Charge and spin interplay in a new spin liquid candidate BEDT-TTF-based organic Mott insulator

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Triangular lattice quasi-two-dimensional Mott insulators based on BEDT-TTF molecule and its analogies present the largest group of spin liquid candidates on triangular lattice. It was shown theoretically that spin liquid state in these materials can arise from a coupling to the fluctuating charge degree of freedom. In this work we discuss magnetic properties of one of such materials, κ-(BEDT-TTF)2Hg(SCN)2Cl, which is known to be at the border of the phase transition from Mott insulator into a charge ordered state, and demonstrates charge order properties in the temperature range from 30 to 15 K. Our magnetic susceptibility and cantilever magnetisation measurements demonstrate an absence of spin order in this material down to 120 mK. We present arguments demonstrating that the charge order melting at low temperatures prevents ordering of spins.

INTRODUCTION

Research in frustrated magnetism is already for some time focused on a search for a quantum spin liquid. This quantum disordered spin state is expected in systems with frustrated or competing interactions, and can be heavily influenced by disorder in the candidate systems [1,2]. Quasi-two-dimensional (2D) Mott insulators based on the organic molecule BEDT-TTF [3] produced the largest number of organic spin liquid candidates [4-9] presumably due to a presence of a ring exchange for S=1/2 system on anisotropic triangular lattice [10,11]. Another path to a spin liquid state was suggested for organic Mott insulators, where the driving force are on-site fluctuating electrical dipole moments coupled to on-site S=1/2 degree of freedom [12,14]. These fluctuating dipole moments, and associated with them quantum dipole liquid state, were detected experimentally [15,16]. Studies of magnetic effects that can be brought about by a fluctuating charge degree of freedom coupled to spins in a Mott insulator are of high interest.

In this work we probe experimentally magnetic properties of κ-(BEDT-TTF)2Hg(SCN)2Cl (κ-HgCl), which at low temperatures presents is a good model of a Mott insulator possessing an electrical dipole degree of freedom. In κ-HgCl structure, (BEDT-TTF)2 dimers form a triangular lattice in the BEDT-TTF-based layer, with an average charge of one hole per (BEDT-TTF)2 and S=1/2 achieved by a charge transfer between anion and cation layers (Fig. 1a). A metal at high temperatures, κ-HgCl undergoes a charge order metal-insulator transition at 30 K, and then a continuous melting of this charge order below 15 K. This behavior allows us to study coupling between charge (electric dipole) and spin degrees of freedom.

Melting of the charge order can lead to inhomogeneities, appearance of domain walls, and charge disorder. An interplay of disorder and low-dimensionality is an important direction of research for spin liquid materials. One of the recent examples on a triangular lattice is YbMgGaO4, where structural disorder controls magnetic state [17]. Many materials, of which YbMgGaO4 is an example, possess intrinsic structural disorder. In order to study disorder effects in some situation disorder is introduced by X-ray irradiation [18]. κ-HgCl provides a unique situation where charge inhomogeneities are present only in a temperature range below 15 K, and their scale is temperature dependent. It can give an additional insight of how inhomogeneities control magnetic state of the system.

The behavior of the charge degree of freedom in κ-HgCl is well studied by now. On the charge order transition, a small charge difference of Δn=0.2e between charge-poor and charge rich molecules of a dimer leads to a dipole solid state [19,20]. This charge distribution in the insulating state is schematically indicated by red and blue color for the (BEDT-TTF)2 layer in Fig. 2. The charge order transition drives a large increase of d.c. resistivity [19,21] and a notable feature in heat capacity (Fig. 2) [16,20]. While the lattice response is detected on this first order phase transition [20], and some lattice phonons change [17], the lattice change has not been detected by the XRD studies which were performed so far [19]. Optical, Raman, and...
length change measurements suggest, that on the ordering transition the electronic system changes dimensionality from 2D to 1D due to the formation of charge stripes along the c axis [10, 19, 20]. In accord with the experiments, calculations by Ref. [22] suggest that the charge order in \(\kappa\)-HgCl results in a high in-plane anisotropy of magnetic exchange interactions \(J\), leading to an effectively 1D magnetism for \(\kappa\)-HgCl in contrast to \(\kappa\)-(BEDT-TTF)\(_2\)Cu\(_4\)(CN)\(_3\). 1D antiferromagnetic (AF) stripes can result in a 1D spin liquid, presenting another possible way to reach a spin liquid state for \(\kappa\)-HgCl [23, 24]. Alternatively, a strong coupling of spin degrees of freedom to the lattice can result in a formation of a spin singlet state [25], as observed, for example, in \(\theta\)-(BEDT-TTF)\(_2\)RbZn(SCN)\(_4\) [20].

Here we present our results on heat capacity, SQUID magnetic susceptibility, and cantilever torque magnetometry measurements of \(\kappa\)-HgCl. As expected for a compound with a complicated phase diagram related to the charge degree of freedom, magnetic properties of \(\kappa\)-HgCl also show complex temperature dependence. The main result of our work is that no magnetic order is detected in this system down to at least 120 mK, while the exchange interactions are on the order of at least 100 K. In contrast to the majority of organic triangular lattice spin liquid candidates, \(\gamma\) linear term is heat capacity is negligibly small in this system. This points on a new path to a spin liquid state in \(\kappa\)-HgCl.

On metal-insulator transition in \(\kappa\)-HgCl at \(T=30\) K, heat capacity shows a distinct peak (see Fig. 2(a)). No other phase transition is detected down to 100 mK, the extrapolation down to 0 K suggests a negligible linear component of \(\gamma\) term in heat capacity \(C_p = A T^\gamma + B T^\alpha\).

Magnetic susceptibility \(\chi_M(T)\) of a polycrystal sample of 2.451 mg measured at 1 T (Fig. 2(b)) reveals a complex temperature dependence. Above the metal-insulator transition, \(\kappa\)-HgCl shows Pauli susceptibility of about \(4 \times 10^{-4}\) emu/mol, which is a value close to the other BEDT-TTF-based organic conductors [27]. On the metal-insulator transition at 30 K magnetic susceptibility \(\chi_M(T)\) does not show any change within the noise of the measurements. Instead, magnetic susceptibility starts to decrease abruptly on cooling below about 24 K. However, instead of decreasing down to the lowest values with \(\chi_M = 0\), as is expected in case of a spin gap or an antiferromagnetic ordering, magnetic susceptibility starts to rise again on cooling the sample below 15 K. \(\chi_M(T)\) saturates below about 5 K, with the saturation values of about \(3.5 \times 10^{-4}\) emu/mol. No indication of magnetic ordering is found in \(\chi_M(T)\) of \(\kappa\)-HgCl measured down to 2 K.

BEDT-TTF based crystals are typically very small, and posses very low magnetic susceptibility (Fig 2). In order to detect possible magnetic ordering or singlet formation in the charge ordered state, and to understand the nature of the low temperature magnetic state, we performed measurements of cantilever torque magnetization for single crystals of \(\kappa\)-HgCl. This method proved to be the most sensitive to detect magnetic order, and was successfully applied to organic Mott insulators [28, 30]. Magnetic torque signal measured for \(\kappa\)-HgCl is described well by the following equation:

\[
\chi_M(T) = \frac{\text{experimental data}}{\text{Bonner-Fisher}}
\]
\[ \tau = \tau_0 + \tau_0 \sin(\theta - \theta_1) + \tau_2 \sin(2\theta - \theta_2) \]  

(1)

In \( \kappa \)-HgCl torque response, \( \tau_1 \sin(\theta - \theta_1) \) component does not change with applied magnetic field at all measured temperatures (see Supplement Information). We conclude that it fully corresponds to the gravity force, no ferromagnetic component of torque was detected. The \( \tau_2 \sin(2\theta - \theta_2) \) component in the torque response of \( \kappa \)-HgCl corresponds to the paramagnetic behavior.

Cantilever torque magnetization measurements show the persistence of paramagnetic response when \( \kappa \)-HgCl is cooled through the charge order transition at 30 K and below this temperature, but detect an abrupt increase of torque amplitude \( \tau_{2\theta} \) at \( T=30 \) K, as shown in Fig. 3. Torque amplitude \( \tau_{2\theta} \) for the rotation in \( ab \) plane at 1 T roughly follows the temperature dependence of magnetic susceptibility, with a decrease at about 20 K, and an increase below 15 K. The phase of \( 2\theta \) for rotation in \( ac \) plane follows this temperature behavior, while the amplitude stays constant on cooling. These effects are weak, and are suppressed at 3 T and higher fields.

![FIG. 3. (a) Scheme of cantilever torque magnetometry experiment with rotation direction for \( ab \) plane shown with blue arrow, and magnetic field direction shown in black. (b) Angle dependence of paramagnetic component \( \tau_{2\theta} \) at 5 T, rotation in \( ab \) plane for temperatures related to the different charge states of \( \kappa \)-HgCl. (c)-(d) Temperature dependence of an amplitude and phase of paramagnetic component of magnetic torque \( \tau_{2\theta} \). (c) shows a temperature dependence of paramagnetic torque amplitude \( \tau_{2\theta} \) in \( ac \) plane and \( ab \) planes. (c) shows temperature dependence of the phase \( \theta_2 \) in \( ac \) and \( ab \) planes.](image)

Magnetization was measured by following the torque amplitude dependence on magnetic field \( H \) at an angle where the amplitude of torque is maximum, see Fig. 4. At temperatures \( T=20, 10, 5, 1.9 \) K for the filed up to \( H = 5 \) T torque \( \tau \) shows parabolic dependence \( \tau \propto H^2 \), suggesting a paramagnetic state and absence of magnetic order. To probe the low temperature magnetic state we performed cantilever torque magnetometry measurements down to 120 mK and up to 17.5 T (Fig. 4), which confirmed \( \tau \propto H^2 \) behavior at this temperature up to the highest measured field.

First, we will discuss magnetic properties of \( \kappa \)-HgCl around the temperature of the charge order phase transition. An absence of a change of magnetic susceptibility at \( T=30 \) K is unexpected: The character of \( \chi_M(T) \) is expected to change from Pauli to a behavior of an insulator with unpaired spins or a spin singlet state. The absence of a change in \( \chi_M(T) \) is in contrast to the behavior of magnetic susceptibility observed on charge order metal-insulator transitions in other 2D BEDT-TTF-based materials, which showed a formation of a spin singlet in the charge ordered insulating state [26, 31]. The paramagnetic behavior below the transition temperatures is confirmed by the cantilever magnetic torque measurements. The jump of the amplitude of paramagnetic torque \( \tau_{2\theta} \) at 30 K detects a change of the anisotropy of g-factor, which can occur due to a crystal or electronic structure change [32]. The structural change on the charge ordering transition is not detected by XRD so far [19], but the lattice phonons show some changes [14]. A large change of electronic structure which acquires 1 D character [19, 22] can be a source of this change.

An absence of an observable change in magnetic susceptibility can be explained by a coincidence of absolute values in the metallic and insulating regimes. On the other hand, a similar absence of a change in magnetic susceptibility on charge localization in TMTTF-based materials [33] was suggested as an evidence of charge and spin degrees of freedom being decoupled [34]. These materials show 1D electronic behavior, and are well-described by the Bonner-Fisher (BF) model of magnetic susceptibility. Typically, they show a transition into a magnetically ordered or spin-Peierls state at temperatures about ten times lower than the temperature of the metal-insulator transition [34]. There is an apparent qualitative similarity between the decoupling of the spin
and charge degrees of freedom in 1D TMTTF salts and the behavior of charge and spin properties of \(\kappa-HgCl\), though the difference between the temperatures of the insulating transition and the decrease of \(\chi_M(T)\) is much smaller.

An evidence of an emergent 1D behavior of the charge degree of freedom \cite{16,19,20} suggests, that a suitable model is a BF model for magnetic susceptibility of \(S=1/2\) antiferromagnetic 1 D chains. \cite{35,36}. While the temperature range of 24 K-30 K is too narrow to extract values of magnetic exchange \(J\) from a fit to the experimental data, we can still compare the relevant temperature dependence. Fig.\(\text{2}(a)\) green curve shows susceptibility calculated by the numerical approximation of the BF model \cite{37} with one electron per (BEDT-TTF)\(_2\) dimer and \(J=400\) K. The decrease of \(\chi_M(T)\) on cooling below \(T=24\) K is much faster than the BF or triangular lattice magnetic susceptibility \cite{21}, and cannot be understood without considering AF or spin singlet correlations or ordering. The decrease of susceptibility was also observed in ESR measurements \cite{21}. Decreasing susceptibility in a small temperature range between 24 K and 15 K can be fit by a magnetic susceptibility of a gapped system \(e^{-\frac{\Delta}{k_BT}}\), which yields a gap \(\Delta=36\) K=1.5 Tc. A transition to a spin-singlet or antiferromagnetically ordered state can be expected in this charge ordered system, based both on theory \cite{25} and on experimentally observed behavior of other charge-ordered materials \cite{26,33}.

Heat capacity in the region of 24 K does not show any phase transition features, but this measurements method is known to be not to be a sensitive indicator of a magnetic transition neither in 1 D \cite{35}, nor in 2 D \cite{39} organic-based systems.

Due to its high sensitivity, the most reliable information is obtained by the cantilever torque measurements. On a spin singlet transition an amplitude of magnetic torque should decrease down to zero, however magnetic torque of \(\kappa-HgCl\) preserves its paramagnetic character below 24 K, and does not detect any signatures of magnetic ordering. A weak decrease of torque amplitude \(\tau_\theta\) in \(ab\) plane, and of phase values in \(ac\) plane observed at 1 T (Fig. 2) follow the susceptibility behavior. As a whole, this decrease of susceptibility without long range order detected suggests that AF order or spin singlet pairs might be formed with a certain correlation length in the temperature range between 24 and 15 K.

Below 15 K magnetic susceptibility starts to increase again. This change occurs when \(\kappa-HgCl\) enters the temperature regime where the re-entrant behavior resulting in melting of the charge order is observed by Raman scattering \cite{10}. The increase of \(\chi_M(T)\) below 15 K cannot be fully described as a response of magnetic impurities producing the Curie-like behavior: It shows weaker temperature dependence and flattens below 5 K, instead of diverging as 1/T.

In the temperature regime where the charge order is melting, magnetic susceptibility will present a superposition of the susceptibility of charge-ordered static or slowly fluctuating (\(\chi_{CO}\)) and non-ordered (\(\chi_H\)) components of the system, as well as susceptibility of domain walls between ordered and non-ordered fractions \(\chi\) : \(\chi_M = \rho \chi_H + (1-\rho)\chi_{CO} + \chi_D\). Here \(\rho\) is a part of the system where the charge order is melted. It is controlled by temperature, increasing from \(\rho = 0\) in the charge ordered system above 15 K, to \(\rho = 1/3\) at 2 K \cite{16}. It would be natural to expect that the scale of the ordered chains decreases, and the number of domain walls increases with the increase of \(\rho\).

Basing on the behavior of susceptibility in the 24-15 K range, we can assume \(\chi_{CO}=0\). The susceptibility of the non-charge-ordered fraction of the system \(\chi_H\) would depend on the dimensionality; BF susceptibility in the Fig.\(\text{2}(a)\) provides some estimate for non-ordered susceptibility for \(\rho = 1\). The increase of \(\chi_M(T)\) on cooling between 15 and 5 K can be associated an increase of \(\rho\) on cooling, but would also include the response of the domain walls between ordered and non-ordered domains. It is known, that non-interacting free spins at the ends of charge ordered chains can produce a Curie law dependence in \(\chi_H(T)\) \cite{37}, while interactions between domain walls lead to a more complicated picture (Ref. \cite{10} and references therein), which can be related to the magnetic susceptibility of \(\kappa-HgCl\). Two spins on the ends of fluctuating charge order chains interacting through a non-charge-ordered dimer domain wall are suggested to produce dynamic ferromagnetic interactions. The relevant response observed in an increase of \(\chi_M(T)\) on cooling for the dipole liquid candidate \(\kappa-(BEDT-TTF)_2Hg(SCN)_2Br\) \cite{11}. It worth noting, that the increase and saturation of \(\chi_M(T)\) below 15 K in \(\kappa-HgCl\) is similar to this response, but on a much smaller scale. Ref. \cite{10} demonstrates that orphan spins of domain walls produce a paramagnetic behavior in torque, with temperature and magnetic field dependence of the phase \(\theta_2\) and amplitude \(\tau_\theta\) of the paramagnetic component. In \(\kappa-HgCl\) torque data show this effect. It is weak, and is only observed at 1 T, suggesting that the impurity spins are saturated at higher fields.

Overall the data suggest that the increase of the \(\chi_M(T)\) on cooling and the temperature dependence of torque at low fields is produced by interacting domain walls, which are fully polarized already at 3 T according to the torque measurements, and the torque signal in \(\kappa-HgCl\) is dominated by the bulk response of paramagnetic spins. This result is in agreement with a suppression of a peak in \(T^{-1}\) in NMR \cite{42} response by the magnetic field directed perpendicular to BEDT-TTF-based layers, and confirms that the peak is due to the response of the domain walls. According to Raman data in magnetic field in this direction, the charge distribution itself does not change in field up to 30 T \cite{43}. 
No indication of magnetic ordering is observed in magnetic cantilever torque studies of $\kappa$-HgCl down to 120 nK, with paramagnetic torque amplitude $\tau_{yz} \propto H^2$ up to the highest measured field of 17.5 T, and the phase being constant with field. This absence of magnetic order or of a spin singlet state in an insulator $\kappa$-HgCl with one unpaired electron ($S=1/2$) and estimated magnetic exchange $J$ of the order of 100 K or higher suggests of a spin liquid state, the same conclusion that came from NMR measurements. However, the low temperature magnetic state in $\kappa$-HgCl has signatures different from spin liquid candidates triangular 2D organic Mott insulators.

The present essential difference between $\kappa$-HgCl and other triangular lattice Mott insulators is the spectrum of magnetic excitations. In S=1/2 triangular lattice organic Mott insulators without a detected charge degree of freedom, such as (BEDT-TTF)$_2$Cu$_2$(CN)$_3$, (BEDT-TTF)$_2$Ag$_2$(CN)$_3$, and Pd(dmit)$_2$-based materials Raman scattering spectroscopy detects a continuum of magnetic excitations that corresponds to theoretically suggested excitation spectrum of a triangular lattice with S=1/2. This continuum is absent in $\kappa$-HgCl. While magnetic excitations is this material are still to be detected, the difference indicates a different magnetic state, possibly due to 1D properties of $\kappa$-HgCl below 30 K, or magnetic interactions decreased by more than one order of magnitude.

In contrast to 2D triangular spin liquid candidates in $\kappa$-HgCl shows $\gamma=0$ linear term in the heat capacity. This is an expected result for a non-ordered S=1/2 antiferromagnetic chain, and is another evidence of 1D behavior.

Below 15 K the system looses signatures of short range magnetic correlations, with charge fluctuations and response of domain walls becoming dominant. Basing on a relatively weak response on the domain walls, we can argue that their concentration is pretty small. As apparent from the data, and do not lead to a possible random singlet state that can be induced by disorder. This suggests that a scenario of 1D S=1/2 chains where fluctuating charge degree of freedom is coupled to spins and prevents their order is the most relevant.

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A seemingly similar material κ-ET$_2$Cu$_2$(CN)$_3$ that shows a very close magnetic susceptibility values of $\chi_M = 5 \times 10^{-3}$ emu mol$^{-1}$ at 30 K [4] is not the right compound to compare with. This system shows magnetic excitations of a two-dimensional triangular lattice of ET-dimers with $J=250$ K, and lacks any charge disproportionation [35].

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Supplement information

Synthesis Single crystals of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl ($\kappa$-HgCl) were prepared by electrochemical oxidation of the BEDT-TTF solution in 1,1,2-trichloroethane (TCE) at a temperature of 40°C and a constant current of 0.5 μA. A solution of Hg(SCN)$_2$, [Me$_4$N]SCN-KCl, and dibenzo-18-crown-6 in 1:0.7:1 molar ratio in ethanol/TCE was used as supporting electrolyte for the $\kappa$-HgCl preparation. The composition of the crystals was verified by electron probe microanalysis and X-ray diffraction.

Heat capacity Heat capacity was measured using Quantum Design PPMS system equipped with the DR option for crystals of the mass 2-4 mg.

![Heat capacity](image)

FIG. 5. Heat capacity of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl in the range 100 mK - 3 K. Note γ = 0 within the error of the measurements.

Magnetic susceptibility

Bonner-Fisher susceptibility (Fig. 2(a), green curve) was calculated following the numerical approximation form Ref. 37

$$\chi_{BF} = \frac{N g^2 \mu_B^2}{k_B T} \left( 1 + \frac{0.25 + 0.14995 x + 0.30094 x^2}{x^2} \right),$$

where $x = |J|/k_B T$ with one electron per (BEDT-TTF)$_2$ dimer and $J=400$ K.
Fig. 6 shows magnetic susceptibility data in the whole measured range. The figure also demonstrated a curve of \( \chi_{\text{dimer}} = A e^{-\frac{T}{\Delta}} \) which can describe \( \chi_M(T) \) in the temperature range between 24 and 15 K, and \( \chi_{\text{Curie}} = C/T \) to compare to the low-temperature behavior of \( \chi_M(T) \).

Cantilever magnetic torque measurements

Fig. 7 presents an example of analysis of the cantilever magnetic torque data. The full torque \( \tau \) (black curve) is reproduced well by the sum of \( \tau_0 \sin(\theta - \theta_1) \), and \( \tau_2 \theta \sin(\theta - \theta_1) \) components. Calibration of the cantilever response by gravity signal is discussed in details in Ref. [50].
FIG. 7. Upper panel: Cantilever magnetic torque data analysis, and example for the data for the rotation in ab plane at 5 K in magnetic field of 5 T. The figure shows original data, and $\tau_{\theta}\sin(\theta - \theta_1)$, and $\tau_{2\theta}\sin(2(\theta - \theta_1))$ components with the respective fitting curves. Lower panel: Raw data of $\kappa$-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl obtained by cantilever magnetic torque measurements. Measurements are done for rotation in ab plane, H= 5T. Angle dependence of $\tau_{2\theta}$ extracted from these measurements is presented in Fig. 3(b)