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

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The thermal conductivity of organic superconductor κ-(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 $\boldsymbol{b}$ and $\boldsymbol{c}$ axes of the crystal, was resolved. The determined nodal structure is inconsistent with recent theoretical predictions of superconductivity induced by the antiferromagnetic spin fluctuation.

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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 κ-(BEDT-TTF)$_2X$ salts [κ-(ET)$_2X$], 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 high-T_c cuprates [2], it was pointed out by many authors that the AF spin fluctuation should play an important role for the occurrence of superconductivity [3,4].

Unconventional superconductivity is characterized by a superconducting (SC) gap with nodes along certain crystal directions. Since the gap structure is intimately related to the pairing interaction, its identification is crucial for understanding the pairing mechanism. Although the structure of the SC order parameter of κ-(ET)$_2X$ salts has been examined by several techniques, it is still controversial [1]. Results strongly in favor of unconventional pairing symmetry came from NMR experiments in which the absence of the Hebel-Slichter peak and cubic T dependence of the spin lattice relaxation rate $1/T_1$ were interpreted as an indication of d-wave pairing with line nodes [1,5]. The existence of the T-linear term in the thermal conductivity κ at low temperatures also supported the presence of line nodes [6]. However, some of the specific heat and penetration depth studies on these materials led to conflicting results. For example, recent specific heat measurements reported a fully gapped superconductivity [7]. Very recently, an attempt to measure the in-plane anisotropy directly 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. 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 κ-(ET)$_2X$ salts is far from settled and the situation strongly confronts us with the need for a powerful directional probe of the SC 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 that the thermal conductivity is a powerful tool for probing the gap structure [12–18]. Thermal conductivity has some advantages, compared to other experiments. First, it is a unique transport quantity which responds to the 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. In fact, a clear fourfold modulation of the in-plane κ 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$_{7-\delta}$ [12,13] and 2D heavy fermion superconductor CeCoIn$_5$ [18], while such a modulation was absent in Nb and the B phase of UPt$_3$ with an isotropic gap in the basal plane [13,19]. These facts demonstrate that the thermal conductivity can be a relevant probe of the SC gap structure. In this Letter, we have measured the thermal conductivity of κ-(ET)$_2$Cu(NCS)$_2$ in magnetic field rotating within the 2D SC planes. The SC gap structure was successfully determined by the angular variation of κ.

Single crystals κ-(ET)$_2$Cu(NCS)$_2$ were grown by a conventional electrochemical method and their approximate sizes are $2 \times 1 \times 0.1$ mm^3. Thermal conductivity was measured by the steady-state method. The heat current $\boldsymbol{q}$ was applied along the $\boldsymbol{b}$ direction. In the present measurements, it is very important to rotate $\boldsymbol{H}$ 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 (lock-in state). For this purpose, we used a system with two superconducting magnets generating $\boldsymbol{H}$ in two mutually orthogonal directions and a ^{3}He cryostat equipped on a mechanical rotating stage. Computer controlling two magnets and the rotating stage, we were able to rotate $\boldsymbol{H}$ continuously within the 2D planes with a misalignment of less than 0.01° from the plane.

We first discuss the T and H dependence of κ. The observed T and H dependence were very similar to the results of Ref. [6]. Figure 1 depicts the T dependence of κ. Upon entering the SC state, κ exhibits a kink and rises to the maximum value just below T_c. As discussed in detail in Ref. [6], the enhancement of κ below T_c reflects the increase of the phonon mean free path by the electron condensation, which is so because the phonon thermal conductivity κ^{ph} well dominates over the electronic thermal conductivity κ^{el} near T_c. Figures 2(a) and 2(b) depict the H dependence of κ in a perpendicular ($\boldsymbol{H} \perp bc$-plane) and parallel ($\boldsymbol{H} \parallel bc$-plane) field, respectively. In a 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 as a result of a competition between κ^{ph} which always decreases with H and κ^{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; $\kappa_n^{\mathrm{el}}/\kappa_n$ is roughly estimated to be $\gtrsim 5\%$ at 0.7 K and $\gtrsim 15\%$ at 0.42 K, where κ_n^{el} and κ_n are the electronic and total thermal conductivity in the normal state above H_{c2}, respectively. This dramatic increase of $\kappa_n^{\mathrm{el}}/\kappa_n$ is caused by κ^{ph} which decreases much faster than κ^{el} with decreasing T. In parallel field with much higher H_{c2} ($\gtrsim 30$ T), $\kappa(H)$ decreases monotonically at all temperatures. While $\kappa(H)/\kappa(0)$ shows a similar H dependence at 0.71 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 κ^{el}. In the inset of Fig. 2(b), we show $\Delta\kappa^{\mathrm{el}}(H)/\kappa(0)$ $[\equiv \frac{\kappa^{\mathrm{el}}(H)-\kappa^{\mathrm{el}}(0)}{\kappa(0)}]$ at 0.4 K, assuming that $\kappa^{\mathrm{ph}}/\kappa(0)$ has the same H dependence.

We now move on to the angular variation of κ as $\boldsymbol{H}$ is rotated within the 2D planes. Figures 3(a)–3(c) display $\kappa(\boldsymbol{H},\theta)$ as a function of $\theta = (\boldsymbol{q},\boldsymbol{H})$ at low temperatures, which are measured in rotating θ after field cooling at $\theta = 0°$ ($\boldsymbol{H} \parallel \boldsymbol{b}$). The consecutive measurement with an inverted rotating direction did not produce any hysteresis in $\kappa(\boldsymbol{H},\theta)$, which demonstrate that the field trapping

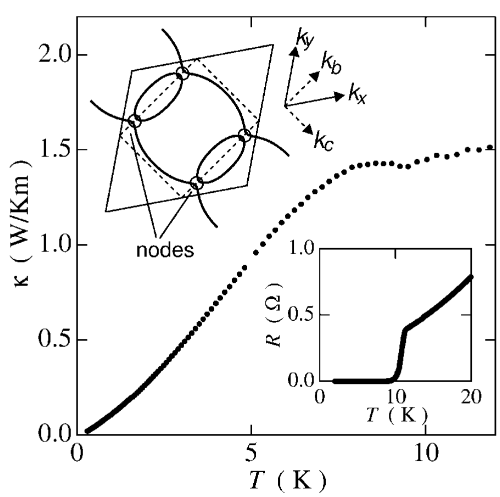

FIG. 1. T dependence of the thermal conductivity in zero field. The heat current $\boldsymbol{q}$ was applied along the $\boldsymbol{b}$ direction. Lower inset: The resistive transition at T_c. Upper inset: The Fermi surface of κ-(ET)$_2$Cu(NCS)$_2$ (solid lines). The dashed lines show the first Brillouin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

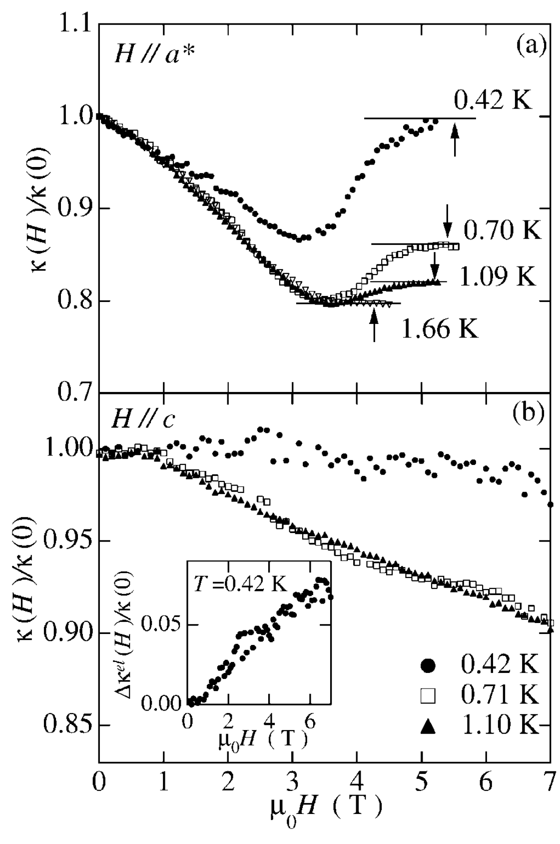

FIG. 2. H dependence of the in-plane κ (a) in perpendicular and (b) in parallel field ($\boldsymbol{H} \parallel c$). Deviation from the horizontal line shown by arrows marks H_{c2}. Inset: H dependence of $\Delta\kappa^{\mathrm{el}}/\kappa(0)$ in parallel field. For details, see the text.

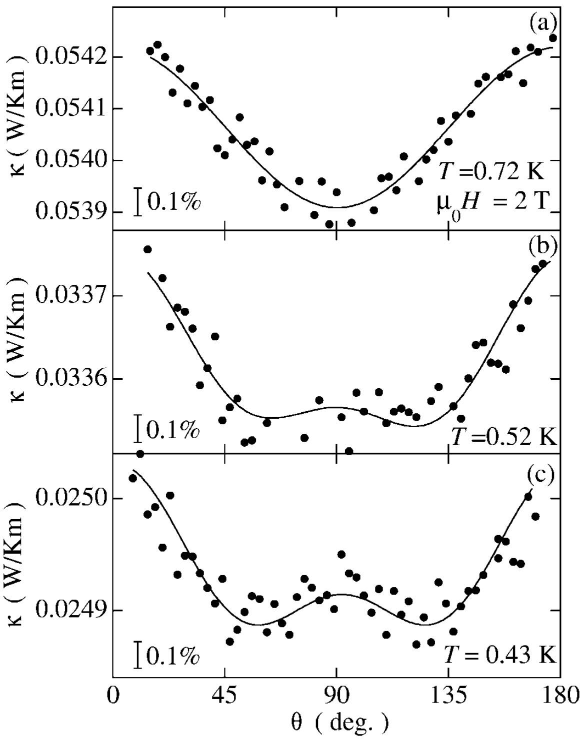

FIG. 3. (a)–(c) Angular variation of $\kappa(\boldsymbol{H},\theta)$ in $|\mu_0\boldsymbol{H}| = 2$ T for different temperatures. $\theta = (\boldsymbol{q},\boldsymbol{H})$. The solid lines represent the results of the fitting by the function $\kappa(H,\theta) = C_0 + C_{2\theta}\cos 2\theta + C_{4\theta}\cos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

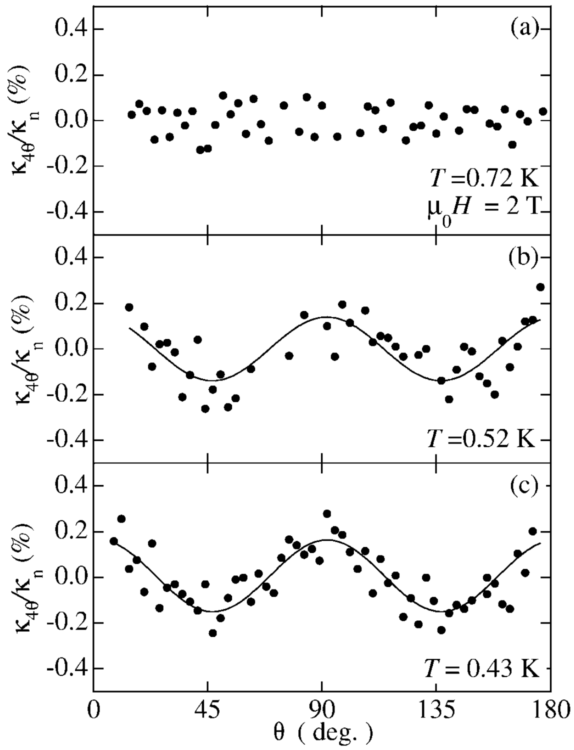

FIG. 4. (a)–(c) The fourfold symmetry $\kappa_{4\theta}$ obtained from Figs. 3(a)–3(c). The solid lines represent $C_{4\theta}\cos 4\theta$. For details, see the text.

related to the pinning of the Josephson vortices is negligibly small. At 0.72 K, $\kappa(\boldsymbol{H},\theta)$ shows a minimum at $\theta = 90°$. Similar θ 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 3(c). In all data, as shown by the solid lines in Figs. 3(a)–3(c), $\kappa(\boldsymbol{H},\theta)$ can be decomposed into three terms with different symmetries; $\kappa(\theta) = \kappa_0 + \kappa_{2\theta} + \kappa_{4\theta}$ where κ_0 is a θ-independent term, and $\kappa_{2\theta} = C_{2\theta}\cos 2\theta$ and $\kappa_{4\theta} = C_{4\theta}\cos 4\theta$ are terms with twofold and fourfold symmetry with respect to the in-plane rotation, respectively. The term $\kappa_{2\theta}$, which has a minimum at $\boldsymbol{H} \perp \boldsymbol{q}$, 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 $\kappa^{\rm ph}$ dominates, $\kappa_{2\theta}$ 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)–4(c) display $\kappa_{4\theta}$ normalized by κ_n after the subtraction of the κ_0 and $\kappa_{2\theta}$ terms from the total κ. At $T = 0.72$ K, the fourfold component is extremely small; $|C_{4\theta}|/\kappa_n < 0.1\%$. On the other hand, a clear fourfold component with $|C_{4\theta}|/\kappa_n \sim 0.2\%$ is resolved at 0.52 and 0.43 K. Since the contribution of $\kappa^{\rm el}$ grows rapidly below 0.7 K and occupies a substantial portion of the total κ at 0.4 K, it is natural to consider that *the fourfold oscillation is purely electronic in origin.* Although $|C_{4\theta}|$ at 0.42 K is as small as 0.2% in κ_n, it occupies approximately 1.5%–2% in $\kappa_n^{\rm el}$ and occupies a few % in $\kappa^{\rm el}(0)$ assuming $\kappa_n^{\rm el}/\kappa_n \sim 0.15$. We now address the origin for the fourfold symmetry. The most important issue here is whether or not the observed fourfold symmetry in $\kappa^{\rm el}$ is 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 $\kappa^{\rm el}$ due to a fourfold distortion of the FS is of second order relative to the leading terms, since the thermal conductivity κ_{xx} is a second rank tensor [20]. In addition, the crystal structure of κ-$(ET)_2Cu(NCS)_2$ 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 $\Delta\sigma(\boldsymbol{H}) = \sigma(\boldsymbol{H}) - \sigma(H = 0)$ 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 $\kappa_{\rm el}$ 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*.

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 [21]. While the Doppler shift increases $\kappa^{\rm el}$ with H through the enhancement of the DOS, it can also lead to a decrease of $\kappa^{\rm el}$ 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 [22]. Since $\kappa^{\rm el}$ 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 $\kappa^{\rm el}$ at 0.42 K. In this case, rotating $\boldsymbol{H}$ within the 2D plane gives rise to the fourfold oscillation in $\kappa^{\rm el}$ associated with the DOS oscillation [15,16]. This effect arises because the DOS depends sensitively on the angle between $\boldsymbol{H}$ 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 $\kappa^{\rm el}$ which attains its maximum value when $\boldsymbol{H}$ is directed to the antinodal directions and turns minimum when $\boldsymbol{H}$ is directed along the nodal directions (see Fig. 2 in Ref. [16]). According to Ref. [15], the amplitude of the fourfold symmetry in the d-wave superconductors arising from the DOS oscillation is roughly estimated as $|C_{4\theta}|/\kappa^{\rm el}(0) = 0.082\frac{v_F v_F' eH}{3\pi\Gamma\Delta}\ln(\sqrt{32\Delta/\pi\hbar\Gamma})$. Here Δ is the SC gap, Γ is the QP relaxation rate, v_F and v_F' are the in-plane and out-of-plane Fermi velocity, respectively. Using $\Gamma \sim 2 \times 10^{11}$ s^{-1}, $2\Delta/k_BT_c = 3.54$, $v_F \sim 5 \times 10^4$ m/s, and $v_F' \sim 2.5 \times 10^3$ m/s, gives $|C_{4\theta}|/\kappa^{\rm el}(0) \sim 3\%$. Thus the DOS oscillation yields $|C_{4\theta}|/\kappa^{\rm el}(0)$ 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. $\kappa_{4\theta}$ exhibits a maximum when $\boldsymbol{H}$ is applied parallel to the $\boldsymbol{b}$ and $\boldsymbol{c}$ axes of the crystal, showing *the gap nodes along the directions rotated* 45° *relative to the* $\boldsymbol{b}$ *and* $\boldsymbol{c}$ *axes* (see the upper inset of Fig. 1). 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 $\boldsymbol{b}$ and $\boldsymbol{c}$ directions. This is because the AF ordering vectors become parallel to the $\boldsymbol{b}$ 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. [3]], the SC gap symmetry of κ-(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 [23]. Our results may bear implications on this issue.

We finally comment on the recent heat capacity measurements which report a fully gaped superconductivity [7]. In our view, their temperature range ($T > T_c/5$) is not low enough to conclude the exponential behavior of the heat capacity.

In summary, the thermal conductivity tensor of κ-(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 κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

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