PHYSICAL REVIEW LETTERS **120,** 247601 (2018)

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

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(Received 20 November 2017; published 14 June 2018)

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 that is driven by the 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 nondimerized or weakly dimerized systems at 1/4 filling, exhibiting a charge order. Our results indicate that intradimer 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-one-dimensional spin liquids.

DOI: 10.1103/PhysRevLett.120.247601

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 the 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 on site Coulomb repulsion U along with a sizable intersite 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 interdimer 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 $T_{\rm FE}$ [25–27], which coincides with the long-range antiferromagnetic (AFM) order [28] at $T_N \simeq T_{\rm FE}$. 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 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 $T_{\rm MI} = T_{\rm CO} \approx$ 25–30 K is accompanied by the formation of ferroelectric order of an order-disorder type, where disordered electric dipoles exist already in the paraelectric phase, and become ordered below $T_{\rm FE} = T_{\rm MI}$. Our results highlight the role of *intra*dimer degrees of

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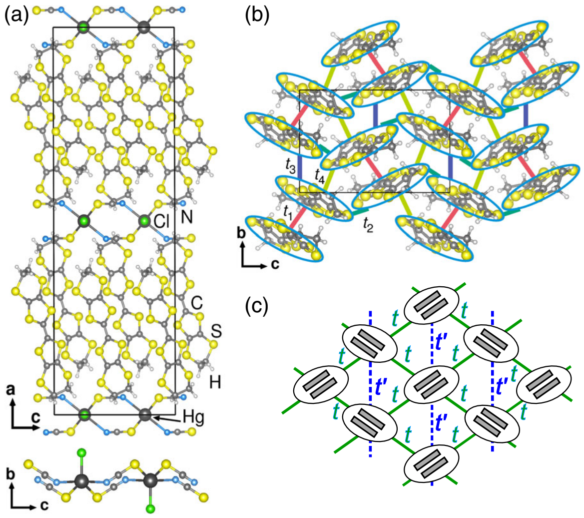

FIG. 1. (a) Crystal structure of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl along the out-of-plane a axis (top), and a side view on the anion layer (bottom) [36]. (b) View on the $(\mathrm{ET})_2^+$ plane showing the typical κ-type arrangement of molecules. The cyan ellipses surround single ET molecules. Two parallel-aligned 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).

freedom in creating novel states, such as electronically driven multiferroicity or CO-induced quasi-one-dimensional (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 [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 band structure. 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 Supplemental Material (SM) [42] 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 SM [42]). 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' (the 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 the relative length change $\Delta L_i(T)/L_i$, with $i = a$, b, c, were performed using a home-built capacitive dilatometer [43] 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 $T_{\mathrm{FE}} \approx 25$ 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, $\epsilon' - \epsilon_{\mathrm{off}} = C/(T - T_{\mathrm{CW}})$, with a Curie-Weiss temperature $T_{\mathrm{CW}} = (17 \pm 2)$ K and an offset ϵ_{off}, likely of an extrinsic nature. The relatively small magnitude of the Curie constant of $C = (2500 \pm 600)$ K is consistent with order-disorder ferroelectricity [75], while C for displacive ferroelectrics [76] is usually of the order of 10^5. By using a simple expression [77] to relate the Curie constant to the size of an individual dipole [78] p, we find

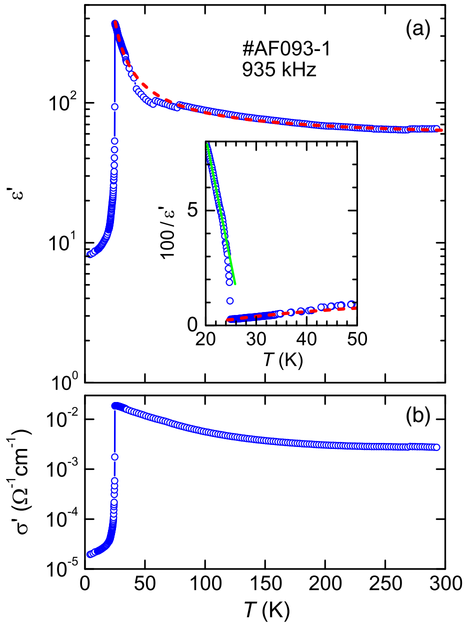

FIG. 2. Temperature dependence of the dielectric constant $\epsilon'(T)$ (a) and conductivity $\sigma'(T)$ (b) of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl crystal #AF093-1 measured at 935 kHz. Data were taken upon warming. The dashed line in (a) is a fit with a Curie-Weiss law ($T_{\mathrm{CW}} = 17.4$ K, $C =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

$p \approx 0.4ed$, 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 $T < T_{\mathrm{FE}}$ 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 $T_{\mathrm{FE}} \approx 30$ K (see SM [42], Fig. 3). We did not observe any significant frequency dependence of the dielectric properties for frequencies below about 1 MHz (see SM [42], Fig. 2). However, in high-frequency measurements up to about 1 GHz (see SM [42], Fig. 4), we found an increasing suppression of the peak in $\epsilon'(T)$ with increasing frequency that resembles the typical behavior of order-disorder ferroelectrics [76].

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 $T_{\mathrm{MI}} \simeq T_{\mathrm{FE}}$. Similarly, for crystals #JAS1721 and #AF087 (see SM [42], Fig. 8), we find a rapid drop in $\sigma(T)$ at $T_{\mathrm{MI}} \simeq T_{\mathrm{FE}} \sim 30$ K. These findings, which are in good qualitative accord with results in the literature [44], provide additional evidence that the dielectric measurements indeed detect the intrinsic sample properties.

The characteristics of $\epsilon'(T)$, revealed in Fig. 2(a) [and SM [42] 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 $\mathrm{BaTiO_3}$ or $\mathrm{AgNa(NO_2)_2}$ (Refs. [76,79,80]). 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 $T_{\mathrm{CW}} < T_{\mathrm{FE}}$. Second, the observed temperature {Fig. 2(a) and SM [42] Fig. 3(a)} and frequency dependences {SM [42] Fig. 2 and Fig. 4} indicate that κ-$\mathrm{(ET)_2Hg(SCN)_2Cl}$ represents an order-disorder-type ferroelectric. This contrasts with relaxor-type ferroelectricity, characterized by a pronounced frequency dependence in ϵ' [27,76]. In fact, a relaxor-type ferroelectricity has been observed for the related κ-$\mathrm{(ET)_2Hg(SCN)_2Br}$ salt [81], 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 [45,82].

We stress that, a definite proof of ferroelectricity, which usually includes measurements of polarization hysteresis, or so-called positive-up-negative-down measurements [25,83], 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

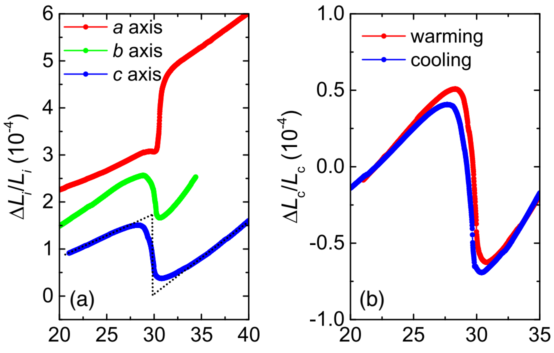

FIG. 3. (a) Relative length change $\Delta L_i/L_i$ vs. T with $i = a, b, c$ of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl (crystal #AF087-4) around the charge-order metal-insulator transition at $T_{\mathrm{MI}} \approx 30$ K. Data were collected upon warming. The individual data sets were offset for clarity. Dotted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

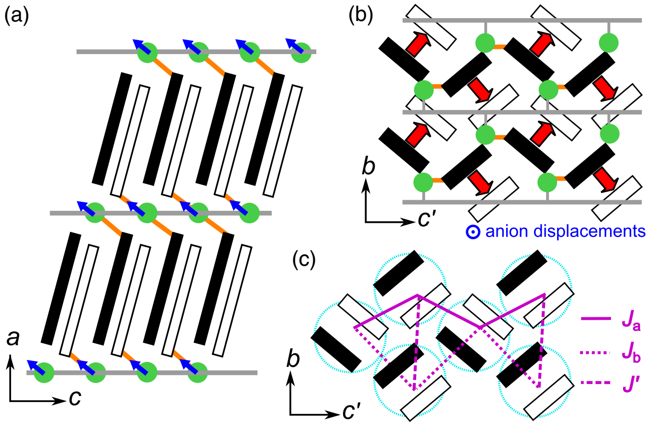

FIG. 4. Proposed CO pattern in κ-$\mathrm{(BEDT\text{-}TTF)_2Hg(SCN)_2Cl}$, viewed within the ac plane (a) and the bc' plane (b). c' accounts for a small rotation of the c axis with respect to the a axis due to the inclination of the BEDT-TTF molecules. Grey lines correspond to the anions, green circles correspond to $\mathrm{Hg(SCN)_2Cl}$ 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.

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.

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 $T_{\mathrm{MI}} \simeq T_{\mathrm{CO}} \approx 30$ K (see SM [42] 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 counter ions in the anion layer [84]. We therefore include the anions in the discussion of possible CO patterns in κ-(ET)$_2$Hg(SCN)$_2$Cl in analogy to Ref. [85]. 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 chainlike 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 $+0.5e$ 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. Figs. 4(a) and 4(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, three-dimensional 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)$_2X$ materials, we use the ratio t_1/t' to quantify the strength of dimerization. In the limit of weak or no dimerization, a nonmagnetic 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 [46,47,86], 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)$_2X$ 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 intradimer 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 $t_1 ... t_4$ 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 intradimer degrees of freedom even for stronger dimerization.

In light of the peculiar multiferroic state with $T_{\mathrm{FE}} \sim T_N$ 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.* [44] 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 SM [42], 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 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 κ-(ET)$_2$Cu[N(CN)$_2$]Cl. However, the charge order must have an effect on the local magnetic interactions due to the redistribution of the charge within each dimer [4,87], i.e., in the first approximation $J_i \propto t_i^2(1 \pm A_i\delta)$ with a proportionality constant A_i. Following Naka and Ishihara [4,87], 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 the CO. We propose that this modification of the interactions may lead to an effective dimensional reduction [88] due to the underlying frustration ($J' \sim J_b$) that 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 [37,89] or thermal transport anisotropy [90].

Summary.—Clear evidence is provided for an order-disorder type ferroelectric state in dimerized κ-$(\mathrm{ET})_2\mathrm{Hg(SCN)}_2\mathrm{Cl}$ [42], driven by charge order within the $(\mathrm{ET})_2$ 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 intradimer degrees of freedom in dimerized $(\mathrm{ET})_2X$ materials in promoting intriguing states. Besides the possibility for electronically driven multiferroicity, for the present material, we propose that the charge order in the presence of a 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. J. A. S. 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.

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