Investigation of Low-Frequency Charge- and Spin-Dynamics in Correlated π-Electron Systems with Multi-Degrees of Freedom

We have investigated the dynamics of correlated charge carriers in the square-lattice dimer Mott insulator β'-(BEDT-TTF)$_2$ICl$_2$ by means of low-frequency fluctuation spectroscopy. The conductance noise power spectral density increases by seven orders of magnitude from room temperature to 70 K, the lowest temperature of our measurements, and can be described by localized fluctuations in a resistor network with variable range hopping. In a characteristic temperature region of 110 – 140 K a crossover of different transport and fluctuation regimes is observed. The localization of carriers at these temperatures is accompanied by the formation of polar nanoclusters and a slowing down of the fluctuation dynamics. From the break-up of the 1/f-type noise spectra into Lorentzian constituents which exhibit a peculiar temperature and electric field dependence we deduce the energy of the two-level fluctuation processes and a cluster size of nanopolar regions of about 20 nm.

Intradimer charge degrees of freedom in recent years have been recognized as key to understand the wealth of exotic ground states in correlated π-electron systems, as e.g. charge-order, ferroelectric order (the combination of which may provide a new mechanism for multiferroicity recently observed in organic charge-transfer salts [1]), magnetism and superconductivity. In particular, their role for the often anomalous dielectric response of different materials/samples exhibiting short-range relaxor-type and/or long-range order currently is a matter of considerable interest.

In order to better understand the role of charge fluctuations for the observed frequency dependent dielectric properties, we designed experiments aiming to study the low-frequency charge carrier dynamics by measuring the conductance noise power spectral density of β'-(BEDT-TTF)$_2$ICl$_2$, a typical square-lattice dimer Mott system, which is a model system for testing charge fluctuations on the dimer and may serve as a reference material for the triangular lattice spin-liquid candidate κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. The technique of measuring the conductance noise power spectral density (PSD) S_G, where $G = I/V$ is the conductance, has been developed and tested in the framework of a previous exchange of students between IMR, Sendai, and Goethe-University Frankfurt.

β'-(BEDT-TTF)$_2$ICl$_2$ orders antiferromagnetically at T_N = 22 K. The temperature dependence of the dielectric constant ε(T,ω) shows a peak structure obeying a Curie-Weiss law with a strong frequency dependence and a Curie temperature T_C = 67 K. The anisotropic ferroelectricity is found to be glassy in nature and the electrical dipoles are suggested to stem from charge disproportionation within the dimer [2,3].

Figure 1 shows the temperature dependence of the magnitude (main panel) and frequency exponent (inset) of the normalized conductance noise power spectral density (PSD) $S_I/I^2 \sim 1/f^\alpha$ taken at f = 1 Hz. The overall behavior resembles that of the resistance which reaches high values of order 10 GΩ at T ~ 70 K due to the Mott gap. The fluctuations, however, increase even more strongly and reveal additional information [4,5]. The strong increase of S_I/I^2 of seven orders of magnitude upon decreasing temperature from room temperature to 70 K of magnitude is well described by an exponential increase

$$\ln(S_I/I^2) = \text{const.} \times (T_0/T)^2,$$

where T_0 marks the crossover from nearest neighbor hopping to variable range hopping (VRH) [6]. In this model, the strong low-frequency dynamics is caused by localized slow fluctuations of the Coulomb potential, which modulates the conductance of nearby elements
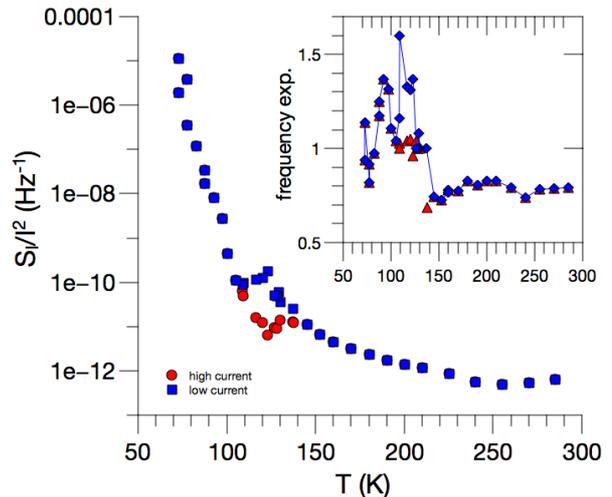
in the resistor network.

Fig.1 Conductance noise PSD of β'-(BEDT-TTF)$_2$ICl$_2$ measured in the low (blue) and high-current (red) limit. Inset shows the frequency exponent ⟨(T) from $S_I/I^2 \sim 1/f^\alpha$.

The frequency exponent α(T) shown in the inset if Fig. 1 shows a step-like increase below about 130 K from values of α ~ 0.8 to α ~ 1 or larger corresponding to a shift of spectral weight to low frequencies and a slowing down of the charge

fluctuations.

In the temperature region between 110 K - 140 K the resistivity starts to strongly increase and the conductance noise PSD exhibits a change in the scaling exponent ξ in $S_G / G^2 \sim G^\xi$ (not shown). In the same temperature range 110 K < T < 140 K, we consistently have observed Lorentzian noise spectra superimposed on a 1/f-like background and were able to fit the spectra accordingly, see Fig 2. Strikingly, as shown in Fig. 2 exemplarily for T = 123 K, above a threshold electric field E applied to the sample, the Lorentzian contribution becomes suppressed and its corner frequency f_c shifts to higher frequencies, while the 1/f^α background also becomes suppressed (shown in Fig. 1). We suggest that in this crossover region where pronounced two-level fluctuations are observed, switching entities, i.e. nano polar regions (NPR) that couple to the external electric field, are formed. The corner frequencies f_c at small currents, i.e. below the threshold electric field, can be described by a thermally activated behavior yielding an activation energy of about E_a = 2800 K, which is comparable to the intradimer transfer energy. However, a Vogel-Fulcher fit to the data $f_c(T)$ works equally well and yields a Vogel-Fulcher temperature of T_{VF} = 32 K, not far from the charge freezing temperature T_{VF} determined from the frequency-dependent peak in the dielectric function [2]. The electric-field dependence $f_c(E)$ above the threshold can be fitted by

$$f_c = f_0 \text{ x } \exp[-(E_a + pE)/k_BT]$$

from which we were able to estimate the total dipolar moment p. With the local moment on the dimer of 0.13ed [2] a nanoscale cluster (NPR embedded in a paraelectric matrix) size of radius ~ 20 nm is estimated.

References
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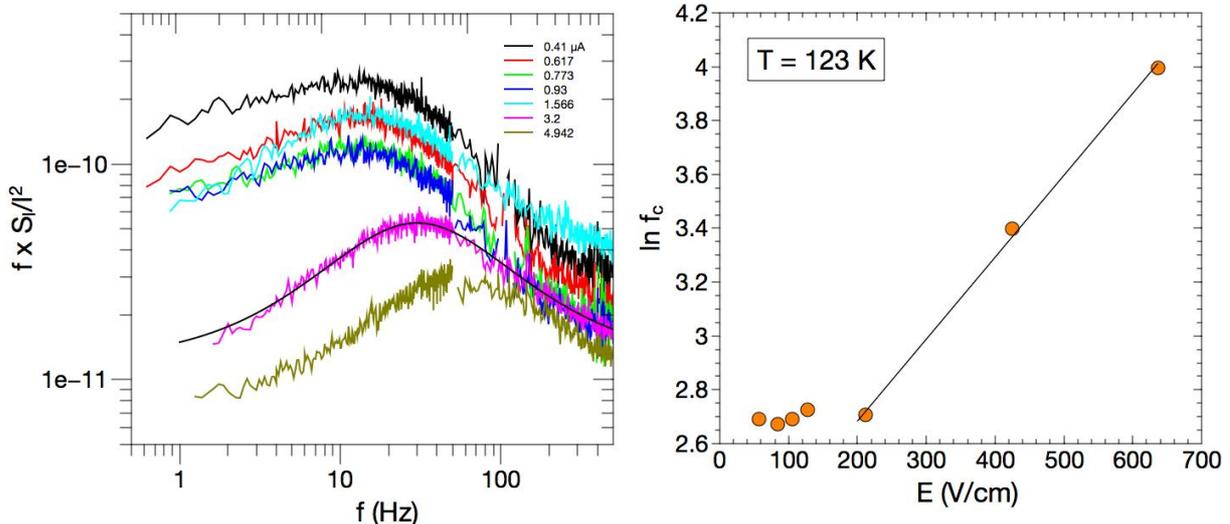
Fig. 2 Left: Lorentzian spectra at T = 123 K superimposed on a 1/f^$\langle$ background for different currents. Solid line is the corresponding fit to the data (exemplarily shown for one curve). Right: Corner frequency f$_c$ for different electric fields.