Evidence for Electronically Driven Ferroelectricity in a Strongly Correlated Dimerized BEDT-TTF Molecular Conductor


Phys. Rev. Lett. 120, 247601 — Published 14 June 2018

DOI: 10.1103/PhysRevLett.120.247601
Evidence for electronically-driven ferroelectricity in a strongly correlated dimerized BEDT-TTF molecular conductor

Elena Gati¹, Jonas K.H. Fischer², Peter Lunkenheimer², David Zielke¹, Sebastian Köhler¹, Felizitas Kolb³, Hans-Albrecht Krug von Nidda², Stephen M. Winter³, Harald Schubert¹, John A. Schlueter⁴,⁵, Harald O. Jeschke³,⁶, Roser Valentí³, and Michael Lang¹

¹ Institute of Physics, Goethe-Universität, Max-von-Laue-Straße 1, 60338 Frankfurt am Main, Germany
² Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86159 Augsburg, Germany
³ Institute for Theoretical Physics, Goethe-Universität, Max-von-Laue-Straße 1, 60338 Frankfurt am Main, Germany
⁴ Division of Materials Research, National Science Foundation, Arlington, VA 22230, USA
⁵ Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA and
⁶ Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan
(Dated: May 14, 2018)

By applying measurements of the dielectric constants and relative length changes to the dimerized molecular conductor κ-(BEDT-TTF)₂Hg(SCN)₂Cl, we provide evidence for order-disorder type electronic ferroelectricity which is driven by charge order within the (BEDT-TTF)₂ dimers and stabilized by a coupling to the anions. According to our density functional theory calculations, this material is characterized by a moderate strength of dimerization. This system thus bridges the gap between strongly dimerized materials, often approximated as dimer-Mott systems at 1/2 filling, and non- or weakly dimerized systems at 1/4 filling exhibiting charge order. Our results indicate that intra-dimer charge degrees of freedom are of particular importance in correlated κ-(BEDT-TTF)₂X salts and can create novel states, such as electronically-driven multiferroicity or charge-order-induced quasi-1D spin liquids.

PACS numbers: 77.80.-e, 77.84.Jd, 71.30.+h, 71.15.Mb

Introduction. — Electronic ferroelectricity, where electrons play the role of the ions in conventional displacive ferroelectrics, has recently become an active area of research¹⁻⁵. Characteristic of this novel type of ferroelectricity is that the polar state is controlled by electronic degrees of freedom of charge, spin and orbital nature, implying the intriguing possibility of cross-correlations with the material’s magnetic properties.

A key phenomenon for electronic ferroelectricity is charge order (CO), resulting from strong electronic correlations, and being ubiquitous in doped transition-metal oxides, such as high-Τc cuprates⁶ or manganites⁷. Particularly clear examples of CO have been found in the families of TMTTF⁸ and BEDT-TTF⁹⁻¹² (in short ET) molecular conductors with 1/4-filled hole bands. It has been established that in these systems, CO and accompanying ferroelectric properties¹³⁻¹⁵ result from the combined action of a strong onsite Coulomb repulsion U along with a sizable inter-site interaction V¹⁶⁻¹⁸.

More recently, the research in this area has gained a new twist by the observation of strong hints for ferroelectricity in some dimerized ET-based materials¹⁵,¹⁹⁻²¹. This came as a surprise as these systems have been primarily discussed in the so-called dimer-Mott limit²²⁻²⁴, where the Mott insulating state is solely driven by a strong U, and lacks a CO instability. In this limit, (ET)₂ dimers are considered as single sites due to a strong intermolecular interaction t₁ (cf. Fig. 1(b)), being much larger than the inter-dimer interactions t and t’ (Fig. 1(c)). This results in a 1/2-filled band, in which intradimer charge degrees of freedom are completely frozen. However, remarkably, for κ-(ET)₂Cu[N(CN)₂]Cl, ferroelectric order was found at T_{FE}²⁵⁻²⁷ which coincides with long-range antiferromagnetic (afm) order²⁸ at T_N ≈ T_{FE}. It has been suggested that in these dimerized systems the electric dipoles originate from CO⁴,²⁰,²⁵,²⁹⁻⁳², i.e., a charge disproportionation by ±δ within the ET dimers, suggesting an essential breakdown of the dimer-Mott scenario. However, this view has been challenged as a definite proof of CO for this family of dimerized ET systems is still missing³³⁻³⁵.

In this Letter, we provide evidence for an electronically-driven ferroelectricity in the related dimerized salt κ-(ET)₂Hg(SCN)₂Cl, where CO was clearly identified by vibrational spectroscopy³⁶,³⁷. Based on our density functional theory calculations, this material has a moderate strength of dimerization thus bridging the gap between 1/4-filled CO and 1/2-filled dimer-Mott systems. We demonstrate that the transition from a metal to a CO insulator in this compound at T_{MI} = T_{CO} ≈ 25 – 30 K is accompanied by the formation of ferroelectric order of order-disorder-type, where disordered electric dipoles exist already in the paraelectric phase, and become ordered below T_{FE} = T_{MI}. Our results highlight the role of intra-dimer degrees of freedom in creating novel
states, such as electronically-driven multiferroicity or CO-induced quasi-1D spin-liquids. In addition, our findings underline the model character of the $\kappa$-(ET)$_2$X systems in studying the interplay of charge-, spin- and lattice$^{38}$-degrees of freedom in the presence of geometrical frustration$^{24}$ close to the Mott transition.

Structure and ab initio-derived hopping integrals. —
$\kappa$-(ET)$_2$Hg(SCN)$_2$Cl, crystallizing in the monoclinic structure$^{36,39} C2/c$, consists of alternating thick layers of organic ET molecules, separated by thin anion sheets, cf. Fig. 1(a). *Ab initio* density functional theory calculations were performed using the full potential local orbital (FPLO)$^{40}$ basis and generalized gradient approximation$^{41}$ for the experimentally determined structure$^{36}$ at room temperature. The tight binding parameters $(t_1, t_2, t_3, t_4)$ (see Fig. 1(b)) were extracted from fits to the bandstructure. We find values at 296 K of $t_1 = 126.6$ meV, $t_2 = 60.0$ meV, $t_3 = 80.8$ meV, and $t_4 = 42.0$ meV (see SI for $T$ dependence of the $t_i$’s). We use the usual geometric formulas $t = (t_2 + t_4)/2$, $t’ = t_3/2$ for assessing the hopping parameters $t = 51.0$ meV and $t’ = 40.4$ meV of the effective-dimer model (see Fig. 1(c)).

Experiments. — Single crystals of $\kappa$-(ET)$_2$Hg(SCN)$_2$Cl were grown by electrocrystallization (see SI). Overall 4 crystals (3 for dielectric measurements, 1 for thermal expansion measurements) of two different sources (labeled with either AF or JAS) were studied to check for sample-to-sample variations. Dielectric measurements were performed with the electric field applied along the out-of-plane $a$ axis, the only possible configuration because of the distinctly lower conductance along this axis. In the low-frequency range ($\nu < 1$ MHz), the dielectric constant $\epsilon’$ (real part of the permittivity) and the real part of the conductivity $\sigma’$ were determined using a frequency-response analyzer (Novocontrol alpha-Analyzer) and an autobalance bridge (Agilent 4980). The system’s high conductivity and the small sample size cause some uncertainties in the absolute values of $\epsilon’$. Measurements of relative length change $\Delta L_i(T)/L_i$, with $i = a, b, c$, were performed using a home-built capacitive dilatometer$^{42}$ with a resolution $\Delta L_i/L_i \geq 10^{-10}$.

Figure 2 shows the dielectric constant $\epsilon'(T)$ (a) and the real part of the conductivity $\sigma'(T)$ (b) of crystal #AF093-1. We find an increasing $\epsilon'(T)$ with decreasing temperature, culminating in a sharp peak at $T_{FE} \approx 25$ K, indicative of a ferroelectric transition (peak value $\approx 400$). As shown by the dashed line in Fig. 2(a), this increase can be well described by a Curie-Weiss law, $\epsilon’ - \epsilon_{off} = C/(T - T_{CW})$, with a Curie-Weiss temperature $T_{CW} = (17 \pm 2)$ K and an offset $\epsilon_{off}$, likely of extrinsic nature. The relatively small magnitude of the Curie constant of $C = (2500 \pm 600)$ K is consistent with order-disorder ferroelectricity$^{43}$ while $C$ for displacive ferroelectrics$^{44}$ is usually of the order of $10^5$. By using a simple expression$^{45}$ to relate the Curie constant to the size of an individual dipole$^{46}$ $p$, we find $p \approx 0.4ed$, with $e$ the electronic charge and $d \approx 4.0$ Å the distance between two ET molecules within the dimer. In light of the strong simplifications involved in this relation and the experimental uncertainties associated with the absolute values of $\epsilon’$, this value of $p$ is in reasonable agreement with the expected out-of-plane dipole moment of 0.13$ed$ created by the observed charge disproportionation$^{36}$ of $\pm 0.1e$ and the relative shift of the molecules within the dimer resulting in a tilt of the dipole moment by $\approx 50^\circ$ with respect to the out-of-plane $a$ axis. Below 25 K, $\epsilon'(T)$ exhibits an abrupt drop and levels off at $\epsilon’ \approx 8$ at low temperatures. By looking at the inverse dielectric constant in the inset of Fig. 2, we find that, in a limited temperature range, $\epsilon'(T)$ for $T < T_{FE}$ can also be described by a Curie-Weiss behavior (solid line), albeit with a distinctly larger slope $[d(1/\epsilon’)/dT]$.

Corresponding measurements on a second crystal (#JAS1721) from a different source, performed with a different measurement device, revealed qualitatively similar behavior with $T_{FE} \approx 30$ K (see SI, Fig. 3). We did not observe any significant frequency dependence of the dielectric properties for frequencies below about 1 MHz (see SI, Fig. 2). However, in high-frequency measurements up to about 1 GHz (see SI, Fig. 4), we found an increasing suppression of the peak in $\epsilon'(T)$ with increasing
The characteristics of $\varepsilon'(T)$, revealed in Fig. 2(a) (and SI Fig. 3(a)), are remarkable in terms of the following aspects. First, the phenomenon closely resembles textbook examples of first-order ferroelectric transitions reported, e.g., for BaTiO$_3$ or AgNa(NO$_2$)$_2$ (Refs. [44, 48, 49]). This includes a Curie-Weiss temperature dependence both above and below $T_{FE}$ with strongly different slopes $|d(1/\varepsilon)/dT|$, together with a Curie-Weiss temperature $T_{CW} < T_{FE}$. Second, the observed temperature (Fig. 2(a) and SI Fig. 3(a)) and frequency dependences (SI Fig. 2 and 4) indicate that $\kappa-(ET)$_2$Hg(SCN)$_2$Cl represents an order-disorder-type ferroelectric. This contrasts with relaxor-type ferroelectricity, characterized by a pronounced frequency dependence in $\varepsilon''$. In fact, a relaxor-type ferroelectricity has been observed for the related $\kappa-(ET)$_2$Hg(SCN)$_2$Br salt which also stands out by its anomalous Raman response$^{37}$. In this and in other charge-transfer salts, the relaxational response was ascribed to the dynamics of CO domain-walls or solitons$^{51,52}$.

We stress that, a definite proof of ferroelectricity, which usually includes measurements of polarization hysteresis or so-called positive-up-negative-down measurements$^{25,53}$, was not possible for the present compound due to its rather high conductivity, especially close to $T_{FE}$. However, taking into account the observed characteristic temperature and frequency dependences in $\varepsilon'$ and the fact that very similar results in $\varepsilon'(T)$ were obtained for samples from different sources, by using different devices, the present data provide strong indications for ferroelectricity in $\kappa-(ET)$_2$Hg(SCN)$_2$Cl.

A thermodynamic investigation of the character of the CO transition is provided by measurements of the relative length change $\Delta L_i(T)/L_i$. Figure 3(a) shows the result of $\Delta L_a(T)/L_a$ along the out-of-plane $a$ axis (see Fig. 1) and the two in-plane $b$ and $c$ axes around 30 K. We observe pronounced, slightly broadened jumps in the sample length along all three axes at $T_{MI} \simeq T_{CO} \approx 30$ K.

**Figure 2.** Temperature dependence of the dielectric constant $\varepsilon'(T)$ (a) and conductivity $\sigma'(T)$ (b) of $\kappa$-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl crystal #AF093-1 measured at 935 kHz. Data were taken upon warming. The dashed line in (a) is a fit with a Curie-Weiss law ($T_{CW} = 17.4$ K, $C = 2500$ K) with an additional offset. The solid line connects the data points. The inset shows the inverse dielectric constant; the lines correspond to Curie-Weiss behavior.

**Figure 3.** (a) Relative length change $\Delta L_i/L_i$ vs. $T$ with $i = a, b, c$ of $\kappa$-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl (crystal #AF087-4) around the charge-order metal-insulator transition at $T_{MI} \approx 30$ K. Data were collected upon warming. The individual data sets were offset for clarity. Dotted line indicates an idealized sharp jump for the $c$-axis data. (b) Relative length change along the $c$ axis, $\Delta L_c/L_c$, around $T_{MI}$ measured upon warming and cooling.
the following discussion, we assume that the charge order modifies the electrostatic interactions between the cations and anions, which involve close contacts between the electropositive S and H atoms in the donors, and the electronegative Cl and C atoms in the anion layer. Through these interactions, each (Hg(SCN)2Cl)s unit in the anion chain is linked to two ET molecules belonging to different layers (shown schematically by orange lines in Fig. 4(a)). Above $T_{CO}$ the charge is homogeneously distributed on the ET molecules ($\delta = 0$), corresponding to a charge of $+0.5e$ per ET. Thus, the position of the Cl$^-$ ion is symmetric with respect to the surrounding (ET)$^{1+0.5}$ molecules. Upon cooling through $T_{CO}$, the charge distribution is modulated by $\pm \delta$ within the ET layer. As a consequence, in order to minimize the overall Coulomb energy, the anions slightly shift towards the charge-rich sites (white rectangles), as indicated by the blue arrows in Fig. 4(a). As this motion, which results in a dominant effect along the $a$ axis, is uniform for all chains it identifies the CO pattern unambiguously, cf. Fig. 4(a) and (b).

In the resulting CO pattern the charge-rich molecules are arranged in stripes along the $c$ axis and alternate with charge-poor stripes along the $b$ axis (see Fig. 4(b)). This CO pattern is consistent with the suggestion put forward in Ref. [36] based on the anisotropy of conductivity spectra. We stress that this type of CO breaks the inversion symmetry both within and between the layers, ensuring long-range 3D ferroelectric order. However, the conclusions on the structural change at the CO transition are only speculative at present, as X-ray investigations at 10K, aimed at detecting the CO pattern, failed to resolve the predicted symmetry-breaking shifts.

For discussing these results in the wider context of dimerized (ET)$_2$X materials, we use the ratio $t_1/t'$ to quantify the strength of dimerization. In the limit of weak or no dimerization, a non-magnetic CO ground state is adopted, as has been well established in $\phi$-phase salts. On the other hand, for $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, where $t_1/t' \sim 5$ reflects a relatively strong dimerization, the notion of a dimer-Mott insulating state has been widely used, and the existence of CO as the origin of the observed ferroelectricity has been debated. Hence, the present $\kappa$-(ET)$_2$Hg(SCN)$_2$Cl system, with $t_1/t' \sim 3$, being located in the middle between these two extreme cases, may provide the key for a better understanding of the physics in the wide class of dimerized (ET)$_2$X materials. Our finding of ferroelectricity in $\kappa$-(ET)$_2$Hg(SCN)$_2$Cl, which is most likely driven by the observed CO within the ET dimers, clearly demonstrates the importance of intra-dimer charge degrees of freedom in these materials. Hence, the minimal model able to capture these effects has to include two molecular orbitals on each dimer and a 3/4 band filling. In fact, by using the hopping parameters $t_1...t_4$ relevant for the rather strongly dimerized $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, and by using an extended
two-orbital Hubbard model on a triangular lattice at 3/4-electron filling, Kaneko et al. recently revealed the possibility for a CO ground state for this material, pointing to the relevance of intra-dimer degrees of freedom even for stronger dimerization.

In light of the peculiar multiferroic state with $T_{FE} \sim T_N$ proposed for $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, one may ask how charge order interacts with the magnetic degrees of freedom in the present $\kappa$-(ET)$_2$Hg(SCN)$_2$Cl material. Initially, Yasin et al. suggested an order to coincide with $T_{CO}$ in $\kappa$-(ET)$_2$Hg(SCN)$_2$Cl, based on the result of electron spin resonance (ESR) measurements. However, as discussed in detail in the SI, our own ESR investigations along with specific heat measurements fail to reveal any clear signature of a magnetic transition around $T_{MI}$. Naively, one may assign the absence of long-range magnetic order to the geometric frustration, inherent to the $\kappa$-type triangular arrangement of dimers. In fact, for the frustration parameter $t'/t$ we find 0.79 in the effective-dimer model, which neglects CO, - a value significantly larger than $t'/t \sim 0.43$ for $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl. However, charge order must have an effect on the local magnetic interactions due to the redistribution of charge within each dimer, with a proportionality constant $A_i$. Following Naka and Ishihara, we anticipate that the CO pattern in Fig. 4 would enhance interactions $J'_b$, while suppressing the coupling $J_b$ (see Fig. 4(c)). At the same time, $J'_b$ would not be strongly affected by CO. We propose that this modification of the interactions may lead to an effective dimensional reduction due to the underlying frustration ($J'_b \sim J_b$) which promotes a quasi-1D spin-liquid state. This novel CO-driven effect could then explain the absence of magnetic order in the present material. A crucial test of this proposal would be to probe the dimensionality of spin correlations below $T_{CO}$, via e.g. polarized Raman scattering or thermal transport anisotropy.

Summary. — Clear evidence is provided for an order-disorder type ferroelectric state in dimerized $\kappa$-(ET)$_2$Hg(SCN)$_2$Cl, driven by charge order within the (ET)$_2$ dimers and stabilized by a coupling to the anions. According to our ab initio density functional theory calculations, this material is characterized by a moderate strength of dimerization $t_1/t' \sim 3$. Our results highlight the role of intra-dimer degrees of freedom in dimerized (ET)$_2X$ materials in promoting intriguing states. Besides the possibility for electronically-driven multiferroicity, we propose for the present material that charge order in the presence of strong frustration may induce a quasi-1D spin-liquid state as a consequence of dimensional reduction.

This work was supported by the Deutsche Forschungsgemeinschaft through the Transregional Collaborative Research Centers TR49 and TRR 80. JAS acknowledges support from the Independent Research and Development program from the NSF while working at the Foundation. We thank Ryui Kaneko for theoretical input, and Mamoun Hemmida, Martin Dressel and Tomislav Ivek for useful discussions of the magnetic properties.

[22] P. Lunkenheimer, J. Müller, S. Krohns, F. Schrettle,


The absence of any indications for a displacive-type of ferroelectricity implies that the dielectric response can be assigned solely to the electric dipoles within the ET layers without any contribution from the alternating anion-system.


\[ \varepsilon = \varepsilon_0 + \varepsilon_1 \left( 1 + \frac{T - T_{CW}}{T_{CW}} \right) \left[ 1 + \frac{T_{CW}}{T} (\varepsilon_L - 1) \right] \]

with \( T \) the Curie constant, \( T_{CW} \) the Curie-Weiss temperature, \( \varepsilon_0 \) the dielectric permittivity of vacuum, \( n \) the dipole density, \( p \) the dipole moment, \( k_B \) the Boltzmann constant and \( \varepsilon_L \) the low-temperature dielectric constant.


The same conclusion was drawn from the anisotropic lattice effects revealed at the CO transition in the quasi-1D (TMTTF)2X salts\(^{57}\).


See Supplemental Material [url] for details on the band-structure calculations, on the dielectric properties and discussion of the magnetic properties, which includes references\(^{36,38,39,42,47,52,56,57,64-96}\).


R. Blinc and B. Žekš, Soft Modes in Ferroelectrics and Antiferroelectrics (North-Holland, Amsterdam, 1994).


[85] W. Kraak, U. Schaller, and R. Herrmann, physica status solidi (a) 85, K183 (1984), ISSN 1521-396X.