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High-resolution ac-calorimetry studies of the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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We report high-resolution specific-heat measurements on the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, performed by using a sensitive ac-modulation technique. The main observations are (i) a discontinuity at T_c much in excess of what is expected for a weak-coupling BCS superconductor and (ii) a quasiparticle contribution to the specific heat with an exponentially weak temperature dependence at $T \ll T_c$. The latter finding is incompatible with an order parameter that vanishes at certain parts of the Fermi surface. The data for $T \leq T_c$ can be well described by a strong-coupling extension of the BCS theory — the α-model — similar to what has been recently found for the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt [Elsinger *et al.*, Phys. Rev. Lett. **84**, 6098 (2000)].

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The quasi-two-dimensional organic charge-transfer salts κ-(BEDT-TTF)$_2X$ based on the electron-donor molecule bis(ethylenedithio)-tetrathiafulvalene, commonly abbreviated to BEDT-TTF or simply ET, are of particular interest because of their rich phase diagram including superconductivity at relatively high temperatures next to an antiferromagnetic insulating state.[1,2] The pressure-induced transition from an antiferromagnetic insulator to a superconductor for X = Cu[N(CN)$_2$]Cl is one of the intriguing observations that places these materials in line with other exotic superconductors where pairing mechanisms that are different from the conventional electron-phonon interaction might be of relevance. In fact, the proximity of magnetic order and superconductivity along with the presence of spin fluctuations above T_c as inferred from ^{13}C-NMR measurements,[3–5] have been taken as strong indications for a spin-fluctuation-mediated superconductivity[6–10] similar to that that has been proposed first for the high-T_c cuprates.[11] Since the identification of the relevant pairing interaction is a very difficult problem, many experiments have focused on the determination of the structure of the superconducting order parameter — the gap amplitude $\Delta(\boldsymbol{k})$ — which is intimately related to the pairing mechanism. However, despite intensive experimental efforts devoted to this issue, no consensus has been achieved yet.[12] Arguments in favor of an unconventional order parameter with *d*-wave symmetry for the above κ-(ET)$_2X$ salts have been derived from temperature-dependent investigations, notably NMR measurements,[5,13,14] thermal conductivity[15] and one specific-heat study.[16] More recent attempts such as STM spectroscopy,[17] millmeter-wave transmission,[18] or thermal conductivity[19] have focused on orientational-dependent investigations aiming at a direct determination of the gap anisotropy. Although a modulation of the gap structure has been seen in all of these studies, they come to quite different conclusions on the direction of the gap zeros, see e.g., Ref. 19.

Conversely, there are numerous experimental studies that are consistent with a conventional BCS-type of superconductivity. Among them are measurements of the magnetic penetration depth[20] and surface impedance[21] as well as the observation of a BCS-like mass isotope effect[22] and a pronounced superconductivity-induced phonon renormalization.[23] The latter two experiments clearly demonstrate the relevance of intermolecular phonons for the pairing interaction.

A very powerful method to probe certain aspects of the gap structure — in particular, the question whether gap zeros exist or not — is provided by specific-heat measurements. In case this integral thermodynamic technique were to find a low-temperature electronic quasiparticle contribution C_{es} that varies exponentially weakly with the temperature, the existence of gap zeros on the Fermi surface could be definitely ruled out. On the other hand, the observation of a nonexponential temperature dependence does not represent a clear proof of gap zeros as it may also originate in extraneous contributions such as impurity phases, normal-conducting regions, or pair breaking. In fact, an exponential low-T specific-heat behavior implying a finite energy gap has been found in recent high-resolution specific-heat measurements on the X = Cu[N(CN)$_2$]Br salt.[24] Moreover it has been shown in this study that the T^2 dependence in C_{es} reported for the same compound by Nakazawa and Kanoda[16] most likely originates in their incorrect determination of the phonon background.

Here we present high-resolution specific-heat measurements on the related κ-$(ET)_2$Cu(NCS)$_2$ salt with the inten-

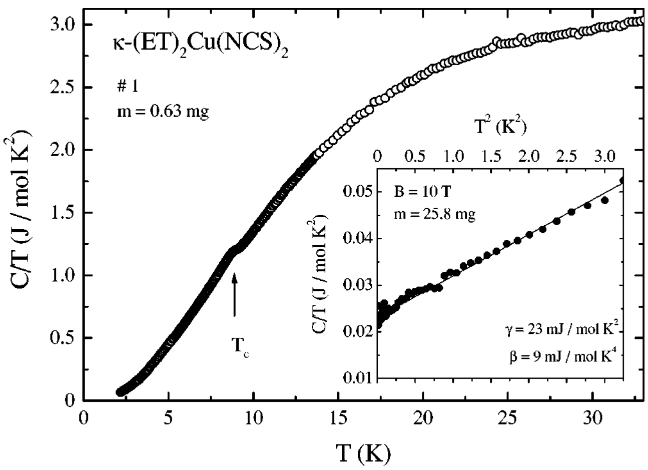

FIG. 1. Specific-heat data as C/T vs T of κ-$(ET)_2$Cu(NCS)$_2$, crystal 1. The inset shows data as C/T vs T^2 on a compilation of several single crystals with a total mass of 25.8 mg taken at low temperatures in a magnetic field $B=10$ T. The solid line is a linear fit of the form $C/T=\gamma+\beta T^2$ to the data below $T=2$ K.

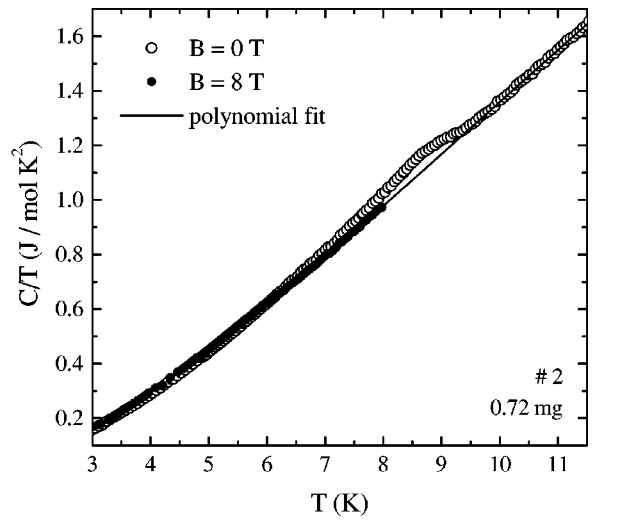

FIG. 2. Specific-heat data as C/T vs T of κ-$(ET)_2$Cu(NCS)$_2$, crystal 2, in the vicinity of the superconducting transition. Data have been taken in zero field and in an overcritical field $B=8$ T. The line represents a polynomial fit to the data $C(T\leqslant 8\,\mathrm{K}, B=8\ \mathrm{T})$ and $C(T\geqslant 10\,\mathrm{K}, B=0)$, see text.

tion to clarify the existence or absence of gap nodes for this compound.

The single crystals used were synthesized by the standard electrocrystallization technique as described elsewhere.[25] For the present investigations, two high-quality single crystals with regular platelike shapes and masses of 0.63 mg (1) and 0.72 mg (2) have been selected. The specific heat has been measured utilizing a high-resolution ac-modulation technique.[26] The setup has been designed for investigating very small platelike single crystals such as the present compounds. The sample holder consisting of a resistive thermometer (Cernox CX-1080-BG) and heater is attached to a ^{4}He-bath cryostat equipped with an 8 T superconducting solenoid. The calorimeter has been checked by measuring high-purity samples of Cu and Ag with typical masses of about 3–4 mg that have absolute heat capacities comparable to those of the small crystals studied here. In the temperature range $2\,\mathrm{K}\leqslant T\leqslant 30\,K$, the maximum deviations from the literature results amount to $\pm 2\%$.

Figure 1 shows the specific heat as C/T vs T of crystal 1 over the entire temperature range investigated.[27] The phase-transition anomaly at T_c is clearly visible although it amounts to only about five percent of the total specific heat at this temperature. To determine the quantity of interest — the quasiparticle specific heat in the superconducting state C_{es} — one has to get rid of the large phonon background C_{ph}. It is known for these molecular systems that, due to low-lying optical phonon modes, C_{ph} starts to deviate from a Debye-like behavior already at low temperatures.[28,29] To avoid uncertainties related to C_{ph}, we proceed in analyzing the difference $\Delta C(T)=C(T,B=0)-C(T,B=8\ \mathrm{T})$. For the field orientation used in our experiment, $B\| a^*$, where the upper critical field is $B_{c_2}\approx 6\ T$,[30] the data taken at 8 T represent the normal-state specific heat C_{n}. Provided that C_{n} is field independent, which has been found in previous measurements for the present compound[31,32] and also for $X=$Cu[N(CN)$_2$]Br,[24] the quantity ΔC has the advantage that the unknown C_{ph} and all other extraneous contributions (such as a small amount of Apiezon grease used to improve the thermal contact to the thermometer and heater) cancel each other out. The experimental fact that C_{n} is independent of the magnetic field within the experimental resolution[24,31] is consistent with $C_{\mathrm{n}}=C_{\mathrm{ph}}+\gamma T$,[33] where γ is the Sommerfeld coefficient.

Figure 2 shows the specific-heat data for $B=0$ and $B=8\,\mathrm{T}$ applied along the a^* axis, i.e., perpendicular to the conducting planes. For technical reasons, measurements in fields of $B=8$ T were limited to $T\leqslant 8$ K. For $C(T,B=8\ \mathrm{T})=C_{\mathrm{n}}(T)$ at $T\geqslant 8$ K, an interpolation based on a polynomial fit between the $C(T<8\,\mathrm{K},B=8\ \mathrm{T})$ and $C(T>10\,\mathrm{K},B=0)$ data was used, cf. the solid line in Fig. 2. The so derived $\Delta C=C(0\ \mathrm{T})-C(8\ \mathrm{T})=C_{\mathrm{es}}-\gamma T$ of crystal 2 is shown in Fig. 3 together with ΔC expected from the BCS weak-coupling theory.[34] The theoretical curve is based on a Sommerfeld coefficient $\gamma=(23\pm 1)$ mJ/(mol K^2) as determined by low-temperature $C(T)$ measurements employing a thermal-relaxation technique on a compilation of three single crystals with total mass of 25.8 mg, see inset of Fig. 1.[35] This γ value is consistent with $\gamma=(25\pm 3)$ mJ/(mol K^2) derived from an earlier specific-heat study on the same compound[31] by analyzing the data in the range $1.3\,\mathrm{K}<T<3\,\mathrm{K}$ which is slightly above that used here.[36] We note that the above $\Delta C(T)$ data are in good agreement with the results of an earlier ac-calorimetry study[32] which focused on the temperature range around T_c, i.e., $6\,\mathrm{K}<T<12\,\mathrm{K}$.[37]

Figure 3 demonstrates that, similarly to what has been recently observed for the $X=$Cu[N(CN)$_2$]Br salt,[24] $\Delta C(T)$ deviates markedly from the weak-coupling BCS-behavior in both the jump height at T_c as well as the overall temperature dependence. However, as for $X=$Cu[N(CN)$_2$]Br, a much better description of the data is obtained by using the semi-empirical extension of the BCS formalism to strong-coupling

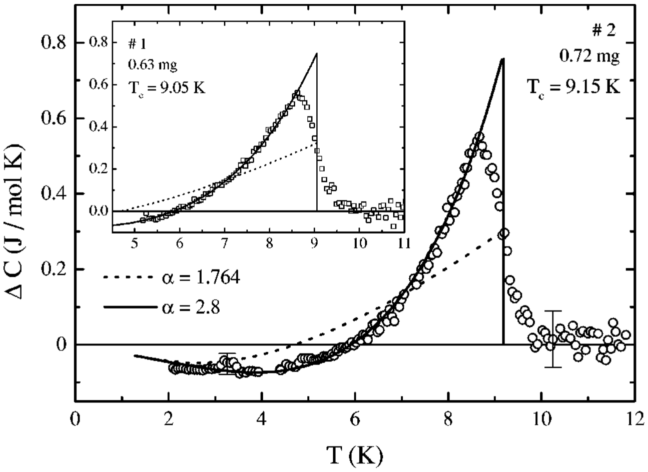

FIG. 3. Specific-heat difference $\Delta C = C(0\ \mathrm{T}) - C(8\ \mathrm{T}) = C(0\ \mathrm{T}) - C_\mathrm{n}$ of crystals 2 and 1 (inset). The dotted and solid thick lines represent the BCS curves for weak and strong coupling, respectively.

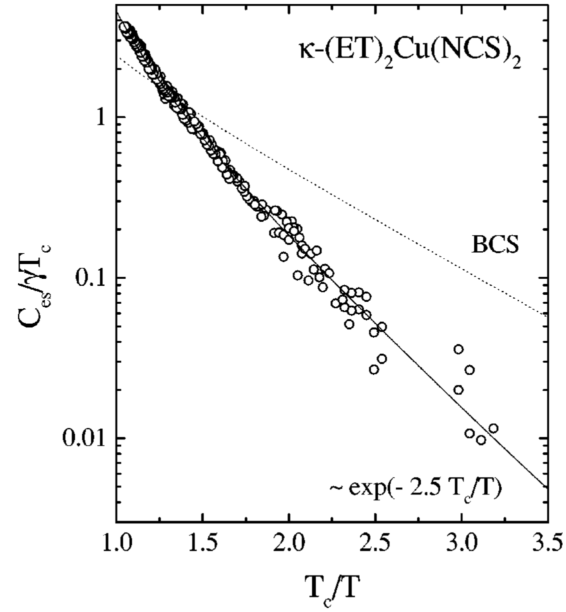

FIG. 4. Semilogarithmic plot of the electronic contribution to the specific heat in the superconducting state as $C_\mathrm{es}/\gamma T_c$ vs T_c/T. The dotted and solid lines represent the weak- and strong-coupling BCS behavior, respectively, see text.

superconductors, the so-called α model.[38] It contains a single free parameter $\alpha \equiv \Delta(0)/k_B T_c$ (k_B being the Boltzmann constant) that scales the BCS energy gap $\Delta(T) = (\alpha/\alpha_\mathrm{BCS}) \cdot \Delta_\mathrm{BCS}(T)$ with $\alpha_\mathrm{BCS} = 1.764$. As Fig. 3 clearly demonstrates, the strong-coupling BCS model with $\alpha = 2.8 \pm 0.1$ provides an excellent description of the data over the entire temperature range investigated. The error margins in α account for the uncertainties in both γ as well as T_c. In the inset of Fig. 3 we show ΔC data of crystal 1 together with the theoretical results of the α model. Although T_c of crystal 1 is slightly reduced compared to that of crystal 2, we find again an excellent agreement with the strong-coupling results employing the same parameter $\alpha = 2.8$. The fact that both data sets in Fig. 3 are well described within the strong-coupling BCS model implies (i) that C_es reveals an exponentially weak temperature dependence at low temperatures and (ii) the thermodynamic consistency of the data, i.e., entropy conservation. The exponential variation of C_es becomes clearer in Fig. 4, where $C_\mathrm{es}/\gamma T_c$ is shown in a semilogarithmic plot as a function of T_c/T. Here, $C_\mathrm{es} = \Delta C + \gamma T$ with $\gamma = (23 \pm 1)$ mJ/(mol K^2) has been used. The solid line represents the same strong-coupling curve shown in Fig. 3. The figure also includes the weak-coupling BCS result (dashed line) that predicts $C_\mathrm{es}/\gamma T_c \propto \exp(-a_\Delta T_c/T)$ with $a_\Delta = 1.44$ for $2.5 \leqslant T_c/T \leqslant 6$.[39] The data of κ-$(ET)_2$Cu(NCS)$_2$ presented here follow $C_\mathrm{es}/\gamma T_c \propto \exp(-2.5 T_c/T)$ down to the lowest accessible temperature. The enhanced prefactor in the exponent of $a_\Delta = 2.5$ as compared to 1.44 for the weak-coupling BCS model reflects the strong-coupling character of the present superconductor.

Figure 4 demonstrates that our results are fully consistent with an exponentially vanishing C_es at low temperatures and, thus, an energy gap without zeros at the Fermi surface. The same conclusions have been drawn from a similar analysis of $C(T,B)$ data on κ-(ET)$_2$Cu[N(CN)$_2$]Br.[24] As the specific heat is an integral technique that picks up all excitations at the Fermi surface, the above findings are incompatible with the existence of gap zeros as claimed by other experiments, notably NMR.[5,13,14] Since the latter results have been obtained in a finite magnetic field applied parallel to the conducting planes, the discrepancies are possibly related to an as yet not understood influence of the magnetic field. In conclusion, high-resolution specific-heat measurements on small high-quality single crystals of $\kappa-$(BEDT-TTF)$_2$Cu(NCS)$_2$ have been performed in both the normal and superconducting state. The data analysis employed, which minimizes uncertainties associated with the unknown, large phonon background reveals an electronic quasiparticle contribution to the specific heat that varies exponentially weakly with temperature at $T \ll T_c$. This behavior is fully consistent with a finite-energy gap all over the Fermi surface and rules out the existence of gap nodes. Moreover, we find an excellent agreement with the predictions of the strong-coupling variant of the BCS model employing an α parameter 2.8 that slightly exceeds the one found recently for the related κ-(ET)$_2$Cu[N(CN)$_2$]Br salt.[24]

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[35] The straight line of the $C(10\mathrm{T})=C_{\mathrm{n}}$ data in the representation C/T vs T^2 is consistent with $C_{\mathrm{n}}=C_{\mathrm{ph}}+\gamma T=\beta T^3+\gamma T$. We find $\beta=9$ mJ/(mol K^4) that corresponds to a Debye temperature of $\Theta_D=(230\pm15)$ K in good agreement with the value of (215 ± 10) K from Ref. 31.
[36] Due to a significant nonsuperconducting volume fraction of about 10% found in these low-temperature studies on the composite samples with $m=25.8$ mg that most likely originates in the irregular and porous surface of one of the crystals and the pressure exerted by frozen-in Apiezon grease, a reliable determination of the low-temperature C_{es} was impeded. This, however, does not affect the determination of γ within the error margins specified.
[37] Note that the conclusion drawn in Ref. 32 of a weak-coupling BCS-type behavior was based on (i) a too large γ value of 34mJ/(mol K^2) and (ii) using an incorrect BCS fit. According to BCS, $\Delta C=0$ at $T/T_c\approx0.5$ (Ref. 34), whereas in their (and the present) data $\Delta C=0$ at $T/T_c\approx2/3$. However, as stated in a ''Note added in proof'' of Ref. 32, an intermediate-to-strong rather than weak coupling is suggested when using the γ value of Ref. 31 of $\gamma=(25\pm3)$mJ/(mol K^2).
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