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Superconductor-insulator phase separation induced by rapid cooling of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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We present measurements of the low-temperature specific heat of single crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br as a function of the cooling rate through the glasslike structure transition at ~80 K. We find that rapid cooling produces a small ($\lesssim$4%) decrease in the superconducting transition temperature accompanied by a substantial (up to 50%) decrease in the normal-state electronic specific heat. A natural explanation of our data is that there is a macroscopic phase separation between superconducting and insulating regions in rapidly cooled samples.

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Organic superconductors based on the BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene] molecule (also abbreviated to ET), with general formula (BEDT-TTF)$_2X$, are composed of conducting cation (ET) layers separated by "insulating" anion (X) layers. The weak overlap between the conducting layers means that their electronic properties are quasi-two-dimensional. These materials display a rich phase diagram as a function of temperature and pressure. For example, at low temperature and ambient pressure κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl is an antiferromagnetic insulator (AFI). Application of moderate pressure (~300 bars) causes an insulator-superconductor (IS) transition with a maximum $T_c \simeq 13$ K.[1] Close to this transition there is multiphase region where the superconducting and insulating phases coexist.[1,2] There is strong evidence that the superconductivity is unconventional, with d-wave-like nodes in the superconducting energy gap.[3,4] Although the phase diagram is similar to the high-T_c cuprate superconductors, here the pressure-induced IS transition is caused by a reduction of the ratio of on-site Coulomb repulsion U to the conduction electron bandwidth W, rather than a change in carrier density.[3,5,6] The position at ambient pressure of different compounds in the series is controlled by the anion and/or the degree of deuteration of the ET molecules, both of which can be thought of as applying "chemical pressure."

A widely studied member of the κ-phase materials is κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (κ-Br), which is a superconductor with a T_c of ~12.4 K. At ambient pressure κ-Br sits close to the AFI phase boundary and deuteration causes it to move even closer to this boundary.[7] At $T_g \simeq 77$ K there is a glasslike structural transition[8] and the cooling rate through this temperature strongly effects the normal- and superconducting-state properties. The nature of this structural transition is unclear. A widely held hypothesis is that it is associated with a configuration change in the order of the terminal ethylene groups of the ET molecules.[8] Although this theory is supported by the existence of an isotope effect on T_g, a recent high-resolution x-ray structural study[9] found that, even in fast-cooled samples, the ethylene groups are almost completely ordered at the lowest temperatures (9 K). It was suggested that the disorder may instead be associated with the polymeric anion chain.[9]

One consequence of rapid cooling through T_g in this compound is a reduction in the superconducting transition temperature T_c.[10,11] This effect has been shown to vary over four orders of magnitude of cooling rate.[10] Magnetization measurements have shown that fast cooling also causes a marked decrease in the magnetic screening which was interpreted as either a decrease in the superconducting volume fraction or an increase in the magnetic penetration depth λ.[12] Scanning microregion infrared reflectance spectroscopy (SMIRS) measurements[13] have shown evidence for macroscopic insulating and metallic region phase separation at the *surface* of fast-cooled samples. In deuterated κ-Br ^{13}C-NMR (Ref. 14), and magnetoresistance measurements[7] show evidence for phase separation even in slowly cooled samples.

In this paper, we report measurements of the specific heat of single crystals of κ-Br as the cooling rate through T_g is varied from ~0.02 K/min to ~100 K/min. By applying a large magnetic field ($\mu_0 H = 14$ T) perpendicular to the conducting planes we can suppress the superconductivity and study the evolution of the normal-state electronic specific heat. We find that the Sommerfeld constant γ is reduced by up to a factor of 2 by fast cooling which we suggest is caused by insulating and metallic region phase separation occurring throughout the bulk of the whole sample.

Single crystals of κ-Br were grown by a standard electrochemical technique.[15] The specific heat was measured using a "long-relaxation" calorimetry technique[4,16] using a bare Cernox[17] chip as the sample platform, heater, and thermometer. The performance of the calorimeter was extensively checked by measuring samples of Ag. The maximum absolute error was $\sim \pm 1\%$. The field dependence of the Cernox thermometer was measured against a capacitance thermometer and checked by measuring the specific heat of Ag which is virtually field independent in our temperature range.

Two samples of κ-Br were measured. Sample A had a mass of 249 μg and dimensions $0.66 \times 0.61 \times 0.30$ mm^3 (the shortest dimension is the low-conductivity b axis) and sample B had a mass of 545 μg and dimensions $0.90 \times 0.85 \times 0.35$ mm^3. These samples were repeatedly cooled down from $T = 85$ K to $T = 65$ K, which is the temperature range of the glass transition,[8] at cooling rates between 0.02 K/min and ~100 K/min, then to $T = 1.3$ K at the

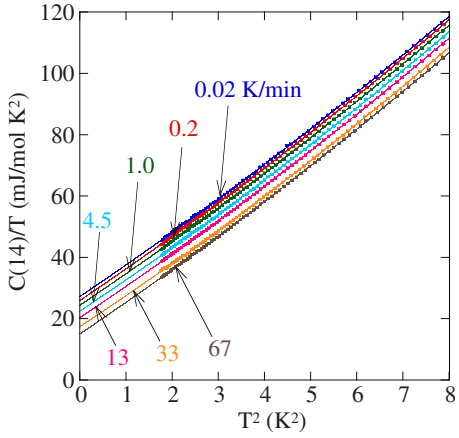

FIG. 1. (Color online) Low-temperature normal-state specific heat measured in a field of 14 T for sample A after it had been cooled, through the glass transition region (85–65 K), at the different rates indicated. The lines are second-order polynomial fits.

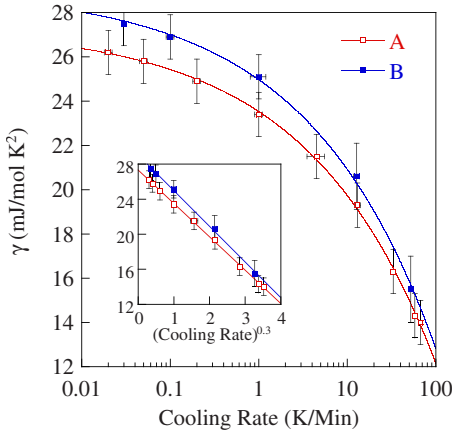

FIG. 2. (Color online) Cooling rate dependence of γ for both samples. The inset shows the same data plotted versus (cooling rate)$^{0.3}$. The solid lines in both parts of the figure are fits to this power law.

maximum cooling rate of the cryostat ($\sim$1–2 K/min for the slow-cooled samples). Rapid cooling above 1.5 K/min was achieved by admitting ^{4}He exchange gas, which was then pumped out while the sample was held at $\approx$20 K to prevent gas absorption on the calorimeter. The specific heat C was measured after each cooldown at various fields between 0 and 14 T, applied perpendicular to the conducting planes. It was shown previously[4] that in κ-Br C becomes field independent above $\mu_0 H_{c2} \simeq 8$ T, and so $C(\mu_0 H = 14\ \mathrm{T})$ can be taken as the normal-state value.

Figure 1 shows the 14-T normal-state specific-heat data plotted as C/T versus T^2 for various cooling rates. It can be seen directly that there is a significant decrease in the Sommerfeld constant γ with increasing cooling rate. The data can be fitted by $C/T = \gamma + \beta_3 T^2 + \beta_5 T^4$ where β_3 and β_5 are the coefficients of the leading-order phonons terms. For the slowest cooling rates, $\gamma = 26 \pm 1$ mJ mol^{-1} K^{-2} and β_3 corresponds to a Debye temperature of 218 ± 10 K, in agreement with previous studies.[18] As the cooling rate was increased we find that β_3 and β_5 remain constant to within 1% and 6%, respectively, whereas γ decreases by up to almost 50%. The dependence of γ on cooling rate is plotted in Fig. 2 for both samples. Although at the lowest cooling rates there is a small difference in γ between the samples, the dependence of γ on cooling rate is very similar. As shown in the inset to Fig. 2 the data approximately obey an empirical power law $\gamma = \gamma_0 - \eta(dT/dt)^n$, with $n = 0.3 \pm 0.05$. This reduction in γ is consistent with the reduction in superconducting volume fraction (or decrease in superfluid density) observed in magnetization measurements.[12]

By subtracting the 14-T normal-state data from the zero-field data the superconducting anomaly at T_c is clearly discernable (see Fig. 3). The anomaly is a rather small proportion of the total specific heat ($\Delta C/C \simeq 3\%$). For simplicity we fit the anomaly to a mean-field theory, neglecting the fact that the anomaly is broadened by both thermal fluctuations and sample inhomogeneity. Specifically, we use a strong-coupling form of the mean-field d-wave theory which was shown to fit the data from the lowest temperatures right up to T_c.[4] We note, however, that an s-wave model works equally well close to T_c.[4] T_c corresponds to the midpoint of the leading edge of the anomaly, and the extrapolated anomaly height ΔC_{MF} is taken from the fit. The figure shows data for the slowest cooling rate and a fast one. Cooling at 52 K/min causes T_c to decrease by 0.6 K and γ to decrease by $\sim$40%. The inset to this figure shows the same data with the axes normalized. It can be seen that the anomaly does not get significantly broader upon rapid cooling.

The decrease in T_c with increased cooling rate is shown in Fig. 4. The data for both samples are in good agreement and also agree reasonably well with previous studies (see Ref. 19 and references therein). The T_c reduction at our maximum cooling rate is $\sim$0.6 K or $\sim$4%. We note that here we have a very small thermometer stage in direct contact with the

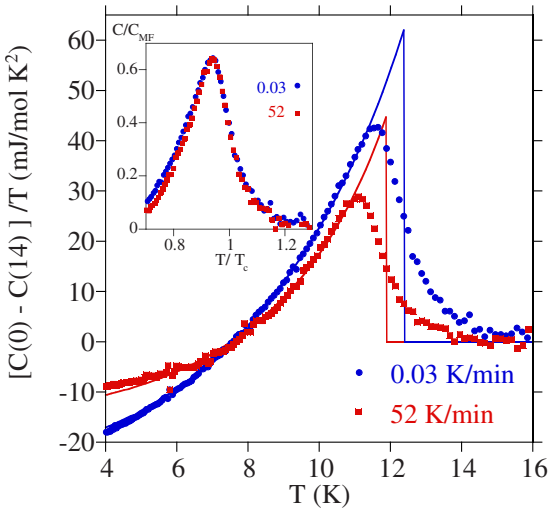

FIG. 3. (Color online) Zero-field electronic specific heat $[C(0) - C(14)]/T$ of sample B, for two different cooling rates. The solid lines are fits to a mean-field model which is used to determine T_c and the height of the specific heat jump at T_c. Inset: scaled plot of the data close to T_c.

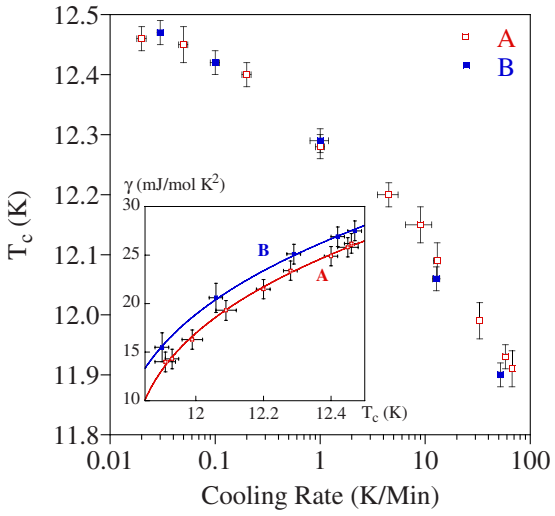

FIG. 4. (Color online) Cooling-rate dependence of T_c for both samples. Inset: γ versus T_c. The lines are guides to the eye.

sample and so the cooling rate registered should be an accurate reflection of that experienced by the sample. At our slowest cooling rates T_c appears to have saturated at its maximum value within our resolution (± 20 mK).

The detailed evolution of the height of the superconducting anomaly can be seen in Fig. 5. Given the dramatic reduction in γ the normalized anomaly height is remarkably constant with cooling rate. For the highest cooling rates $\gtrsim 12$ K/min, $\Delta C_{\mathrm{MF}}/\gamma T_c$ is seen to increase, although this is close to the resolution limit. For these high cooling rates a small upturn in C/T is seen in the 14-T data for $T \lesssim 2$ K, probably because of additional magnetic contributions, which increases the uncertainty of our estimates of γ.

In Fig. 6 we show the low-temperature behavior of the electronic specific heat $[C(0)-C(14)]/\gamma T$ for sample A at two different cooling rates. In both cases, $[C(0)-C(14)]/\gamma T$ is linear with T below ~ 4 K and fits the strong-coupling form of the d-wave model very well (details of the fit can be found in Ref. 4). Hence, at least for moderately fast cooling the order parameter symmetry is unaffected.

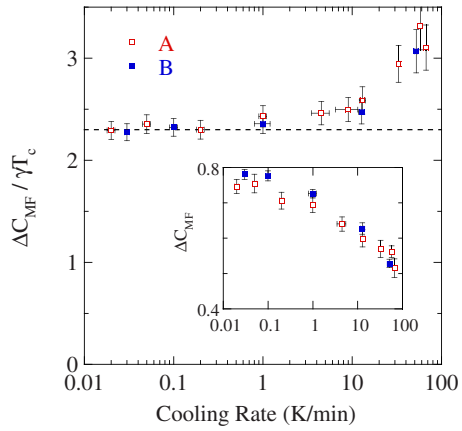

FIG. 5. (Color online) Normalized superconducting anomaly height $\Delta C_{\mathrm{MF}}/\gamma T_c$ as a function of cooling rate for both samples. The inset shows behavior of ΔC_{MF} in units of J mol^{-1} K^{-1}.

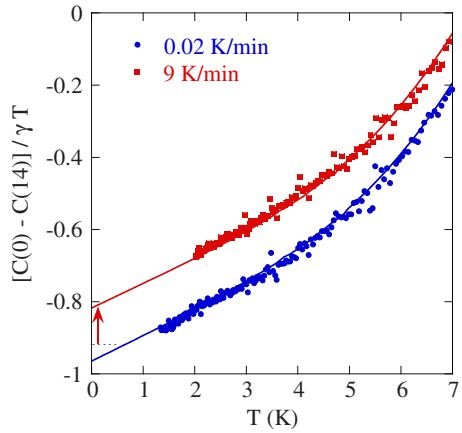

FIG. 6. (Color online) Low-temperature behavior of the electronic specific heat in the superconducting state, $[C(0)-C(14)]/\gamma T$, along with fits to a strong coupling d-wave model, at two different cooling rates (sample A). The 9-K/min data have been offset vertically for clarity by 0.1 as indicated by the arrow.

In conventional models of superconductivity, the density of states at the Fermi level, N_0, is an important factor in determining T_c [in simple BCS theory $T_c \propto \exp(-1/N_0 V)$, where V is the superconducting pairing potential energy]. This continues to be the case even in most more exotic theories, and so it appears very difficult to reconcile the relatively small decrease in T_c with the large decrease in γ (see Fig. 4) which in band theory is proportional to N_0. This behavior is similar to that found upon deuteration of κ-Br, which also produces a large decrease in γ with only a small decrease in T_c.[20] There is clear evidence that deuteration moves the system towards the antiferromagnetic state. In some systems, γ is found to diverge at the metal insulator boundary; however, the behavior in deuterated κ-Br is similar to that observed in the high-T_c cuprates.

A natural explanation of our results is that upon fast cooling κ-Br phase separates into insulating and metallic (superconducting) regions. Given the proximity of κ-Br to the AFI phase boundary this is plausible and explains the reduction of the average value of γ for the whole sample. It is also consistent with the SMIRS results[13] mentioned above. However, it does not, in itself, explain the observed reduction of T_c. One possibility is that fast cooling causes the structure transition at T_g to be incomplete throughout the whole sample and effectively produces a negative pressure moving the system further towards the AFI phase.[7] As the AFI phase transition is first order, the system naturally may then break up into superconducting and insulating regions. This picture also explains the progressive lowering of γ as a function of increased deuteration.[20] The small reduction in T_c could then result, at least partially, from small changes in the intrinsic density of states and/or pairing interaction strength as the phase diagram is transversed. This is similar to the behavior observed upon deuteration of κ-Br, where T_c at first rises slightly and then falls as the AFI boundary is approached.[21]

However, in κ-Cl the opposite trend is found with T_c being maximum close to the phase boundary.[22] Another factor which needs to be taken into account is the direct effect of disorder. As κ-Br has a strongly anisotropic energy gap, even nonmagnetic impurities are expected to decrease T_c rapidly, as observed experimentally for κ-NCS.[23] The correlation of the increase in residual resistance ρ_0 with the decrease of T_c as the cooling rate is increased in κ-Br has been found to be in agreement with that expected for a *d*-wave superconducting energy gap.[24] We note, however, that the presence of insulating regions in rapidly cooled samples, as suggested by the present work, would also cause a substantial increase ρ_0 in addition to the direct effect of disorder. Hence ρ_0 may overestimate the true level of disorder present in the superconducting fraction of the fast-cooled samples.

In summary, we have measured the low-temperature specific heat of κ-Br as a function of cooling rate through the structural phase transition at T_g ($\simeq$78 K). T_c decreases with increased cooling rate and is accompanied by a sharp decrease in the normal-state electronic specific heat. This reduction is up to $\sim$50% at our maximum cooling rate ($\sim$100 K/min). We suggest that this reduction in γ is due to phase separation of superconducting (metallic) and insulating regions, caused by the fast cooling effectively applying negative pressure to the material and thus driving it closer to the first-order antiferromagnetic insulating state.

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