Superconducting Gap Structure of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ Probed by Thermal Conductivity Tensor

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The thermal conductivity of organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($T_c=10.4$ K) has been studied in a magnetic field rotating within the 2D superconducting planes with high alignment precision. At low temperatures ($T \lesssim 0.5$ K), a clear fourfold symmetry in the angular variation, which is characteristic of a $d$-wave superconducting gap with nodes along the directions rotated 45° relative to the $b$ and $c$ axes of the crystal, was resolved. The determined nodal structure is inconsistent with recent theoretical predictions of superconductivity induced by the antiferromagnetic spin fluctuation.

Since the discovery of superconductivity in organic materials about 2 decades ago, the question of the pairing symmetry among this class of materials is one of the most intriguing problems. In particular, the nature of the superconductivity in quasi-2D $\kappa$-(BEDT-TTF)$_2$X salts ($\kappa$-(ET)$_2$X), where the ion X can, for example, be Cu(SCN)$_2$, Cu[N(CN)$_2$]Br or I$_3$, has attracted considerable attention. In these layered organics, Shubnikov-de Haas oscillation experiments have established the existence of a well-defined Fermi surface (FS), demonstrating the Fermi liquid character of the low energy excitation. The large enhancement of the effective mass revealed by the specific heat as well as magnetic susceptibility measurements suggests the strong electron correlation effect in the normal state. Moreover, it was suggested that superconductivity occurs in proximity to the antiferromagnetic (AF) ordered state in the phase diagram [1]. Since some of these unusual properties suggest analogies with the magnetic (AF) ordered state in the phase diagram [1]. Since these measurements rely on the $T$-dependence of the physical quantities, it is more desirable to measure the in-plane anisotropy of the gap directly in order to probe the gap structure. Very recently, such an attempt was made by STM [8] and mm-wave transmission [9] experiments. Although both measurements reported the strong modulation of the gap structure, they led to completely different conclusions on the node directions; the former predicts nodes along the directions rotated 45° relative to the $b$ and $c$ axes while the latter predicts nodes along the $b$ and $c$ directions. In interpreting these experiments, one needs to bear in mind that the STM spectrum parallel to the 2D plane can be strongly affected by the atomic state at the edge. Moreover, an alternative interpretation was proposed for the mm-wave transmission experiments [10]. Thus, the gap structure of $\kappa$-(ET)$_2$X salts is far from settled and the situation strongly confronts us with the need for a powerful directional probe of the superconducting gap.

During the past few years, the understanding of the heat transport in the mixed state of superconductors with anisotropic gap has largely progressed [11]. In particular, it was demonstrated both experimentally and theoretically that the thermal conductivity is a powerful tool for probing the anisotropic gap structure [12,13]. Thermal conductivity has some advantages, compared to other experiments. First, it is an unique transport quantity which does not vanish in the superconducting state, responding to the unpaired quasiparticles (QPs). Second, it is a probe of the bulk free from the surface effect. Third and most importantly, it is indeed a directional probe, sensitive to the relative orientation among the thermal flow, the magnetic field, and nodal directions of the order parameter, as we will discuss in detail later. In fact, a clear fourfold modulation of the in-plane thermal conductivity with an in-plane magnetic field which reflects the angular position of nodes of $d_{x^2-y^2}$ symmetry was observed in...
YBa$_2$Cu$_3$O$_{7-\delta}$ and 2D heavy fermion superconductor CeCoIn$_5$, while such a modulation was absent in Nb and the B-phase of UPt$_3$ with an isotropic gap in the basal plane. These fact demonstrate that the thermal conductivity tensor can be a relevant probe of the superconducting gap structure. In this Letter, we have measured the thermal conductivity tensor of $\kappa$-(ET)$_2$Cu(NCS)$_2$ in magnetic field rotating within the 2D superconducting planes. The superconducting gap structure was successfully determined by the angular variation of $\kappa$. On the basis of these findings, we discuss the nature of the superconductivity of $\kappa$-(ET)$_2$Cu(NCS)$_2$.

Single crystals $\kappa$-(ET)$_2$Cu(NCS)$_2$ were grown by conventional electrochemical method and their approximate sizes are 2x1x0.1mm$^3$. The thermal conductivity was measured by the steady-stated method with one heater and two RuO$_2$ thermometers. The heat current $q$ was applied along the $b$-direction. The upper inset of Fig. 1 shows the FS. In the present measurements, it is very important to rotate $H$ within the 2D $bc$-planes with very high accuracy because a slight field-misalignment produces 2D pancake vortices which might act as a strong scattering center of the thermal current. Special care was therefore taken to keep the perpendicular field due to the misalignment less than $H_{c1}$ perpendicular to the layers, so that the condition for the absence of pancake vortices (lock-in state) was always fulfilled while rotating $H$.

For this purpose, we used a system with two superconducting magnets generating $H$ in two mutually orthogonal directions and a $^3$He cryostat equipped on a mechanical rotating stage with a minimum step of 1/500 degree at the top of the Dewar. Computer-controlling two magnets and the rotating stage, we were able to rotate $H$ continuously within the 2D planes with a misalignment of less than 0.01 degree from the plane, which we confirmed by the simultaneous measurement of the resistivity.

We first discuss the $T$- and $H$- dependence of $\kappa$. The observed $T$- and $H$- dependence were very similar to the results of Ref. 6. Figure 1 depicts the $T$-dependence of $\kappa$. Upon entering the superconducting state, $\kappa$ exhibits a kink and rises to the maximum value just below $T_c$. As discussed in detail in Ref. 6, the enhancement of $\kappa$ below $T_c$ reflects the increase of the phonon mean free path by the electron condensation, which is so because the phonon thermal conductivity $\kappa_{ph}$ well dominates over the electronic thermal conductivity $\kappa_{el}$ near $T_c$.

Figures 2 (a) and (b) depict the $H$-dependence of $\kappa$ in perpendicular ($H \perp bc$-plane) and parallel ($H \parallel bc$-plane) field, respectively. In perpendicular field, $\kappa(H)$ shows a monotonic decrease up to $H_{c2}$ above 1.6 K, which can be attributed to the suppression of the phonon mean free path by the introduction of the vortices. Below 1.6 K, $\kappa(H)$ exhibits a dip below $H_{c2}$. The minimum of $\kappa(H)$ appears

FIG. 1. $T$-dependence of the thermal conductivity in zero field. The heat current $q$ was applied along the $b$-direction. Lower inset: The resistive transition at $T_c$. Upper inset: The Fermi surface of $\kappa$-(ET)$_2$Cu(NCS)$_2$ (solid lines). The Fermi surface consists of quasi-1D and 2D hole pocket. The dashed lines show the first Brillouin zone with $k_b$ and $k_c$ axes. The thin solid lines show the extended Brillouin zone with $k_c$ and $k_q$ axes in the similar coordinate style of the high-$T_c$ cuprates. The node directions determined in our experiment are also shown.

FIG. 2. $H$-dependence of the in-plane thermal conductivity (a) in perpendicular and (b) in parallel field ($H \parallel c$) at low temperatures. Deviation from the horizontal line shown by arrows marks $H_{c2}$. Inset: $H$-dependence of $\Delta\kappa_{el}/\kappa(0)$ in parallel field. For details, see the text.
as a result of a competition between $\kappa^{ph}$ which always decreases with $H$ and $\kappa^{el}$ which increases steeply near $H_{c2}$. Then the magnitude of the increase of $\kappa(H)$ below $H_{c2}$ provides a lower limit of the electronic contribution. As seen in Fig. 2(a), the electronic contribution grows rapidly below 0.7 K; $\kappa^{el}/\kappa_n$ is roughly estimated to be $\geq 5\%$ at 0.7 K and $\geq 15\%$ at 0.42 K, where $\kappa^{el}_n$ and $\kappa_n$ are the electronic and total thermal conductivity in the normal state above $H_{c2}$, respectively. This dramatic increase of $\kappa^{el}/\kappa_n$ is caused by $\kappa^{ph}$ which decreases much faster than $\kappa^{el}$ with decreasing $T$. In parallel field with much higher $H_{c2}$ ($\geq 30$ T), $\kappa(H)$ decreases monotonically at all temperatures. While $\kappa(H)/\kappa(0)$ shows a similar $H$-dependence at 0.71 K and 1.1 K, it deviates from this pattern at 0.42 K. Since the electronic contribution grows rapidly below 0.7 K, this deviation can be attributed to $\kappa^{el}$. In the inset of Fig. 2(b), we show $\Delta\kappa^{el}(H)/\kappa(0) = (\kappa^{el}(H) - \kappa^{el}(0))/\kappa(0)$ at 0.4 K, assuming that $\kappa^{el}/\kappa(0)$ has the same $H$-dependence.

We now move on to the angular variation of $\kappa$ as $H$ is rotated within the 2D planes. Figures 3 (a)-(c) display $\kappa(H, \theta)$ as a function of $\theta = \langle q, H \rangle$ at low temperatures, which are measured in rotating $\theta$ after field cooling at $\theta = 0^\circ \ (H \parallel b)$. The consecutive measurement with an inverted rotating direction did not produce any hysteresis in $\kappa(H, \theta)$, which demonstrate that the field trapping related to the pinning of the Josephson vortices is negligibly small. At 0.72 K, $\kappa(H, \theta)$ shows a minimum at $\theta = 90^\circ$. Similar $\theta$-dependence was observed at higher temperatures. On the other hand, the angular variation changes dramatically at lower temperatures, exhibiting a double minimum as shown in Figs. 3(b) and (c). In all data, as shown by the solid lines in Figs. 3 (a)-(c), $\kappa(H, \theta)$ can be decomposed into three terms with different symmetries; $\kappa(\theta) = \kappa_0 + \kappa_{2q} + \kappa_{4q}$ where $\kappa_0$ is a $\theta$-independent term, and $\kappa_{2q} = C_{2q} \cos 2\theta$ and $\kappa_{4q} = C_{4q} \cos 4\theta$ are terms with two and fourfold symmetry with respect to the in-plane rotation, respectively. The term $\kappa_{4q}$, which has a minimum at $H \perp q$, appears as a result of the difference of the scattering rate for QPs and phonons traveling parallel to the vortex and for those moving in the perpendicular direction. Since a large twofold symmetry is observed even above 0.7 K where $\kappa^{ph}$ dominates, $\kappa_{2q}$ is mainly phononic in origin. In what follows, we will address the fourfold symmetry which is directly related to the electronic structure.

Figures 4 (a)-(c) display $\kappa_{4q}$ normalized by $\kappa_n$ after the subtraction of the $\kappa_0$- and $\kappa_{2q}$-terms from the total $\kappa$. At $T=0.72$ K, the fourfold component is extremely small; $|C_{4q}|/\kappa_n < 0.1\%$. On the other hand, a clear fourfold component with $|C_{4q}|/\kappa_n \sim 0.2\%$ is resolved at 0.52 and 0.43 K. Since the contribution of $\kappa^{el}$ grows rapidly below 0.7 K and occupies a substantial portion of the total $\kappa$ at 0.4 K, it is natural to consider that the fourfold oscillation is purely electronic in origin. Although $|C_{4q}|$ at 0.42 K is as small as 0.2% in $\kappa_n$, it occupies approximately 1.5-2% in $\kappa^{el}_n$ and occupies a few % in $\kappa^{el}(0)$ assuming $\kappa^{el}_n/\kappa_n$.

![FIG. 3. (a)-(c)Angular variation of $\kappa(H, \theta)$ in $|\mu_0 H|=2$ T for different temperatures. $\theta = \langle q, H \rangle$. The solid lines represent the results of the fitting by the function $\kappa(H, \theta) = C_0 + C_{2q} \cos 2\theta + C_{4q} \cos 4\theta$, where $C_0$, $C_{2q}$ and $C_{4q}$ are constants.](image)

![FIG. 4. (a)-(c) The fourfold symmetry $\kappa_{4q}$ obtained from Figs. 3 (a)-(c). The solid lines represent $C_{4q} \cos 4\theta$. For details, see the text.](image)
We note that this value is one order of magnitude larger than that in Sr$_2$RuO$_4$ with an isotropic gap in the plane \[ \text{[7]} \]. We now address the origin for the fourfold symmetry. The most important issue here is "Is the observed fourfold symmetry in $\kappa^el$ a consequence of the line nodes perpendicular to the layer?". We will show that the band structure inherent to the crystal is very unlikely to be an origin of the fourfold symmetry. First of all, it can be shown by the group theoretical consideration that the anisotropic term in $\kappa^el$ due to a fourfold distortion of the FS is of second order relative to the leading terms, since the thermal conductivity $\kappa_{xx}$ is a second rank tensor \[ \text{[24]} \]. In addition, the crystal structure of $\kappa$-(ET)$_2$Cu(NCS)$_2$ is monoclinic and FS is nearly elliptic; the fourfold distortion of the FS should be very small if it exists. Second, the in-plane magnetoconductivity $\Delta\sigma(H) = \sigma(H) - \sigma(H = 0)$ above $T_c$ is undetectably small even at 5 T due to the very strong two dimensionality. In fact, the upper limit of $\Delta\sigma/\sigma(0)$ roughly estimated from the warp of the FS perpendicular to the plane is less than $10^{-5}$ at 2 T. Thus, as far as the Wiedemann-Franz law holds, the fourfold oscillation of $\kappa_{xx}$ arising from the magnetoconductance should be undetectably small. These considerations lead us to conclude that the observed fourfold symmetry originates from the superconducting gap nodes \[ \text{[22]} \].

In the thermal transport in the superconductors with nodes, the dominant effect in a magnetic field is the Doppler shift of the delocalized QP energy spectrum, which occurs due to the presence of a superfluid flow around each vortex, and generates a nonzero QP density of states (DOS) at the Fermi level (Volovik effect) \[ \text{[23]} \]. While the Doppler shift increases $\kappa^el$ with $H$ through the enhancement of the DOS, it can also lead to a decrease of $\kappa^el$ through the suppression of impurity scattering time and Andreev scattering time off the vortices. At high temperatures, the latter effect is predominant, but eventually gives way to the former at low temperatures, as demonstrated in high-$T_c$ cuprates \[ \text{[24]} \]. Since $\kappa^el$ increases with $H$ as shown in the inset of Fig. 2(b), the enhancement of the DOS is the main origin for the $H$-dependence of $\kappa^el$ at 0.42 K \[ \text{[25]} \]. In this case, rotating $H$ within the 2D-plane gives rise to the fourfold oscillation in $\kappa^el$ associated with the DOS oscillation \[ \text{[16]} \].\[ \text{[16]} \]. This effect arises because the DOS depends sensitively on the angle between $H$ and the direction of the nodes of the order parameter, because the QPs contribute to the DOS when their Doppler-shifted energies exceed the local energy gap. The DOS oscillation with fourfold symmetry gives rise to $\kappa^el$ which attains its maximum value when $H$ is directed to the antinodal directions and turns minimum when $H$ is directed along the nodal directions (see Fig. 2 in Ref. \[ \text{[16]} \]). According to Ref. \[ \text{[16]} \], the amplitude of the fourfold symmetry in the $d$-wave superconductors arising from the DOS oscillation is roughly estimated as $|C_{4\theta}|/|\kappa^el(0)| = 0.082 \frac{\nu_F^4/\rho_H}{\pi \mu_B H} \ln(\sqrt{32\Delta/\pi m})$. Here $\Delta$ is the superconducting gap, $\Gamma$ is the QP relaxation rate, $\nu_F$ and $\nu_F'$ are the in-plane and out-of-plane Fermi velocity, respectively. Using $\Gamma \sim 2 \times 10^{11} \text{s}^{-1}$, $2\Delta/k_BT_c = 3.54$, $\nu_F \sim 5 \times 10^4 \text{m/s}$, and $\nu_F' \sim 2.5 \times 10^5 \text{m/s}$, gives $|C_{4\theta}|/|\kappa^el(0)| \sim 3\%$. Thus the DOS oscillation by Volovik effect yields $|C_{4\theta}|/|\kappa^el(0)|$ which is in the same order to the data.

The fourfold symmetry enables us to specify the node directions, which is crucial for understanding the pairing interaction. $\kappa_{10}$ exhibits a maximum when $H$ is applied parallel to the $b$ and $c$ axes of the crystal, showing the gap nodes along the directions rotated $45^\circ$ relative to the $b$ and $c$-axes; the nodes are situated near the band gap between the 1D and 2D bands (see the upper inset of Fig. 1). This result is consistent with the STM experiments \[ \text{[8]} \]. We emphasize here that the determined nodal structure is inconsistent with the recent theories based on the AF fluctuation. If one assumes an AF fluctuation scenario, it is natural to expect the nodes to be along the $b$ and $c$ directions. This is because the AF ordering vectors become parallel to the $b$-axis, which would provide a partial nesting. If we take the same conventions for the magnetic Brillouin zone as the high-$T_c$ cuprates with $d_{x^2-y^2}$ symmetry (see Fig. 1 (c) in Ref. \[ \text{[3]} \]), the superconducting gap symmetry of $\kappa$-(ET)$_2$Cu(NCS)$_2$ is $d_{xy}$. It is interesting to note that superconductivity with $d_{xy}$ symmetry has been theoretically suggested based on the charge fluctuation scenario \[ \text{[28]} \]. Our present results may bear implications on this issue.

We finally comment on the recent heat capacity measurements which report a fully gaped superconductivity \[ \text{[6]} \]. In our view, their temperature range $(T > T_c/5)$ is not low enough to conclude the exponential behavior of the heat capacity; the measurements at temperatures less than $T_c/10$ would be required.

In summary, the thermal conductivity tensor of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ was studied in a magnetic field rotating within the 2D superconducting planes. The observed fourfold oscillation provides a strong evidence of $d$-wave symmetry. From its sign, the node directions are successfully specified. These results place strong constraints on models that attempt to explain the mechanism of the superconductivity of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$.

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