Millimeter-Wave Magneto-optical Determination of the Anisotropy of the Superconducting Order Parameter in the Molecular Superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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We have used a millimeter-wave magneto-optical technique to study the angle dependence of the high-frequency conductivity of the molecular superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The data strongly suggest that the superconducting gap has nodes directed along the **b** and **c** directions of the crystal, in agreement with recent theoretical predictions. This supports the idea that the superconductivity in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is d wave in nature, and is mediated by spin fluctuations.

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The family of superconducting charge-transfer salts κ-(BEDT-TTF)$_2X$, where X can, for example, be Cu(NCS)$_2$, Cu[N(CN)$_2$]Br, or I$_3$, has attracted considerable recent attention. A variety of experiments have suggested that the superconducting gap function may contain nodes at certain points on the Fermi surface; e.g., the ^{13}C NMR spin-lattice relaxation rate [1] varies as T^3 and the thermal conductivity [2] is proportional to T below the superconducting critical temperature T_c. In addition, microwave penetration-depth studies [3] show a non-BCS-like behavior of the penetration depth as a function of T and the electronic component of the specific heat [4] has an unconventional field dependence below T_c. However, Shubnikov–de Haas [5,6], magnetic breakdown [7], and angle-dependent magnetoresistance oscillation [8] experiments demonstrate that these salts have well-defined quasi-two-dimensional (Q2D) Fermi surfaces, indicating that the quasiparticles can be described by Fermi-liquid theory at low temperatures (the Fermi surface is shown schematically as an inset of Fig. 1). Furthermore, it has been possible to fit experimental Fermi-surface-topology data to a simplified model of the tight-binding band structure (the so-called effective dimer model) to a good degree of accuracy [5,9–11].

The combination of unconventional superconductivity and a tractable analytical representation of the band structure makes the κ-(BEDT-TTF)$_2X$ superconductors attractive for theoretical studies, and a number of authors [9,10,12,13] have explored the possibility of d-wave superconductivity mediated by spin fluctuations. Such approaches predict that the superconducting order parameter will have four, roughly perpendicular, gap nodes, the exact orientation of the nodes depending on the underlying details of the Fermi surface [10,12]. Experiments performed thus far have merely detected the probable presence of the gap nodes, without giving information about their relative orientation. In this paper, we use a millimeter-wave magneto-optical technique to determine the orientation of the gap nodes in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The data appear to be in good qualitative agreement with the predictions of Schmalian [10].

The experiments were carried out on a number of crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, grown by

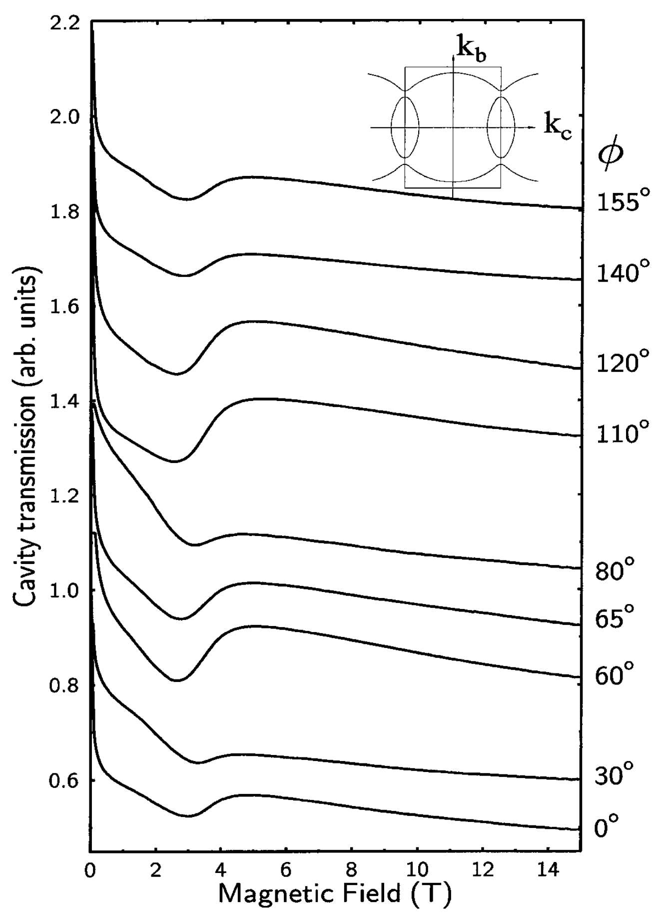

FIG. 1. Main figure: Cavity transmission as a function of magnetic field for several orientations ϕ of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal in the oscillating H field ($T = 1.4$ K). Inset: Schematic of the Fermi surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (after Refs. [5] and [10]).

conventional electrochemical means [14] and of approximate size $1 \times 0.5 \times 0.05\ \mathrm{mm}^3$. A single crystal was placed at the center of a silver rectangular resonant cavity of dimensions $6 \times 3 \times 1.5\ \mathrm{mm}^3$, resonating in the TE_{102} mode at around 70 GHz; the quality factor of the cavity is ~1500 when empty, falling to ~1000 when it is loaded with the sample. The high-frequency field distribution in the cavity is very well defined, and the sample is placed in an antinode of the oscillatory magnetic field $\mathbf{H}_{\mathrm{osc}}$, such that $\mathbf{H}_{\mathrm{osc}}$ is parallel to the highly conducting Q2D planes of the sample. Oscillatory circulating currents are induced in the plane perpendicular to $\mathbf{H}_{\mathrm{osc}}$; hence they always have a component in the low conductivity direction (i.e., perpendicular to the high-conductivity planes). The skin depth in this regime is larger than the sample dimensions and the millimeter-wave field penetrates the sample completely [15]. The currents induced in the sample dissipate power from the cavity's millimeter-wave field, and for small changes, the change in the cavity's quality factor is proportional to the change in the sample's conductivity. The cavity system therefore allows the sample's bulk conductivity to be measured at GHz frequencies [15,16].

In the current experiment, the sample was placed on a mount which allowed it to be rotated about the normal to its highly conducting Q2D planes within the cavity; thus the orientation of $\mathbf{H}_{\mathrm{osc}}$ within the highly conducting planes can be varied. In the discussion that follows, the orientation of $\mathbf{H}_{\mathrm{osc}}$ will be defined by the azimuthal angle of rotation ϕ; $\phi = 0$ corresponds to $\mathbf{H}_{\mathrm{osc}}$ being parallel to the **b** direction of the lattice. In such an arrangement, the induced circulating currents always have the same interplane component; however, the direction of the in-plane component of the induced current can be changed by rotating the sample. The cavity was placed in a variable temperature insert within a 17 T superconductive magnet. The quasistatic field B provided by the magnet was applied perpendicular to the sample's Q2D planes.

Figure 1 shows the cavity transmission at a temperature $T = 1.4$ K as a function of B for several different orientations (denoted by ϕ) of the oscillatory field $\mathbf{H}_{\mathrm{osc}}$ within the sample's Q2D conducting planes. At high B, the cavity transmission is dominated by the normal-state conductivity of the sample, which includes Shubnikov–de Haas oscillations [15,16] (see Fig. 2, right-hand inset), and which is virtually independent of ϕ [17]. At low B, the cavity transmission decreases steeply with increasing B before reaching a minimum (between 3 and 4 T in Fig. 1). The depth of the minimum changes markedly as ϕ is altered; note that its depth is particularly large at $\phi = 60°$, 65°, and 110°, but small at $\phi = 0$, 30°, 80°, 140°, and 155°. In marked contrast, the Shubnikov–de Haas oscillation amplitude, which is a reliable gauge of the sensitivity of the cavity to changes in the sample's normal-state conductivity [15,16], is virtually the same at $\phi = 30°$ and 65° (Fig. 2, right-hand inset) [17].

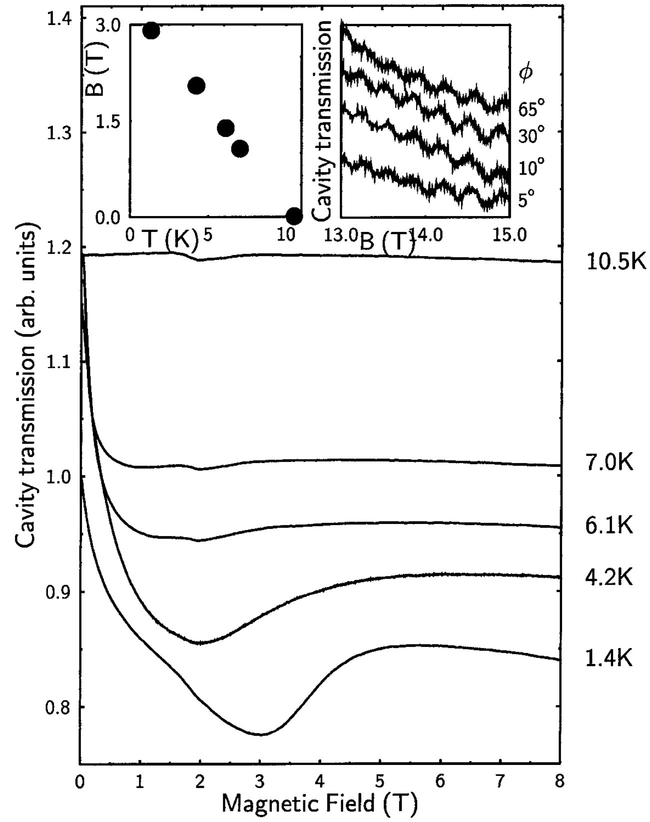

FIG. 2. Main figure: Cavity transmission at fixed ϕ for several temperatures. Left-hand inset: Magnetic field B of the minimum in transmission versus T. Right-hand inset: Plot of cavity transmission at $T = 1.4$ K on an expanded scale showing Shubnikov–de Haas oscillations and their approximate ϕ independence.

Figure 2 shows the cavity transmission as a function of magnetic field for various temperatures T. Note that our experimental apparatus has a slight background absorption [15] which may be seen as a small "kink" at $B \approx 2$ T; this feature is present in the absence of a sample and is independent of T and sample orientation. However, the most prominent feature at low T is again the minimum. As T increases, the minimum moves to lower fields, until it vanishes completely just below $T \approx 10.5$ K; apart from the cavity background kink, the transmission is virtually featureless at and above this temperature. The resistive onset of superconductivity of this particular batch of samples occurs at $T_c = 10.4$ K, showing that the minimum is associated with the field-driven transition from superconducting to normal. Further support for this proposal is given in the left-hand inset of Fig. 2, which shows the field position of the minimum as a function of T; the data closely mimic the known T dependence of the upper critical field of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [18].

A number of mechanisms for millimeter-wave power dissipation are known to occur within the superconducting state [19,20]. The dissipation due to these mechanisms becomes larger than that due to the normal-state electrons close to the phase transition (magnetic field- or temperature-driven) to normal behavior [19,20]. The data in Figs. 1 and 2 support such a picture; the fact that a *minimum* in the cavity transmission occurs just below the superconducting to normal transition shows that the dissipation in the cavity is *larger* in the superconducting state just below the upper critical field than it is in the normal state just above it [21].

We now consider the ϕ dependence of the cavity transmission in Fig. 1. We have already noted that at high B, the cavity transmission is dominated by the normal-state conductivity, which is almost ϕ independent (see the right-hand inset of Fig. 2). In contrast, the low-field cavity transmission, and, in particular, the depth of the minimum denoting the superconducting to normal transition, varies markedly with ϕ. As described above, the minimum occurs because of differences between the amount of dissipation in the superconducting and normal states [19,20]; the fact that the minimum varies with ϕ indicates that the relative strengths of the dissipative mechanisms in the superconducting and normal states depends on the direction in which the oscillatory current induced by $\mathbf{H}_{osc}$ flows.

The geometry of the experiment dictates that $\mathbf{H}_{osc}$ always lies perpendicular to the interplane direction, so that the circulatory induced current must have a component flowing in the interplane direction for all ϕ. Because of the very large conductivity anisotropy of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [18], the size of the circulating current will almost entirely be determined by the interplane conductivity, so that it will be almost ϕ independent [15]; this explains the approximate ϕ independence of the cavity transmission in the normal state in Fig. 1 (see also the right-hand inset of Fig. 2). Therefore the variation with ϕ of the mechanisms which cause the minimum in Fig. 1 must be due to the direction in which the *in-plane* component of the induced current flows.

The Fermi surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is shown as an inset of Fig. 1. The flow of in-plane currents at low temperatures will be due to quasiparticles with energies within $\sim k_B T$ of the Fermi energy; as the quasiparticle velocities $\mathbf{v}$ are given by $\hbar \mathbf{v} = \nabla_{\mathbf{k}} E(\mathbf{k})$, where $\nabla_{\mathbf{k}}$ is the gradient operator in k space, these will have velocities directed perpendicular to the Fermi surface [22]. By choosing an in-plane current direction, we are chiefly selecting quasiparticles with a particular direction of $\mathbf{v}$, and hence probing a particular section of the Fermi surface [22]. If there is a node in the superconducting gap at that point, the dissipative mechanisms which affect the induced current will be very similar in the superconducting and normal states (the number of normal quasiparticles involved in the current flow will be very similar in the normal and superconducting states). Hence, the depth of the minimum in the cavity dissipation close to the phase boundary will be small. On the other hand, if the superconducting gap function is large on that part of the Fermi surface, there will be a large difference in the dissipative mechanisms affecting the induced current as one moves from the superconducting state to the normal state; hence the minimum will be deep. In this way, the ϕ dependence of the superconducting gap can be mapped out by examining the depth of the minimum.

Figure 3 shows the depth of the minimum below the extrapolated normal-state cavity transmission as a function of azimuthal angle ϕ. In order to remove any possible effects caused by the sample's geometry [17], the depth of each minimum has been normalized by dividing by the Fourier amplitude of the Shubnikov–de Haas oscillations at the same angle ϕ (see Fig. 2, right-hand inset); in such a cavity measurement, the size of the Shubnikov–de Haas oscillations is a good absolute indication of the interplane conductivity [15,16] and so can be used to normalize out variations in the coupling between the sample and the millimeter-wave fields. The normalized minimum depth shows a clear "X" shape, with nodes directed along the **b** and **c** directions of the crystal [23]. This strongly suggests that the superconducting order parameter also possesses nodes in these directions, in agreement with the calculations of Schmalian [10].

It should also be noted that the antinodes of Fig. 3 are of a qualitatively similar form to the predicted antinodes in the superconducting gap shown in Fig. 3 of Ref. [10] [in Ref. [10], the y and x directions correspond to the **c** and **b** crystal directions of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, respectively], although the very narrow "suppressed gap" regions are not visible in our data, possibly because of the limited angular resolution.

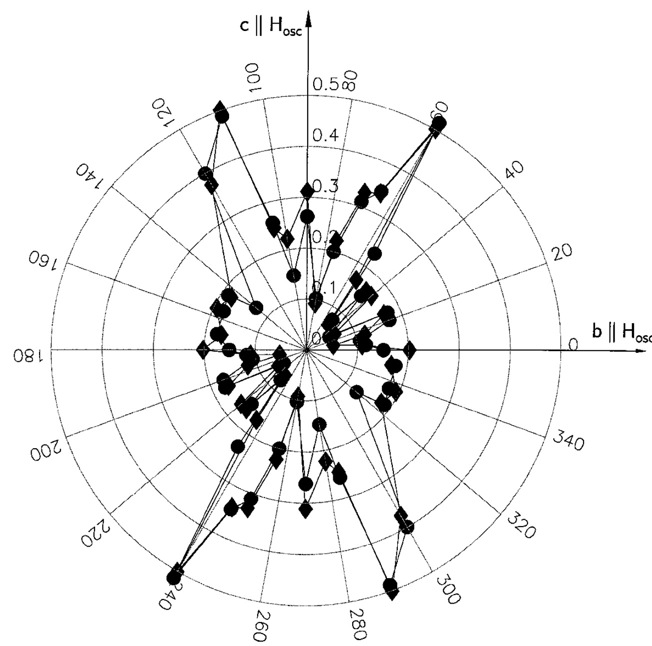

FIG. 3. Normalized amplitude of the minimum in transmission versus azimuthal angle ϕ; $\phi = 0$ corresponds to $\mathbf{H}_{osc} \parallel \mathbf{b}$ (i.e., induced currents $\parallel$ **c**) and $\phi = 90°$ corresponds to $\mathbf{H}_{osc} \parallel$ **c** (i.e., induced currents $\parallel$ **b**).

In summary, we have used a millimeter-wave magneto-optical technique to study the superconducting to normal transition of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The data strongly suggest that the superconducting gap has nodes directed along the **b** and **c** directions of the crystal, in agreement with recent theoretical predictions [10]. This provides support for the idea that the superconductivity in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and other κ-phase BEDT-TTF salts is *d* wave in nature, and is at least partly mediated by spin fluctuations. It is hoped that this observation will stimulate similar experiments on other "exotic" superconductors such as the cuprates and Sr_2RuO_4.

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[1] S. M. de Soto *et al.*, Phys. Rev. B **52**, 10 364 (1995); **54**, 16 101 (1996); H. Mayaffre *et al.*, Phys. Rev. Lett. **75**, 4122 (1995); K. Kanoda *et al.*, Phys. Rev. B **54**, 76 (1996).
[2] S. Belin *et al.*, Phys. Rev. Lett. **81**, 4728 (1998).
[3] Stephan Friemel, Thesis, Universite Paris XI, 1997.
[4] Y. Nakazawa and K. Kanoda, Phys. Rev. B **55**, R8670 (1997).
[5] J. M. Caulfield *et al.*, J. Phys. Condens. Matter **6**, 2911 (1994).
[6] C. M. Mielke *et al.*, Phys. Rev. B **56**, R4309 (1997).
[7] M. V. Kartsovnik *et al.*, Phys. Rev. Lett. **77**, 2530 (1996); N. Harrison *et al.*, J. Phys. Condens. Matter **8**, 5415 (1996).
[8] Y. Yamochi *et al.*, J. Phys. Soc. Jpn. **65**, 354 (1996); M.-S. Nam *et al.*, Synth. Met. **103**, 1905 (1999).
[9] R. Louati *et al.*, Synth. Met. **103**, 1857 (1999).
[10] Jörg Schmalian, Phys. Rev. Lett. **81**, 4232 (1998).
[11] G. Visentini *et al.*, Europhys. Lett. **42**, 467 (1998).
[12] K. Kuroki and H. Aoki, e-print cond-mat/9812026.
[13] K. Maki *et al.*, Synth. Met. **103**, 1933 (1999).
[14] M. Kurmoo *et al.*, Solid State Commun. **61**, 459 (1987).
[15] A. Ardavan *et al.*, Phys. Rev. Lett. **81**, 713 (1998).
[16] A. Polisskii *et al.*, J. Phys. Condens. Matter **8**, L195 (1996).
[17] The slight variation with ϕ of the normal-state response appears to be due to the shape of the crystal, and does not seem to be related to the underlying band structure.
[18] T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors* (Springer-Verlag, Berlin, 1998), Chap. 5.
[19] J. Corson *et al.*, Nature (London) **398**, 221 (1999).
[20] See, e.g., Chap. 2 of M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).
[21] Some of the dissipation within the superconducting state will be due to the presence of normal carriers above the gap [20]. As B increases, the gap will decrease, increasing the number of normal carriers present; this is thought to be the reason for the decrease in cavity transmission between 0 and $\sim$2 T in Fig. 2.
[22] S. J. Blundell and J. Singleton, Phys. Rev. B **53**, 5609 (1996).
[23] The normalization process has little effect on the overall shape of Fig. 3, as the Shubnikov–de Haas oscillation amplitude is relatively independent of ϕ (see Fig. 2, right-hand inset).