# Specific-Heat Measurements of the Gap Structure of the Organic Superconductors $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu(NCS)_2$

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(Received 26 March 2007; published 30 July 2007)

We present high resolution heat capacity measurements of the organic superconductors $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu(NCS)_2$ in fields up to 14 T. We use the high field data to determine the normal state specific heat and hence extract the behavior of the electronic specific heat $C_{el}$ in the superconducting state in zero and finite fields. We find that in both materials for $T/T_c \lesssim 0.3$, $C_{el}(H = 0) \sim T^2$ indicating $d$-wave superconductivity. The data are well described by a strong coupling $d$-wave model from our base temperature ($T/T_c \sim 0.1$) right up to $T_c$. Our data help to resolve the controversy regarding the order parameter symmetry in these materials.

DOI: 10.1103/PhysRevLett.99.057001 PACS numbers: 74.70.Kn

The organic superconductors $\kappa$-$(ET)_2X$ [ET represents bis(ethylenedithio)-tetrathiafulvalene] have many similarities to the high temperature cuprate superconductors (HTSC) [1]. In both cases, the electronic structure is quasi-two-dimensional and the superconducting phase emerges from an antiferromagnetic insulating (AFI) state as the phase diagram is transversed. In the case of the cuprates, the structure is ''tuned'' away from the AFI state either by varying the oxygen content or making nonisovalent substitutions, whereas in $\kappa$-$(ET)_2X$ it is achieved either by changing the anion $X$ or by applying external pressure. It is natural then to speculate that the mechanism for superconductivity in these two materials may be related even though $T_c$ is up to an order of magnitude higher in HTSC.

A first step towards determining if this is indeed the case is to determine the symmetry of the superconducting energy gap functions in the two families of materials. The case of the cuprates has been very well studied and the overwhelming consensus is that these materials have a gap with predominately $d_{x^2-y^2}$ symmetry [2]. In the organic materials the situation is more controversial [3].

The two most widely studied materials are $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ and $\kappa$-$(ET)_2Cu(NCS)_2$ (hereafter abbreviated to $\kappa$-Br and $\kappa$-NCS) as these have the highest $T_c$ at ambient pressure ($\sim$12 and $\sim$9.5 K, respectively). As yet, no direct phase sensitive determinations of the gap function have been reported; however, there have been numerous experiments which have probed its anisotropy. Some early experimental determinations of the temperature dependence of the penetration depth $\lambda(T)$ reported behavior which was consistent with a $d$-wave gap whereas others were consistent with $s$ wave [3]. The discrepancies stem from experiments not having been carried out at sufficiently low temperature and/or with high enough precision to be conclusive. More recent measurements performed down to $T/T_c \lesssim 0.03$ showed clearly the existence of low energy excitations which were consistent with a $d$-wave gap [4,5]. Thermal conductivity $\kappa(T)$ data shows a low temperature $T$-linear term [6] and a fourfold variation with basal plane angle in an applied magnetic field [7]. Both of these results indicate a $d$-wave gap as do tunneling [8] and NMR experiments [9].

Specific heat $C$ has an advantage over many other techniques in that it is a bulk thermodynamic probe. For example, it is largely insensitive to surface contamination (or thin layers of damaged material) which may adversely affect probes such as $\lambda(T)$ (in the Meissner state) or tunneling. A disadvantage is that the electronic component $C_{el}$ is often only a few percent of the total at $T_c$. It is difficult to accurately extract $C_{el}$ from the total which is dominated by phonon contributions. In Ref. [10] $C_{el}$ of $\kappa$-Br was determined by subtracting an estimate of the phonon contribution obtained from a nonsuperconducting quench cooled deuterated version of the same compound. These authors found that $C_{el} \sim T^2$ as expected for a $d$-wave gap. However, this approach was criticized by Elsinger *et al.* [11] and Müller *et al.* [12] who instead determined the phonon contribution by applying a high magnetic field to destroy the superconductivity. These authors claimed that their data for both $\kappa$-Br and $\kappa$-NCS were well described by an $s$-wave gap. It should be mentioned, however, that in neither of these two reports were explicit attempts made to fit their data to a $d$-wave model.

Here we report high resolution measurements of $C_{el}$ for $\kappa$-Br and $\kappa$-NCS which are well described by a strong coupling model which assumes a $d$-wave form of the superconducting gap. Our data therefore resolves the above-mentioned inconsistency between some previously reported heat capacity measurements [11,12] and other probes of the superconducting gap.

Samples of both compounds were grown by the usual electrochemical method [13] in Argonne, and had masses in the range of 80–600 $\mu$g. Specific-heat measurements were conducted in a purpose built calorimeter which uses a long relaxation method similar to that described in

 

Ref. [14]. Briefly, a Cernox [15] chip resistor (CX-1030-Br) is suspended by silver coated glass fibers in vacuum. The Cernox material acts as both thermometer and heater. The sample was attached to the calorimeter chip with Apiezon N grease. The addenda (chip, grease, and leads) was determined in a separate run immediately prior to the main experiment. The thermometer was calibrated in field, in 1 T increments up to 14 T, by stabilizing the temperature with a capacitance thermometer. The performance of the experiment was extensively studied by measurement of high purity samples of Ag (with masses in the range 0.3–5 mg). In the range 1.3–20 K the absolute values of the Ag data agreed with standard values to within 1%. Small (<4 mK) adjustments to the calibration points were made to ensure that the measured $C$ for all Ag samples were smooth and field independent within experimental error.

Heat capacity data for both materials is shown in Fig. 1. In this raw data the ~3% anomaly at $T_c$ is barely discernible. In order to subtract the large phonon contribution we have made measurements in magnetic fields up to 14 T, applied perpendicular to the basal plane. For both materials, the maximum field is significantly in excess of the upper critical field $H_{c2}$, and so at 14 T both materials are in the normal state. In Fig. 1 we show the low temperature portion of the 14 T data plotted as $C/T$ versus $T^2$. Fitting this with a second order polynomial, we determine the Sommerfeld coefficient $\gamma$ as well as the coefficients of the leading phonon terms, $\beta_3$ and $\beta_5$ ($C = \gamma T + \beta_3 T^3 + \beta_5 T^5$). The field dependence of $\gamma$ is shown in Fig. 1 and is seen to saturate at $\gamma = 28 \pm 2$ mJ/mol K$^2$ for $\mu_0 H \gtrsim 8$ T in $\kappa$-Br and $\gamma = 35 \pm 2$ mJ/mol K$^2$ for $\mu_0 H \gtrsim 3$ T in $\kappa$-NCS. In what follows we make the assumption that the 14 T data are equivalent to that of the normal state in zero field (i.e., the only field dependence in $C$ is due to the superconductivity). In principle, there could be magnetic contributions which vary with field. However, the insensitivity of $C$ to $H$ at high fields indicates that these contributions are negligible. Indeed, in Ref. [16] a sizable magnetic contribution in high field was only found for $T$ well below 1 K.

In Figs. 2 and 3 we show $\Delta C = C(0) - C(14\ \mathrm{T}) = C_{\mathrm{el}} - \gamma T$ for $\kappa$-Br and $\kappa$-NCS, respectively. The superconducting transitions are now clearly visible, with the midpoint of the transition giving $T_c = 12.25$ and 9.56 K, respectively. Note that the noise in the data is larger at higher temperature because the fractional resolution of the calorimeter $\Delta C/C$ is roughly constant with $T$ whereas the phonon background increases $\sim T^3$.

In many superconductors, the weak-coupling form of the BCS theory is inadequate to describe in detail the physical properties. A full solution to the strong coupling theory is

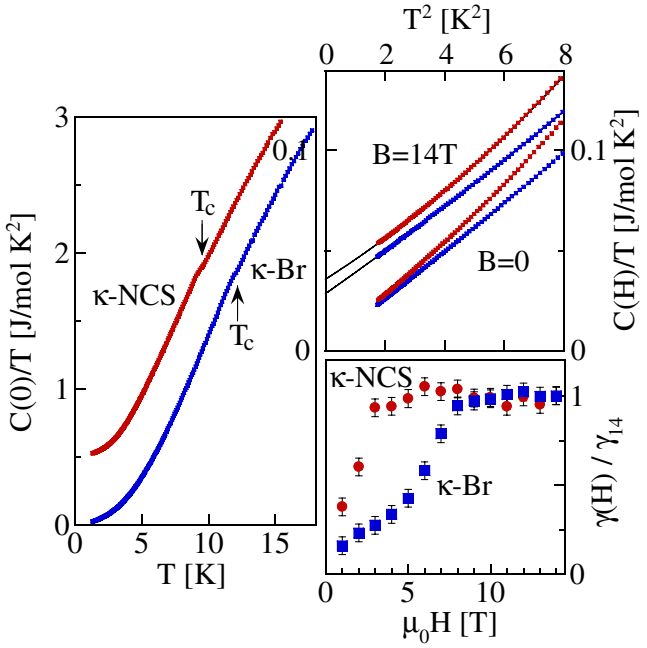


FIG. 1 (color online). Left: Zero field specific-heat data for $\kappa$-Br and $\kappa$-NCS. Upper right-hand panel: $C/T$ vs $T^2$ for both compounds in fields of 0 and 14 T. The upper curve for each field is $\kappa$-NCS. Lower right-hand panel: Field dependence of $\gamma$ for both compounds.

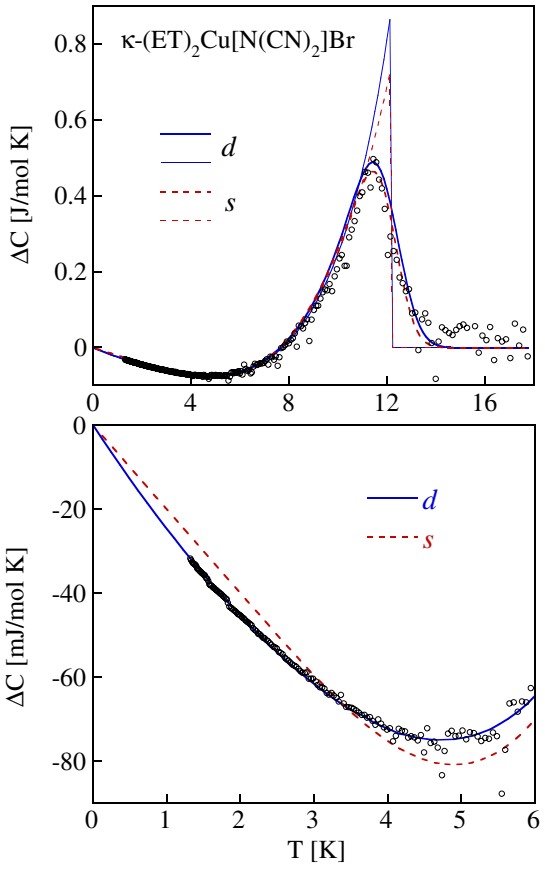


FIG. 2 (color online). Top: $\Delta C = C(0) - C(14\ \mathrm{T})$ vs $T$ for $\kappa$-Br, along with several fits. The thin solid line is a fit to the strong coupling $d$-wave model, whereas the thick solid line is the same fit convoluted with a Gaussian. Similarly, the dashed lines are fits to the strong coupling $s$-wave model. Bottom: Enlarged view of the low temperature part of the upper panel (the convoluted fits are indistinguishable and are omitted for clarity).

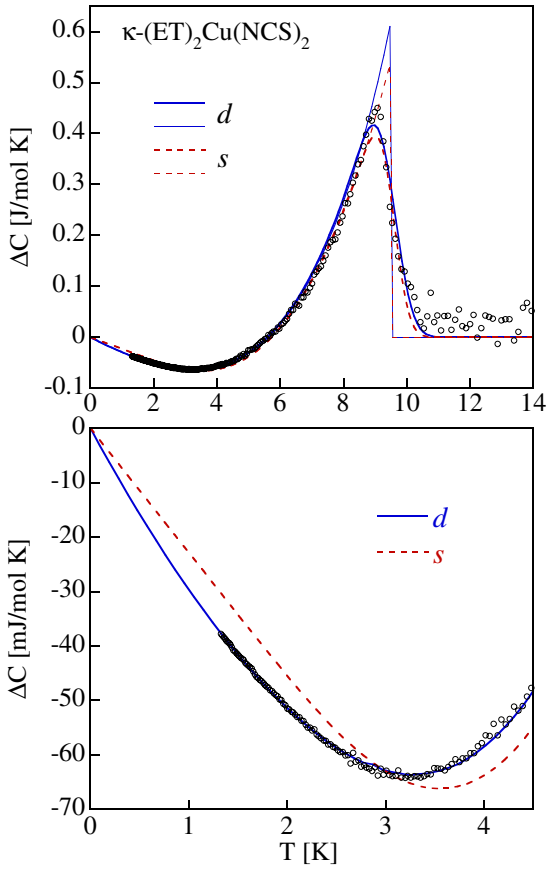


FIG. 3 (color online). The same plots as Fig. 2 but for $\kappa$-NCS.

complicated, and dependent on microscopic details, but it is found that many properties can be explained satisfactorily with the so-called $\alpha$ model [17]. Here, the temperature dependence of the energy gap $\Delta$ is approximated by the weak-coupling behavior but the value at zero temperature is an adjustable parameter. This model has been used to describe a wide range of superconductors including ''exotic'' materials such as $MgB_2$ [18] and $NbSe_2$ [19].

Within the $\alpha$ model, the entropy $S$ in the superconducting state for a two-dimensional cylindrical Fermi surface is given by

$$\frac{S}{\gamma_n T_c} = \frac{3}{\pi^3}\int_0^{2\pi}\int_0^{\infty} f\ln f + [1-f]\ln[1-f]d\varepsilon d\phi, \tag{1}$$

where the Fermi function $f = [\exp(E/k_BT) + 1]^{-1}$, the quasiparticle energy $E^2 = \varepsilon^2 + \Delta^2(\phi)$, $\gamma_n$ is the normal state $\gamma$, and the energy gap $\Delta$ is a function of the in-plane angle $\phi$. The specific heat $C_{\rm el} = T(\partial S/\partial T)$. For conventional isotropic $s$-wave superconductivity the gap function $\Delta(\phi, T) = \alpha\Delta^s_{\rm BCS}(T)$, whereas in the simplest case for $d$ wave $\Delta(\phi) = \alpha\Delta^d_{\rm BCS}(T)\cos 2\phi$. In these expressions $\Delta^{s,d}_{\rm BCS}$ takes the usual $s$- or $d$-wave weak-coupling form.

To allow for the possibility of any part of the sample being nonsuperconducting (and metallic), we allow $\gamma_n$ to vary in the fit, so the free parameters are $\alpha$, $\gamma_n$, and $T_c$. As can be seen in the top panels of Figs. 2 and 3, at high temperatures the fits to the $s$ and $d$ models are virtually indistinguishable and both fit the data very well. Close to $T_c$ the superconducting transition is broadened by inhomogeneity and fluctuation effects and the fit is considerably improved by convolution with a Gaussian (of width $\sigma =$ 0.65 and 0.43 K for $\kappa$-Br and $\kappa$-NCS, respectively).

At lower temperature (bottom panels of Figs. 2 and 3) there is a very significant difference between the two models. The $d$-wave model fits the data almost exactly over the full temperature range whereas the $s$-wave model completely fails at low temperature. The parameters derived from the fits are given in Table I. In both materials, for the $d$-wave fit $\gamma_n$ is found to be very close to the value found from the direct fit to the 14 T data $\gamma_{14}$, whereas the $s$-wave fit is about 30% smaller. If $\gamma_n$ were fixed at $\gamma_{14}$ the $s$-wave fit would be considerably worse. Clearly, optimizing $\gamma_n$ for a fit to the low temperature data will not significantly improve the $s$-wave fit. The values of $\alpha$ found show that the $d$-wave coupling is rather strong.

The difference between the $s$-wave and $d$-wave fits is perhaps shown more clearly in Fig. 4, where we have plotted $\Delta C/T$ versus $T/T_c$. In the low temperature limit, the clean $d$-wave model predicts $C_{\rm el} \sim T^2$ so we expect $\Delta C/T \simeq aT - \gamma_n$. The $s$-wave model predicts $\Delta C/T \simeq a'T^{-5/2}\exp(-\Delta_0/k_BT) - \gamma_n$. The lines on the figure are the same fits as in Figs. 2 and 3. Figure 4 shows that below $T/T_c \simeq 0.3$ $\Delta C/T$ varies linearly with $T$, and the full $d$-wave model fits the data over the full temperature range. Again, clearly the $s$-wave model does not fit the data at low temperature. A linear fit to the $\Delta C/T$ for $T/T_c < 0.3$ gives $a = 2.33 \pm 0.03$ mJ/mol K$^3$ and $a = 4.21 \pm 0.04$ mJ/mol K$^3$ for $\kappa$-Br and $\kappa$-NCS, respectively.

The data in this Letter are representative of results taken on a large number of different crystals. In total, 6 samples of $\kappa$-Br (with $T_c$ values in the range $11.5 < T_c < 12.4$ K) and 3 samples of $\kappa$-NCS (with $T_c$ values in the range $9.3 < T_c < 9.6$ K) were measured and all were found to have the same behavior as that reported here. For $\kappa$-Br it is known that fast cooling through the temperature region 60–85 K depresses $T_c$ [20]. The sample reported here was cooled very slowly (at 0.72 K/h) through this region. Data were also taken for higher cooling rates, which we find significantly decreases $\gamma_n$ and $T_c$ but leaves the $T$ dependence of $C$ unchanged, except close to $T_c$. These results will be reported in detail separately.

TABLE I. Parameters derived from the $s$- and $d$-wave fits to the data in Figs. 2 and 3. The units of $\gamma$ are mJ/mol K$^2$. $\gamma_{14}$ is the value of $\gamma_n$ derived from a fit to the 14 T data. The maximum gaps at zero temperature $\Delta_0 = 2.14\alpha k_BT_c$ for the $d$-wave fits.

| | | | $d$ wave | | $s$ wave | |
|---|---|---|---|---|---|---|
| | $T_c$ | $\gamma_{14}$ | $\alpha$ | $\gamma_n$ | $\alpha$ | $\gamma_n$ |
| $\kappa$-Br | 12.25 K | 28 ± 2 | 1.73 | 26.6 | 1.47 | 20.0 |
| $\kappa$-NCS | 9.56 K | 35 ± 2 | 1.45 | 33.3 | 1.34 | 22.8 |

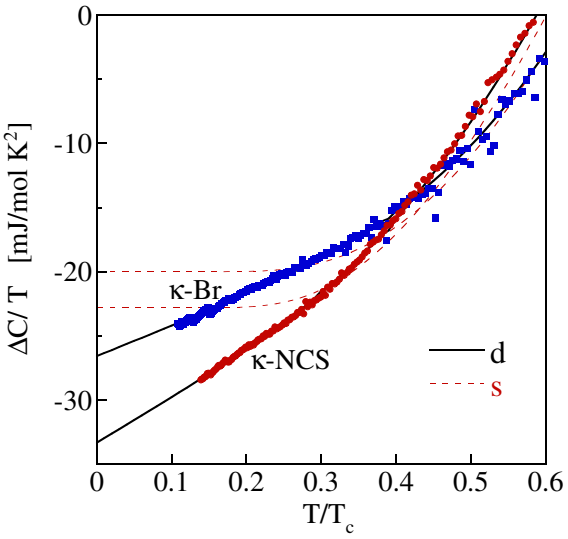


FIG. 4 (color online). $\Delta C/T$ vs $(T/T_c)$ for $\kappa$-Br and $\kappa$-NCS. The solid lines are fits to the $d$-wave model and the dashed and dotted lines are the $s$-wave fits for each compound, respectively.

Within the $d$-wave model, by linearizing the angle dependence of the gap near the nodes it can be shown that at low temperature, for a two-dimensional cylindrical Fermi surface, $C_{\rm el}/T^2 = 54\zeta(3)k_B\gamma_n/\pi^2\mu\Delta_0$, where $\mu\Delta_0 = d\Delta(\phi)/d\phi|_{\rm node}$. Hence, the coefficient of the $T^2$ term in the specific heat determines only the slope of the energy gap near the nodes, $\mu\Delta_0$. In general, the energy gap may not simply vary like $\cos(2\phi)$ and so $\mu$ may differ from 2. We have considered this possibility by fitting the data to a linearized gap model, where $\Delta(\phi) = \mu\Delta_0\phi$ for $|\phi - \frac{\pi}{4}| < \frac{1}{\mu}$ and $\Delta(\phi) = \Delta_0$ otherwise. The behavior of the data at $T/T_c \gtrsim 0.3$, in particular, the size of the jump at $T_c$, constrains the values of $\mu = 2.0 \pm 0.4$, although clearly this depends, to some extent, on our assumed weak-coupling form of $\Delta(T)$.

We have also considered the possibility of a mixed order parameter, or more generally an anisotropic gap which does not go to zero at the "nodes"; for example, $d_{x^2-y^2} + i\epsilon s$. Our data constrains $\epsilon \lesssim 0.1$, so the minimum gap at the nodes is $\lesssim 10\%$ of the maximum.

The main difference between this and previous studies is that our noise level is considerably lower. The data of Elsinger *et al.* [11] for $\kappa$-Br and Müller *et al.* [12] for $\kappa$-NCS cover a similar range of temperature and field to that here. However, their noise level is $\sim$10 times higher, which makes it much more difficult to distinguish between the $s$ and $d$ models. The data of Nakazawa *et al.*[10] for $\kappa$-Br cover a lower temperature range. Between $\sim$0.3 and $\sim$2 K they find that $C_{\rm el}$ follows a $T^2$ power law with slope ($a$) very similar to that reported here. For $T \gtrsim 2$ K their data deviate markedly from ours presumably because of the above-mentioned uncertainties in their phonon subtraction which become more important at higher temperature.

We find that our $d$-wave model also accounts well for the superfluid density data of Le *et al.* [5]. A fit to their data gives $\alpha = 1.7 \pm 0.2$ and $\alpha = 1.4 \pm 0.2$ for $\kappa$-Br and $\kappa$-NCS, respectively. These values are consistent with those found here. A quantitative analysis of the penetration depth data of Ref. [4] is complicated by uncertainties in the assumed value of the penetration depth at zero temperature; however, the measured temperature dependence of $\lambda$ is in very good agreement with predictions from the current model, once impurity effects are included.

In conclusion, we have measured the specific heat of an extensive set of samples of $\kappa$-Br and $\kappa$-NCS and find that in all cases the data are well fitted by a strong coupling $d$-wave model. Our data firmly rule out an isotropic $s$-wave gap in these samples.

Work at Argonne National Laboratory is sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract No. DE-AC02-06CH11357.

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