

Low-temperature specific heat of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br in the superconducting state

Y. Nakazawa and K. Kanoda

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

(Received 17 December 1996)

The low-temperature specific heat of single crystals of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br was studied in the temperature range between 0.11 and 4.5 K. The electronic specific heat, C_{el} , in the superconducting state shows a quadratic temperature dependence that is most reasonably attributed to the quasiparticle excitations found in unconventional superconductors with line nodes in the gap structure. The magnetic-field dependence of the temperature-linear term in C_{el} is also consistent with this picture of superconductivity. [S0163-1829(97)50714-4]

The problem of pairing mechanism in organic superconductors is one of the hot topics in condensed matter physics. Since the discovery of superconductivity in (TMTSF)₂X salts in 1980,¹ more than 50 salts are recognized as organic superconductors up to now. Although material research in this field has been greatly stimulated and accelerated by the discovery of BEDT-TTF based salts, which yielded many quasi-two-dimensional superconductors, the pairing mechanism of the superconductivity in organic systems is still an open question at present. The first experimental study on this problem was for (TMTSF)₂ClO₄, where the absence of coherence peak and a power-law temperature dependence of the nuclear magnetic resonance (NMR) relaxation rate have been reported as a sign of unconventional electron pairing in the organic superconductor.²

The κ -(BEDT-TTF)₂Cu[N(CN)₂]Br is known as the highest- T_c (11.6 K) salt at ambient pressure. This material consists of two-dimensional donor sheets, each of which is separated by insulating anion layers with a multilayer period of about 15 Å. In the donor layers, BEDT-TTF dimers are arranged in nearly orthogonal coordination to form a zigzag network. More interesting to notice is the electronic phase diagram of the κ -phase family, κ -(BEDT-TTF)₂X, in that the superconducting phase of this family is situated very close to the Mott insulating phase with an antiferromagnetic ground state. Recently, strong antiferromagnetic spin fluctuations were observed in both superconducting [X =Cu(NCS)₂ and Cu[N(CN)₂]Br] and insulating [X =Cu[N(CN)₂]Cl] salts.³⁻⁵ These fluctuations develop into an antiferromagnetic long-range ordering at T_N =27 K in the Cu[N(CN)₂]Cl salt,⁵ while in the former two salts the fluctuations are depressed below 50 K and superconductivity appears around 10 K instead of magnetic ordering.

In the superconducting state, ¹³C-NMR study has recently been performed by three groups, who measured the nuclear spin-lattice relaxation rate in different conditions to avoid effects of the vortices in different ways and gave the same conclusion; there observed no Hebel-Slichter coherence peak just below T_c and a T^3 dependence of relaxation rate at low temperatures.⁶⁻⁸ These results support a possibility of unconventional pairing with line nodes in the gap. The electronic specific heat of superconductors which have nodes in the gap structure is known to show a power-law temperature dependence, while an exponential dependence would be seen in

case of fully gapped superconductors. The quadratic temperature dependence of electronic specific heat was reported in heavy-electron compounds of UPt₃ below 0.3 K,⁹ and more recently in the 90 K phase of YBa₂Cu₃O₇ which has now been widely discussed in terms of the $d_{x^2-y^2}$ pairing symmetry.¹⁰

In this paper, we present the temperature and field dependence of electronic specific heat in the superconducting state of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br in a temperature range between 0.11 and 4.5 K. Since this contribution is much smaller than that of lattice specific heat, high-resolution experiments and an accurate estimation of lattice specific heat are required. By applying magnetic fields higher than H_{c2} , it may be possible to extract temperature dependences of lattice specific heat. In such experiments, however, some additional terms due to possible paramagnetic localized moments or impurities, often observed as an upturn of C_p/T at low temperatures, show complicated magnetic field dependence and obscure the reliability of lattice specific heat especially below 1 K, which is the most important temperature range to obtain reliable data of electronic specific heat. We have previously reported that the deuterated salt, when cooled rapidly, is situated in the insulating region which does not have any fine γ value by confirming that γ keeps vanishing even in a magnetic field of 8 T.¹¹ This fact justifies a use of the specific heat value of the deuterated salt as the lattice specific heat of the κ -(BEDT-TTF)₂Cu[N(CN)₂]Br salt. By improving resolution of our calorimeter and using the deuterated salt as a proper reference material, we discuss temperature dependence of specific heat due to quasiparticle excitations over the gap in the superconducting state of this material. Its magnetic field dependence in a low field region below 2 T is also presented.

The samples used for this work was grown by electrochemical oxidation method in the so-called H -type cells. We used 1,1,2-trichloroethane as a solvent and applied constant current of 1.0 μ A for about two weeks to obtain single crystals for this calorimetry work. The weight of the crystals used in this study was 4.3 mg for κ -(BEDT-TTF)₂Cu[N(CN)₂]Br sample and 3.7 mg for the deuterated sample. The specific heat measurements were performed with the thermal relaxation calorimeter of ³He type in the temperature range between 0.85 and 4.5 K. The data

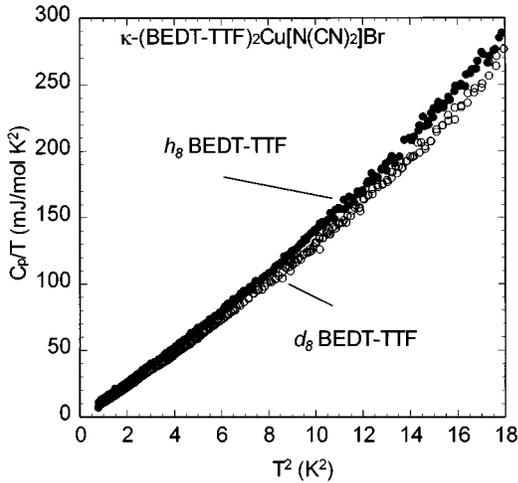


FIG. 1. C_p/T vs T^2 plot for κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br (denoted by h_8 BEDT-TTF) and the rapidly cooled deuterated salt (denoted by d_8 BEDT-TTF) in a temperature range between 0.85 and 4.2 K.

between 0.11 and 1.15 K were obtained by the similar type of calorimeter mounted on a dilution refrigerator.¹² We used a thin sapphire plate ($2 \times 2 \times 0.12$ mm 3) as a bolometer, to which a small chi-type of RuO $_2$ thermometer and a film heater are attached. The bolometer is suspended by thin constantan wires from the copper block. The wires also serve as a heat leak for temperature relaxation. In order to eliminate uncertainties as much as possible, we first measured the heat capacity of bolometer with small amounts of Apiezon N grease typically weighing about 0.1–0.2 mg before the sample is mounted. After this blank measurement a single piece of crystal was set on the bolometer without any additional grease and the total heat capacity was measured. The contribution of bolometer plus grease to the total heat capacity is 90% at 0.2 K, 60% at 0.9 K, and 40% at 4.0 K.

The specific heat per formula unit is displayed in C_p/T vs T^2 plot in Fig. 1. We also show low-temperature data in the same plot in Fig. 2. An appreciable difference between the C_p/T values of the two salts is observable in the whole temperature range studied. The small upturns observed at the lowest temperatures for both salts are due to some tiny impurities and considered not to be intrinsic. In organic materials, contribution of the lattice specific heat which arises from acoustic phonon is still large even at low temperatures, as compared with inorganic compounds. The lattice contribution obeys the T^3 law only in the restricted temperature range below about 2 K and above this temperature it starts to deviate upward from the T^3 dependence due to higher-order contribution as in several BEDT-TTF based salts.^{11–13} Therefore, to estimate γ and β values in the formula of $C_p = \gamma T + \beta T^3$ accurately, low-temperature data below about 2 K is required. The least-square fitting (the solid line in Fig. 2) of the C_p/T vs T^2 data of the present deuterated salt below 1.7 K gives values of $\gamma = 0.06 \pm 0.43$ mJ/molK 2 and $\beta = 12.0$ mJ/molK 4 . The calculated Debye temperature is 212.0 K. This value is very close to the experimental value of the nondeuterated salt in an external field of 14 T determined by Andracka *et al.*¹⁴ According to the Debye theory, Θ_D is in proportion to the sound velocity and therefore in proportion

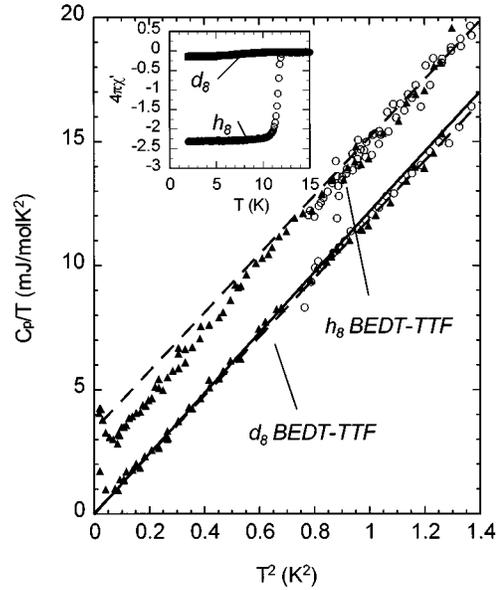


FIG. 2. The low-temperature data of (h_8 BEDT-TTF) and (d_8 BEDT-TTF) salts. The open circles denote data obtained by 3 He refrigerator and the filled triangles denote those obtained by dilution refrigerator. The solid and dashed lines in the figure represent the slope due to the lattice specific heat with $\Theta_D = 212.0$ K and 213.7 K, respectively. The inset shows the real part of ac susceptibility of both salts, with ac field perpendicular to the layers. Demagnetization correction is not made.

to the square root of molecular weight. The difference of 1.7% of molecular weight between deuterated and nondeuterated salts may reasonably give rise to the difference of the Debye temperature and β value. The expected values of these parameters for nondeuterated salts are $\beta = 11.7$ mJ/molK 4 and $\Theta_D = 213.7$ K, which give the dashed line in Fig. 2. Another possible correction may be for a contribution due to the spin wave excitation in the antiferromagnetically ordered state of the deuterated salt. However, it is negligible, since almost all magnetic entropy of $S = R \ln 2$ appears at higher temperatures as two-dimensional short-range ordering dominated by the magnetic coupling of $J = 0.04$ eV, which gives T^2 term with a coefficient smaller than 10^{-2} mJ/molK 3 at low temperatures, just as in the case of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl salt.¹¹ Therefore, by subtracting the contribution of lattice specific heat evaluated using the difference of molecular weight, we can extract the electronic part of C_{el}/T in the superconducting state. The contribution of C_{el} to the total heat capacity including bolometer is 6% at $T = 0.3$ K, 4% at $T = 1.7$ K, and 5% at $T = 2.5$ K. These values are sufficiently larger than the present experimental resolution, better than 1% between 0.11 and 4.5 K. We would like to emphasize that the low-temperature profile of C_{el}/T revealed here is not influenced by possible ambiguity in estimation of the nondeuterated lattice specific heat. At 0.5 K ($T^2 = 0.25$ K 2) for example, one can see in Fig. 2 that the electronic contribution is more than 40% of the total specific heat and is not influenced by ambiguity of the order of 1%, if any, in the lattice part. The downward deviation, especially below about 1.0 K, from the dashed line which is drawn to compare the upper data points with the expected lattice slope for h_8 salt demonstrates the existence of electronic specific

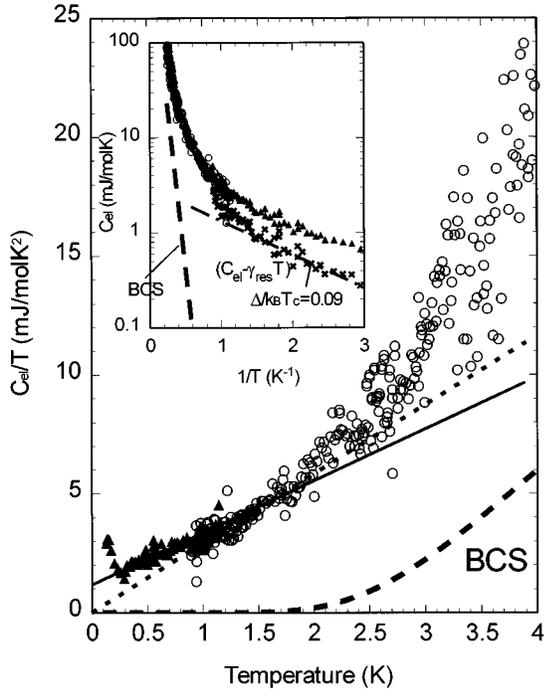


FIG. 3. Temperature dependence of electronic specific heat divided by temperature for κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br. The open circles denote data obtained by 3 He refrigerator and the filled triangles denote those obtained by the dilution refrigerator. The solid line and dotted line stand for the slope of $C_{el}/T = \alpha T$ with $\alpha = 2.2$ mJ/molK 3 and 2.8 mJ/molK 3 (see text). The dashed curve stands for a prediction of BCS weak coupling theory with $2\Delta/k_B T_c = 3.52$. Inset shows an activation plot of C_{el} as a function of $1/T$. The BCS curve is given by the dashed curve and a slope for extremely anisotropic s wave is displayed by dot-dashed line.

heat term discrepant with the $C_p/T = \gamma + \beta T^2$ type of temperature dependence.

Figure 3 shows plot of C_{el}/T vs T . If an isotropic gap of $2\Delta/k_B T_c = 3.52$ exists around the Fermi level as is predicted by the BCS-weak coupling theory, C_{el}/T would show an activation type of temperature dependence such as $\exp(-\Delta/k_B T)$ as shown by the dashed lines, which are far below the experimental values. From the plot in the linear scale, one can see that the low-temperature data of C_{el}/T do not saturate but vary linearly even below 2 K. This means that the C_{el} obeys a quadratic temperature dependence with a coefficient of $\alpha = 2.2$ mJ/molK 3 (the solid line in Fig. 3). An additional feature of the data is that C_{el}/T shows a finite value of $\gamma_{res} = 1.2$ mJ/molK 2 in the limit of 0 K. An explanation of the finite γ_{res} value is made in the context of the unconventional pairing with electron scattering by nonmagnetic centers. In this case, a finite density of states appear around a zero energy in the linear energy dependence expected in the clean case and leads to generation of the γ_{res} term and deviation of the low-temperature variation in C_{el}/T from the clean case.¹⁵ In the present compound, the residual $\gamma_{res} (= 1.2$ mJ/molK 2) is very small compared with the normal state γ_n value, namely $\gamma_{res}(0T)/\gamma_n = 0.05$, and may be reasonably understood by the occurrence of the incommensurate superlattice,¹⁶ which is specific for this compound among κ -(BEDT-TTF) $_2$ X family, or frozen disorder in the ethylene conformation. In reality, the present salt has

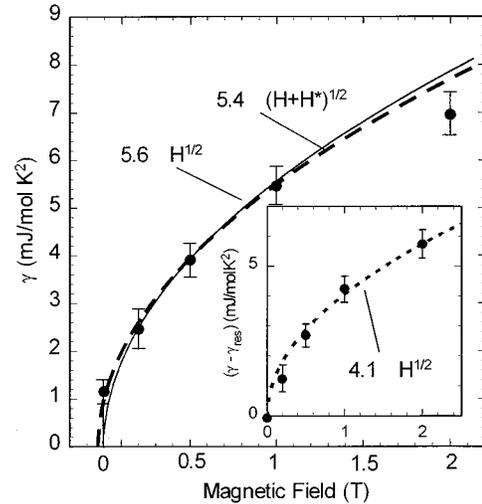


FIG. 4. Field dependence of the γ term in the electronic specific heat. The external fields were applied perpendicular to the conducting layer. The solid and dashed curves show fitted results of the data to $\gamma(H) = AH^{1/2}$ and $\gamma(H) = A(H+H^*)^{1/2}$, respectively. Magnetic field dependence of $(\gamma - \gamma_{res})$ is shown in the inset.

relatively low residual-resistance ratio and show no quantum oscillations at ambient pressure unlike the other salts. In the case of clean unconventional superconductivity with line nodes in the gap, the coefficient in the quadratic temperature dependence, $C_{el} = \alpha T^2$, is predicted to be $\alpha = 3.3k_B \gamma_n / \Delta_{max}$ with Δ_{max} the maximum of the gap in the study of the electronic specific heat of YBa $_2$ Cu $_3$ O $_7$.¹⁰ If we assume, as Δ_{max} , a BCS value mentioned above and use the γ_n value of 22 mJ/molK 2 in Ref. 14, α is predicted to be about 3.5 mJ/molK 3 . The direct comparison of this prediction with the above experimental slope ($\alpha = 2.2$ mJ/molK 3) is not valid because the latter is modified from the value of the clean case by the finite density of states corresponding to the γ_{res} . The dotted line ($\alpha = 2.8$ mJ/molK 3) in Fig. 3 can be taken as the slope of C_{el}/T vs T expected in a clean case without the γ_{res} term for the present salt. In any case, the experimental value of α is of the same order of the theoretical prediction.

The alternative interpretation of the finite γ_{res} is the presence of a normal phase. On this assumption, the electronic specific heat in the superconducting phase is given by $C_{el} - \gamma_{res}T$, which is plotted by crosses in the inset of Fig. 3. There is still a large discrepancy between the data and the BCS behavior. However, there may be a case of an extremely anisotropic s -wave gap with a minimum value of $\Delta_{min}/k_B T_c = 0.09$, which corresponds to the dot-dashed line in the inset.

In order to get further insight into the pairing state, it is quite informative to examine the recovery of the electronic specific heat coefficient, γ , with increasing fields. The $\gamma(H)$ is predicted to be in proportion to the square root of external field, H , for $H_{c1} \ll H \ll H_{c2}$ for superconductivity with line nodes in the gap,¹⁹ while $\gamma(H)$ varies linearly in the gapped state without nodes. Figure 4 shows the field dependence of the γ term in C_{el} . It is seen that the recovery of γ is not linear but can be fitted to a form of $\gamma = 5.6H^{1/2}$ as shown in the solid curve in the figure. The theoretical prediction of the form is $\gamma = k\gamma_n(H/H_{c2})^{1/2}$ with k of order unity. Using the values of $H_{c2} = 10$ T and $\gamma_n = 22$ mJ/molK 2 for the present

salt, the fitted coefficient gives $k=0.80$, which is in agreement with the prediction. In the picture of dirty superconductivity with line nodes, the disorder giving γ_{res} plays essentially the same pair-breaking role as the magnetic field does. In this context, the data of $\gamma(H)$ may be analyzed in a form of $A \times (H + H^*)^{1/2}$ where H^* is an effective field of disorder equivalence. The dashed curve is a fitting to this form, resulting in $A = 5.4 \text{ mJ/molK}^2\text{T}^{1/2}$, $H^* = 3.4 \times 10^{-2} \text{ T}$ and $k = 0.77$. In the picture of two phases, on the other hand, $\gamma(H) - \gamma_{\text{res}}$ is considered to be intrinsic in the superconducting phase. The inset shows fields dependence of this quantity. The nonlinear behavior is fitted by $A \times H^{1/2}$ with $A = 4.1 \text{ mJ/molK}^2\text{T}^{1/2}$, giving $K = 0.59$. In any case, it is evident that $\gamma(H)$ shows a noticeable deviation from linearity but is well described by square root dependence.

These results support the existence of line nodes in the superconducting gap and therefore suggests that the symmetry of electron pairs in this material is unconventional with anisotropic wave function. This is consistent with the NMR experiments.⁶⁻⁸ The existence of line nodes is most reasonably attributable to the two-dimensional $d_{x^2-y^2}$ wave model¹⁷ or anisotropic $d+s$ wave model recently discussed for high- T_c cuprates.¹⁸

In conclusion, we have studied the electronic specific heat of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br salt and found that the low-temperature specific heat can be expressed as $C_p/T = \gamma_{\text{res}}T + \alpha T^2 + \beta T^3$. The observed temperature and field dependence of electronic part are consistent with unconventional superconductivity with line nodes in the gap parameter. The specific heat behavior of superconductors with $T_c = 3-4 \text{ K}$, such as β -(BEDT-TTF)₂AuI₂ (Ref. 13) and κ -(BEDT-TTF)₂I₃ (Ref. 20) were reported to be explained in the frame of BCS theory. If these are true, the comprehensive understanding of the variety of pairing state in BEDT-TTF salts is not straightforward but requires some additional mechanism. It is guessed that the antiferromagnetic spin fluctuations enhanced in the normal state of the present salt^{3,4} have something to do with the unconventional nature of pairing and the T_c enhancement.

The authors thank A. Kawamoto and K. Miyagawa for their useful discussions. The technical support of K. Kato and T. Takayama at the Low-temperature Center of IMS are also acknowledged. This work was financially supported by Grant-in-Aid for Scientific Research Nos. 06452064 and 07649497 from the Ministry of Education, Science, Sports and Culture, Japan.

¹D. Jérôme *et al.*, J. Phys. (Paris) **41**, 98 (1980).

²M. Takigawa *et al.*, J. Phys. Soc. Jpn. **56**, 873 (1987); Y. Hasegawa and H. Fukuyama, *ibid.* **56**, 877 (1987).

³A. Kawamoto *et al.*, Phys. Rev. Lett. **74**, 3455 (1995); Phys. Rev. B **52**, 15 522 (1995).

⁴H. Mayaffre *et al.*, Europhys. Lett. **28**, 205 (1994).

⁵K. Miyagawa *et al.*, Phys. Rev. Lett. **75**, 1174 (1995).

⁶K. Kanoda *et al.*, Phys. Rev. B **54**, 76 (1996).

⁷S. M. De Soto *et al.*, Phys. Rev. B **52**, 10 364 (1995).

⁸H. Mayaffre *et al.*, Phys. Rev. Lett. **75**, 4122 (1995).

⁹D. Jaccard, J. Flouquet, P. Lejay, and J. L. Tholence, J. Appl. Phys. **57**, 3082 (1985).

¹⁰K. A. Moler *et al.*, Phys. Rev. Lett. **73**, 2744 (1994), and references therein.

¹¹Y. Nakazawa and K. Kanoda, Phys. Rev. B **53**, 8875 (1996); it should be noted that the deuterated salt is situated so close to the boundary of metallic phase and insulating phase, that all of the crystals we measured contain superconducting and magnetic insulating phases with comparable volume fraction. (This is not

due to the deteriorated quality of the crystals.) More important for this paper is our finding that the relative fraction seriously depends on the cooling rate through 80 K. [A. Kawamoto *et al.* (unpublished)]. This explains the incompleteness and sample dependence of the superconductivity in earlier reports. In the case of rapid cooling performed in this work and in the above issue, the superconducting volume is negligibly small (less than few percent, see the inset of Fig. 2) as was confirmed by ac magnetic susceptibility and specific heat experiment in the magnetic field.

¹²Y. Nakazawa, A. Kawamoto, and K. Kanoda, Phys. Rev. B **52**, 12 890 (1995).

¹³K. Andres *et al.*, Physica **143B**, 334 (1986).

¹⁴B. Andracka *et al.*, Solid State Commun. **79**, 57 (1991).

¹⁵M. Prohammer *et al.*, Phys. Rev. B **47**, 15 152 (1993).

¹⁶Y. Nogami *et al.*, Solid State Commun. **89**, 113 (1993).

¹⁷D. J. Scalapino *et al.*, Phys. Rep. **250**, 329 (1995).

¹⁸K. Maki and M. T. Beal-Monod, Phys. Lett. A **208**, 365 (1995).

¹⁹G. E. Volovik, JETP Lett. **58**, 469 (1993).

²⁰J. Wosnitzer *et al.*, Phys. Rev. B **50**, 12 747 (1994).