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Specific heat of the organic superconductor κ-(BEDT-TTF)$_2$I$_3$

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We present high-resolution specific-heat, C, measurements on a large (4.47 mg) single crystal of κ-(BEDT-TTF)$_2$I$_3$ from 0.25 to 20 K in zero and different magnetic fields. The electronic specific-heat coefficient in the normal state is extracted to $\gamma = (18.9 \pm 1.5)$ mJ K^{-2} mol^{-1}. For the ratio $\Delta C/(\gamma T_c)$, where ΔC is the jump of C at $T_c = 3.4$ K, a value of 1.6 ± 0.2 consistent with the BCS prediction of 1.43 is found. The exact form of $\Delta C(T)$, the specific-heat difference between the superconducting and the normal state, however, deviates somewhat from the BCS dependence but might be explained by strong coupling. In magnetic fields applied perpendicular to the highly conducting b-c plane the height of the jump in C is strongly reduced and broadened with a concomitant reduction of T_c. In a field of $B = 0.5$ T above B_{c2} at low temperatures a hyperfine contribution to C is found which is larger than the value expected by nuclear hyperfine interaction alone.

I. INTRODUCTION

Organic metals like the quasi-one-dimensional (1D) Bechgaard salts or the quasi-two-dimensional (2D) materials as, e.g., BEDT-TTF (=ET or bisethylenedithiotetrathiafulvalene) show a remarkable variety of unusual physical phenomena. Especially the properties of the up to date approximately 50 superconducting organic materials[1] have received broad attention. One of the prime questions still under considerable discussion is the nature of the superconducting state. Experimental results are often controversial and both BCS-like and unconventional behavior have been suggested.[2]

One thermodynamic property, the specific heat C, however, has very rarely been investigated in these materials. One problem here might be that the available crystals mostly are very small with masses less than 1 mg. Another difficulty evolves from the low density of electrons which makes it very hard to resolve the superconducting jump ΔC at T_c from the phonon background. To date, only a few measurements of C near T_c are known.[3–8] These experiments seem to indicate an almost BCS-like behavior with a value of $\Delta C/\gamma T_c$ close to the BCS prediction 1.43, respectively, a tendency to slightly stronger coupling.[4,5,7] In most of these measurements, however, a collection of crystals was glued together onto the sample holder to increase the heat-capacity contribution from the sample with respect to the addenda. In this investigation we used one large (4.47 mg) single crystal of κ-(ET)$_2$I$_3$ and extended our study down to very low temperatures (~ 0.2 K).

(ET)$_2$I$_3$ is the organic salt that exhibits the most different phases. In this stoichiometry up to six modifications of this compound with sometimes strongly different physical properties and largely varying T_c are known.[1] κ-(ET)$_2$I$_3$ has the relatively moderate superconducting transition temperature of $T_c \approx 3.4$ K. Other ET salts of the κ phase, however, show the highest T_c (up to approximately 13 K) of the 2D organic materials known to date.[9] Nevertheless, the lower T_c of κ-(ET)$_2$I$_3$ allows a somewhat better resolution of the specific-heat jump because of the lower Debye contribution to C at this temperature. On the other hand, we could extend our measurements to low enough temperatures to fully see the vanishing of the electronic contribution to C in the superconducting state. Furthermore, measurements in high magnetic fields above B_{c2} allowed the extraction of the Sommerfeld coefficient γ of the electrons in the normal state.

II. EXPERIMENT

The crystal measured in this work has been prepared electrochemically in the standard way described earlier.[10] The specific heat was measured with the standard heat-pulse technique both in a ^{4}He and a dilution refrigerator. Both cryostats are equipped with superconducting magnets for fields up to 6 T. In the ^{4}He cryostat the sample was glued with a small amount of Apiezon N grease onto a sapphire plate. An evaporated manganin film serves as a sample heater and a calibrated RuO$_2$-SMD (surface mounted device) resistor which is glued to the sapphire is used as a thermometer. In the dilution refrigerator a small silver foil with a Pt-W heater was especially prepared as a sample holder for the measurement. Here a Matsushita carbon resistor was used as sample thermometer. In both cases the temperature was measured with a high-resolution ac resistance bridge. With this bridge we could reach an absolute temperature resolution of the order $\delta T/T \approx 10^{-5}$ that allowed us to reduce the temperature steps in each heating pulse especially close to T_c to much less than $\Delta T/T = 1\%$. The empty sample holders were measured separately, the silver foil also in $B = 0.5$ T, to obtain a reliable value of the addenda contribution. For $B = 0$ and $T \leq 0.5$ K the addenda was too large ($\geq 90\%$) to resolve C of the sample. Therefore, these data are omitted in the following. For higher temperatures and fields, however, the sample contributed up to approximately 50% to the total heat capacity. The overall accuracy of the absolute value of C conservatively estimated is 5%, the relative accuracy $\Delta C/C \approx 0.5\%$.

III. RESULTS AND DISCUSSION

The specific heat of κ-$(ET)_2I_3$ in $B = 0$ and 0.5 T over the whole investigated temperature range is shown in Fig. 1. At $T_c = 3.4$ K the anomaly in C is hardly visible on the large phonon background. At temperatures below ~ 6 K, C is somewhat steeper than the usual Debye T^3 law. At higher temperatures C levels off towards a weaker T dependence (cf. also Fig. 3). In a magnetic field of 0.5 T, sufficient to suppress the superconductivity completely for B perpendicular to the highly conducting b-c plane, a somewhat unexpected behavior is observed. Towards low temperatures below $T \approx 0.4$ K, C is increasing again. This part of the specific heat is shown in Fig. 2 in an enlarged scale (only the data taken in the dilution refrigerator are shown). The solid line is a fit to the data of the form

$$C = a_{hf} T^{-2} + \gamma T + \beta T^3 + \delta T^5 \; . \tag{1}$$

Thereby the first term represents the high-temperature tail of a Schottky anomaly due to hyperfine interaction and γ is the Sommerfeld coefficient of the electronic

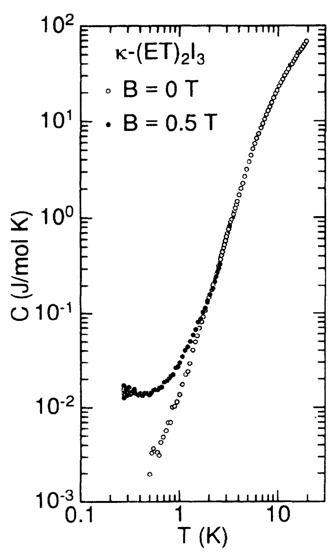

FIG. 1. Specific heat of κ-$(ET)_2I_3$ in zero field and in $B = 0.5$ T applied perpendicular to the highly conducting b-c plane.

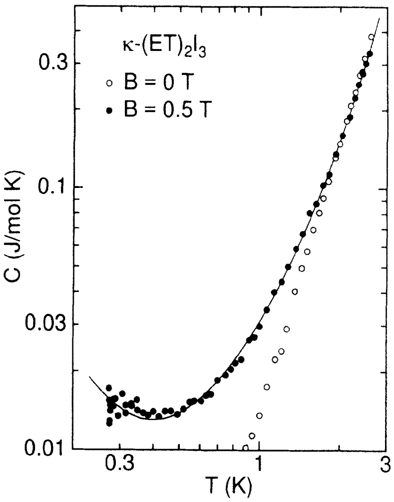

FIG. 2. Low-temperature part of the specific heat of κ-$(ET)_2I_3$. The solid line is a fit with (1) as described in the text.

specific heat in the normal state. The phonon contribution to C is approximated with the cubic Debye term and a T^5 term describing higher-order deviations from the Debye law. The coefficients for the fit shown in Fig. 2 are $a_{hf} = (0.77 \pm 0.05)$ mJ K mol^{-1}, $\gamma = (18.9 \pm 1.5)$ mJ K^{-2} mol^{-4}, $\beta = (10.3 \pm 1)$ mJ K^{-4} mol^{-1}, and $\delta = (1.03 \pm 0.2)$ mJ K^{-6} mol^{-1}. The only possible origin for the low-temperature Schottky anomaly seems to be the hyperfine interaction of the nuclear magnetic moments with the applied external magnetic field. No T^{-2} contribution, whatsoever, was found in the measurement for $B = 0$ (see Fig. 1). The coefficient due to magnetic hyperfine interaction can be calculated by[11]

$$a_{hf} = R \sum_i a_i \frac{I_i + 1}{3 I_i} \left[\frac{\mu_i B}{k_B} \right]^2 , \tag{2}$$

where R is the gas constant, k_B is the Boltzmann factor, a_i is the natural abundance of the nucleus i with spin I_i and magnetic moment μ_i. In κ-$(ET)_2I_3$, the main contribution to a_{hf} comes from the eight hydrogen of the ethylene groups with $I_1 = \frac{1}{2}$ and $\mu_1 = 2.79\ \mu_N$, where μ_N is the nuclear magnetic moment. An additional contribution comes from the iodine (^{127}I) with $I_{127} = \frac{5}{2}$ and $\mu_{127} = 2.808$. All other nuclei either have no nuclear magnetic moment or the natural abundance is negligible. The result in $B = 0.5$ T is $a_{hf} = 0.02$ mJ K mol^{-1}, a value by far too small compared to the measured hyperfine contribution. Other specific-heat measurements of different ET salts in applied magnetic fields show no signs of a hyperfine contribution. This result, however, is somewhat surprising especially for one experiment where C of κ-$(ET)_2Cu[N(CN)_2]Br$ up to 14 T and down to 1.25 K was measured.[7] In this measurement the hyperfine contribution of the hydrogen atoms calculated with (2) principally should have shown up. This, on the other hand, is evidence that for κ-$(ET)_2I_3$ in an applied magnetic field, an additional magnetic contribution to C is present. The origin, however, of the large hyperfine coefficient a_{hf} is unclear at the moment.

The value of the linear coefficient γ is slightly lower than values obtained for other compounds of the ET group[3,4,6,7] where γ was found in the range between (22 ± 3) mJ K^{-2}mol^{-1} for κ-$(ET)_2Cu[N(CN)_2]Br$ and (29 ± 2) mJ K^{-2}mol^{-1} for κ-$(ET)_2NH_4Hg(SCN)_4$. In these investigations, however, γ and β are always extracted from a rather limited temperature range. As can be seen by the investigation presented here the usual linear fit of C/T vs T^2 yields quite ambiguous results depending on the field and temperature range where the fit is employed. Therefore, Eq. (1), taking into account the low-temperature hyperfine contribution and the deviation from the Debye T^3 behavior at higher temperatures, was used to obtain the most reliable results for γ and β.

On a piece of the same sample where the specific-heat measurements were done, de Haas-van Alphen (dHvA) studies were also made.[12] In agreement with previous investigations[13] a dHvA frequency of $F_0=(3860\pm20)$ T and an effective mass of $m_0=(3.9\pm0.1)m_e$ for the field applied perpendicular to the b-c plane was obtained. With the assumption of a circular Fermi surface,[14] i.e., $\varepsilon_F=\hbar^2A_k/2\pi m_0$, where ε_F is the Fermi energy and $A_k=(2\pi e/\hbar)F_0$ is the area of the Fermi surface, the Sommerfeld coefficient for a 2D electron gas $\gamma=\pi^2Rk_B/3\varepsilon_F=(20.5\pm0.5)$ mJ K^{-2}mol^{-1} is obtained. Calculation of γ directly with the 2D free-electron model and an effective mass of 3.9 m_c yields a value of 20.9 mJ K^{-2}mol^{-1}. These results are in excellent agreement with the specific-heat value. Obviously, κ-$(ET)_2I_3$ can be very well described by the 2D free-electron model.

The Debye temperature is $\Theta_D=(\frac{12}{5}\pi^4Rnl\beta)^{1/3}=(218\pm7)$ K, where n is the number of atoms per formula unit [55 for κ-$(ET)_2I_3$]. This is within the range of Θ_D values reported so far for the ET compounds.[3,4,6–8] As mentioned before, in κ-$(ET)_2I_3$ a clear deviation from the simple Debye T^3 behavior is observed. For the data below approximately 3 K this fact was taken into account by the additional T^5 term (cf. Fig. 2). This additional phonon contribution can be seen more clearly in the inset of Fig. 3 where C/T^3 vs T is plotted. Besides the sharp anomaly around the superconducting transition at $T_c\approx3.4$ K which is now clearly visible the specific heat shows an enormous peak at approximately 6 K (note that in Fig. 3 a Debye T^3 behavior would yield a constant value of T). Obviously, in κ-$(ET)_2I_3$ low-lying phonon excitations with presumably a very small dispersion are present. A fit assuming Einstein-like excitation spectra can be used to give a rough description of the excess phonon specific heat by

$$C_{\text{exc}}=N_Ek_B\left[\frac{\Theta_E}{T}\right]\frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T)-1]^2}\ , \tag{3}$$

where Θ_E is the characteristic Einstein temperature and N_E represents the number of Einstein modes per mol. A reasonable fit was obtained with $\Theta_E=28$ K and $N_E=1.4\times10^{24}$ mol^{-1}, which would account for approximately an optical-phonon triplet at the low energy of ~2.3 meV, respectively ~19.4 cm^{-1}. For other phases of $(ET)_2I_3$ around this wave number, optical modes probably due to librations of the ET molecules were observed by resonant Raman scattering.[15]

The main frame of Fig. 3 shows the specific heat close to the phase transition in 0 and fields up to 0.05 T. Already in these moderate fields $T_c(B)$ is strongly reduced (cf. also Fig. 5). The specific-heat anomaly is very much broadened and reduced in intensity reminiscent of the behavior observed in cuprate high-T_c material.[16,17] For $B=0$, $T_c=3.4$ K, and a height of the specific-heat jump at T_c of $\Delta C=(103\pm10)$ mJ K^{-1}mol^{-1} was extracted from a plot of C/T vs T taking into account the usual equal entropy (=area) condition. With these results $\Delta C/\gamma T_c=1.6\pm0.2$ is obtained which is in full accordance with the BCS value of 1.43. However, a closer examination of the jump in C reveals some distinctive deviations from the simple BCS behavior. In order to calculate $\Delta C(T)=C_S(T)-C_N(T)$, the specific-heat difference of C in the superconducting and the normal state, we estimated C_N by subtracting the hyperfine contribution which is not present in $B=0$ from the data in $B=0.5$ T, and fitting the rest up to 5 K by a polynomial. Subtraction of the resulting curve from the data in the zero field yields the data shown in Fig. 4 together with the BCS fit[18] as the solid line. Below T_c a clear deviation of fit and data can be seen. Obviously, with decreasing temperature the electronic specific heat of the quasiparticles is vanishing faster than predicted by BCS. This kind of behavior is more typical for a superconductor with strong coupling. Indeed, tunneling measurements on the β phase of $(ET)_2I_3$ have yielded an electron-phonon coupling constant λ of approximately 1.[19] However, from dHvA experiments on other ET compounds[20] a λ of the order 0.25 was estimated suggesting rather weak-coupling limit.

Comparing our results with the high-precision data of Graebner *et al.*[5] for κ-$(ET)_2Cu(NCS)_2$ we realized that the apparently good BCS-like behavior of C in this com-

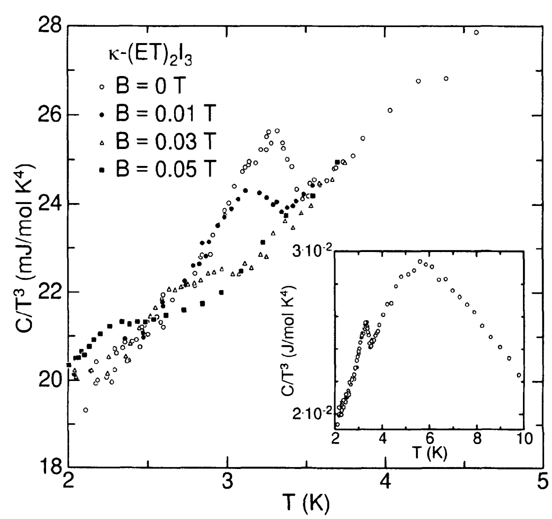

FIG. 3. Specific heat divided by T^3 vs T close to the superconducting transitions in zero and three fields up to $B=0.05$ T. The inset shows in an enlarged temperature range the strong deviation of the zero-field data from simple Debye T^3 law.

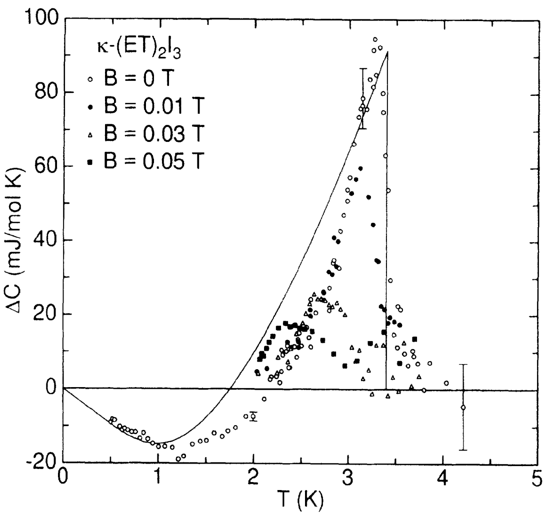

FIG. 4. Specific-heat difference ΔC between superconducting and normal C for zero and three fields up to $B = 0.05$ T. The solid line represents the BCS-like specific-heat anomaly with the measured $\gamma = 18.9$ mJ K^{-2} mol^{-1}.

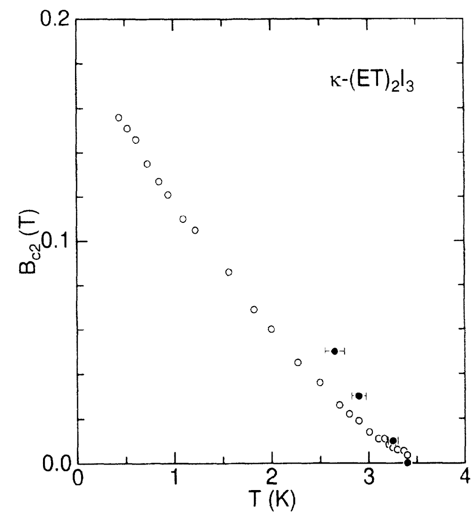

FIG. 5. Upper critical field B_{c2} of κ-(ET)$_2$I$_3$ obtained by ac-susceptibility (open circles) and specific-heat measurements (closed symbols).

pound (cf. Fig. 3 of Ref. 5) with the fitted $\gamma = 36$ mJ K^{-2} mol^{-1} (Ref. 21) is accidentally obtained through a wrong BCS-fit to the data. Taking the tabulated data of Mühlschlegel[18] where T/T_c and $C_S/\gamma T_c$ (not $C_S/\gamma T$) is given ΔC should be zero for $T \approx 0.5 T_c$ (see Fig. 4). The data for κ-(ET)$_2$Cu(NCS)$_2$, however, cross $\Delta C = 0$ at $T/T_c \approx 0.66$ (Ref. 5). For κ-(ET)$_2$I$_3$ this crossing is found for $T/T_c \approx 0.63$, respectively, $T \approx 2.15$ K (see also Fig. 2). Therefore, except for the strongly more rounded phase transition in κ-(ET)$_2$Cu(NCS)$_2$ (Ref. 5) the overall dependence of $\Delta C(T)$ is very similar for these two compounds but clearly different from the simple BCS behavior.

Although the measured sample was of excellent quality, as is definitely proven by the observation of dHvA oscillations and the extracted Dingle temperature of $T_D \approx 0.5$ K,[12] the anomaly in $B = 0$ at T_c is strongly rounded. This fact also cannot be explained by experimental resolution. One possible explanation for this observation are fluctuation effects which should become increasingly dominant for strong type-II superconductors with short coherence length.[22] Especially, in an applied magnetic field the fluctuation regime should increase considerably according to the field-dependent Ginzburg criterion.[23] This broadening effect has very recently been verified by magnetization measurements of κ-(ET)$_2$I$_3$ in fields down to 1 μT.[12] These experiments have shown that already the earth field of approximately 50 μT (also present in the C data at $B = 0$) broadens the transition width by ~ 0.2 K. Therefore, even the zero-field data might have effectively been influenced by the earth field. The strong two dimensionality of the ET salts seems to increase the fluctuation regime further. In cuprate high-T_c materials different attempts were made to describe the rounded specific-heat anomaly for $B = 0$ with either Gaussian corrections to mean-field theory[16] or very recently with a fit known for the critical behavior of the conventional XY model.[17] In addition, the C data in a magnetic field have tried to scale on the basis of the Ginzburg-Landau fluctuation theory for 3D superconductors,[22] respectively, 3D XY scaling.[17] The former scaling has successfully been employed for magnetization data of κ-(ET)$_2$Cu(NCS)$_2$.[24] In the present case for κ-(ET)$_2$I$_3$ the C data also seem to scale slightly better with the method as described in Ref. 22. However, the very small C contribution of the critical fluctuations in the applied fields and the still not negligible scatter of the data hampers the distinctive decision between the different models. Altogether, however, the field and temperature dependence of the fluctuating C close to T_c in the ET compounds is strongly reminiscent of the behavior found in the cuprate superconductors.

The last point we want to discuss is the magnetic phase diagram obtained by specific heat and ac-susceptibility (χ) measurements.[12] Figure 5 shows $B_{c2\perp}$ vs T for fields applied perpendicular to the highly conducting b-c plane. The data extracted from the specific heat are obtained by the equal area condition in a plot of C/T vs T assuming an ideal mean-field jump at T_{c2}. These data are lying fairly well on a straight line with a slope of $\Delta B_{c2\perp}/\Delta T \approx 0.067$ T/K, whereas the χ data show an upward curvature towards lower temperatures often found in resistivity and χ measurements of organic superconductors. This discrepancy is thought to be due to flux-flow effects. χ presumably measures the irreversibility line rather than the true $B_{c2\perp}$.[24] Therefore, the critical field at $T = 0$ can only be approximated to $B_{c2\perp}(0) = (0.18 \pm 0.02)$ T. With this value the correlation length within the b-c plane $\xi_\parallel \approx 43$ nm is calculated using the relation $B_{c2\perp} = \Phi_0 / 2\pi\xi_\parallel^2$.

IV. SUMMARY

In conclusion, high-resolution specific-heat measurements of κ-(ET)$_2$I$_3$ are presented. Although the value of $\Delta C/\gamma T_c = 1.6 \pm 0.2$ seems to be consistent with the BCS prediction the exact shape of the anomaly deviates clearly from BCS behavior. The superconducting transitions, especially in applied fields, are broadened indicating the importance of fluctuation effects due to the reduced dimensionality. In a field above B_{c2} a hyperfine contribution to C larger than expected from the nuclear magnetic moments of the involved isotopes is found. The critical fields determined from C measurements deviate from values obtained by ac-susceptibility measurements showing the importance of flux flow in the ET salts even at this comparatively low temperature.

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