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Evidence for electronically-driven ferroelectricity in a strongly correlated dimerized BEDT-TTF molecular conductor

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By applying measurements of the dielectric constants and relative length changes to the dimerized molecular conductor κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl, 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)$_2$X salts and can create novel states, such as electronically-driven multiferroicity or charge-order-induced quasi-1D spin liquids.

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Introduction. — Electronic ferroelectricity, where electrons play the role of the ions in conventional displacive ferroelectrics, has recently become an active area of research[1–5]. 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-T_c cuprates[6] or manganites[7]. Particularly clear examples of CO have been found in the families of TMTTF[8] and BEDT-TTF[9–12] (in short ET) molecular conductors with 1/4-filled hole bands. It has been established that in these systems, CO and accompanying ferroelectric properties[13–15] result from the combined action of a strong onsite Coulomb repulsion U along with a sizable inter-site interaction V[16–18].

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 materials[15,19–21]. This came as a surprise as these systems have been primarily discussed in the so-called *dimer-Mott* limit[22–24], 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 t_1 (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)$_2$Cu[N(CN)$_2$]Cl, ferroelectric order was found at T_{FE}[25–27] which coincides with long-range antiferromagnetic (afm) order[28] at $T_N \simeq T_{FE}$. It has been suggested that in these dimerized systems the electric dipoles originate from CO[4,20,25,29–32], i.e., a charge disproportionation by $\pm\delta$ 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 missing[33–35].

In this Letter, we provide evidence for an electronically-driven ferroelectricity in the related dimerized salt κ-(ET)$_2$Hg(SCN)$_2$Cl, where CO was clearly identified by vibrational spectroscopy[36,37]. 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 $T_{MI} = T_{CO} \approx 25 - 30\,$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

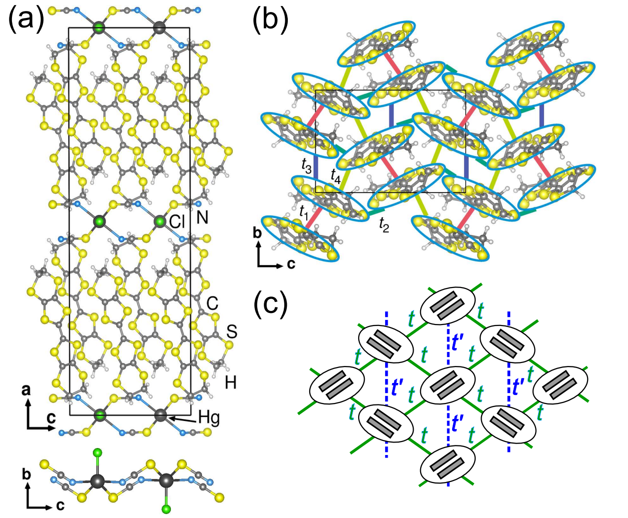

FIG. 1. (a) Crystal structure of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl along the out-of-plane a axis (top) and side view on the anion layer (bottom)[36]; (b) View on the (ET)$_2^+$ plane showing the typical κ-type arrangement of molecules. The cyan ellipses surround single ET molecules. Two parallel-aligned ET molecules form dimers. The four dominant hopping terms are denoted by t_1 (pink), t_2 (dark green), t_3 (blue) and t_4 (light green); (c) Schematic of the *effective-dimer* model with hopping parameters t (green) and t' (blue).

states, such as electronically-driven multiferroicity or CO-induced quasi-1D spin-liquids. In addition, our findings underline the model character of the κ-(ET)$_2X$ 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. — κ-(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 κ-(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 ϵ' (real part of the permittivity) and the real part of the conductivity σ' 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 ϵ'. 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 ≈ 400). As shown by the dashed line in Fig. 2(a), this increase can be well described by a Curie-Weiss law, $\epsilon' - \epsilon_{off} = C/(T - T_{\text{CW}})$, with a Curie-Weiss temperature $T_{\text{CW}} = (17 \pm 2)$ K and an offset ϵ_{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 ϵ', this value of p is in reasonable agreement with the expected out-of-plane dipole moment of $0.13ed$ 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 $\approx 50°$ 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 $T < T_{\text{FE}}$ 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 $T_{\text{FE}} \approx 30$ 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

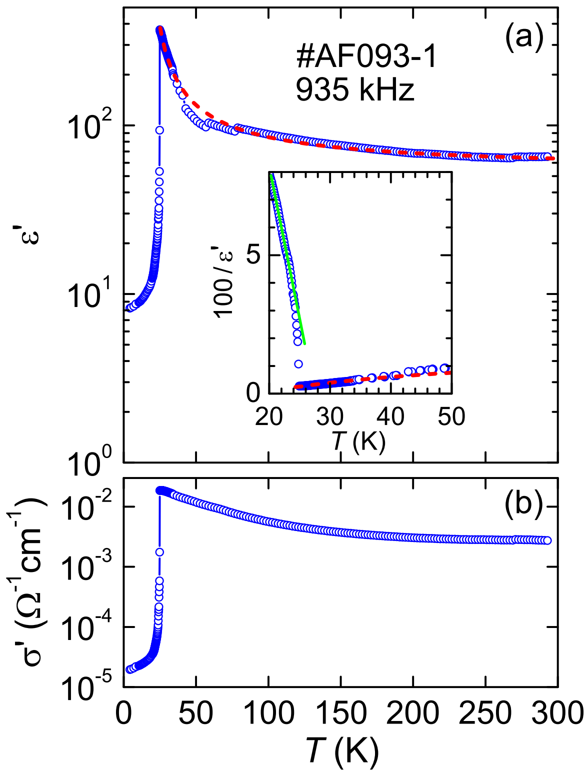

FIG. 2. Temperature dependence of the dielectric constant $\varepsilon'(T)$ (a) and conductivity $\sigma'(T)$ (b) of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl crystal #AF093-1 measured at 935 kHz. Data were taken upon warming. The dashed line in (a) is a fit with a Curie-Weiss law ($T_{\rm CW} = 17.4\,$K, $C = 2500\,$K) 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.

frequency that resembles the typical behavior of order-disorder ferroelectrics[44].

The real part of the conductivity shown in Fig. 2(b) shows metallic behavior at higher temperatures. Below 25 K, $\sigma'(T)$ rapidly drops by about three orders of magnitude, indicating that $T_{MI} \simeq T_{FE}$. Similarly, for crystals #JAS1721 and #AF087 (see SI, Fig. 8), we find a rapid drop in $\sigma(T)$ at $T_{MI} \simeq T_{FE} \sim 30\,$K. These findings, which are in good qualitative accord with literature results[47], provide additional evidence that the dielectric measurements indeed detect the intrinsic sample properties.

The characteristics of $\epsilon'(T)$, revealed in Fig. 2(a) (and SI Fig. 3(a)), are remarkable in terms of the following aspects. First, the phenomenology 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 $|d(1/\epsilon)/dT|$, together with a Curie-Weiss temperature $T_{\rm CW} < T_{FE}$. Second, the observed temperature (Fig. 2(a) and SI Fig. 3(a)) and frequency dependences (SI Fig. 2 and 4) indicate that κ-(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 ϵ'[27,44]. In fact, a relaxor-type ferroelectricity has been observed for the related κ-(ET)$_2$Hg(SCN)$_2$Br salt[50] 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 $T_{\rm FE}$. However, taking into account the observed characteristic temperature and frequency dependences in ϵ' and the fact that very similar results in $\epsilon'(T)$ were obtained for samples from different sources, by using different devices, the present data provide strong indications for ferroelectricity in κ-(ET)$_2$Hg(SCN)$_2$Cl.

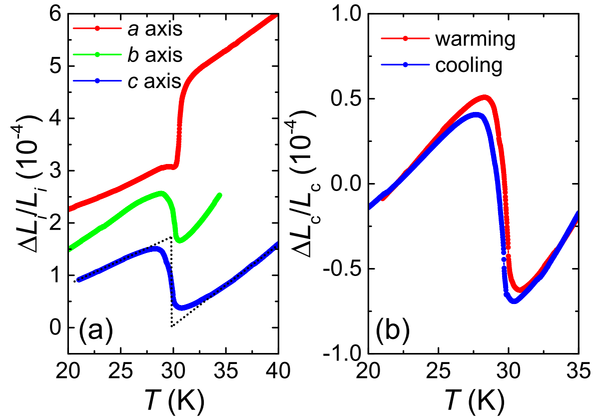

FIG. 3. (a) Relative length change $\Delta L_i/L_i$ vs. T with $i = a, b, c$ of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl (crystal #AF087-4) around the charge-order metal-insulator transition at $T_{MI} \approx 30\,$K. Data were collected upon warming. The individual data sets were offset for clarity. Dotted line 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.

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 $\Delta L_i(T)/L_i$ 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

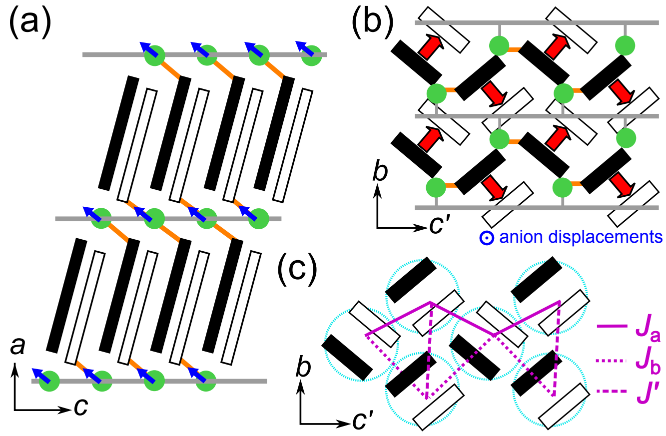

FIG. 4. Proposed CO pattern in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl, viewed within the ac plane (a) and the bc' plane (b). c' accounts for a small rotation of the c axis with respect to the a axis due to the inclination of the BEDT-TTF molecules. Grey lines correspond to the anions, green circles correspond to Hg(SCN)$_2$Cl units of the anion layer. White (black) rectangles correspond to charge-rich (charge-poor) BEDT-TTF molecules with charge $0.5 + \delta\,(0.5 - \delta)$ in the charge-ordered state. Orange solid lines illustrate the interaction path between the S and H atoms in the BEDT-TTF layer and the Cl and C atoms in the anion layer. Blue arrows indicate the shift of the anions in response to the charge order in the BEDT-TTF layer. Thick red arrows indicate electric dipoles p. (c) Dominant magnetic exchange-coupling paths J_a, J_b and J' (see main text) for the proposed CO state.

(see SI for a detailed determination of T_{MI} from the present data set). The jump-like anomalies in $\Delta L_i(T)/L_i$ and the observation of thermal hysteresis between warming and cooling (Fig. 3 (b)) are clear signatures of the first-order character of the CO transition, consistent with the conclusion drawn above from the $\epsilon'(T)$ results.

Surprisingly, the dominant lattice response to CO is found along the out-of-plane a axis, yielding a pronounced decrease upon cooling below T_{CO}. This highlights a strong involvement of the anion layer in the formation of the CO state as a result of the ionic character of the material: The change in the charge distribution within the ET layers from a homogeneous distribution above T_{CO} to a charge-modulated state below will necessarily induce finite shifts of the counterions in the anion layer[54]. We therefore include the anions in the discussion of possible CO patterns in κ-(ET)$_2$Hg(SCN)$_2$Cl in analogy to Ref. [55]. Figure 4 shows a schematic view of the structure of κ-(ET)$_2$Hg(SCN)$_2$Cl including the ET molecules (rectangles) and the nearby anion layers. The anions form a chain-like structure along the c axis (grey lines in Fig. 4) with short-side chains formed by the terminal ligand Cl (green circles) along the b axis. For 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)$_2$Cl)$^-$ 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 $+0.5\,e$ per ET. Thus, the position of the Cl$^-$ ion is symmetric with respect to the surrounding (ET)$^{+0.5}$ molecules. Upon cooling through T_{CO}, the charge distribution is modulated by $\pm\,\delta$ within the ET layer[36]. 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 10 K[36], 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 θ-phase salts[10]. On the other hand, for κ-(ET)$_2$Cu[N(CN)$_2$]Cl, where $t_1/t' \sim 5$ reflects a relatively strong dimerization[56–58], the notion of a dimer-Mott insulating state[22–24] has been widely used, and the existence of CO as the origin of the observed ferroelectricity has been debated[33–35]. Hence, the present κ-(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 κ-(ET)$_2$Hg(SCN)$_2$Cl, which is most likely driven by the observed CO within the ET dimers[36], clearly demonstrates the importance of intra-dimer charge degrees of freedom in these materials. Hence, the minimal model able to capture theses effects has to include two molecular orbitals on each dimer and a 3/4 band filling. In fact, by using the hopping parameters $t_1 \ldots t_4$ relevant for the rather strongly dimerized κ-(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.*[32] 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 κ-(ET)$_2$Cu[N(CN)$_2$]Cl, one may ask how charge order interacts with the magnetic degrees of freedom in the present κ-(ET)$_2$Hg(SCN)$_2$Cl material. Initially, Yasin *et al.*[47] suggested afm order to coincide with T_{CO} in κ-(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 κ-type triangular arrangement of dimers. In fact, for the frustration paramter 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 κ-(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[4,59], i.e., in first approximation $J_i \propto t_i^2(1 \pm A_i\delta)$ with a proportionality constant A_i. Following Naka and Ishihara[4,59], we anticipate that the CO pattern in Fig. 4 would enhance interactions J_a, while suppressing the coupling J_b (see Fig. 4(c)). At the same time, J' would not be strongly affected by CO. We propose that this modification of the interactions may lead to an effective dimensional reduction[60] due to the underlying frustration ($J' \sim J_b$) 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[37,61] or thermal transport anisotropy[62].

Summary. — Clear evidence is provided for an order-disorder type ferroelectric state in dimerized κ-(ET)$_2$Hg(SCN)$_2$Cl[63], 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.

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[1] N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, et al., Nature **436** (2005).
[2] J. van den Brink and D. I. Khomskii, J. Phys.: Condens. Matter **20**, 434217 (2008).
[3] K. Yamamoto, A. A. Kowalska, and K. Yakushi, Appl. Phys. Lett. **96**, 122901 (2010).
[4] M. Naka and S. Ishihara, J. Phys. Soc. Jpn. **79**, 063707 (2010).
[5] S. Ishihara, J. Phys. Soc. Jpn. **79**, 011010 (2010).
[6] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature **375**, 561 (1995).
[7] S. Mori, C. H. Chen, and S.-W. Cheong, Nature **392**, 473 (1998).
[8] D. S. Chow, F. Zamborszky, B. Alavi, D. J. Tantillo, A. Baur, C. A. Merlic, and S. E. Brown, Phys. Rev. Lett. **85**, 1698 (2000).
[9] H. Mori, S. Tanaka, and T. Mori, Phys. Rev. B **57**, 12023 (1998).
[10] K. Kuroki, Sci. Technol. Adv. Mater. **10**, 024312 (2009).
[11] F. Kagawa, T. Sato, K. Miyagawa, K. Kanoda, Y. Tokura, K. Kobayashi, R. Kumai, and Y. Murakami, Nat. Phys. **9**, 419 (2013).
[12] S. Sasaki, K. Hashimoto, R. Kobayashi, K. Itoh, S. Iguchi, Y. Nishio, Y. Ikemoto, T. Moriwaki, N. Yoneyama, M. Watanabe, et al., Science **357**, 1381 (2017).
[13] P. Monceau, F. Y. Nad, and S. Brazovskii, Phys. Rev. Lett. **86**, 4080 (2001).
[14] F. Nad and P. Monceau, J. Phys. Soc. Jpn. **75**, 051005 (2006), http://dx.doi.org/10.1143/JPSJ.75.051005.
[15] P. Lunkenheimer, B. Hartmann, M. Lang, J. Müller, D. Schweitzer, S. Krohns, and A. Loidl, Phys. Rev. B **91**, 245132 (2015).
[16] H. Seo, Physica B: Cond. Mat. **69**, 805 (2000).
[17] T. Takahashi, Y. Nogami, and K. Yakushi, J. Phys. Soc. Jpn. **75**, 051008 (2006).
[18] H. Seo, J. Merino, H. Yoshioka, and M. Ogata, J. Phys. Soc. Jpn. **75**, 051009 (2006).
[19] K. Yamamoto, S. Iwai, S. Boyko, A. Kashiwazaki, F. Hiramatsu, C. Okabe, N. Nishi, and K. Yakushi, J. Phys. Soc. Jpn. **77**, 074709 (2008).
[20] M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, Phys. Rev. B **82**, 125119 (2010).
[21] S. Iguchi, S. Sasaki, N. Yoneyama, H. Taniguchi, T. Nishizaki, and T. Sasaki, Phys. Rev. B **87**, 075107 (2013).
[22] H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. **64**, 2726 (1995).
[23] K. Kanoda, Hyperfine Interact. **104**, 235 (1997), ISSN 1572-9540.
[24] B. J. Powell and R. H. McKenzie, Rep. Prog. Phys. **74**, 056501 (2011).
[25] P. Lunkenheimer, J. Müller, S. Krohns, F. Schrettle,

A. Loidl, B. Hartmann, R. Rommel, M. de Souza, C. Hotta, J. Schlueter, et al., Nat. Mater. **11**, 755 (2012).
[26] M. Lang, P. Lunkenheimer, J. Müller, A. Loidl, B. Hartmann, N. H. Hoang, E. Gati, H. Schubert, and J. A. Schlueter, IEEE Trans. Magn. **50**, 2700107 (2014).
[27] P. Lunkenheimer and A. Loidl, J. Phys.: Condens. Matter **27**, 373001 (2015).
[28] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).
[29] C. Hotta, Phys. Rev. B **82**, 241104 (2010).
[30] R. Clay, H. Li, and S. Mazumdar, Physica B: Condensed Matter **405**, S253 (2010), ISSN 0921-4526, proceeding of the 8th International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets; Yamada Conference LXIV.
[31] H. Gomi, M. Ikenaga, Y. Hiragi, D. Segawa, A. Takahashi, T. J. Inagaki, and M. Aihara, Phys. Rev. B **87**, 195126 (2013).
[32] R. Kaneko, L. F. Tocchio, R. Valentí, and F. Becca, New J. Phys. **19**, 103033 (2017).
[33] K. Sedlmeier, S. Elsässer, D. Neubauer, R. Beyer, D. Wu, T. Ivek, S. Tomić, J. A. Schlueter, and M. Dressel, Phys. Rev. B **86**, 245103 (2012).
[34] S. Tomić, M. Pinterić, T. Ivek, K. Sedlmeier, R. Beyer, D. Wu, J. A. Schlueter, D. Schweitzer, and M. Dressel, J. Phys.: Condens. Matter **25**, 436004 (2013).
[35] M. Pinterić, P. Lazić, A. Pustogow, T. Ivek, M. Kuveždić, O. Milat, B. Gumhalter, M. Basletić, M. Čulo, B. Korin-Hamzić, et al., Phys. Rev. B **94**, 161105 (2016).
[36] N. Drichko, R. Beyer, E. Rose, M. Dressel, J. A. Schlueter, S. A. Turunova, E. I. Zhilyaeva, and R. N. Lyubovskaya, Phys. Rev. B **89**, 075133 (2014).
[37] N. Hassan, S. Cunningham, M. Mourigal, E. I. Zhilyaeva, S. A. Torunova, R. N. Lyubovskaya, and N. Drichko, arXiv:1704.04482 (2017).
[38] E. Gati, M. Garst, R. S. Manna, U. Tutsch, B. Wolf, L. Bartosch, H. Schubert, T. Sasaki, J. A. Schlueter, and M. Lang, Science Advances **2** (2016).
[39] S. V. Konovalikhin, G. V. Shilov, O. A. D'yachenko, R. N. Lyubovskaya, M. Z. Aldoshina, and R. B. Lyubovskii, Bulletin of the Russian Academy of Sciences, Division of chemical science **41**, 704 (1992), ISSN 1573-9171.
[40] K. Koepernik and H. Eschrig, Phys. Rev. B **59**, 1743 (1999).
[41] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[42] R. Pott and R. Schefzyk, J. Phys. E: Sci. Instrum. **16**, 444 (1983).
[43] 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-cation system.
[44] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
[45] $\epsilon = C/(T - T_{CW}) = \frac{1}{3\epsilon_0} n \frac{p^2}{k_B(T-T_{CW})}[1 + \frac{T_{CW}}{C}(\epsilon_L - 1)]$ with C the Curie constant, T_{CW} the Curie-Weiss temperature, ϵ_0 the dielectric permittivity of vacuum, n the dipole density, p the dipole moment, k_B the Boltzmann constant and ϵ_L the low-temperature dielectric constant.
[46] W. P. Mason and B. T. Matthias, Phys. Rev. **74**, 1622 (1948).
[47] S. Yasin, E. Rose, M. Dumm, N. Drichko, M. Dressel, J. Schlueter, E. Zhilyaeva, S. Torunova, and R. Lyubovskaya, Physica B: Cond. Mat. **407**, 1689 (2012), ISSN 0921-4526.
[48] C. J. Johnson, Appl. Phys. Lett. **7**, 221 (1965).
[49] K. Gesi, J. Phys. Soc. Jpn. **28**, 395 (1970).
[50] T. Ivek, R. Beyer, S. Badalov, M. Čulo, S. Tomić, J. A. Schlueter, E. I. Zhilyaeva, R. N. Lyubovskaya, and M. Dressel, Phys. Rev. B **96**, 085116 (2017).
[51] T. Ivek, B. Korin-Hamzić, O. Milat, S. Tomić, C. Clauss, N. Drichko, D. Schweitzer, and M. Dressel, Phys. Rev. Lett. **104**, 206406 (2010).
[52] H. Fukuyama, J. Kishine, and M. Ogata, J. Phys. Soc. Jpn. **86**, 123706 (2017).
[53] J. F. Scott, *Ferroelectric Memories* (Springer, Berlin, 2000).
[54] The same conclusion was drawn from the anisotropic lattice effects revealed at the CO transition in the quasi-1D $(TMTTF)_2X$ salts[55].
[55] M. de Souza, P. Foury-Leylekian, A. Moradpour, J.-P. Pouget, and M. Lang, Phys. Rev. Lett. **101**, 216403 (2008).
[56] H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. Lett. **103**, 067004 (2009).
[57] D. Guterding, R. Valentí, and H. O. Jeschke, Phys. Rev. B **92**, 081109 (2015).
[58] D. Guterding, M. Altmeyer, H. O. Jeschke, and R. Valentí, Phys. Rev. B **94**, 024515 (2016).
[59] M. Naka and S. Ishihara, Sci. Rep. **6** (2016).
[60] O. A. Starykh and L. Balents, Phys. Rev. Lett. **98**, 077205 (2007).
[61] P. Lemmens, G. Güntherodt, and C. Gros, Phys. Rep. **375**, 1 (2003), ISSN 0370-1573.
[62] C. Hess, Eur. Phys. J. Special Topics **151**, 73 (2007), ISSN 1951-6401.
[63] See Supplemental Material [url] for details on the band-structure calculations, on the dielectric properties and discussion of the magnetic properties, which includes references[36,38,39,42,47,52,56,57,64–90].
[64] M. Altmeyer, R. Valentí, and H. O. Jeschke, Phys. Rev. B **91**, 245137 (2015).
[65] H. Eschrig and K. Koepernik, Phys. Rev. B **80**, 104503 (2009).
[66] R. Böhmer, M. Maglione, P. Lunkenheimer, and A. Loidl, J. Appl. Phys. **65**, 901 (1989).
[67] E. Gati, S. M. Winter, J. A. Schlueter, H. Schubert, J. Müller, and M. Lang, Phys. Rev. B **97**, 075115 (2018).
[68] R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1994).
[69] F. Sandy and R. V. Jones, Phys. Rev. **168**, 481 (1968).
[70] Y. Takayama, K. Deguchi, and E. Nakamura, J. Phys. Soc. Jpn. **53**, 4121 (1984).
[71] P. F. Sullivan and G. Seidel, Phys. Rev. **173**, 679 (1968).
[72] J. Müller, M. Lang, R. Helfrich, F. Steglich, and T. Sasaki, Phys. Rev. B **65**, 140509 (2002).
[73] J. Wosnitza, X. Liu, D. Schweitzer, and H. J. Keller, Phys. Rev. B **50**, 12747 (1994).
[74] P. Foury-Leylekian, S. Petit, I. Mirebeau, G. André, M. de Souza, M. Lang, E. Ressouche, A. Moradpour, and J.-P. Pouget, Phys. Rev. B **88**, 024105 (2013).
[75] R. Świetlik, H. Grimm, D. Schweitzer, and H. J. Keller, Z. Naturforsch. A **42**, 603 (1987).

[76] B. Andraka, G. R. Stewart, K. D. Carlson, H. H. Wang, M. D. Vashon, and J. M. Williams, Phys. Rev. B **42**, 9963 (1990).
[77] B. Andraka, J. S. Kim, G. R. Stewart, K. D. Carlson, H. H. Wang, and J. M. Williams, Phys. Rev. B **40**, 11345 (1989).
[78] S. Katsumoto, S. ichi Kobayashi, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **57**, 3672 (1988).
[79] P. Garoche, R. Brusetti, D. Jérome, and K. Bechgaard, J. Physique Lett. **43**, 147 (1982).
[80] S. Barnes, Adv. Phys. **30**, 801 (1981).
[81] R. Jin, M. H. Pan, X. B. He, G. Li, D. Li, R. wen Peng, J. R. Thompson, B. C. Sales, A. S. Sefat, M. A. McGuire, et al., Supercond. Sci. Technol. **23**, 054005 (2010).
[82] M. Heinrich, H.-A. Krug von Nidda, R. M. Eremina, A. Loidl, C. Helbig, G. Obermeier, and S. Horn, Phys. Rev. Lett. **93**, 116402 (2004).
[83] M. Hemmida, H.-A. Krug von Nidda, B. Miksch, L. L. Samoilenko, A. Pustogow, J. Schlueter, A. Loidl, and M. Dressel, arXiv:1710.04028 [cond-mat.str-el] (2017).
[84] J. Müller, M. Lang, F. Steglich, J. A. Schlueter, A. M. Kini, U. Geiser, J. Mohtasham, R. W. Winter, G. L. Gard, T. Sasaki, et al., Phys. Rev. B **61**, 11739 (2000).
[85] W. Kraak, U. Schaller, and R. Herrmann, physica status solidi (a) **85**, K183 (1984), ISSN 1521-396X.
[86] A. Löhle, E. Rose, S. Singh, R. Beyer, E. Tafra, T. Ivek, E. I. Zhilyaeva, R. N. Lyubovskaya, and M. Dressel, J. Phys.: Condens. Matter **29**, 055601 (2017).
[87] Y. Kurosaki, Y. Shimizu, K. Miyagawa, K. Kanoda, and G. Saito, Phys. Rev. Lett. **95**, 177001 (2005).
[88] P. Limelette, P. Wzietek, S. Florens, A. Georges, T. A. Costi, C. Pasquier, D. Jérome, C. Mézière, and P. Batail, Phys. Rev. Lett. **91**, 016401 (2003).
[89] S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jérome, C. Mézière, M. Fourmigué, and P. Batail, Phys. Rev. Lett. **85**, 5420 (2000).
[90] C. Strack, C. Akinci, V. Pashchenko, B. Wolf, E. Uhrig, W. Assmus, M. Lang, J. Schreuer, L. Wiehl, J. A. Schlueter, et al., Phys. Rev. B **72**, 054511 (2005).