c$ has the largest anomaly $\Delta C/T|_{T_c} \approx 28.6$ mJ/mol K^2. This value is quite comparable with that reported by other groups.[29, 30, 31] In each doping side (underdoping or overdoping), $\Delta C/T|_{T_c}$ seems to display a monotonic increase with $T_c$. This behavior is qualitatively consistent with that reported in Ref. [31] where a scaling behavior of $\Delta C/T|_{T_c} \propto (T_c)^2$ was reported. However, we note that there is a clear difference between the underdoped and the overdoped regions. For example, the sample with $x =$ 0.07 has a higher $T_c$ while showing a smaller $\Delta C/T|_{T_c}$ compared with that of the sample with $x =$ 0.12. As will be discussed below, we attribute this difference in the underdoping and overdoping regions to...
under zero temperature. One can see a nonmonotonic evolution of temperature SH data for samples with different doping levels. (b) Low-temperature SH data for samples with different doping levels under zero temperature. One can see a nonmonotonic evolution of the residual value $\gamma_0$ with doping. The departure from linear behavior at about 7 K for the sample with $x = 0.15$ was caused by the superconducting transition.

In Fig. 3(b), we present the low-T SH data at zero field. A linear extrapolation of the low-T data finds immediately that there is a sizeable value of the residual SH coefficient $\gamma_0$ for all samples. A closer scrutiny realizes that $\gamma_0$ has a nonmonotonic doping dependence on the Co-doping concentration $x$. We must stress that the sizeable value of $\gamma_0$ found in present samples is not simply attributed to the superconducting fraction. The reasons are as following: (1) A minimum of $\gamma_0$ was observed just at the optimal doping point (see below). From the chemistry point of view, however, there is no reason to believe that the non-superconducting fraction should be the lowest in the optimally doped sample; (2) Counting the magnetization signal in the low temperature region finds that the magnetic shielding is beyond 95 % for all the samples.

In order to clarify the origin of $\gamma_0$ in present samples, we have extrapolated the low-T SH data shown in inset (a) of Fig. 2 to zero temperature linearly and obtained the field-induced term $\Delta\gamma(H) = (C(H) - C(0))/T$ at 0 K, which was shown in inset (b) of Fig. 2 for the optimally doped sample. One can see that $\Delta\gamma(H)$ rises up quickly and shows a nonlinear tendency below about 1 T. Whereas it displays a clear linear behavior above 1 T. Similar feature was observed in samples with other doping levels. We at first attempted to fit the data with the relation $\Delta\gamma(H) = A\sqrt{H}$ predicted for d-wave symmetry in the clean limit. The result was displayed by the green solid line in the inset (b) of Fig.2. It is clear that this fitting curve cannot describe the experimental data at all. Secondly, we fitted our data using the relation for d-wave superconductors in the dirty limit, $\Delta\gamma(H) = \Lambda(H/H_{c2}^\alpha)\log[H/(H_{c2}^\alpha)]$. Here $B$ is a constant which approximates 7.26 for a triangular vortex lattice. We left $\Lambda$ and $H_{c2}^\alpha$ as the free fitting parameters. The best fitting result was shown by the red dash-dotted line. Again this curve departs from the experimental data, especially it cannot reflect the kink feature around 1 T and the linear feature above 1 T. So we can exclude the presence of the superconducting gap with d-wave symmetry, either in the clean or dirty limit. Consequently, the finite DOS found in the present system cannot be attributed to the impurity scattering effect for a d-wave superconductor.

The doping dependence of the extracted $\gamma_0$, along with $T_c$, was shown in Fig. 4(a). The curve of $T_c$ vs $x$ formed an asymmetric dome, while the $\gamma_0$ vs $x$ curve showed an anti-correlated behavior. We argue that this behavior can be explained by the Co-induced impurity-scattering effect. Numerical calculations using the T-matrix method have shown that, in a superconductor with $S^{\pm}$ pairing symmetry, the fully opened gap of a clean state will be filled up by impurity states. Therefore a finite DOS at $E_F$ may rise up (forming the so-called gapless state) if the scattering strength becomes stronger. In the unitary limit, the residual SH coefficient $\gamma_0$ may be expressed by the impurity concentration $n_{imp}$ and the superconducting gap $\Delta_\alpha$ in a simple form $\gamma_0 \propto (n_{imp}/\Delta_\alpha)^\alpha$, with $\alpha > 0$. The index $\alpha$ approximates 0.5 for a d-wave superconductor.

In the underdoped region, assuming a proportionality between $n_{imp}$ and the number of Co-dopant, since the magnitude of $\Delta_s$ increases with $x$ more rapidly (see discussion later on Fig. 4(d)) than a linear increase of $n_{imp}$, therefore $\gamma_0$ was reduced with the increase of doping, one thus qualitatively understands that $\gamma_0$ anti-correlates with $\Delta_s \propto T_c$. Actually the realistic case is more complicated: the superconductivity and AF states compete with each other in the underdoped region, and there will be less and less contributions of DOS given by the AF state in the $T = 0$ K approach with adding more Co-dopants into the system. These two factors lead to the dropping-down behavior of $\gamma_0$ versus $x$. In the overdoped region, the AF order was suppressed completely. However, as we have addressed, the Co-
doping will deteriorate the spin-fluctuations and weaken the pairing strength, resulting in the decrease of $\Delta_s$. Meanwhile $n_{imp}(\propto x)$ keeps rising. These two factors lead to the quick increase of $\gamma_0$ with doping in the overdoped region. In Fig.4(b) we also showed $-\gamma_0$ together with $T_c$. Surprisingly one can see a quite good consistency between the doping dependence of $-\gamma_0$ and $T_c$. This good consistency is understandable because $\gamma_0$ reflects how many spin-fluctuation-mediated scattering channels, which are responsible for the Cooper pairing, are blocked away by the impurities.

As for the doping dependence of the SH jump $\Delta C/T|_{T_c}$, which were shown in Fig. 4(c), we can explain it based on the variation of $\gamma_0$ with $x$. The BCS theory tells that the height of SH jump is proportional to the effective normal state SH coefficient $\gamma_{eff}$:

$$\frac{\Delta C}{T}|_{T_c} \propto \gamma_{eff} \propto (\gamma^{bare}_{m} - \gamma_0)^{\beta}. \quad (1)$$

Here $\gamma^{bare}_{m}$ is the bare value of SH coefficient in the normal state (weakly dependent on doping[35]) if the impurity scattering and the competition of the AF state would not exist, and $\beta \geq 1$. The impurity-scattering may modify the DOS spectrum $\rho(\omega)$ in the $\omega \sim \Delta$ approach and suppress the height of the SH jump $\Delta C/T|_{T_c}$, giving a value of $\beta$ larger than 1. From equation (2), we can expect a roughly consistent tendency between $\Delta C/T|_{T_c}$ and $-\gamma_0$. Recalling the fact that $T_c$ correlates linearly with $-\gamma_0$, one can easily see the reason for the similar evolvement tendency between $T_c$ and $\Delta C/T|_{T_c}$ with $x$, as shown in Fig. 4(c).

In above discussion, we have shown that the parameters $-\gamma_0$, $\Delta C/T|_{T_c}$ and $T_c$ share a similar doping dependence. The key player here is actually $\Delta_s$ which is estimated in the following. In Fig. 4(d), we show the doping dependence of the square root of the upper critical field $H_{c2}^\parallel$ along with $T_c$, where $H_{c2}^\parallel$ was determined using the Werthamer-Helfand-Hohenberg relation[36] from the field dependent resistivity data (not shown here). One can see that both set of data overlap quite well. This is understandable because the Ginzburg-Landau theory has given the relation

$$H_{c2}^\parallel = \frac{\Phi_0}{2\pi \xi_{c,ab}} \propto \Delta_s^2, \quad (2)$$

where $\Phi_0$ is the flux quantum and $\xi_c (\xi_{ab})$ is the coherence length in the direction of $c$ axis (ab plane). As a result, $\sqrt{H_{c2}^\parallel}$ is proportional to $\Delta_s \propto T_c$. 

In summary, we studied the low-temperature SH and resistivity on Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals in wide doping region. A sizeable residual SH coefficient $\gamma_0$ in the low-T limit and clear SH jumps were detected in all samples. It is found that $-\gamma_0$, $\Delta C/T|_{T_c}$, $\sqrt{H_{c2}^\parallel}$, and $T_c$ all share a similar evolution with doping amount $x$. All these behaviors were interpreted within the model of $S^\parallel$ pairing symmetry considering the Co-doping induced scattering effect in this system.

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