Nodal Gap in Fe-Based Layered Superconductor $LaO_{0.9}F_{0.1-\delta}FeAs$ Probed by Specific Heat Measurements *

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We report the specific heat measurements on the newly discovered Fe-based layered $LaO_{0.9}F_{0.1-\delta}FeAs$ superconductor with the onset transition temperature $T_c \approx 28$ K. A nonlinear magnetic field dependence of the electronic specific heat coefficient $\gamma(H)$ has been found in the low temperature limit, which is consistent with the prediction for a nodal superconductor. The maximum gap value $\Delta_0 \approx 3.4 \pm 0.5$ meV is derived by analysing $\gamma(H)$ based on the d-wave model. We also detected the electronic specific heat difference between 9 T and 0 T in a wide temperature range, a specific heat anomaly can be clearly observed near T_c. The Debye temperature of our sample is determined to be about 315.7 K. Our results suggest an unconventional mechanism for this new superconductor.

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In the superconducting state, conduction electrons pair and condense into a low energy state leading to the formation of a gap at the Fermi energy E_F. It is this gap that protects the superconducting condensate. Based on the general space group of the material, and together with the detailed pairing interaction between the two electrons, the superconducting gap should have a specific symmetry for an individual superconductor. This gap symmetry is very important for understanding the underlying mechanism of a superconductor. For example, a $d_{x^2-y^2}$ symmetry has been proven by tremendous experiments for the cuprate superconductors.[1] One effective way to detect the gap symmetry is to generate quasiparticles (QP) from the condensate and then trace out the detailed way for the accumulation of the QP density of states (DOS). Specific heat (SH) is one of the powerful tools to measure the DOS at the Fermi level. Textbook knowledge tells us that the low temperature electronic SH for an s-wave gap should have an exponential temperature dependence, namely $C_e \propto \exp(-T_0/T)$, where T_0 is a characteristic temperature related to the magnitude of the energy gap. For a superconductor with nodal gap symmetry, the DOS is a power law of energy leading to a power law dependence of temperature for the electronic SH:$C_e \propto T^2$ for the gap with line nodes and $C_e \propto T^3$ for point nodes.[2] For example, in cuprate superconductors, there are line nodes in the gap function, this results in[3] an electronic SH $C_e = \alpha T^2$, where $\alpha \propto \gamma_n/T_c$ and γ_n is the specific heat coefficient reflecting the DOS at the Fermi level of the normal state. In the mixed state, the magnetic vortices will induce depairing both within and outside the vortex cores leading to the localized and delocalized QP DOS, respectively. Volovik [4] pointed out that for d-wave superconductors in the mixed state, supercurrents around a vortex core lead to a Doppler shift to the quasi-particle excitation spectrum, which affects strongly the low energy excitation around the nodes. It was shown that the contribution from the delocalized part will prevail over the core part and the SH is predicted to behave as[3,4] $C_{vol} = k\gamma_n T\sqrt{H/H_{c2}}$ with k in the order of unity, H_{c2} the upper critical field. This prediction has been verified by many measurements which were taken as the evidence for d-wave symmetry in cuprate superconductors.[5−12]

In past years, superconductivity at several Kelvins was observed in some quaternary oxypnictides with a general formula as $LnOMPn$ (where $Ln=$ La or Pr; $M =$ Mn, Fe, Co or Ni; $Pn =$ P or As).[13−15] It was found that T_c can be increased by partially substituting the element O with F.[14] Recently, it was reported that the superconducting transition temperature can be increased to 26 K in the material $La[O_{1-x}F_x]FeAs$ ($x = 0.05 \sim 0.12$).[16] This is surprising since the iron elements normally give rise to magnetic moments, and in many cases they form a long-range ferromagnetic order, and are thus detrimental to the superconductivity with singlet pairing. Therefore it is highly desired to know the gap symmetry of this new superconductor. In this Letter, we report the measurements on low-temperature specific heat under different magnetic fields. A nonlinear field dependence of the electronic SH coefficient γ is discovered. Our data together with a detailed analysis indicate that the new superconductor $La[O_{1-x}F_x]FeAs$ may have a nodal gap.

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The polycrystalline samples were synthesized by using a two-step solid state reaction method. First the starting materials Fe powder (purity 99.95%) and As grains (purity 99.99%) were mixed in 1:1 ratio, ground and pressed into a pellet shape. Then it was sealed in an evacuated quartz tube and followed by burning at 700°C for ten hours. Then the resultant pellet was smashed and ground together with the LaF_3 powder (purity 99.95%), La_2O_3 powder (purity 99.9%) and grains of La (purity 99.99%) in stoichiometry as the formula $LaO_{0.9}F_{0.1}FeAs$. Again it was pressed into a pellet and sealed in an evacuated quartz tube and burned at about 940°C for two hours, followed by a burning at 1150°C for 48 h. Then it was cooled down slowly to room temperature. Since a little amount of F may escape during the second step fabrication, in the formula for our sample, we use $(0.1-\delta)$ as the possible concentration of F. X-ray diffraction patterns in this sample show that the dominant component is from $LaO_{0.9}F_{0.1-\delta}FeAs$.

The ac susceptibility were measured based on an Oxford cryogenic system (Maglab-Exa-12). The resistivity and the specific heat was measured on the Quantum Design instrument physical property measurement system (PPMS) with temperature down to 1.8 K. We employed the thermal relaxation technique to perform the specific heat measurements. For the SH measurements, we used a latest improved SH measuring puck 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.

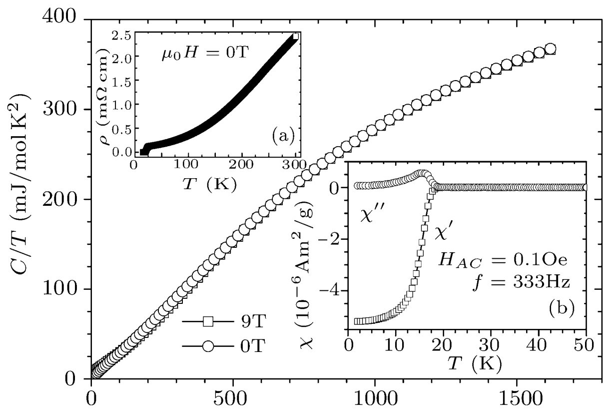

Fig. 1. Raw data of specific heat plotted as C/T vs T^2, shown in the main frame. Insets (a) and (b) show the temperature dependence of the resistivity and the ac susceptibility at zero dc magnetic field, respectively.

In the main frame of Fig. 1 we show the raw data of specific heat plotted as C/T vs T^2 under two different magnetic fields 0 T and 9 T. Very similar to the case in cuprate superconductors, no visible superconducting jump can be seen from the raw data at zero field, indicating a rather small superfluid density or condensation energy in the present system. By extrapolating the data in the superconducting state at zero field down to 0 K, it is surprising to see a rather small residual term $\gamma_0 \approx 0.69\,\mathrm{mJ/mol\,K^2}$, indicating a very small non-superconducting volume or little impurity scattering centres in our present sample (Here one mole means one unit cell or two molecules, i.e., $(LaO_{0.9}F_{0.1-\delta}FeAs)_2$). Inset (a) in Fig. 1 shows the temperature dependence of resistivity at 0 T in a wide temperature range up to 300 K. The onset transition temperature is about 28 K. One can also see that the residual resistivity ratio (RRR) is about 18.5, which is a rather large value for a polycrystalline sample. The residual resistivity at 30 K is only $0.13\,\mathrm{m\Omega\,cm}$, which is several times smaller than the data reported by other groups.[16] All these suggest that our samples are much cleaner with fewer scattering centres or smaller non-superconducting volume. The ac susceptibility data measured at zero dc magnetic field are shown in inset (b) of Fig. 1.

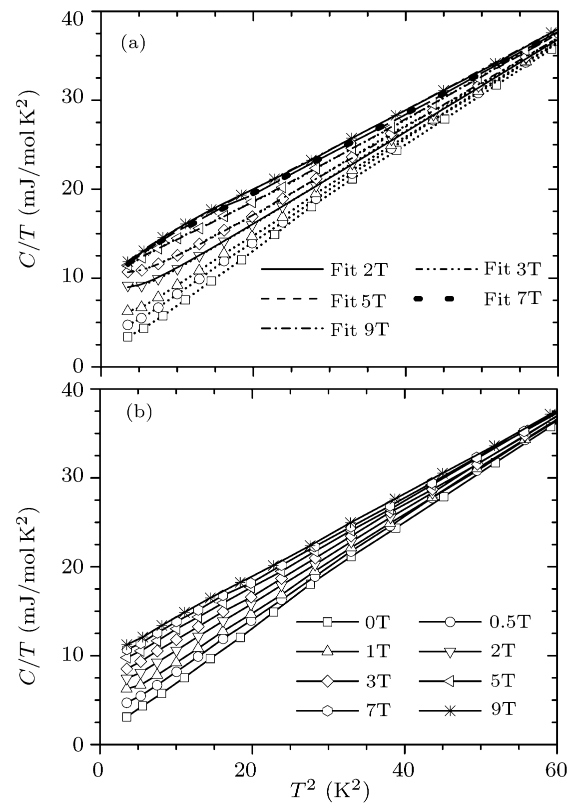

Fig. 2. Temperature and magnetic field dependence of the specific heat in C/T vs T^2 in the low-temperature range. (a) Raw data before removing the Schottky anomaly. We can see that the Schottky anomaly becomes visible when the field is higher than 2 T. The solid, dashed, dot-dashed, dot-dot-dashed and dotted lines represent the theoretical fit (see text) containing all terms in Eq. (1). (b) Replot of the data after the Schottky anomaly is subtracted. The short dotted lines in (a) and solid lines in (b) are guiding to the eyes.

The raw data of the specific heat in various magnetic fields at $T < 7.7\,\mathrm{K}$ are shown in Fig. 2(a). One can see that the Schottky anomaly is visible when $\mu_0 H \geq 2\,\mathrm{T}$, while it is negligible at lower fields because the SH peak due to the Schottky anomaly still locates in the lower temperature region (e.g. lower than 1.8 K) when the field is low. Thus we just need to consider the correction from the Schottky anomaly at high fields when fitting the data to separate the electronic contribution from other contributions. As we all know, the total specific heat of a superconductor can be expressed as

$$C(T,H) = [\gamma_0 + \gamma(H)]T + \beta T^3 + C_{Sch}(T,H), \quad (1)$$

where the four terms represent the residual electronic specific heat, the electronic contribution, the phonon contribution and the magnetic impurity contribution (the so-called Schottky anomaly), respectively. The two-level Schottky anomaly is given by $nx^2e^x/(1+e^x)^2$ ($x = g\mu_B H/k_B T$) at nonzero fields, where μ_B is the Bohr magneton and n is the concentration of paramagnetic centres. As revealed by the thick solid lines in Fig. 2(a), the data under the fields $\mu_0 H \geq 2\,\mathrm{T}$ can be fitted very well by Eq. (1). For the data of lower fields, we just simply extrapolated them down to 0 K linearly and consequently the electronic contribution and the phonon contribution were separated.

Table 1. Fitting parameters by Eq. (1).

$\mu_0 H$ (T)	$\gamma(H)$ (mJ/mol K^2)	β (mJ/mol K^4)	n (mJ/mol K)	g
0.0	0.000	0.586	-	-
0.5	1.684	0.584	-	-
1.0	2.914	0.560	-	-
2.0	4.810	0.522	9.58	2.01
3.0	6.026	0.504	9.70	1.85
5.0	7.326	0.486	10.50	2.18
7.0	8.310	0.470	11.68	2.07
9.0	8.910	0.466	10.84	1.79

From the treatment of the data as described above, we obtain the fitting parameters for different fields, as shown in Table 1. Here we take the average value $\beta \sim 0.49\,\mathrm{mJ/(mol\,K^4)}$. The residual term γ_0 is determined to be $0.69\,\mathrm{mJ/(mol\,K^2)}$, which is an extremely small value compared with that in other systems. The small contribution from Schottky anomaly and residual term make our data analysis more easy and reliable. Using the obtained value of β and the relation $\Theta_D = (12\pi^4 k_B N_A Z/5\beta)^{1/3}$, where $N_A = 6.02 \times 10^{23}\,\mathrm{mol^{-1}}$ is the Avogadro constant, $Z = 8$ is the number of atoms in one unit cell, we obtain the Debye temperature $\Theta_D = 315.7\,\mathrm{K}$ for the present sample. Suppose that it is in the weak electron–phonon coupling regime, we then use the McMillan equation to evaluate the electron–phonon coupling strength λ_{e-ph} via.[17]

$$T_c = \frac{\Theta_D}{1.45}\exp\Big[-\frac{1.04(1+\lambda_{e-ph})}{\lambda_{e-ph} - \mu^*(1+0.62\lambda_{e-ph})}\Big], \quad (2)$$

where μ^* is the Coulomb pseudopotential taking about 0.10. Using $\Theta_D = 315.7\,\mathrm{K}$ and $T_c = 26\,\mathrm{K}$, we obtain a very large value for the electron–phonon coupling: $\lambda_{e-ph} = 1.2$. This may suggest that a simple model based on electron–phonon coupling and the McMillan equation cannot interpret the high transition temperature in the present system.

In the following we investigate the magnetic-field-induced change of the SH coefficient $\gamma(H)$. After removing the Schottky anomaly for each field, we are left with only the first three terms in Eq. (1). The results are shown in Fig. 2(b). It is clear that the low temperature part is quite straight for all fields, this allows to determine the zero temperature value of $\gamma(H)$ at different fields. As shown in Fig. 3, $\gamma(H)$ increases nonlinearly as the magnetic field increases from 0 T to 9 T. In fact, the nonlinear behaviour can be roughly described by a simple equation $\gamma(H) = \mathrm{A}\sqrt{H}$ as shown by the solid line, which is actually the theoretical prediction for superconductors with line nodes in the gap function.[4] This suggests that in the 10% F-doped LaOFeAs sample the gap clearly has a nodal structure.

Although our data shows a relation being close to the d-wave prediction $\gamma(H) \propto \sqrt{H}$, it is by no means to say that the gap in the present sample is definitely of d-wave type, since other type of pairing symmetry with nodes can also give rise to a nonlinear $\gamma(H)$. While we can nevertheless use the d-wave model to derive some important parameters. For example, we can obtain the maximum gap value by investigating the field-induced term $\gamma(H)$ quantitatively, as we have performed successfully in LaSrCuO single crystals.[11,18] The term $\gamma(H)$, which mainly arises from the Doppler shift of the quasi-particle excitation spectrum near the nodes induced by the supercurrent flowing around vortices, has a direct relation to the slope of the gap at the node, $v_\Delta = 2\Delta_0/\hbar k_F$ with Δ_0 the d-wave maximum gap in the gap function $\Delta = \Delta_0\cos(2\phi)$, k_F the Fermi vector (taking $k_F \approx \pi/a \sim 0.78\,\text{Å}^{-1}$, where $a = 4.03\,\text{Å}$ is the in-plane lattice constant). We have known that the relation between v_Δ and the prefactor A is given by

$$A = \frac{4k_B^2}{3\hbar}\sqrt{\frac{\pi}{\Phi_0}}\frac{nV_{mol}}{d}\frac{a_L}{v_\Delta}, \quad (3)$$

where Φ_0 is the flux quantum, n is the number of conduction planes per unit cell, d is the c-axis lattice constant, V_{mol} is the volume per mole, and $a_L = 0.465$ for a triangular vortex lattice.[19,20] The value of the prefactor A, which is about $3.2\,\mathrm{mJ/(mol\,K^2\,T^{0.5})}$, has been obtained from fitting the data in Fig. 3. Thus we can extract gap value $\Delta_0 \approx 3.4 \pm 0.5$ meV using the known parameters for our sample. It is a reasonable value with the ratio $2\Delta_0/k_BT_c \approx 4.0$, if we take $T_c = 20$ K. This ratio is quite close to the prediction ($2\Delta_0/k_BT_c = 4.28$) for the weak coupling d-wave superconductors.

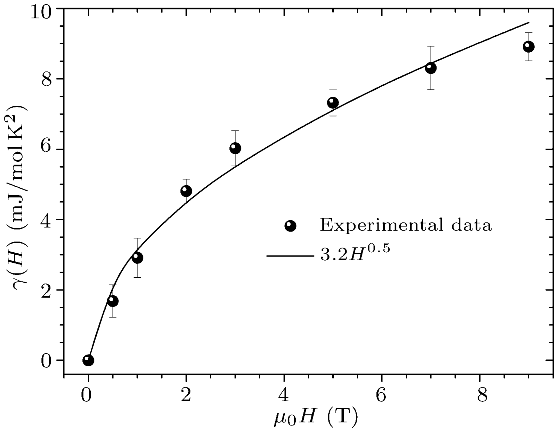

Fig. 3. Field dependence of the field-induced term $\gamma(H)$ at $T = 0$ K (symbols). The solid line is the fit to $\gamma(H) = A\sqrt{H}$.

The nonlinear $\gamma(H)$ found here cannot be simply attributed to the multigap effect as observed in MgB_2[21] and $2H$-$NbSe_2$[22] in which the $\gamma(H)$ is nonlinear. The reason is that, even if there are multigaps in these two systems, the zero-field SH data $\gamma(T)$ shows a clear flattening in low-temperature range corresponding to the weak excitation of QPs for an s-wave superconductor. This is completely absent in the present system, as shown in Fig. 2. One may further ascribe the nonlinearity found for $LaO_{1-x}F_xFeAs$ to the granular feature of the sample: the grains are randomly aligned within the bulk sample, when a field is applied, the creating rates of DOS by a magnetic field are different among the grains with different orientations. In this case, a non-linear $\gamma(H)$ may be observed, especially in a system with high anisotropy. This possibility cannot be ruled out, but it is difficult to understand why the relation $\gamma(H) \propto \sqrt{H}$ is roughly satisfied here.

In Fig. 4 we present the temperature dependence of $\gamma(0\text{T})-\gamma(9\text{T})$, one can see that a shallow SH anomaly starts at about 25 K and ramps up slowly with decreasing temperature, and shows a peak at about 15 K, which is just the middle resistive transition point at 9 T (see the inset in Fig. 4). This broadened anomaly may be induced by both the broad transition at zero field (the superconducting phase is still not perfectly uniform) and the very low superfluid density leading to a strong phase fluctuation. Future experiments on improved samples will fix these problems. Although a magnetic field of 9 T is still difficult to suppress the superconductivity completely, it is clear that the difference between 9 T and 0 T does not show a flattening down to about 2.8 K. This is not expected by an s-wave BCS superconductor with T_c beyond 20 K. This fact may also corroborate our conclusion derived from the nonlinear behaviour of $\gamma(H)$ at zero K that there are nodes on the gap function.

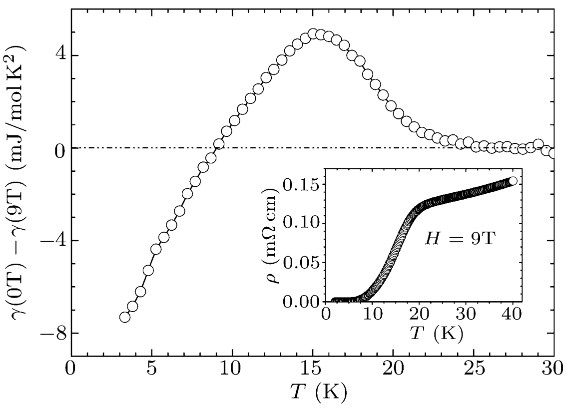

Fig. 4. Temperature dependence of $\gamma(0\text{T}) - \gamma(9\text{T})$ up to 30 K, shown in the main frame. One can see a clear specific heat anomaly near T_c. The inset shows the temperature dependence of resistivity at 9 T from 2 K to 40 K.

In summary, the low temperature specific heat measurements reveal that the new superconductor $LaO_{1-x}F_xFeAs$ has a rather low superfluid density and condensation energy. The field induced extra DOS $\gamma(H)$ follows a nonlinear behaviour which is roughly proportional to $\sqrt{H}$. This may suggest that $LaO_{1-x}F_xFeAs$ superconductors have a nodal gap and are probably unconventional superconductors.

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