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Vortex phase transition and superconducting properties of organic quasi-two-dimensional κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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Abstract : We report investigations of the low temperature dc susceptibility and the magnetization on the layered organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br near 80K and the effect of disorder on the superconducting transition temperature T_c. The shielding effect (S) and the critical current density J_c were studied (with H parallel to the c axis of the crystal). J_c can be estimated by analysis of magnetic hysteresis measurement using the Bean model. For each temperature value, we observed two regimes in the critical current density J_c(H). This result implies that there exists a first-order phase transition in the vortex system in this organic superconductor. Our results show that the magnetic properties of these compounds depend strongly on the cooling rate. The structural transformation which occurs at the vicinity of 80K very strongly influences the physics of vortex lattice and the associated magnetic behavior.

Keywords : ORGANIC SUPERCONDUCTOR, CRITICAL CURRENT, SHIELDING EFFECT, MAGNETIC SUSCEPTIBILITY, VORTEX PINNING.

Introduction

The layered organic molecular crystals κ-(BEDT-TTF)$_2X$ based on a donor molecule bis(ethylenedithio)-tetrathiafulvalene (abbreviated as BEDT-TTF) have been recognized as highly correlated electron systems [1]. They have a layered structure with alternating sheets of metallic (dimerized ET molecules) and insulating (anion, X) planes. Among them, compounds of the family κ-(BEDT-TTF)$_2X$ have recently attracted considerable attention because of their similarity to the high T_c cuprates and the possibility that they may also have a non-conventional paring state [2]. Organic superconductors exhibit other typical features like a structural transformation occurring around 80K for κ-(BEDTTTF)$_2$Cu[N(CN)$_2$]Br and introduces a certain degree of disorder in the conducting planes. That can influence considerably the physics of vortex lattices of these compounds and the associated magnetic behavior. Organic charge transfer salts are excellent model systems in which to study many of the questions about the strongly correlated phenomena described above. Band structure suggests that these materials

should be metals at all experimentally relevant pressures and temperatures.

Further, organic chemistry allows the organic charge transfer salts to be subtly tuned in ways that have never been achieved in inorganic materials. The compound κ-$(ET)_2Cu[N(CN)_2]Br$ constitutes a beautiful example, for which, the Mott transition can be driven by replacing the eight hydrogen atoms in the ET molecule with deuterium [3].

A remarkable feature of the electronic state of *κ*-(BEDT-TTF)$_2$X compound is that, the native quarter filled band is modified to the effective half filled band by the strong dimer structure consisting of two BEDT-TTF molecules. In fact, the BEDT-TTF molecule has two ethylene groups at the end; the two-dimensional conduction planes consist of BEDT-TTF molecular dimers, which form an anisotropic triangular lattice.

When the terminal ethylene groups in each ET molecule contain all possible eight hydrogen atoms (H_8), the material shows bulk superconductivity. Upon replacing the hydrogen by deuterium (D_8), T_c gets considerably reduced, the phase transition becomes broader, and no volume superconductivity is observable.

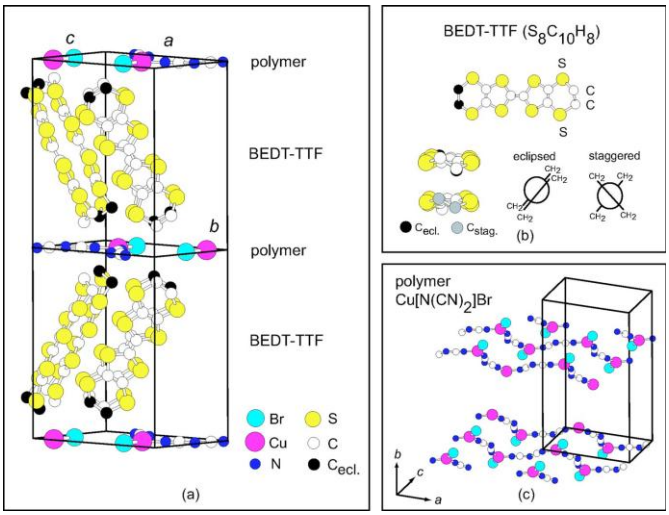

Figure 1: (a) Crystal structure of *κ*-Br; (b) Eclipsed and staggered configurations of the ethylene groups $(CH_2)_2$ of BEDT-TTF molecule from a dimerized structure. Organic BEDT-TTF molecules stack in conducting planes separated by inorganic insulating layers, giving rise to a highly anisotropic quasi-two dimensional band structure; (c) View of the packing of the polymeric anion chains in *κ*-Br. Protons on the BEDT-TTF molecule are omitted for clarity.

The layered structure of *κ*-(BEDT-TTF)$_2$*X* family of organic molecular metals is shown in figure 1(a). BEDT-TTF molecules dimerize, forming molecular units that stack on a triangular lattice in two-dimensional planes. The removal of one electron from each BEDT-TTF dimer causes the tight-binding band to be half filled, and to balance the charge, layers of anion *X* are located between the partially oxidized BEDT-TTF sheets.

The flat BEDT-TTF molecules (Figure 1(b)) dimerize to form molecular units that stack in planes on a triangular lattice [4]. The anions, X, separate the planes and accept one electron from each BEDT-TTF dimer.

Influence of the superconducting transition temperature T_c of *κ*-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br was found in one of the first investigations after synthesis of the compound [5]. Recently this effect has been the subject of numerous studies in the salt with both usual H_8-BEDT-TTF and deuterium substituted D_8-BEDT-TTF molecules (which we will subsequently abbreviate as *κ-H$_8$*-Br and *κ-D$_8$*-Br salts, respectively) [6-11]. There is growing evidence that a proper cycling is important for electronic properties [6. 7. 9-11]. The effect is related to the phase transition at 80K, due to the order-disorder transformation of the terminal ethylene groups of the BEDT-TTF molecules [12-13].

In this paper, we report on an extensive experimental study of the effect of the cooling rate on the interlayer transports properties at T_c and on the magnetic susceptibility and magnetization. By freezing the sample into different disordered states, we found that there is a strong evidence for a structural transformation at around 80K. The results of the critical current and the shielding effect for the *κ*-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br sample are also present as function of magnetic field at different temperatures with magnetic fields applied perpendicular to the conducting planes.

EXPERIMENTAL SECTION

Single crystals of the *κ*-(BEDT-TTF)$_2$Cu[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 have average dimensions: $0.7\times0.7\times0.2mm^3$ and $1\times1\times0.25mm^3$, respectively. Our samples had good magnetic quality and were stable; the results remained unchanged despite repeating the experiment several times. The block-like crystals weighing m=0.59mg for *κ-H$_8$*-Br and m=2.07mg for *κ-D$_8$*-Br. Before starting each measurement, the sample was first warmed to a given temperature well above T_c. Once the residual field is eliminated, the sample was zero field cooled (ZFC) or field cooled (FC) to a desired temperature. Magnetic measurements were done with a commercial conducting quantum interference device (SQUID), which produces a magnetic field up to 5T. Magnetic field was applied perpendicular to the sample plane. The superconducting magnet was reset such that the remaining field was less than 1μT.

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 160–90K at a cooling rate of about 2K/min and then from 90–70K, at a cooling rate of 0.1K/min. Furthermore, the sample is then kept at the temperature of 70K during 20h

and then cooled directly to 2K at a cooling rate of 5K/min. In the rapid cooling condition, the sample was submerged directly in the Dewar at a temperature of the order of 2K.

RESULTS AND DISCUSSION

The superconducting transition temperature was measured by use of a dc susceptibility, and the magnetic field was applied perpendicularly to the conducting layers.

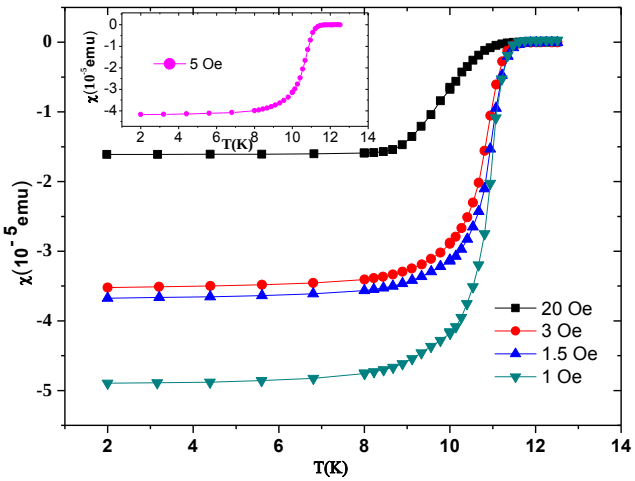

Figure 2: Magnetic susceptibility as a function of temperature, at for different magnetic field values for hydrogenated κ-H_8-Br in slow cooling. The inset shows the susceptibility versus temperature at field 5Oe.

We present in figure 2 the susceptibility variations versus temperature for hydrogenated κ-H_8-Br sample in slow cooling conditions, at different fields (H=1Oe, H=1.5Oe, H=3Oe and H=20Oe) and for H=5Oe in the onset. Values of the superconducting transition temperature have been taken here from the diamagnetic transition curve at the crossing point of the interpolation lines from the normal and superconducting regions. We can plot thus defined T_c (i.e., suppression of superconductivity) as a function of field with overlaid for the slow-cooled, as shown in figure 3. Clearly, the critical T_c decreases with increasing field monotonically. On the other hand, a strong increase of T_c, as large as 1K was reported, in the case of deuterated (κ-D_8-Br) sample [14].

Temperature 80K corresponds to a structural phase transition temperature in the anion chain. Cooling through 80K at different rates will freeze the high-temperature phase to low temperatures and the presence of local moment suppresses the superconducting transition temperature. Scanning microregion infrared reflectance spectroscopy measurements have shown evidence for macroscopic insulating/metallic region phase separation at the surface of fast cooled samples [15].

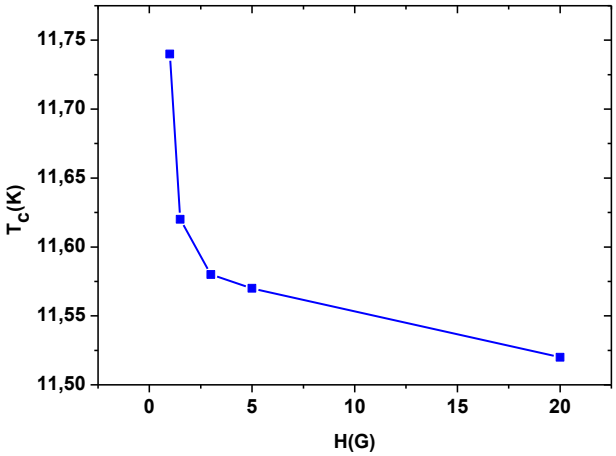

Figure 3: Superconducting critical temperature versus magnetic field for hydrogenated κ-H_8-Br.

Let us now look at the amplitude of the real part of dc susceptibility (Figure 4) which is nothing but the shielding effect (S) [16]. Furthermore, on the basis of data shown in figure 2, we obtained the shielding effect dependence of the magnetic field. The shielding effect represents the exclusion of magnetic flux by the sample in alternative dynamic mode. S was set arbitrarily equal to 1 for H_{dc}=1Oe. It can be seen from the curves that the shielding effect depends strongly on both temperature and applied magnetic field. Further, the decrease in S as a function of the temperature was much slower in the case of the low field. It clearly shows an improvement of the quality of the grains and intergranular coupling in the sample.

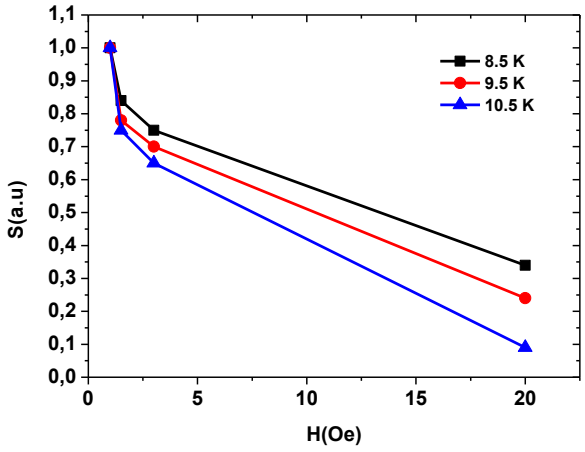

Figure 4: Shielding effect (S) in arbitrary units as a function of the magnetic field, for three different temperatures.

Magnetization hysteresis cycles measurements have played an important role in understanding the critical characteristics of superconductor. In particular, it makes possible a contactless determination of the critical current density using the critical state model [17]. It is well known that the critical current

density J_c depends on the flux pinning properties of a superconductor.

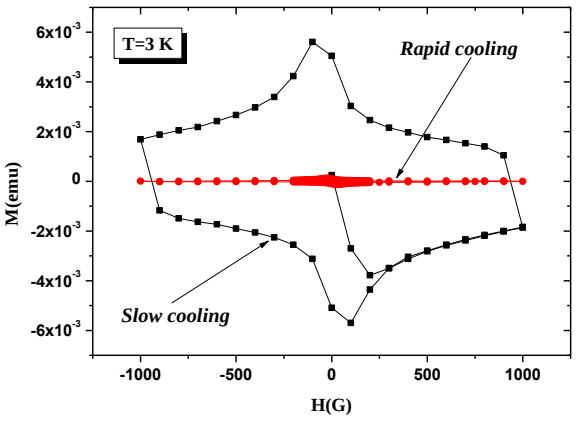

Figure 5: Magnetization hysteresis cycle at T=3K in slow and rapid cooling of deuterated *κ*-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br sample.

Figure 5 shown the magnetic hysteresis loops of (*κ*-D$_8$-Br) compound at T=2K after slow and rapid cooling rate, in the magnetic field range of (−1KG; 1KG). In the case of the slow cooling rate, a wide cycle is observed. The hysteresis results from flux pinning, and when the pinning is absent, the magnetic behavior of the superconductor is fully reversible. The presence of several pining centers provides high currents. When the magnetic field increases, the magnetic flux continues to penetrate the sample and the diamagnetism is not perfect.

It is important to note the absence of the secondary peak in the whole temperature range. Furthermore, the secondary peak has been observed both in iron-pnictides [18-19] and in cuprate high T_c superconductors [20].

The hysteresis cycles depend strongly on the cooling rate V_c of the samples through the order–disorder transformation which affects the ethylene groups C_2H_4 and which occurs at the vicinity of 80K [9]. The value of 80K was speculated to correspond to a structural transition temperature in the anion chain.

Taniguchi et al [21] reported the cooling-rate dependence of the magnetization curves, where the hysteretic magnetization width becomes narrow by cooling fast. One may consider that cooling fast introduces a much larger number of the ethylene-disorders, and leads to much stronger vortex pinning on the basis of a concept of the simple pinning effect by disorder.

The critical current density was determined using the Bean critical state model, from the irreversible parts of the magnetization curves with the formula [17]:

$$J_c = 30\frac{\Delta M}{d} \quad (1)$$

Where d is the size of the simple and ΔM is the difference between the magnetizations measured while decreasing and increasing field in the perpendicular field orientation. In figure 6, we present the critical current density $J_c(H)$ variations. As can be seen in this figure J_c depend strongly on both temperature and magnetic field.

It is important to note that in the case of *κ*-D$_8$-Br sample, the $J_c(H)$ dependence can be divided into two regimes, e.g. $J_c(H)$ exhibits a slight decrease below some an applied magnetic field H^*. The latter being the field where the slope of $J_c(H)$ curve change. A gradual transition to a power low behavior, that is $J_c(H) \propto H^{-\alpha}$ is found above this field. Thus, this regime, named the power law region, is usually attributed to strong pinning centers. Furthermore, the second regime shows a sharp drop in the J_c occurring because of a fast creeping of vortices.

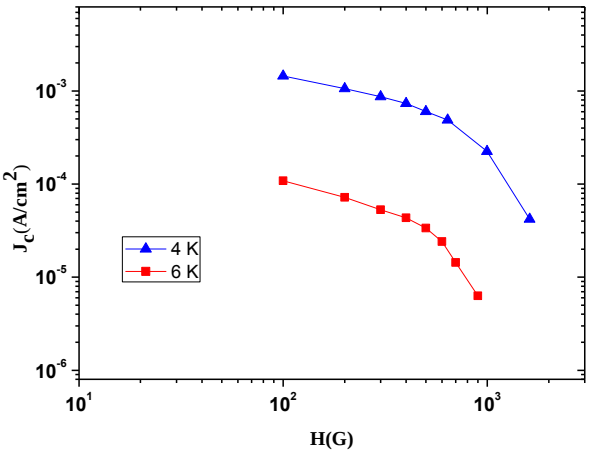

Figure 6: Critical current density versus magnetic field, for two different temperatures (T=4K and T=6K) and for deuterated *κ*-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br sample in slow cooling.

The strong decrease of the current density J_c(H), when H>H* can be explained by a collective pinning behavior of vortices. The vortices number becomes greater when the applied magnetic field increases.

CONCLUSIONS

As conclusion, we reported the magnetic susceptibility and the magnetization measurements to investigate the disorder effect and the first-order phase transition in the vortex system in organic superconductor *κ*-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Our

results show that both shielding effect and the critical current depend strongly on the temperature and magnetic field. The cooling rate has a considerable effect on the superconducting properties; the effect is much less in the case of hydrogenated salts. In particular, the cooling rate near 80K controls the amount of disorder at low temperature. Superconducting transition temperature T_c is determined using the dc magnetic susceptibility.

Finally, it is clear from all the above discussions and results that organic superconductors offer a unique opportunity to study (and perhaps to distinguish between) the contribution of various physical defects and thermal fluctuations to the broadening of the superconducting transition around T_c.

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REFERENCES

1. B. J. Powell, and R. H. McKenzie, *Journal* of *Physics: Condensed Matter*, **vol.18**, p 827 (2006)
2. R. H. McKenzie, *Sciences*, **vol.278**, p 820-821 (1997)
3. H. Taniguchi, K. Kanoda, and A. Kawamoto, *Physical Review B*, **vol.67**, p 014510 (2003)
4. T. Ishiguro, K. Yamaji and G. Saito, *Organic Superconductors 2nd edn*, Springer, Berlin (2006)
5. W. K. Kwok, U. Welp, K. D. Carlson, G. W. Crabtree, K. G. Vendervoort, H. H. Wang, A. M. Kini, J. M. Williams, D. L. Stupka, L. K. Montgomery and J. E. Thompson, *Physical Review B*, **vol.42**, p 8686 (1990)
6. A. Kawamoto, K. Miyagawa and K. Kanoda, *Physical Review B*, **vol.55**, p 14140 (1997)
7. M. Tokumoto, N. Kinoshita, Y. Tanaka and H. Anzai, *Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV*, edited by J. R. Reynolds *et al.*, MRS Symposia Proceedings **N°.488** (Materials Research Society, Pittsburgh), p 903 (1998)
8. J. E. Eldridge, Y. Lin, H. H. Wang, J. M. Williams and M. Kini, *Physical Review B*, **vol.57**, p 597 (1998)
9. X. E. Su, F. Zuo, J. Schlueter, M. E. Kelly and J. E. Williams, *Physical Review B*, **vol.57**, p 14056 (1998)
10. A. Aburto, L. Fruchter and C. Pasquer, *Physica C*, **vol.303**, p 185 (1998)
11. M. A. Tanatar, T. Ishiguro, T. Kondo and G. Saito, *Physical Review B*, **vol.59**, p 3841(1999)
12. M. Kund, H. Muller, W. Biberacher, K. Andres and G. Saito, *Physica B*, **vol.191**, p 274 (1993)
13. S. Senoussi and F. Pesty, *Studies of High Temperature Superconductors: Diverse Superconducting Systems and Some Miscellaneous Applications*, **vol.37**, ed. A. Narlika (Nova Science Publishers, Huntington, NY, USA), p 205–248 (2001)
14. A. Tirbiyine, A. Taoufik, A. Nafidi, H. El Ouaddi, S. Snoussi, H. Chaib, S. Bahsine, O. Touraghe and N. Hassanaine, *IOP Conf. Series: Mater. Sciences and Engineering*, **vol.13**, p 012036 (2010)
15. N. Yoneyama, T. Sasaki, N. Kobayashi, Y. Ikemoto and H. Kimura, *Physical Review B*, **vol.72**, p 214519 (2005)
16. R. A. Hein, T. L. Francavilla and D. H. Leinberg, Eds., *Magnetic Susceptibility of Superconductors and Other Spin Systems*. New York: Plenum, **ch.3** (1991)
17. C. P. Bean, T. Sasaki, N. Kobayashi, Y. Ikemoto and H. Kimura, *Physical Review Letters*. **vol.8**, p 250 (1962)
18. W. Zhou, X. Xing, W. Wu, H. Zhao and Z. Shi, *Scientific Reports*, **vol.6**, p 22278 (2016)
19. A. K. Pramanik, L. Harnagea, C. Nacke, A. U. B. Wolter, S. Wurmehl V. Kataev and B. Büchner, *Physical Review B*, **vol.83**, p 094502 (2011)
20. Y. Yeshurum, N. Bontemps, L. Burlachkov and A. Kapitulnik, *Physical Review B*, **vol.49**, p 1548 (1994)
21. H. Taniguchi, A. Kawamoto, K. Kanoda. *Physical Review B*, **vol.59**, p 8424 (1999)