DYNAMIC DISORDER AT INTERMEDIATE TEMPERATURE AND ITS EFFECT ON THE MAGNETIC PROPERTIES OF THE ORGANIC SUPERCONDUCTOR κ-(BEDTTTF)$_2$Cu[N(CN)$_2$]Br

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Abstract:
The k-(BEDT-TTF)X superconducting salts, [where BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene, abbreviated as ET, and X is a monovalent anion like *Cu*[*N*(*CN*)]*Br* 2 , and for either *Cu*[*N*(*CN*)]*Cl* 2 or ( )2 *Cu NCN* and so on], exhibit interestinmagnetic and superconducting phase transitions [1]. They are quasi-two-dimensional and the interplane coupling is very weak. The basic structural unit is a dimer consisting of two BEDTTTF molecules stacked on top of one another. This layered structure leads to highly
anisotropic electronic properties. These organic superconductors have similar characteristic superconducting properties including the intrinsic Josephson Effect and the mixed-state properties. This similarity suggests the existence of the vortex phase transition in the organic layered superconductors as observed in HTSC. Because the temperature scale is much lower in organic materials, the thermal fluctuation is expected to be small compared to HTSC. Thus, the comparison between the high-Tc and organic superconductors can give important clues as to the nature of vortex phase transitions.
Besides these anomalies around 50 K, unusual time dependencies in magnetic and transport properties have been reported for both deuterated and hydrogenated k-Br near 80 K. For - *H* - *Br* 8 k , the superconducting properties have been found to depend on the thermal history, in particular on how fast the sample had been cooled through 80 K. As mentioned above, the ground state of - *D* - *Br* 8 k is strongly sample-dependent: both superconducting as well as non-superconducting crystals are found. Furthermore, superconducting as well as insulating (possibly antiferromagnetic) phases in separated volume parts of the same sample have been reported. Their relative volume fraction was found to depend on the cooling rate Vc employed at around 80 K[2-3-4]: in fast cooled samples, a strong decrease of the diamagnetic signal has been observed, which has been interpreted as indicating a suppression of the superconducting in favour of the magnetic phase.

I. Introduction

Organic charge-transfer salts based on the donor molecule bis(ethylenedithio)tetrathiafulvalene, abbreviated as BEDT-TTF or ET, have been recognized as one of the most highly correlated electron systems [1]. Among them, the system κ-(BEDT-TTF)$_2$X where X indicates a monovalent anion such as Cu[N(CN)$_2$]Br T_c=11.6K), Cu[N(CN)$_2$]Cl (T_c=12.8K), Cu(NCS)$_2$(T_c=10.7K), etc. exhibits interesting magnetic and superconducting phase transitions [2]. The above systems are quasi-two-dimensional and the interplane coupling is very weak. The basic structural unit is a dimer consisting of two BEDT-TTF molecules stacked on top of one another. This layered structure leads to highly anisotropic electronic properties. However, they have a layered structure with alternating sheets of metallic (dimerized ET molecules) and insulating (anion, X) planes, like high-T_c materials. Consequently, these superconductors have similar superconducting properties including the intrinsic Josephson Effect [3]. This similarity suggests the existence of the vortex phase transition in the organic layered superconductors as observed in high-T_c superconductors such as $Yba_2Cu_3O_{7-\delta}$. Because, the temperature scale is much lower in organic materials, the thermal fluctuations are expected to be small compared to the high-T_c compounds. Thus, the comparison between the two type's superconductors gives important clues such as the nature of vortex phase transitions. Furthermore, organic superconductors exhibit other typical features like the structural transformation around 80 K that influence considerably the physics of their vortex lattices and the associated magnetic behaviors. Thus the structural transformation around 80 K will also induce a certain degree of disorder in the conducting planes.

The unusual time dependencies of the magnetic and the transport properties have been reported for both deuterated (D_8-Br) and hydrogenated (H_8-Br) near 80 K [4]. For κ-H_8-Br, the superconducting properties have been found to depend on the thermal history, in particular on how fast the sample has been cooled through 80 K. As a matter of fact, D_8-Br exhibits several

puzzling superconducting properties. Some of these properties were ascribed to the appearance of a magnetic transition at lower temperature (10-20 K) and the meaning of which is still unclear. Several mechanisms have been proposed including spin-density waves, [5] spin canting, [6] or the suppression of superconductivity by dispersed magnetic ions associated with the persistent disorder [7]. Their relative volume fraction was found to depend on the cooling rate V_c employed at around 80 K [8, 9].

In addition to deuteration, the cooling rate of D_8-Br in the vicinity of 80 K appears to affect the proportions of superconducting and antiferramagnetic phases [2, 9, 10, 11]. Although there is some opposition [12], the origin of this effect is believed to originate with the conformational freezing of the terminal ethylene groups. On the other hand, at very high temperature, the pair of ethylene molecules is free to oscillate rapidly and independently between the two equivalent conformations (so-called: "eclipsed" or "staggered"). Upon cooling, these thermal fluctuations gradually slow down and simultaneously a kind of long-range order among the ethylene groups builds up [13, 14]. Depending on the rate at which the temperature drops near 80 K, the system can be forced to freeze into a frustrated state consisting of increased proportions of ethylene groups in the staggered configuration.

In this paper, we report a systematic study of dynamic structural disorders as well as the effect of the cooling rate on the interlayer transport properties at T_c and on the magnetization hysteresis (critical current). By freezing the sample into different disordered states, we found that there is strong evidence for a structural transformation at around 80 K. The resistivity for the quenched sample increases with increasing cooling rate. Consequently T_c decreases linearly with increasing resistivity. The quenched state is also unstable against thermal fluctuations and decays gradually toward an equilibrium state.

II. Experimental section

Single crystals of the κ-$(BEDTTTF)_2Cu[N(CN)_2]Br$ superconductor were synthesized at the Jean Rouxel Institute of Materials. Both hydrogenated and deuterated compounds were used in this study. The two samples are with an average dimension: $0.7\times0.7\times0.2\,mm^3$ and $1\times1\times0.25\,mm^3$, respectively. They were initially cooled slowly from room temperature to liquid helium temperature. Subsequent cooling was done first by warming up the sample slowly to a given temperature above T_c. Magnetic measurements were done with a commercial conducting quantum interference device (SQUID), which produces a magnetic field up to 5 T. Magnetic field was applied perpendicular to the sample plane. The superconducting magnet was reset such that the remaining field was less than 1 μT. Once the field was quenched; the sample was zero field cooled (ZFC) or field cooled (FC) to a desired temperature.

III. Results and discussion

We have investigated the magnetic susceptibility of the superconducting phase as a function of the cooling rate in the ZFC conditions. In the slow cooling rate, the sample was cooled from 160 K to 90 K at a cooling rate of about 2 K/min and then from 90 K to 70 K, at a cooling rate of 0,1 K/min. Furthermore, the sample is keep then at the temperature of 70 K during 20 hours and then cooled directly to 2 K at a cooling rate of 5 K/min. In the rapid cooling condition, the sample was immerged directly in the Dewar at the temperature of 2 K.

Figure 1 shows the temperature dependence of the magnetic susceptibility of hydrogenated (H_8-Br) κ-$(BEDTTTF)_2Cu[N(CN)_2]Br$ sample after slow and rapid cooling rate at magnetic field of 1.5 Oe.

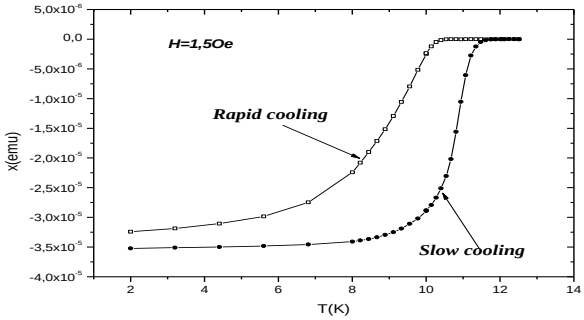

Fig 1. Temperature dependence of the magnetic susceptibility of hydrogenated (H_8-Br) κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ after slow and rapid cooling. The magnetic field is fixed at 1,5 Oe.

The cooling through the structural transformation in the vicinity of 80 K has a strong effect on the superconducting transition. It is clear from this figure that the highest superconducting transition temperature occurs for the susceptibility of the slowly cooled sample. The beginning of the superconductivity occurs at T≈11.7 K in the case of slow cooling for the compound (H_8-Br). A strong decrease of T_c with the increase of the cooling rate is also observed from Fig. 1. Moreover, T_c falls towards T≈11 K in the case of the rapid cooling. The superconducting transition temperature T_c as well as the width of this transition depends on V_c. The effect is very pronounced in the case of the deutrated sample (D_8-Br): the absence of a diamagnetic saturation towards low temperatures and a sensibility much more raised to the cooling are found. It was indicated that the system containing some deuterium is situated in the critical region of the transition between a superconducting phase and an antiferromagnetic phase [4].

It is also shown that rapid cooling suppresses the spin canting as observed from magnetic susceptibility measurement, and produces an increase in the fraction of antiferromagnetic phases. In addition we can conclude that the rapid cooling quenches the sample into a disordered state.

We present in Fig. 2, the magnetization hysteresis loops of deuterated (D_8-Br) sample at T=8 K for two different cooling rates, where the magnetic field varies from -80 G to 80 G. The hysteresis cycles depend strongly on the cooling rate V_c of the sample through the order-disorder transformation which affects the ethylene groups C_2H_4 and which occurs at the vicinity of 80 K. The area of the cycle decreases with increasing the cooling rate, and the cycle shape also changes. Furthermore, these effects are less spectacular in the case of the hydrogenated sample.
Kawamoto *et al* reported that rapid cooling through 80 K drives the superconducting phase into a disordered magnetic phase in the deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br compound [4]. The disorders suppress the antiferromagnetic ordering temperature.

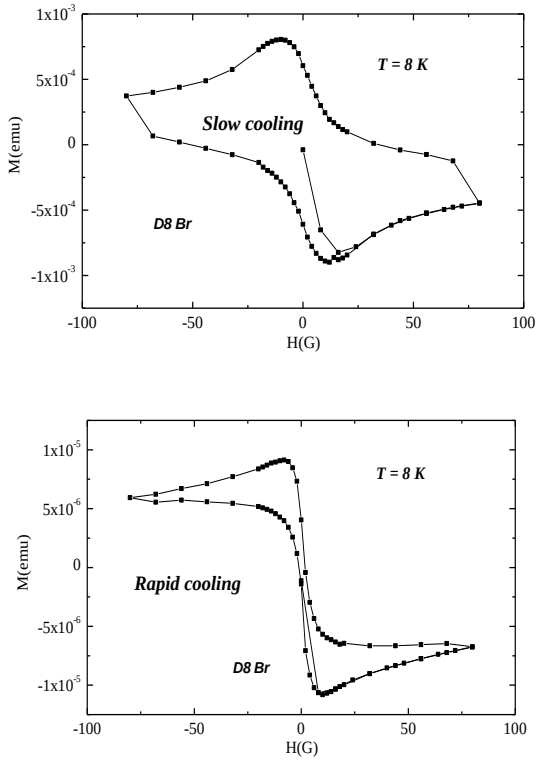

Fig 2. Magnetization hysteresis cycle at T = 8 K in the slow and the rapid cooling rate of D_8-Br sample.

Rapid cooling produces an increase in the fraction of antiferromagnetic phase, suppresses the superconducting phase and increases the magnetic phase.

Figure 3 shows the magnetic hysteresis cycles at T= 2 K after slow and rapid cooling rate of (D_8-Br) compound, in the magnetic field range of (-1; 1 KG). It can be seen, in this figure, that in the case of the slow cooling rate a wide cycle is observed. The hysteresis results from flux pinning, when the pinning is absent, the magnetic behavior of the superconductor is fully reversible. The presence of several pining centers provides high currents.

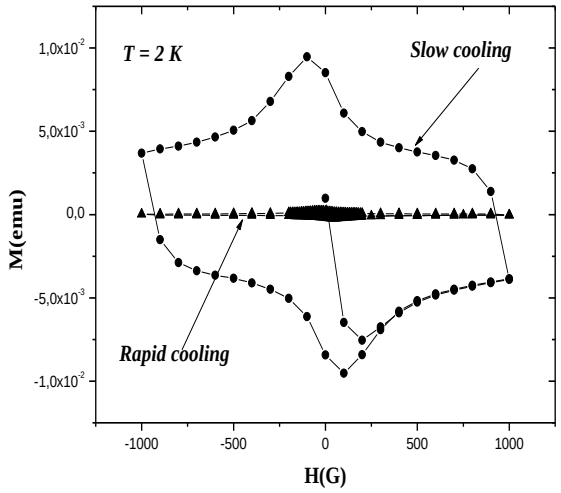

Fig 3. Magnetization hysteresis cycle at T = 2 K in slow and rapid cooling of D_8-Br sample.

When the magnetic field increases, the magnetic flux continues to penetrate the sample and the diamagnetism is not perfect. The value of 80 K corresponds to a temperature of structural transition in the chain anion. Rapid cooling through 80 K will freeze the high temperature magnetic phase to low temperatures and the presence of local magnetic moments suppresses the superconducting transition temperature T_c. These results suggest that rapid cooling is effective in reducing the flux pinning.
The measured hysteresis loops of (D_8-Br) κ-(BEDTTTF)$_2$Cu[N(CN)$_2$]Br for different temperatures (T=2 K, T=3 K and T=4 K) are shown in Fig. 4. The magnetization depends strongly on the temperature; a decrease of the magnetization with increasing temperature is observed.

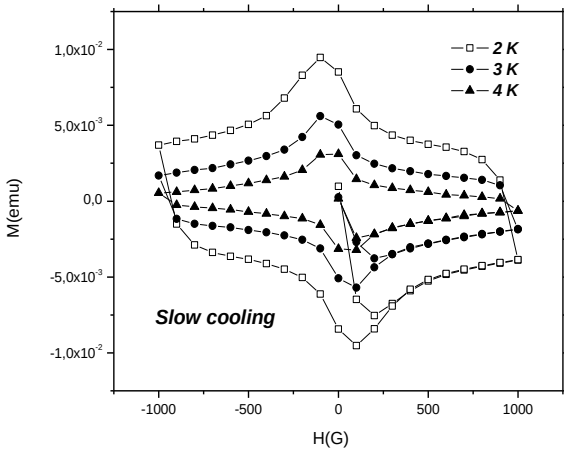

Fig. 4. The magnetic hysteresis cycle of our D8-Br sample at three different temperatures (T=2 K, T=3 K and T=4 K).

The strong temperature dependence of the magnetization may be caused by the large thermally activated flux motion in κ-$(BEDTTTF)_2Cu[N(CN)_2]Br$ system. As mentioned above, when there is no pinning of vortices (temperature increases), the magnetization decreases and the area of the cycle decreases.

IV. Conclusion

We have studied the effect of cooling rate through the order-disorder structural transformation near 80 K for both the hydrogenated and deuterated κ-$(BEDTTTF)_2Cu[N(CN)_2]Br$ samples. This structural transformation influences strongly the physics of the vortex lattice and the associated magnetic behavior. The degree of disorder that persists at low temperature depends on the cooling rate through this transformation. Our results show that the magnetic properties of these compounds depend strongly on the cooling rate V_c. It was shown that the cooling through the order-disorder transformation at the vicinity of 80 K has a pronounced effect on the superconducting transition temperature T_c and on the magnetic hysteresis (critical current density).

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