The superconducting order parameter in the organic layered superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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Abstract: Highly sensitive ac susceptibility measurements were performed in order to resolve the controversy regarding the symmetry of the superconducting order parameter in κ-BEDT-TTF materials. The experimentally obtained superfluid density behaviour qualitatively contradicts *s*-wave symmetry theoretical predictions, but disagrees also quantitatively with the *d*-wave expected behaviour in the weak coupling limit. The mixture of *d*-wave and *s*-wave parameters, with a rather large proportion of the latter, describes well the results; however, it also opens new questions regarding the origin of the superconducting pairing.

Keywords: organic superconductivity, ac susceptibility, magnetic penetration depth

1. INTRODUCTION

For more than a decade, a family of organic materials based on κ-BEDT-TTF attracts a special attention. Not only because members of these achieve the highest superconducting (SC) transition temperatures among organic materials, but also because they share many common properties with the high-temperature cuprate superconductors [1]. First, they are strongly anisotropic, quasi-two-dimensional materials, with a very weak interplane coupling. And second, antiferromagnetic (AF) and SC phases occur next to one another, which suggests that electron correlations play significant role in the establishment of the ground state. Indeed, the ground state of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl material is an insulating AF phase with mildly canted spins [2], while the ground state of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [abbreviated as κ-(ET)$_2$Br] and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [abbreviated as κ-(ET)$_2$NCS] is a SC phase.

Most of newly discovered superconductors share one important common feature: Majority of experimental evidence suggests that the ground state pairing of electrons is not isotropic (non-*s*-wave). Therefore the central point of the investigation in these materials is the determination of the symmetry and the origin of the order parameter. While in high-temperature cuprate superconductors consensus is reached that the symmetry is *d*-wave and the attractive potential is of magnetic origin [3,4], the situation in κ-BEDT-TTF materials remains controversial. For example, different penetration depth studies, as well as specific heat measurements, point to either the *d*-wave or the gapless order parameter. Further, recent angle-resolved measurements of the SC gap structure using STM [5] and thermal conductivity [6] showed the fourfold symmetry in the angular variation characteristic of the *d*-wave superconducting gap.

In order to widen the knowledge about the issue of the SC order parameter, we have experimentally determined superfluid density of κ-(ET)$_2$Br material and compared our results with the theoretical models.

2. RESULTS AND DISCUSSION

Diamagnetic response of several κ-(ET)$_2$Br single crystals was measured in two geometries, with magnetic field parallel and perpendicular to two-dimensional (2D) planes, using ac susceptibility technique [7]. In order to obtain the *absolute* value of diamagnetic susceptibility, we have performed the improved calibration of the system with a piece of specially and carefully designed niobium foil, which shape and dimensions fitted well the ones of the real sample. In order to determine effects regarding the BEDT-TTF ethylene groups ordering, we have also used different cooling rates in the glass transition temperature range. The results for magnetic field perpendicular to 2D planes and for the cooling rates of -300 K/min (quenched) and -0.2 K/min (relaxed) are presented in Fig. 1. We have identified the state with the least remnant disorder, relaxed state, as the ground state of the system. Finally, using simple geometrical relations we can easily extract the in-plane penetration depth $\lambda_{in}(T)$ from the diamagnetic response and construct the in-plane superfluid density using the expression $\rho_{s,in}(T)=[\lambda_{in}(0)/\lambda_{in}(T)]^2$.

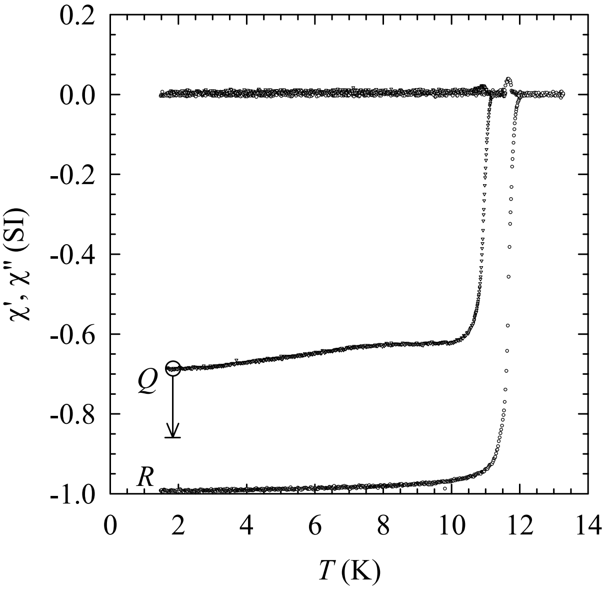

Figure 1: Real and imaginary parts of the susceptibility for relaxed (R) and quenched (Q) states and for the magnetic field perpendicular to 2D planes.

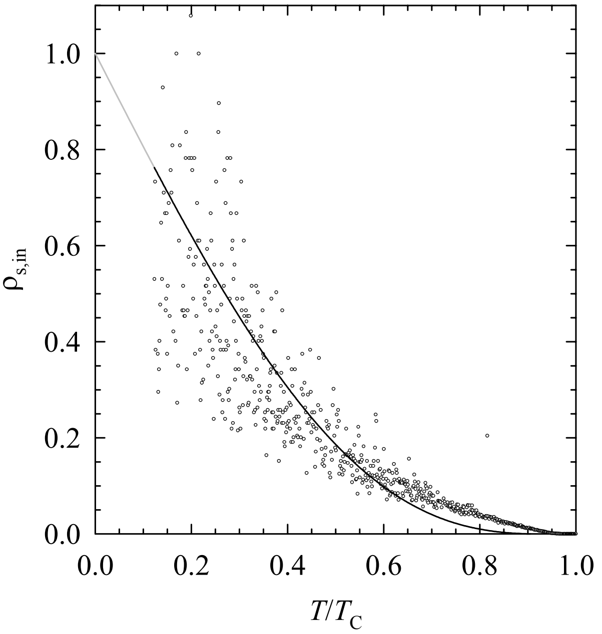

Figure 2: In-plane superfluid density for the ground state. Solid line is fit to the polynomial expression.

The in-plane superfluid density for the ground state is presented in Fig. 2. At low temperatures, it shows strongly linear behaviour in clear contradiction to the *s*-wave behaviour. Since the theoretical expressions cannot be easily handled mathematically, the solution appears to fit the data to the polynomial expressions. In case of the in-plane superfluid density, we obtain

$$\rho_{s,in}(t) = 1 - 1.95\,t + 1.45\,t^3 - 0.09\,t^4 - 0.41\,t^5, \tag{1}$$

where $t = T/T_C$ represents reduced temperature. For *d*-wave behaviour in the week coupling model, the coefficient of the leading term t in the expansion, $1 - a\,t$, amounts to $a = 0.65$, which is much smaller than the obtained experimental result. Since this coefficient depends strongly on the ratio of the superconducting transition temperature and the zero-temperature superconducting order parameter, we are led to conclusion that the latter is much smaller that the one predicted by the weak-coupling model. As a result, this also implies that the nodal region, the volume of which is inversely proportional to the angular slope of the gap near the node $\mu = dg(\varphi)/d\varphi|_{node}$ (Fig 3.(b)), occupies a much larger fraction of the phase space at low temperatures.

One plausible interpretation of our results is to consider the mixture of the *d*-wave and *s*-wave order parameters, which corresponds to the superconducting order parameter $g(\mathbf{k}) = \cos(2\varphi) + r$, with r representing the *s*-wave component (Fig. 3) [8]. The leading linear coefficient a then increases with the increase of r according to the expression

$$a = \frac{2\ln 2}{2.14\sqrt{1-r^2}}\exp\left[\frac{2r^2}{1+2r^2}\right] \tag{2}$$

The shapes of the superfluid density curves for several values of parameter r are given in Fig. 4. For our results, $|r| \sim 0.7$ gives a very good agreement, which is, on the other hand, theoretically very unlikely. We briefly address this issue in the next paragraph.

Recently, an admixture of the *s*-wave component with $r = -0.067$ for κ-$(ET)_2$NCS was suggested [8] based on the angular-dependent magnetothermal conductivity data [6]. These measurements, as well as STM [5], have revealed that nodes are directed along directions rotated by 45° relative to the in-plane crystal axes, indicating $d_{x^2-y^2}$-wave superconductivity (depicted in Fig. 3). Such a nodal structure indicates that both Fermi surfaces (oval-shape quasi-two-dimensional hole cylinder band and an open

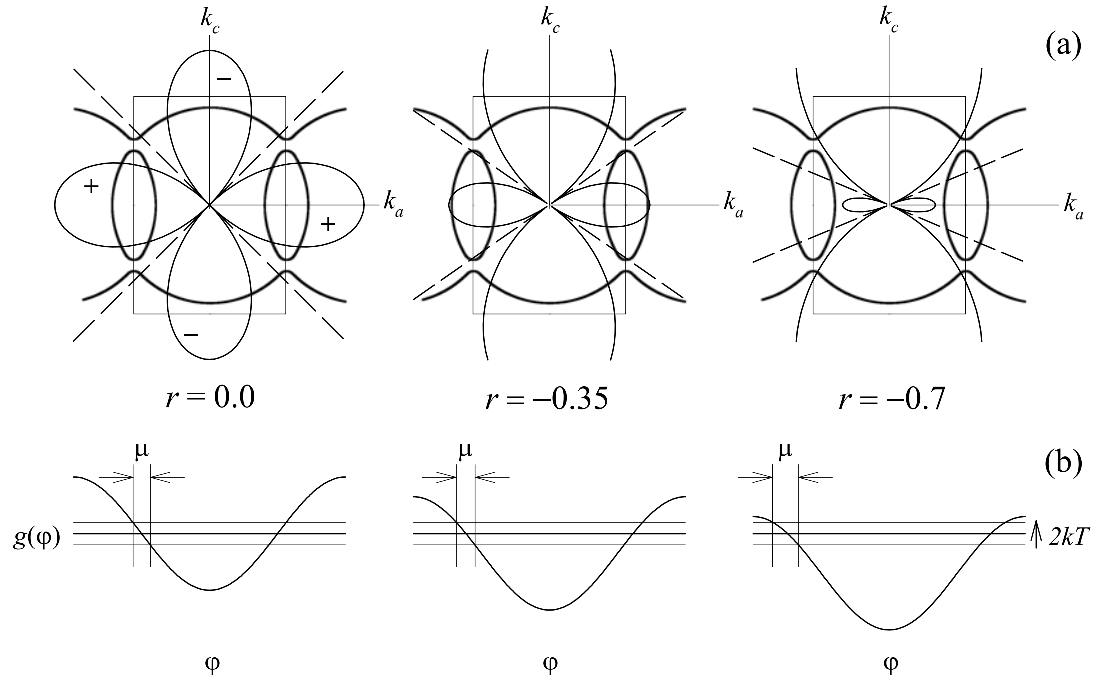

Figure 3: The effects of the admixing of the *s*-wave component to the $d_{x^2-y^2}$-wave, where *r* represents the *s*-wave component parameter. (a) The change of the node directions: Thick lines represent the Fermi surface, lines with a medium thickness superconducting gap and thin lines the Brillouin zone and crystallographic axes. Dashed lines represent node directions in the superconducting gap. (b) The change of the volume of the nodal region μ: The thick horizontal line represents the Fermi energy and thin horizontal lines the limits of the thermal excitations.

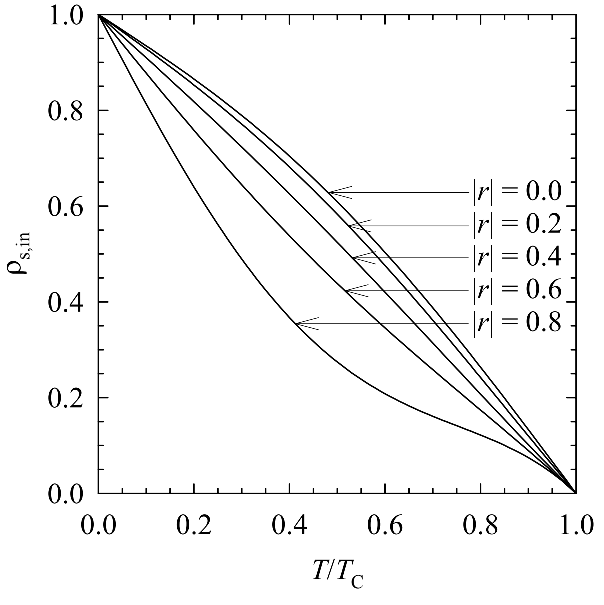

Figure 4: Superfluid density in the (*d*+*s*)-wave model for a few values of the *s*-wave component parameter *r*.

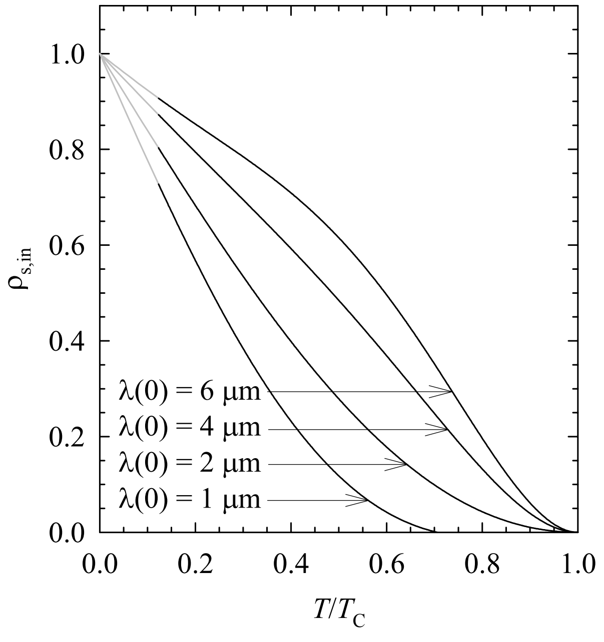

Figure 5: In-plane superfluid density for the ground state for uncalibrated data and few chosen $\lambda_{in}(0)$ values.

quasi-one-dimensional band) should participate in SC pairing in contrast with the theoretical prediction of superconductivity induced by AF spin fluctuations [9]. The Coulomb interaction, which is responsible for the *d*-wave superconductivity, gives rise to both spin and charge fluctuations, so that charge fluctuations might as well play the role in the κ-BEDT-TTF superconductivity. The value $r = -0.067$ suggests that the node lines in $g(\mathbf{k})$ pass through the gap between two Fermi surfaces. This is consistent with the (*d*+*s*)-wave model in which the superconductivity is due to the charge fluctuations between different groups of BEDT-TTF dimers. On the other hand, for $r \sim -0.7$, the nodal directions cross the oval-shaped quasi-two-dimensional cylinders (Fig 3.(a)), and for $r \sim 0.7$, the nodal directions cross a pair of open quasi-one-dimensional sheets. If the *d*+*s* superconductivity model is generated by the charge fluctuations, such a scenario is unlikely to work, since this implies a strong intra-Coulomb repulsion in each energy band. Therefore, the exact mechanism of the pairing remains unclear and further theoretical as well as experimental work should be done to resolve this question.

We point out that the similar ρ_{in} behaviour was also reported by Carrington *et al.* [10]. Since in their measurements only relative dependence of the penetration depth $\lambda_{in}(T)$-$\lambda_{in}(0)$ was obtained, $\lambda_{in}(0)$ values, ranging between 0.5 and 3 μm, were taken from the literature [1]. For $\lambda_{in}(0) \leq 1.3$ μm, Carrington *et al.* found the same behaviour of ρ_{in}, and pointed out that only for $\lambda_{in}(0) \geq 1.8$ μm, the slope does become similar to the one reported for the high-temperature superconducting cuprates and expected in the weak-coupling model. In Fig. 5 we show the analogous analysis of our uncalibrated data. Using various $\lambda_{in}(0)$ values from 1 μm to 6 μm, we get that ρ_{in} crosses-over to the behaviour, as predicted in the weak coupling model, for $\lambda_{in}(0) \sim 3$ μm, in a very good agreement with the results reported by Carrington *et al.* [10].

3. CONCLUSION

We have performed ac susceptibility measurements on κ-(ET)$_2$Br material in order to determine the symmetry of the superconducting order parameter in κ-BEDT-TTF materials. Full characterization of each sample under study was achieved by introducing the improved calibration of the system and by careful monitoring of thermal influences associated with the glass transition. Experimentally determined superfluid density showed the behaviour in clear contradiction to the *s*-wave symmetry and was compared to the theoretical predictions for *d*-wave and (*d*+*s*)-wave symmetries. The latter symmetry gives a good quantitative agreement with the experimental results. However, while our data indicate a rather large component of the *s*-wave parameter, the magnetothermal conductivity data point to a prevailing *d*-wave component. Nevertheless, both results raise new questions regarding the origin of the superconducting pairing. Further experimental and theoretical work is necessary in order to find satisfying explanations.

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