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Genuine superconducting ground state in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br: an understanding after decade of controversy

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Abstract

We overview the state of knowledge regarding the symmetry of the superconducting order parameter in layered organic superconductors based on κ-(BEDT-TTF). A remnant intrinsic disorder at low temperatures in nominally pure single crystals emerges as one of decisive key ingredients that influences the value and the temperature dependence of the penetration depth, while leaving the transition temperature unchanged. However, the microscopic origin of this influence remains still unclear.

Keywords: organic superconductors, magnetic measurements, glass transitions

1. Introduction

The superconducting state of κ-(BEDT-TTF)$_2$X, where X stands for Cu(NCS)$_2$, and for either Cu[N(CN)$_2$]Br or Cu[N(CN)$_2$]Cl, was discovered by Urayama *et al.* in 1988 [1] and Kini *et al.* in 1990 [2]. Since then, the question of the pairing symmetry in this class of materials has remained one of the most intriguing problems, experimentally as well as theoretically [3,4]. Three essential features of these superconductors make them similar to the high-temperature cuprate superconductors. First they 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. The in-plane to out-of-plane conductivity anisotropy is of the order of 10^3. Second, antiferromagnetic and SC phases occur next to one another, and the SC state is created by applying pressure to an insulating AF state. The phase diagram is, therefore, quite similar to that of cuprates if pressure is replaced by doping. Third, the normal state has some properties that are distinct from conventional metals. First is that Knight shift decreases significantly below about 50 K suggesting a suppression of density of states, that is the appearance of a pseudogap near the Fermi energy [5]. A broad dip in the electronic density of states around Fermi energy was also observed by STM measurements below about 45 K [6]. Second there is peak in $1/T_1T$, where T_1 is the spin-lattice relaxation time, which suggests the existence of short range AF correlations [5].

An additional feature of the normal state concerns an order-disorder transition that bears glassy features and happens at $T_G \approx 75$ K for the Cu[N(CN)$_2$]Br system [7,8]. The transition region is situated between 65 K and 85 K, while for the Cu(NCS)$_2$ system is found between 45 K and 75 K. The transition is ascribed to the gradual freezing down of the remaining motion of the ethylene groups of the BEDT-TTF molecules that are thermally activated at high temperatures between two possible conformations. That is, the relative orientation of the outer C-C bonds can be either eclipsed or staggered. Upon lowering the temperature, the former and latter are adopted for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, respectively. X-ray diffraction measurements show that at 125 K, $(CH_2)_2$ groups are ordered in average in the whole bulk. However, the passage through the region of glassy transition appears to play a crucial role regarding the level of residual intrinsic disorder at low temperatures. Rapid cooling rates are reflected in smaller resistivity ratio between T_G and T_C and larger resistivity humps centred at about 60 K [9,10]. The understanding of transport properties in the normal state is further complicated by the fact that the standard resistivity behaviour that resembles of a semicon-

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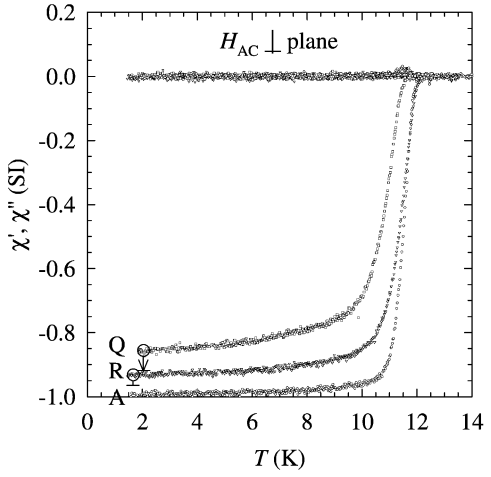

Fig. 1. Complex susceptibility for three different cooling procedures in $H_{AC} \perp$ plane geometry.

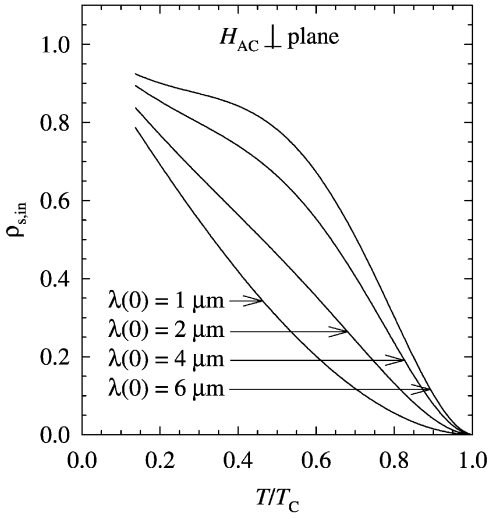

Fig. 2. In-plane superfluid density in the ground state for several values of $\lambda_{in}(0)$

ductor above 100 K, whereas it becomes metallic below, is not reported for all syntheses. In addition, indications are given that some Cu(II), instead of regular Cu(I), are incorporated during synthesis into the system, and that their presence might be related with the resistivity behaviour [11].

The symmetry of the SC order parameter has been examined by various techniques during the last 12 years yielding controversial results. The most recent reports in favour of unconventional *d*-wave symmetry are obtained by thermal conductivity [12], STM [13], tunnel diode oscillator [14] and ac susceptibility [15]. In contrast, the most recent specific heat measurements showed conventional strong-coupling *s*-wave structure [16]. In attempt to reconcile the existing contradictions, we have undertaken an investigation that covered a broad range of single crystals of various syntheses and in which the influence of thermal cycling and sample history is checked in carefully designed experiment [17]. In order to clarify possible sample dependence, we have done a full characterization of each sample under study. In that way we avoid to use the literature values, which are not well defined. Reported in-plane penetration depth values vary between 0.5μm and 2μm, whereas values for the out-of-plane penetration depth vary even more. Reported values range between 40μm and 250μm. The full account of this work will be published elsewhere [18].

2. Results

Complex susceptibility data for three different cooling rates are displayed in Fig. 1. The ground state for a single crystal we show here was established in Annealed state. Annealed state was achieved after keeping the sample for three days between 77 K and 100 K. When this sample was cooled slowly through the region of T_G (60 K – 100 K) by the standard slow cooling rate of -0.2 K/min, the low temperature state (R state) was close but distinct from the ground state. This finding contrasts results obtained on single crystals from the other synthesis, for which the ground state was achieved in R state. For cooling rates of about -300 K/min, Quenched state is established. The susceptibility at low temperatures again varies among samples of different origin.

The temperature behaviour of the in-plane superfluid density in the ground state for several zero temperature values of the in-plane penetration depth is shown in Fig. 2. The leading temperature term of the polynomial fit is the linear term. It should be noted that for $\lambda_{in}(0) \geq 3\mu$m, the behaviour of $\rho_{in}(t)$ corresponds to the one observed in the high temperature cuprate superconductors and expected in the weak coupling limit for *d*-wave SC [14,15]. However, for smaller values of $\lambda_{in}(0)$, the curvature changes and hints an unusually small energy gap. Our data give $\lambda_{in}(0) \approx 1\mu$m what is at the upper limit of the $\lambda_{in}(0)$ reported in the literature. Therefore, we are lead to conclude that the weak coupling model cannot be applied to the SC ground state, and some new ideas and models are needed to account for the superfluid density in κ-(BEDT-TTF)$_2$X superconductors.

In contrast, the in-plane superfluid density for the R state, which is close but distinct from the ground state, can be described properly by quadratic temperature behaviour at low temperatures (Fig. 3). It should be noted that in this state, the temperature behaviour of the SC order parameter is quite close to the one expected in the *s*-wave model, if the experimental error is taken into account. This finding might help to resolve the long standing issue of unconventional versus conventional pairing in this class of layered superconductors. While the quadratic temperature dependence is expected in the standard *d*-wave models with impurities [19–21], no change in T_C in the relaxed state, achieved

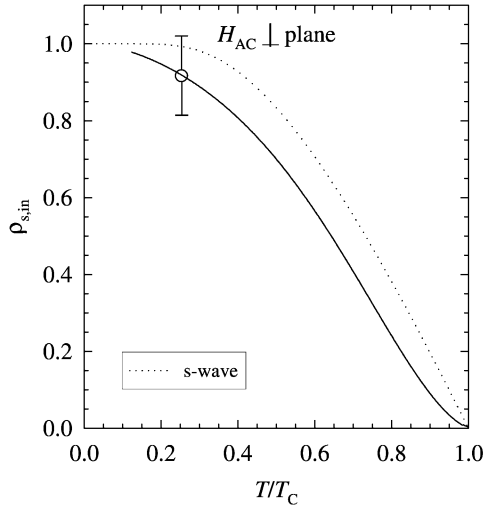

Fig. 3. In-plane superfluid density in the R state, distinct from the ground state. Dashed line shows s-wave result. Error bar stands for a noise in experimental points.

by -0.2 K/min rate, in comparison to the ground state, together with the observed increase of $\lambda_{in}(0)$ by factor of 6, is totally unexpected [20,21]. We note that for faster cooling rates T_C decreases concomitantly with a significant increase of $\lambda_{in}(0)$, what is qualitatively, but still not quantitatively in accord with standard theories for d-wave superconductors. The understanding of the nature of low temperatures states, distinct from the ground state, demands more efforts, since the phase diagram structure of deuterated systems cannot be fully applied to the hydrogenated systems described here [22].

3. Summary

The level of residual disorder and electronic properties at low temperatures are critically determined by the time scale of experiment in the region of the glassy transition. This fact imposes a necessary requirement to get a reliable description of the SC state and that is to perform the full characterization of the SC state in the sample under study in the same well defined and controlled cooling conditions. The bulk superconductivity is established in the ground state and the observed behaviour of the in-plane superfluid density is strongly linear in T, whereas the out-of-plane superfluid density varies as T^2 at low temperatures. Much larger coefficient of the leading temperature term than expected in the weak coupling d-wave model presents a mystery and calls for new challenges in understanding this class of organic layered superconductors.

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