κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br: A Fully Gapped Strong-Coupling Superconductor

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High-resolution specific-heat measurements of the organic superconductor κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Br in the superconducting ($B = 0$) and normal ($B = 14$ T) states show a clearly resolvable anomaly at $T_c = 11.5$ K and an electronic contribution, C_{es}, which can be reasonably well described by strong-coupling BCS theory. Most importantly, C_{es} vanishes exponentially in the superconducting state which gives evidence for a fully gapped order parameter.

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Since the discovery of superconductivity in organic metals about 20 years ago the question of the nature of this state is one of the most intriguing problems in this class of materials. The close neighborhood of antiferromagnetically ordered states in the pressure-temperature phase diagram has spurred speculations of a Cooper-pair coupling which is mediated by antiferromagnetic fluctuations rather than by conventional electron-phonon coupling [1,2]. This notion gained additional feedback by the growing evidence for unconventional behavior of the high-T_c cuprates and heavy-fermion superconductors. A large number of experiments, especially on the quasi-two-dimensional (2D) organic materials, were initiated to elucidate the question of the symmetry of the order parameter, i.e., of the determination of possible gap nodes in the superconducting state. The outcome is rather controversial with an approximately equal distribution of reports which present results in line with conventional BCS-like behavior and others which give support for an unconventional state [3–5]. Here, the term "unconventional superconductivity" is used to denote the fact that either a nonphononic Cooper-pair attraction is present or that, besides the gauge symmetry, additional symmetries are broken at T_{c}.

In the following we restrict ourselves to the 2D organic charge-transfer salts based on the donor molecule BEDT-TTF (bisethylenedithio-tetrathiafulvalene, or ET for short). Materials of the well-studied κ phase reveal a unique phase diagram [6,7] with κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Br, the superconductor with the highest transition temperature ($T_c = 11.5$ K) in this class, being close to an antiferromagnetic (presumably) Mott-insulating ground state. This direct neighborhood of competing ground states strongly motivated the speculations on a nonphononic pairing mechanism.

Results especially in favor of unconventional behavior were supplied by ^{13}C-NMR experiments of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [8–10]. The NMR data were obtained with the necessarily applied field along the BEDT-TTF planes. For this field orientation it is believed that the vortex lattice is trapped in the so-called lock-in state and that one thereby can avoid additional spin-relaxation processes due to the otherwise present flux-line motion. All three experiments [8–10] showed consistently a nonexponential, i.e., non-BCS-like, decrease of the spin-lattice relaxation rate $1/T_1$. The data could approximately be described by a $1/T_1 \propto T^3$ dependence which was interpreted as an indication for d-wave pairing with line nodes in the energy gap. Accordingly, these line nodes should lead to a T^2 behavior of the electronic specific heat in the superconducting state, C_{es}. Recently, indeed specific-heat data were reported [11] which seemingly showed an approximately T^2 dependence of C_{es}. In that experiment, however, the phonon specific heat of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br was tried to be estimated by measuring a quench-cooled nonsuperconducting deuterated sample which is just on the insulating side of the above-mentioned phase diagram [6,7].

Specific-heat experiments are an especially powerful method in order to decide whether nodes of the superconducting gap are present or not. If this integral technique reveals an exponential dependence of C_{es}, nodes of the order parameter, i.e., points where the superconducting gap becomes zero, can unequivocally be ruled out. On the other side, care has to be taken when a nonexponential behavior of C_{es} is observed. Besides the existence of gap nodes, spurious effects like a not completely superconducting sample or an improper subtraction of nonelectronic specific-heat contributions may lead to wrong conclusions. This experiment, i.e., the measurement of the specific heat of one single crystal κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br both in the superconducting ($B = 0$) and in the normal states at a magnetic field of 14 T, was initiated in order to obtain a definitive answer to the possible existence of gap nodes in a reliable way.

Care was taken to reduce the heat capacity of the sample holder. This enabled us to measure one single crystal of 3.26 mg which contributed (50–70)% to the total heat capacity. The heat capacity of the empty sample holder, which consists of a sapphire plate with a thin manganin wire (20 μm diam) as heater and a RuO$_2$ resistor as thermometer, was measured in all relevant fields. The RuO_2 thermometer which shows in the experimental range only a small field dependence was calibrated in fields up to 14 T in steps of 1 T. The specific heat was measured in a ^{4}He cryostat equipped with a 14 T superconducting magnet by the quasiadiabatic heat-pulse technique. The temperature resolution of about $\Delta T/T < 1 \times 10^{-5}$ prevents any rounding effects at the transition due to the experiment.

The specific heat, C, between 1.7 and 21 K in $B = 0$ and $B = 14$ T is shown in Fig. 1. The upper critical field of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is $B_{c2} = (10 \pm 2)$ T which can be estimated from the field dependence of our low-temperature C data (not shown) and which is in line with earlier estimates [12,13]. Therefore, the data in $B = 14$ T are in the normal state comprising the electronic and the phononic contributions truly relevant for the data analysis of this special sample. From our data we determine a Sommerfeld coefficient $\gamma = (25 \pm 2)$ mJ mol^{-1} K^{-2} and a Debye temperature of about $\Theta_D = (200 \pm 10)$ K. These values agree within error bars with earlier literature data [11,14]. The uncertainties in our values originate in the limited T range where we observe a linear plus a cubic temperature dependence of C. Already at about 3 K we observe a deviation from the cubic Debye law, i.e., an additional phononic contribution. These low-lying optical phonon modes are well known from Raman-scattering investigations and previous specific-heat data of other organic superconductors (see Refs. [15,16] for details). At very low temperatures, the nuclear magnetic moments of the hydrogen atoms of the BEDT-TTF molecules should contribute to a Schottky anomaly due to hyperfine interactions (see [15] for details). In 14 T, this hyperfine contribution would be about 3.5% of the total specific heat at 2 K. In our experiment as well as in [14] no indication of a low-temperature upturn of the C data was observed for this field. This is most probably caused by a too long spin-lattice relaxation time compared to the thermal relaxation time of the sample to the bath.

The blowup in Fig. 1(b) shows the region close to $T_c = 11.5$ K. In this scale one can see more clearly the broad anomaly arising from the superconducting transition. In contrast to previous reports [14,17] we were able to unequivocally resolve this anomaly which contributes about 3% to the total specific heat. The broadened jump at T_c is much larger than anticipated from weak-coupling theory. This becomes much clearer when we plot ΔC vs T (Fig. 2), where ΔC is the specific-heat difference between C in the superconducting ($B = 0$) and in the normal states ($B = 14$ T). The latter was approximated by a polynomial [solid line in Fig. 1(b)]. ΔC expected from weak-coupling BCS theory [18] is shown as the dashed line in Fig. 2. It is obvious that the jump at T_c as well as the whole temperature dependence does not follow this behavior. Instead, the experimental data can much better be described by strong-coupling behavior (solid line in Fig. 2). Thereby, we assumed a BCS-like temperature dependence of the energy gap $\Delta(T)$ scaled by one appropriate parameter, i.e., the gap ratio $\alpha = \Delta(0)/k_B T_c$, which is $\alpha_{\mathrm{BCS}} = 1.76$ in the weak-coupling limit [19]. With this simplistic assumption and $\alpha = 2.7$ we obtain the reasonable description shown in Fig. 2. The jump height is reproduced quite well taking into account the fact that we neglected any fluctuations. In the intermediate temperature region the data lie somewhat above the strong-coupling line, whereas at low temperatures, where the data are most precise, perfect agreement is found [20]. We want to note that we did not fit the model to the data but rather compared visually the BCS curves for different α with the data. Therefore, as well as due to the error bar in γ, the uncertainty in α is about ± 0.2.

For strong-coupling superconductors only phenomenological models exist which connect the different

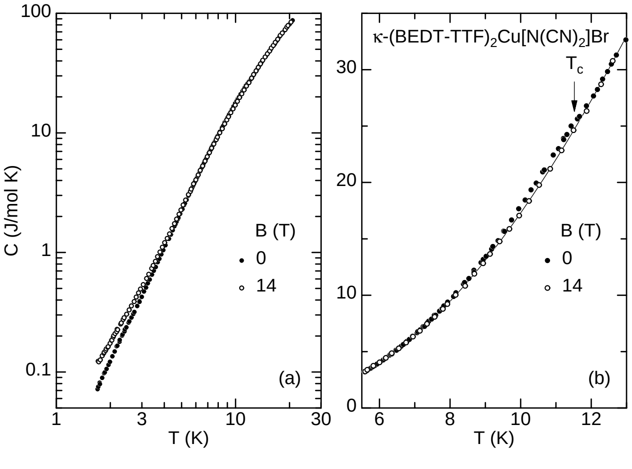

FIG. 1. Temperature dependence of the specific heat of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the superconducting ($B = 0$) and the normal ($B = 14$ T) states shown (a) for the complete temperature range and (b) for the region close to $T_c = 11.5$ K. The solid line in (b) is a polynomial fit to the 14 T data.

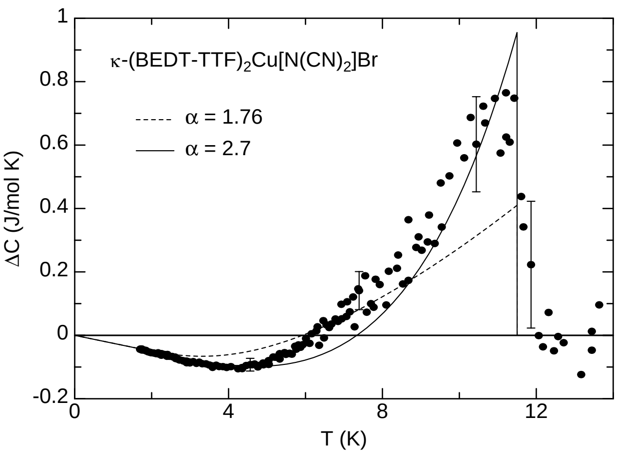

FIG. 2. Specific-heat difference between the superconducting and the normal states with BCS curves for weak (dashed line) and strong (solid line) coupling.

superconducting parameters. By use of a large set of data from conventional superconductors the approximate relation between the specific-heat jump $\Delta C/\gamma T_c$ and T_c/ω_{ln} is known, where ω_{ln} is the average phonon (or, more general, coupling) energy [21]. Further on, the value T_c/ω_{ln} is connected with the coupling strength λ of the superconducting charge carriers by the modified McMillan equation. However, for strong coupling, i.e., λ larger than about 1.5, the McMillan equation is not valid any more and it is more appropriate to use an empirical relation between T_c/ω_{ln} and λ obtained from tunneling data and presented in Ref. [22]. Under the assumption that the organic superconductors can be described by the same strong-coupling theory as conventional superconductors leads to a very large λ of about 2.5. This might be in line with a recent theoretical treatment where enhanced strong-coupling features in quasi-two-dimensional correlated electron systems are expected [23].

The λ values vs T_c for the title material as well as for four other organic superconductors [15,16,24,25] are presented in Fig. 3. Thereby, λ was extracted for all materials in the same way, with $\alpha = 1.76$ for the weak-coupling superconductor α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ [25] and a crudely estimated $\alpha = 2.2$ from the limited set of available literature data for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [24]. A clear systematic increase of λ, i.e., the relative specific-heat jump $\Delta C/\gamma T_c$, as a function of T_c is obvious. According to Fig. 1 of Ref. [21] this indicates that the characteristic average coupling energy ω_{ln} has a similar strength for all shown organic superconductors. Consequently, one can write $\lambda \propto N(E_F)\langle I^2\rangle$ [22], where $N(E_F)$ is the electronic density of states at the Fermi energy and $\langle I^2\rangle$ is the coupling matrix element averaged over the Fermi surface. Our result indicates that mainly $\langle I^2\rangle$ controls T_c, since $N(E_F)$ remains more or less constant as shown by the measured $\gamma \propto N(E_F)$ which is not correlated with T_c for the mentioned organic superconductors. There is, however, a tendency for a slight increase with T_c if one considers only the kappa-phase materials, from $\gamma = (18.9 \pm 1.5)$ mJ mol^{-1} K^{-2} for κ-(BEDT-TTF)$_2$I$_3$ to $\gamma = (25 \pm 2)$ mJ mol^{-1} K^{-2} for the title material. Within a two-dimensional Fermi-liquid picture the γ values lead to effective masses of about $3.6m_e$ and $4.6m_e$, respectively, where m_e is the free-electron mass. This increase of γ and the effective masses is in accordance with results from de Haas–van Alphen or Shubnikov–de Haas experiments which show an increasing effective cyclotron mass from $m_c = 3.9m_e$ for κ-(BEDT-TTF)$_2$I$_3$ [13] to $m_c = 6.6m_e$ for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [26]. These enhanced masses point to the importance of many-body effects, i.e., electron-phonon and electron-electron interactions, in the organic superconductors and are at least qualitatively in line with the estimated large coupling constants λ.

The main point of this paper is the proof of an exponentially vanishing electronic specific heat in the superconducting state. It is clear already from Fig. 2 that no electronic contribution to C remains at low temperatures since otherwise the data would not follow so perfectly the strong-coupling BCS curve. The fact becomes more evident when we plot the electronic part of the specific heat in the superconducting state, C_{es}, as a function of T_c/T (Fig. 4). For the determination of C_{es} we subtracted the phonon part of C which corresponds to C measured in $B = 14$ T $- \gamma T$. The normalized plot in Fig. 4 shows unambiguously that C_{es} vanishes towards low T. The solid line is an exponential fit to the data of the form $C_{es}/\gamma T_c \propto \exp(-2.7T_c/T)$. At $T_c/T \approx 3$, C_{es} is so small that we cannot resolve it any longer leading to the scatter of the data towards lower temperatures. From this result we can conclude that a possible remnant of C_{es}/T is less than about 1 mJ mol^{-1} K^{-2} [27]. Consequently, our data prove

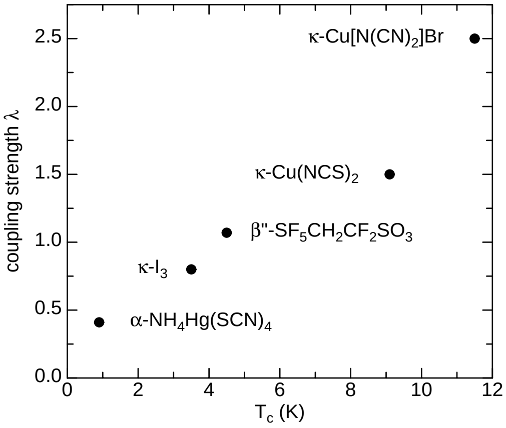

FIG. 3. The estimated coupling strength λ vs the superconducting transition temperatures for different two-dimensional organic superconductors of the general formula P-(BEDT-TTF)$_2X$, where the crystallographic phase P and the anion X are given in the figure.

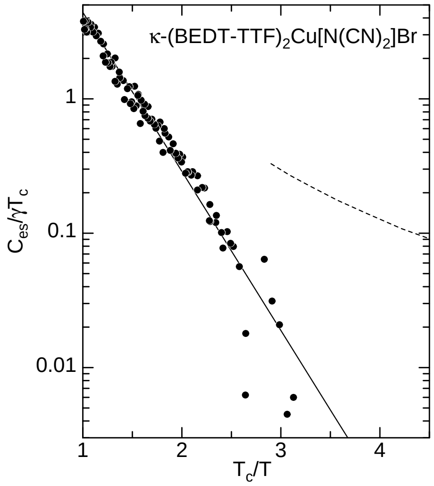

FIG. 4. Normalized plot of the electronic specific heat in the superconducting state vs T_c/T. The solid line shows the exponential vanishing of C_{es}. The dashed line is the approximate estimate of C_{es} from [11].

the absence of gap nodes but, instead, point strongly to the existence of a complete energy gap in the superconducting state. We want to note that our data do not allow us to make any statements on possible gap anisotropies. These may well be the reason for the observed slight discrepancy between the ΔC data and the BCS fit in the intermediate temperature region shown in Fig. 2. In addition, our finding does not exclude an order-parameter symmetry of that kind, that gap nodes could principally exist. It may just happen that because of the 2D character the gap falls outside the actual Fermi surface [28].

Within BCS theory one can approximate $C_{es}/\gamma T_c \propto \exp(-a_\Delta T_c/T)$ for $2.5 < T_c/T < 6$ [29], where the coefficient a_Δ ($= 1.44$ in the weak-coupling limit) is proportional to the energy gap Δ at $T = 0$. The much larger value $a_\Delta \approx 2.7$ we extracted from our data is the behavior expected for strong coupling and consistent with the large λ. The exponential vanishing of C_{es} can equally well be proven for the organic superconductors κ-(ET)$_2$I$_3$ [15] and β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ [16].

In Fig. 4 we included the approximated average of the estimated result for C_{es} from Fig. 3 of Ref. [11] (dashed line). It is evident from our result that one can definitely exclude any remnant contribution as high as proposed in this work (at $T_c/T = 3$ our data are more than a factor of 10 smaller). Indeed, the estimated C_{es} at 4 K in [11] coincides approximately with the normal-state electronic C which would mean a crossing of the C data in the normal and the superconducting states at around this temperature. Figures 1(a) and 2 show that these results must be wrong. It is therefore proven that it is not allowed to estimate the phonon specific heat from a quench-cooled nonsuperconducting deuterated sample.

For superconductors with line nodes a field dependence of γ proportional to $\sqrt{B}$ is predicted [30]. Recently, however, a $\sqrt{B}$ dependence was also observed at low fields in an s-wave superconductor [31] pointing out that the bare observation of this behavior does *not* prove an unconventional pairing state. For the title material a $\sqrt{B}$ dependence of γ at low fields was reported [11]. Since our measurements were made at higher temperatures we cannot make a definitive statement. However, from the field dependence of C at fixed temperature we can describe the data reasonably well by a linear field dependence.

In conclusion, the results of our specific-heat measurements of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the superconducting and normal states can be well described by strong-coupling BCS theory. We extract a large coupling parameter $\lambda \approx 2.5$ which scales well with λ values found for organic superconductors with lower T_c. The electronic specific heat in the superconducting state vanishes exponentially with T_c/T which disproves the T^2 behavior claimed earlier. Our data are fully consistent with a completely gapped order parameter.

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