Magnetic-Field Induced Crossover of Superconducting Percolation Regimes in the Layered Organic Mott System κ-$(ET)_2Cu[N(CN)_2]Cl$

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Introduction

Materials in which magnetic, correlated metallic and superconducting phases compete for stability often show an intrinsic tendency towards electronic phase separation, an effect which is intensively discussed for the high-T_c cuprates and the manganites, see [1, 2] for reviews. Recently, also for quasi-two-dimensional organic conductors κ-$(BEDT\text{-}TTF)_2X$, where BEDT-TTF (or simply ET) is bis(ethylenedithio)tetrathiafulvalene and *X* stands for polymeric anions [3], an inhomogeneous coexistence of antiferromagnetic insulating and superconducting phases is observed when the material is located in the vicinity of the first-order metal-to-insulator transition (MIT). The latter can be tuned either by altering the chemical composition of the material or by applying pressure [4-6]. Pressure studies of the compound with *X* = $Cu[N(CN)_2]Cl$ (κ-Cl hereafter) revealed a first-order MIT line $T_{MI}(p)$ [4,6] indicative of a bandwidth-controlled Mott transition. The region of inhomogeneous phase coexistence in κ-Cl has been studied by simultaneous measurements of ^{1}H-NMR and ac-susceptibility [4], ^{13}C-NMR [5], and resistivity [6]. Despite strong evidence for spatially and statically coexisting phases, the question was raised whether the coexistence was of macroscopic or of mesoscopic type [4], for the details of spatial distribution, domain size, and stability of the inhomogeneous state are still under debate [7]. From resistance measurements, a percolative superconducting phase was suggested where "tiny" superconducting domains are progressively induced into the insulating host phase at small enough pressures [6]. The nature of the percolative phase itself, however, has not been explored in detail, yet. In contrast to κ-Cl, in partially deuterated samples of the material with X = $Cu[N(CN)_2]Br$ (κ-Br) metallic and insulating domains of macroscopic size (50 – 100 μm) were found in real-space imaging employing scanning microregion-infrared spectroscopy [7] below the critical temperature T_0 of the first-order Mott transition.

Fluctuation spectroscopy is a powerful tool to investigate the low-frequency dynamics of interacting electron systems. We have applied this technique to bulk single crystals of the title organic charge-transfer salt aiming to investigate the percolative nature of the superconducting transition in pressurized κ-Cl. We find evidence for different percolation regimes when the superconducting transition is driven by a magnetic field. In the crossover region from "classical" behavior to a new type of percolation that is dominated by instable superconducting clusters or domains, the action of an individual fluctuating entity is enhanced. This enables us to estimate a *mesoscopic* cluster volume in the order of a few hundred nm^3.

Experimental

Single crystals of κ-$(ET)_2Cu[N(CN)_2]Cl$ with platelet-like and rod-like morphology were grown by electrochemical crystallization. In order to produce a small pressure, samples (denoted as κ-Cl* hereafter) have been embedded in a solvent-free epoxy, the slightly larger coefficient of thermal expansion of which results in a finite stress acting on the sample during cooldown. Although the exact pressure is not known *a priori*, the actual conditions have been found to be reproducible for different cooldowns. An effective pressure of ~ 220 – 250 bar on our samples has been estimated. Low-frequency resistance fluctuations have been measured by a standard bridge-circuit ac technique [8] in a five- or six-terminal (κ-Cl*) or four-terminal (κ-Cl) setup. The output signal of a lock-in amplifier (SR830) operating at a driving frequency f_0 of typically 517 Hz was processed by a spectrum analyzer (HP35660A). Care was taken to exclude that spurious noise sources contributed to the results.

Results and Discussion

Figure 1 compares the temperature dependence of the resistivity of κ-Cl* with that of the resistance of κ-Cl located at different positions in the temperature-pressure phase diagram (see inset).
Because of the stress acting on the sample κ-Cl* embedded in epoxy, it exhibits a semiconducting (insulating) behavior down to about 46 K. At lower temperature the resistivity shows a pronounced minimum following the transition into the metallic phase. The S-shaped transition line of the MIT (see inset) is crossed again leading once more to insulating behavior below about 22 K, where a kink in the resistivity curve is observed. Upon further cooling, the sample undergoes an insulator-to-superconductor transition at T_c = 13 K (midpoint of the transition). The transition is rather broad due to the inhomogeneous nature of the coexistence region. The resistivity drops within ΔT_c = 1.9 K from 90 % to 10 % of its normal-state value. Although the transition temperatures for the present sample are somewhat higher, the observed behavior is in good agreement with the phase diagram determined from isobaric temperature and isothermal pressure sweeps by *Kagawa et al.* [6]. The reference samples κ-Cl showed the expected semiconducting behavior down to low temperatures.
A typical noise power spectral density (PSD) of κ-Cl* taken at T = 90 K is shown in Fig. 2 (right inset). At all temperatures above T_c we observe a noise spectrum of generic $1/f^{\alpha}$-type with $0.9 < \alpha < 1.1$. The main panel presents the normalized noise $S_R/R^2(T)$ taken at 1 Hz. We apply a phenomenological random fluctuation model introduced by Dutta, Dimon, and Horn (DDH) [9] based on the assumption that *1/f* spectra are created by the superposition of a large number of random and independent switching entities called "fluctuators", which are assumed to linearly couple to the resistance of the sample:

$$S(f) \propto \int \frac{\tau(E)}{\tau(E)^2 4\pi^2 f^2 + 1} D(E) dE. \qquad (1)$$

Each fluctuator is characterized by a thermally activated time constant $\tau = \tau_0 \exp(E/k_B T)$, where τ_0 is a characteristic attempt time of the order of an inverse phonon frequency, E the activation energy of the process and k_B Boltzmann's constant. *D(E)* represents a certain distribution of activation energies that is deduced from the application of the DDH model to the temperature dependent noise $S_R(T)$ (details of the analysis will be published elsewhere). The resulting *D(E)* (left inset of Fig. 2) exhibits a pronounced, roughly Gaussian peak at an energy of ~ 250 meV. This energy is known as the signature of the orientational degrees of freedom of the ET molecules' terminal ethylene moieties undergoing a glasslike transition at around 70 K [3,10], which corresponds to a certain degree of disorder. The peak energy agrees well with values of 224 − 232 meV reported in the literature, see [3]. This demonstrates that fluctuation spectroscopy provides a promising novel access to the microscopic transitions and dynamical molecular properties of the investigated materials.

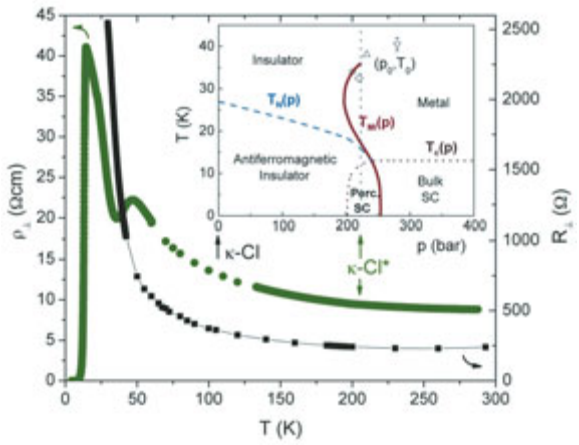

Fig. 1: Resistivity (resistance) of two samples of κ-(ET)$_2$Cu[N(CN)$_2$]Cl. Inset shows the experimentally obtained phase diagram. Arrows indicate the positions of the samples measured at ambient conditions (κ-Cl) and at a finite pressure (κ-Cl).*

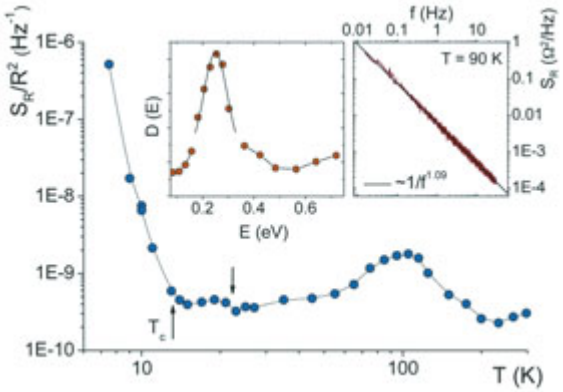

Fig. 2: Temperature dependence of the normalized resistance noise at 1 Hz of κ-Cl. Arrows indicate the superconducting transition (onset of Tc) and the temperature of re-entering the insulating phase. Right inset: PSD of the resistance noise at 90 K in a log-log plot. The line is a linear fit yielding SR ∝ 1/f1.09. Left inset: energy distribution D(E) extracted from the DDH model, see text.*

Upon further cooling the sample, the normalized noise power decreases again, before a small but distinct step-like increase in S_R/R^2 is observed at 22 K (see arrow in Fig. 2), which coincides with a kink in the resistivity (see Fig. 1 and text above). This feature is most likely due to the crossing of the MIT line when reentering the insulating state. In the following we will focus on the transition into the superconducting state which goes along with a substantial rise of the noise level. We interpret its more than two-orders-of-magnitude increase as a result of the percolative nature of the superconducting transition in this sample. Similar behavior has been observed for many high-Tc-cuprate samples, see, e.g., [11], and references therein. Qualitatively, in strongly disordered conductors, the resistance fluctuations are determined not by the entire volume of the conductor but rather by an essentially smaller volume leading to a large noise level. We now apply ideas of percolation theory and treat the coexistence region close to the MIT as a mixture of superconducting and non-superconducting (normal or insulating) phases, i.e., a lattice of resistors with a temperature-dependent fraction p that is short-circuited, simulating the superconducting links. For instance, one can think of a network of p Josephson-coupled junctions formed by connections between superconducting grains or clusters. A wide distribution of junction critical currents $i_c(T)$ means that at a given macroscopic current I, the local current i can be either larger or smaller than i_c which determines whether the junction is superconducting or resistive. In this "classical" percolation model [12], the noise level is determined by fluctuating (non-superconducting) resistors $r_i + \Delta r_i(t)$, i.e., resistive junctions. With decreasing temperature, p increases and hence, the noisy volume contributing to the macroscopic resistance fluctuations $R + \Delta R(t)$ shrinks, which in turn leads to a divergence of the spectral density of fractional resistance fluctuations when approaching the percolation threshold p_c from above, in agreement with our observations shown in Fig. 2.

In the present materials, even when homogeneous, it is known that the effect of fluctuations is strongly enhanced in increasing magnetic fields [3]. Consequently, we have studied the percolation effects at the superconducting transition in more detail by performing isothermal noise measurements in magnetic fields applied perpendicular to the planes. The magnitude of the resistance noise

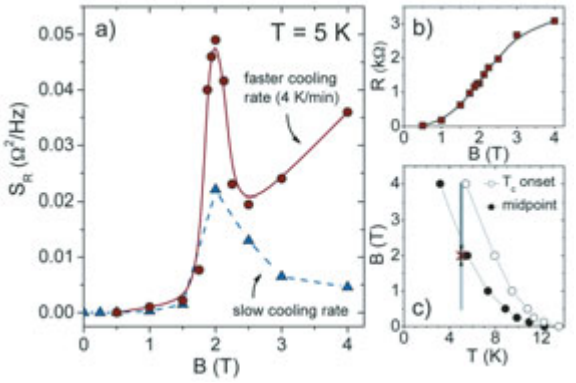

Fig. 3: (a) $S_R(B, T = 5 K)$ at 1 Hz for different cooling rates. (b) Magnetosresistance at 5 K and (c) phase diagram with the onset and midpoint of the superconducting transition at various fields. Dark and light gray lines indicate different scaling regimes (see text and Fig. 4), the cross shows the maximum noise level, and the black line indicates the regime in which the noise deviates from 1/f behavior.

at $T = 5$ K strongly depends on the magnetic field with a pronounced peak at $B = 2$ T, see Fig. 3(a) .

Percolation theory predicts power-law scaling behavior in the variable $(p - p_c)$, which very often cannot be determined accurately. Thus, it is more convenient [11] to consider a scaling law $S_R/R^2 \propto R^{lrs}$, where lrs is the resistor-superconductor (RS) network scaling exponent. Surprisingly, as shown in Fig. 4(a), the transition is not just dominated by a single scaling law but rather by two percolation regimes (different slopes lrs) with an apparent discontinuity corresponding to the peak in the noise level. Deep in the superconducting phase (low fields), the scaling follows the prediction for a "classical" RS network in 3D of $lrs = 0.9 \pm 0.3$ [12], whereas the slope when approaching superconductivity from above (high fields) is significantly larger. The slope we observe is close to the characteristic exponent of $lrs = 2.74$ for the so-called p model in 3D [12,13], which has first been observed for thin-film high-T_c superconductors. p noise leads to a new class of universal scaling exponents. In the above-described picture it corresponds to a random switching (on-off) of superconducting links in the RS network, i.e., spontaneous fluctuations $\Delta p(t)$ of $p(T)$ leading to fluctuations in the macroscopic resistance, which may be due to time-dependent perturbations of the Josephson coupling energy between superconducting clusters. When approaching $T_c(B)$ from high temperatures, percolation due to instable superconducting clusters or domains switching back and

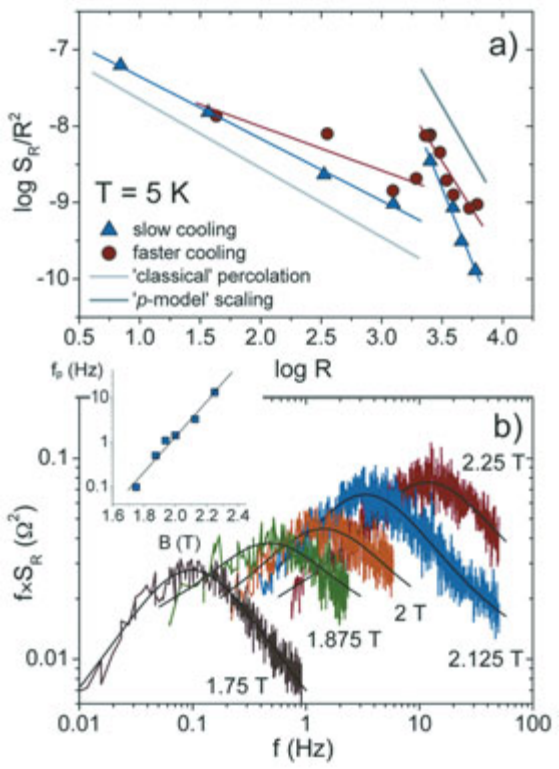

Fig. 4: (a) Scaling of the normalized noise S_R/R^2 versus the resistance R, for the data in Fig. 3. (b) PSD in the vicinity of the maximum noise level as $f \times S_R$ vs f. Lines are fits to Eq. (2) plus a 1/f background term. The inset shows the shift of the peak frequency f_p with applied magnetic field B.

forth dominates over the noise due to the resistive parts of the sample. At a field of 2 T, which is just below the midpoint of the resistive transition, see Figs. 3(b) and 3(c), the noise peaks and shows a crossover to a "classical" percolation regime dominated by the change in the fraction of superconducting domains.

Figure 4(b) shows the PSDs as $f \times S_R$ vs f at various fields in the vicinity of 2 T, where the noise peaks. In this narrow field range we observe clear deviations from *1/f*-type behavior which in this representation appears as a constant background. Obviously, under certain conditions ("noise window") the spectra are resolved into Lorentzian contributions

$$S_R(f) = \frac{4(\Delta R)^2}{(\tau_1 + \tau_2)[(\tau_1^{-1} + \tau_2^{-2})^2 + (2\pi f)^2]} \qquad (2)$$

representing a random telegraph signal between "high" and "low" resistance levels in the time domain [14]. Here τ_i denote the characteristic lifetimes for the high and low states. Lines in Fig. 4(b) are fits to a 1/f background plus Eq. (2) showing that an individual fluctuator dominates the noise.

The inset of Fig. 4 reveals a clear shift of the peak frequency $f_p = (1/2\pi)(\tau_1^{-1} + \tau_2^{-1})$ to higher values with increasing magnetic field. One may assume a thermally activated behavior, for which the energy barrier at a given temperature depends on magnetic field: $f_p = \tau_0^{-1}\exp[-(E + mB)/k_BT]$. Here, E denotes the energy barrier at zero field and mB the magnetic energy. We find a value of $E \sim 3.45$ meV from the fit to our data; see inset of Fig. 4. Considering the fluctuating entity as a cluster that switches between the superconducting and normal state, we compare this energy to the condensation energy density $V_s B_{cth}^2/2\mu_0$, where B_{cth} is the thermodynamic critical field and μ_0 the free space permeability. This approach yields a rough estimate for the fluctuating sample volume of $V_s \sim 340$ nm^3. An alternative explanation would be that in an already superconducting cluster the vortices become temporarily pinned and unpinned, possibly going along with switching between vortex solid and liquid states. Assuming that in such a case mB may simply be compared to the pinning energy we find a value for V_s which is smaller but in the same order as the one above. Thus, in both cases the estimated volume indicates a *mesoscopic* rather than a macroscopic inhomogeneous state.

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