$\kappa$-(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 $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the superconducting ($B = 0$) and normal ($B = 14$T) state show a clearly resolvable anomaly at $T_c = 11.5\text{K}$ 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 on 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 on a Cooper-pair coupling which is mediated by antiferromagnetic fluctuations rather than by conventional electron-phonon coupling [6,7]. 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 on the symmetry of the order parameter, i.e., on 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 giving support for an unconventional state [3,13]. Here, the term ‘unconventional superconductivity’ is used to denote that either a non-phononic Cooper-pair attraction is present or that besides the gauge symmetry additional symmetries are broken at $T_c$.

The most studied family of the 2D organic charge-transfer salts is the $\kappa$-phase based on the donor molecule BEDT-TTF (bisethylenedithio-tetrathiafulvalene or ET for short). Materials of this phase reveal a unique phase diagram [5,6] with $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, the superconductor with the highest transition temperature ($T_c = 11.5\text{K}$) 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 non-phononic pairing mechanism.

Results especially in favour for unconventional behavior were supplied by $^{13}$C-NMR experiments of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [5,6]. 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 [3,6] showed consistently a non-exponential, 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 [1] which seemingly showed an approximately $T^2$ dependence of $C_{es}$. In that experiment, however, the phonon specific heat of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br was tried to estimate by measuring a quench-cooled non-superconducting deuterated sample which is just on the insulating side of the above-mentioned phase diagram [4,8].

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 non-exponential 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 non-electronic specific-heat contributions may lead to wrong conclusions. This experiment, i.e, the measurement of the specific heat of one single crystal $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br both in the superconducting ($B = 0$) and in the normal state at a magnetic field of 14T, 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 3.26mg which contributed 50-70% to the to-
Our low-temperature anomaly due to hyperfine interactions (see [14] 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 blow up 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 $\Delta T/T < 1 \cdot 10^{-5}$ 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 $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br which can be estimated from the field dependence of our low-temperature $C$ data (not shown) and which is in line with earlier estimates [2,3]. Therefore, the data in $B = 14$ T are in the normal state comprising the electronic and the phononic contribution truly relevant for the data analysis of this special sample. From our data we determine a Sommerfeld coefficient $\gamma = (25 \pm 2)$ $\text{mJ mol}^{-1} \text{K}^{-2}$ and a Debye temperature of about $\Theta_D = (200 \pm 10)$ K. These values agree within error bars with earlier literature data [11,13]. 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 of other organic superconductors (see Refs. [2,3] for details). At very low temperatures, the nuclear magnetic moments of the hydrogen atoms of the BEDT-TTF molecules should contribute to a Schottky heat capacity. The heat capacity of the empty sample holder, which consists of a sapphire plate with a thin manganin wire (20 $\mu$m diameter) 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 quasi-adiabatic heat-pulse technique. The temperature resolution of about $\Delta T/T < 1 \cdot 10^{-5}$ prevents any rounding effects at the transition due to the experiment.

FIG. 1. Temperature dependence of the specific heat of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the superconducting ($B = 0$) and normal ($B = 14$ T) state 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 normal state with BCS curves for weak (dashed line) and strong (solid line) coupling.
TTF) organic superconductors of the general formula $P_2$(BEDT-TTF)$_2X$, where the crystallographic phase $P$ and the anion $X$ are given in the figure.

but rather compared visually the BCS curves for different $\alpha$ with the data. Therefore, as well as due to the error bar in $\gamma$, the uncertainty in $\alpha$ is about $\pm 0.2$.

For strong-coupling superconductors only phenomenological models exist which connect the different 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 $T_c/\omega_{ln}$ is known, where $\omega_{ln}$ is the average phonon (or, more general, coupling) energy [20]. Further on, the value $T_c/\omega_{ln}$ is connected with the coupling strength $\lambda$ of the superconducting charge carriers by the modified McMillan equation. However, for strong coupling, i.e., $\lambda$ larger than about 1.5, the McMillan equation is not valid any more and it is more appropriate to use an empirical relation between $T_c/\omega_{ln}$ and $\lambda$ obtained from tunneling data and presented in Ref. [21]. Under the assumption that the organic superconductors can be described by the same strong-coupling theory as conventional superconductors this leads to a very large $\lambda$ 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 [22].

The $\lambda$ values vs $T_c$ for the title material as well as for four other organic superconductors [18,19,23,24] are presented in Fig. 3. Thereby, $\lambda$ was extracted for all materials in the same way, with $\alpha = 1.76$ for the weak-coupling superconductor $\alpha$-(BEDT-TTF)$_2NH_4Hg(SCN)$_4 [24] and a crudely estimated $\alpha = 2.2$ from the limited set of available literature data for $\kappa$-(BEDT-TTF)$_2Cu(NCS)$_2 [23]. A clear systematic increase of $\lambda$, 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 $\omega_{ln}$ has a similar strength for all shown organic superconductors. Consequently, one can write $\lambda \propto N(E_F) \langle I^2 \rangle$ [21], 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 $\gamma = (18.9 \pm 1.5) \text{mJ mol}^{-1} \text{K}^{-2}$ for $\kappa$-(BEDT-TTF)$_2I_3$ to $\gamma = (25 \pm 2) \text{mJ mol}^{-1} \text{K}^{-2}$ for the title material. Within a two-dimensional Fermi-liquid picture the $\gamma$ values lead to effective masses of about 3.6 $m_e$ and 4.6 $m_e$, respectively, where $m_e$ is the free-electron mass. This increase of $\gamma$ 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 $m_c = 3.9 m_e$ for $\kappa$-(BEDT-TTF)$_2I_3$ [13] to $m_c = 6.6 m_e$ for $\kappa$-(BEDT-TTF)$_2Cu[N(CN)$_2]Br [25]. 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 $\lambda$.

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 $B = 14 \text{T}$ minus $\gamma T$. 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 $C_{es}/\gamma T_c \propto \exp(-2.7 T_c/T)$. At $T/T_c \approx 3$, $C_{es}$ 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$^{-2}$. Consequently, our data prove 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 to make any statements on possible gap anisotropies. These may well be the reason for the observed slight discrepancy between the $\Delta C$ data and the BCS fit in the intermediate temperature region shown in Fig. 3.

Within BCS theory one can approximate $C_{es}/\gamma T_c \propto \exp(-a_{\Delta} T_c/T)$ for $2.5 < T_c/T < 6$ [26], where the coefficient $a_{\Delta} (= 1.44$ in the weak-coupling limit) is proportional to the energy gap $\Delta$ 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 $\lambda$. The exponential vanishing of $C_{es}$ can equally...
This work (at exclude any remnant contribution as high as proposed in line). It is evident from our result that one can definitely estimated result for $C_\text{es}$ of 10 smaller. Indeed, the estimated $C_\text{es}$ at 4K in [11] coincides approximately with the normal-state electronic $C$ which would mean a crossing of the $C$ data in the normal and superconducting state at around this temperature. Figures 1(a) and 2 show that this results must be wrong. It is therefore proven that it is not allowed to estimate the phonon specific heat from a quench-cooled non-superconducting deuterated sample.

For superconductors with line nodes a field dependence of $\gamma$ proportional to $\sqrt{B}$ is predicted [27]. Recently, however, a $\sqrt{B}$ dependence was also observed at low fields in an s-wave superconductor [25] 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 $\gamma$ 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 the organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the superconducting and normal state can be well described by strong-coupling BCS theory. We extract a large coupling parameter $\lambda \approx 2.5$ which scales well with $\lambda$ 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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