# Evidence for line nodes in the energy gap of the overdoped $Ba(Fe_{1-x}Co_x)_2As_2$ from low-temperature specific heat measurements

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Low-temperature specific heat (SH) is measured on $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals in a wide doping region under different magnetic fields. For the overdoped sample, we find the clear evidence for the presence of the $T^2$ term in the SH data, which is absent both for the underdoped and optimal doped samples, suggesting the presence of line nodes in the energy gap of the overdoped samples. Moreover, the field-induced electronic specific heat coefficient $\Delta\gamma(H)$ increases more quickly with the field for the overdoped sample than the underdoped and optimal doped ones, giving more support to our arguments. Our results suggest that the superconducting gap(s) in the present system may have different structures strongly depending on the doping regions.

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## I. INTRODUCTION

Plenty of efforts have been made on the study of the iron-pnictide superconductors, since the discovery of superconductivity with $T_c = 26$ K in $LaFeAsO_{1-x}F_x$.[1] An important issue concerning this new family of high-$T_c$ superconductors is about the gap structure, which should provide clues to the understanding of the microscopic pairing mechanism.[2] Presently, consensuses have been reached on several systems, e.g., LaFePO, $KFe_2As_2$, $BaFe_2(As_{1-x}P_x)_2$, and so on, whereby nodes exist on the gap structure.[3–9] However, experimental results gave rather contradicting conclusions on this issue in other systems of the iron-pnictide superconductors.[10–20] One problem here may come from the different qualities of the samples studied by different groups. Recently, annealing of the single crystals in the 122 phase was reported to be an effective route to improve the quality of the samples.[21–24] Especially, it was found that annealing can considerably decrease the residual specific heat (SH) coefficient $\gamma_0$ in the superconducting state and suppress the Schottky anomaly in low temperature, which may suggest that fewer impurities exist in the annealed samples.[24] This supplies a better platform both for investigating the intrinsic properties of the samples and for analyzing the SH data. Moreover, some groups also point out that the gap structure shows a strong evolution with the doping concentration.[18,19,24]

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. The variation of electronic SH versus temperature and magnetic field can differ in the superconducting materials with different gap structures. From textbook knowledge we know that the low-temperature electronic SH $C_{el}$ for a superconductor with an isotropic gap should have an exponential temperature dependence, namely $C_{el} \propto e^{-\Delta_0/k_BT}$, where $\Delta_0$ is the magnitude of the energy gap. However, for a superconductor with nodal gap(s), a power-law dependence of temperature for $C_{el}$ has been predicted theoretically: $C_{el} \propto T^2$ for the gap with line nodes and $C_{el} \propto T^3$ for point nodes.[25,26] In fact, the quadratic term has been observed in cuprate superconductors, suggesting that line nodes exist in the gap function.[27–29] In the mixed state, the magnetic vortices in superconductors will induce a depairing effect within and outside the vortex cores, leading to the localized and delocalized quasiparticle DOS, respectively. In general, the field-induced electronic SH coefficient will show a rapid increase with the increase of magnetic field in the low field region when the system has the energy gap(s) with a rather small minimum value.[30–33]

For the iron-pnictide superconductors, it is rather difficult to get the pure electron contribution from the total SH, since the upper critical field is very high and the normal state cannot be obtained by suppressing the superconductivity using a magnetic field. Nevertheless, many methods have been used by some groups to subtract the phonon contribution from the SH data, which, however, always inevitably brings about uncertainties.[17,34,35] In this paper, we report the clear evidence of the presence of the $T^2$ term in electronic SH of the overdoped $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals from the raw data, which is consistent with the prediction of superconductors with line nodes. Moreover, the field-induced electronic SH coefficient $\Delta\gamma(H)$ increases very quickly with magnetic field for the overdoped sample, suggesting a rather small minimum value of the energy gap. This further confirms the conclusion that we stated above. These behaviors give a sharp comparison with that observed in the underdoped and optimal doped samples, where a rather small anisotropy is implied in the gap structure.

## II. EXPERIMENTAL DETAILS AND SAMPLE CHARACTERIZATION

The $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals were grown by the self-flux method.[36] The as-grown samples were annealed under high vacuum at 800 °C for 20 days. The samples for the SH measurement have typical dimensions of $2.5 \times 1.5 \times 0.2$ mm$^3$. The dc magnetization measurements were done with a superconducting quantum interference device (Quantum Design, MPMS7). The specific heat were measured with a Helium-3 system based on the Quantum Design instrument physical property measurement system (PPMS). We employed the thermal relaxation technique to perform the specific heat measurements. The thermometer was calibrated under different magnetic fields beforehand. The external magnetic field is applied perpendicular to the $c$ axis of the single crystals.

 

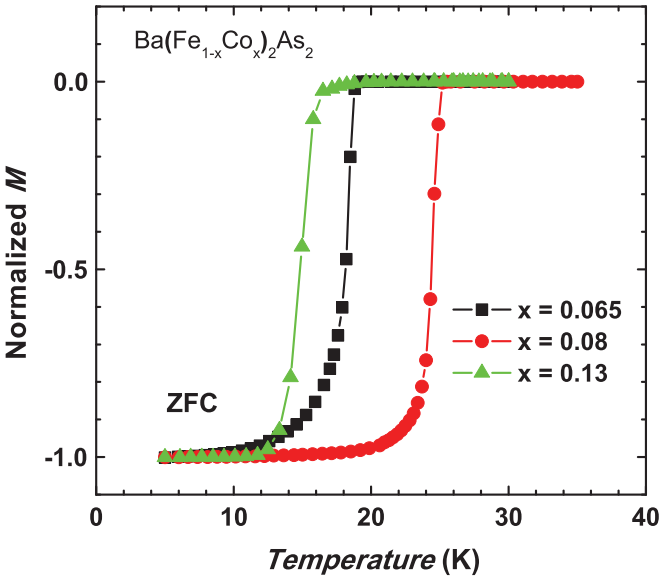


FIG. 1. (Color online) Temperature dependence of dc magnetization for three $Ba(Fe_{1-x}Co_x)_2As_2$ samples with $x = 0.065$, 0.08, and 0.13, which are determined to be in the underdoped, optimal doped, and overdoped regions, respectively. The data are collected with field $H = 10$ Oe using the zero field cooling process. The curves are normalized by the magnetization data obtained at 5 K.

The superconducting transitions of the single crystals are checked by the dc magnetization measurements. In Fig. 1, we show the temperature dependence of the dc magnetization data for $Ba(Fe_{1-x}Co_x)_2As_2$ samples with nominal doping contents $x = 0.065$, 0.08, and 0.13. The data were collected under a dc field of 10 Oe, which were normalized by the values obtained at 5 K. The sample with $x = 0.08$ is found to be optimally doped with the highest onset transition temperature $T_c^{\text{onset}} \approx 25.2$ K, which is about 1 K higher than that of the as-grown sample. Accordingly, the samples with $x = 0.065$ and 0.13 are in the underdoped and overdoped regions, respectively.

## III. RESULTS AND DISCUSSION

The raw data of SH for the three samples with $x = 0.065$, 0.08, and 0.13 under different fields are plotted as $C/T$ versus $T^2$ in Fig. 2. Here we focus on the behaviors of our data in the low-temperature region below 4.5 K. One can see clear different behaviors among the three samples. For the underdoped and optimal doped samples, the curves display clear linear tendency in this low temperature region, which can actually be described by

$$C(T,H) = \gamma(H)T + \beta T^3, \tag{1}$$

where $\gamma(H)$ is the electronic SH coefficient under a magnetic field of $H$ and $\beta$ is the phonon SH coefficient. We show three typical fitting curves based on Eq. (1) in Figs. 2(a) and 2(b). From the fitting process, the residual SH coefficient under zero field $\gamma_0$ $[\equiv\gamma(0)]$ is determined to be 1.7 and 1.5 mJ/mol $K^2$ for the two samples, respectively. A slight deviation from the linear behavior under high magnetic fields in low temperatures may come from the influence of the Schottky anomaly of the sample platform. We note that the linear behavior is rather

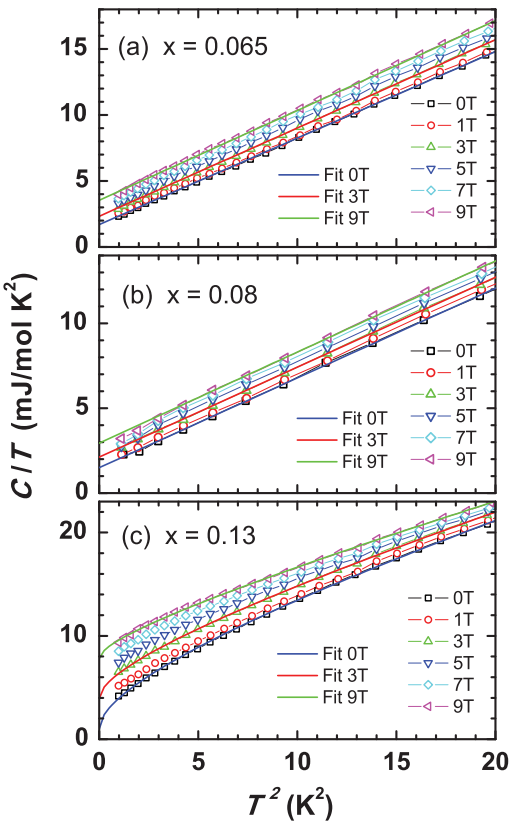


FIG. 2. (Color online) The raw data of the SH for three $Ba(Fe_{1-x}Co_x)_2As_2$ samples with $x = 0.065$ (a), $x = 0.08$ (b), and $x = 0.13$ (c) under different fields in the low temperature region. The data are shown in $C/T$ versus $T^2$ plot. We also show three solid lines of the theoretical fitting (see text) in each figure.

similar to the previous report.[37] For the overdoped sample, however, the data show a clear negative curvature rather than a straight line in all the curves up to 9 T, in sharp contrast with the result of the underdoped and optimal doped samples. We argue that this behavior suggests the presence of the $T^2$ term in the electronic SH, which is expected for the superconductors with line nodes in the energy gap.[25,26] Consequently, the data in Fig. 2(c) can be described by

$$C(T,H) = \gamma(H)T + \alpha(H)T^2 + \beta T^3, \tag{2}$$

with $\alpha(H)$ the coefficient of the $T^2$ term under the field $H$. As shown by the solid lines, the fitting result is rather good. We must note that the negative-curvature feature observed here cannot be attributed to the Schottky anomaly. In general, the behavior of the Schottky anomaly in SH should display a very strong evolution with magnetic field and, moreover, a steep peak in the low-temperature region under low fields should be observed, both of which are missing in our experimental data. This gives direct evidence for the presence of line nodes in the energy gap of the overdoped $Ba(Fe_{1-x}Co_x)_2As_2$. From the fitting, we find that the residual term $\gamma_0 \approx 1.0$ mJ/mol $K^2$ for this sample, which is not larger than that of the optimal doped sample. This differs from the results on the as-grown samples.[37] The situation is reasonable since the annealing process can dramatically suppress the number of the impurity scatterers in the sample, as pointed by K. Gofryk *et al.*[24]

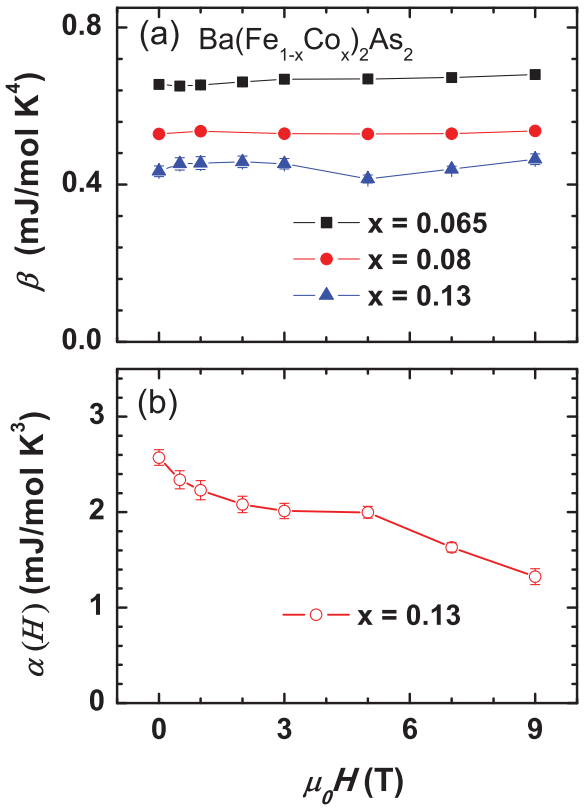


FIG. 3. (Color online) Field dependence of the fitting parameters $\beta$ and $\alpha(H)$ for the three samples. It is clear that $\beta$ is almost independent of the field, while $\alpha(H)$ of the overdoped sample decreases monotonously with the increase of the field.

Accordingly, we know why the $T^2$ term can only be detected in the annealed samples. As shown by the theoretical work, the intraband impurity scattering tends to make the gap(s) more isotropic and may result in the removal of the low-energy excitations.[38,39]

The fitting parameters for the three samples, $\beta$ and $\alpha(H)$, are shown in Figs. 3(a) and 3(b). One can see that the value of $\beta$ is almost independent of field for the three samples, which confirms the reliability of our analysis and fitting process. Moreover, $\alpha(H)$ of the overdoped sample decreases monotonously with the increase of magnetic field up to 9 T. For the superconductors with a singlet $d$-wave gap (e.g., the cuprate superconductors), it has been pointed out theoretically that the $T^2$ term can exist only in moderate-temperature regions ($\sqrt{H/H_{c2}} \ll T/T_c \ll 1$) in the mixed state because of the so-called Volovik effect.[30,31,40] Our observation here may suggest that some segments of the line nodes are not affected by the Volovik effect because the Fermi surface where they reside in is perpendicular to the magnetic field. For the cuprate superconductors, the value of $\alpha(H)$ under zero field was estimated to be $\alpha(0) \sim \gamma_n/T_c$, with $\gamma_n$ the electronic SH coefficient in the normal state.[28] Applying this relation, $\alpha(0)$ is estimated to be about 1 mJ/mol K$^3$. The value obtained from our data is about 2 times larger than this estimation. This may suggest that the simple relation is not suitable for the present multigap system, which needs more investigations from the theoretical side. In addition, we note that the values of $\beta$ decrease with the increase of the doping content $x$. One possible origin of this behavior is that, for the underdoped sample, a part of the $T^3$ term comes from the contribution of the antiferromagnetic state, which coexists with the superconducting state. There is another possibility. As mentioned above, the electronic SH in a superconductor with point nodes can also contribute the $T^3$ term. So the behavior of the data in Fig. 3(a) may be interpreted in terms of the presence of point nodes in the energy gap of the underdoped and optimal doped samples. However, this argument is rather incompatible with the behavior observed in Fig. 4, where the electronic SH coefficient increases very slowly with the magnetic field both for the underdoped and optimal doped samples (see below). One natural argument is that the phonon SH differs slightly among the samples with different doping contents.

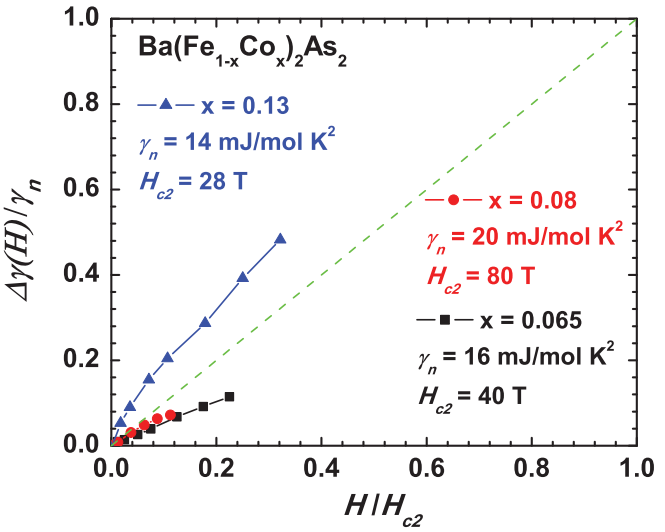


FIG. 4. (Color online) The magnetic field dependence of the low-temperature electronic SH coefficient plotted as $\Delta\gamma(H)/\gamma_n$ versus $H/H_{c2}$. The values of $\gamma_n$ and $H_{c2}$ for the three samples are estimated based on the result of other groups.[24,41,42] The green dashed line is a guide for eyes, which shows the theoretical curve for the samples with an isotropic superconducting gap.

The field dependence of the electronic SH coefficient $\Delta\gamma(H) = \gamma(H) - \gamma(0)$ for the three samples is shown in Fig. 4. The data are plotted as $\Delta\gamma(H)/\gamma_n$ versus $H/H_{c2}$, where $H_{c2}$ is the upper critical field. The values of $\gamma_n$ and $H_{c2}$ are estimated according to the results of other reports[24,41,42] and shown in this figure. We must point out here that the uncertainty of the estimated values of $\gamma_n$ and $H_{c2}$ will not affect the conclusions deduced in the following. In this figure we also display a theoretical curve for a conventional superconductor with an isotropic superconducting gap by the green dashed line. One can see that different behaviors of the three samples in different doping regions are distinct. The data of the optimal doped sample seems rather close to the green line under low magnetic fields and even evolves to be below it when the field increases. The underdoped sample behaves similarly to the optimal doped sample. On the other hand, the data of the overdoped sample increase more quickly and are clearly above the green line. The behavior of the overdoped sample is quite similar to those reported by others, although they have the magnetic field along the $c$ axis of the crystals.[24] We note here that it is not easy to describe the data in Fig. 4 using

a simple formula, because the present system was found to display multiband and even multigap features. Nevertheless, from the present data we can draw the conclusion qualitatively that the energy gap(s) of the overdoped sample has a rather large anisotropy, compared with that of the underdoped and optimal doped samples. Obviously, this argument is consistent with our above-mentioned conclusion that line nodes exist in the energy gap of the overdoped sample.

Our results suggest that the gap structure of the $Ba(Fe_{1-x}Co_x)_2As_2$ system shows a clear evolution with the doping content $x$. Actually, doping dependence of the gap structure has been detected by other experiments, including penetration depth, heat transport, specific heat, point-contact Andreev reflection, and so on.[18,19,24,43] These results share the same tendency with the present work that nodes should exist in the overdoped samples, although there is discrepancy concerning the underdoped and optimal doped regions. The detailed mechanism of this behavior is still vague at this time. Even so, we can unambiguously obtain important implications that the emergence of line nodes in the overdoped sample is related to the evolution of the topology of the Fermi surface and the pairing interaction with the doping of electrons into the system, rather than the intrinsic symmetry of the energy gap.

## IV. CONCLUDING REMARKS

In summary, we studied the low-temperature specific heat on the $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals in a wide doping region. Before measurements, the single crystals were carefully annealed to improve the sample quality. We found a clear evidence for the presence of $T^2$ term from the raw SH data on the overdoped sample, which is absent both for the underdoped and optimal doped samples, suggesting that line nodes must exist in the energy gap of the overdoped sample. On the other hand, the underdoped and optimal doped samples display a rather small anisotropy in the gap structure. Moreover, the field-induced term $\Delta\gamma(H)$ increased more quickly with magnetic field for the overdoped sample than the underdoped and optimal ones, being consistent with the above conclusions. Our results suggest that the superconducting gap(s) in the present system may have different structures depending on the different doping regions. More investigations on this issue on other systems of the iron-pnictide superconductors are needed in the future.

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