Multiferroicity in an organic charge-transfer salt that is suggestive of electric-dipole-driven magnetism

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Multiferroics, showing simultaneous ordering of electrical and magnetic degrees of freedom, are remarkable materials as seen from both the academic and technological points of view.1,2 A prominent mechanism of multiferroicity is the spin-driven ferroelectricity, often found in frustrated antiferromagnets with helical spin order.3–5 There, as for conventional ferroelectrics, the electrical dipoles arise from an off-centre displacement of ions. However, recently a different mechanism, namely purely electronic ferroelectricity, where charge order breaks inversion symmetry, has attracted considerable interest.6 Here we provide evidence for ferroelectricity, accompanied by antiferromagnetic spin order, in a two-dimensional organic charge-transfer salt, thus representing a new class of multiferroics. We propose a charge-order-driven mechanism leading to electronic ferroelectricity in this material. Quite unexpectedly for electronic ferroelectrics, dipolar and spin order arise nearly simultaneously. This can be ascribed to the loss of spin frustration induced by the ferroelectric ordering. Hence, here the spin order is driven by the ferroelectricity, in marked contrast to the spin-driven ferroelectricity in helical magnets.

Here, we have investigated single-crystalline κ-(BEDT-TTF)2Cu[N(CN)2]Cl (κ-Cl), where BEDT-TTF stands for bis(ethylenedithio)-tetrathiafulvalene (often abbreviated as ET). Three crystals with different geometries and contact materials were investigated (see Methods). In these compounds, dimers of ET molecules form an anisotropic triangular lattice with a half-filled dimer band, where the strong on-dimer Coulomb interaction U drives the system to a Mott insulating state.7,8 In addition, the importance of intra-dimer degrees of freedom and inter-site interactions V has been pointed out.9–11. κ-Cl consists of alternating conducting ET layers and insulating anion sheets (see Supplementary Fig. S1). Within the ET layers, adjacent molecules form dimers on which a single hole is located. Below \( T_N \approx 27 \) K, intralayer antiferromagnetic and interlayer ferromagnetic ordering of hole spins occurs, followed by weak ferromagnetic canting below \( 23 \) K (refs 12,13). κ-Cl becomes superconducting below \( 12.8 \) K, when applying pressures of 300 bar (ref. 14).

Figure 1 shows the temperature-dependent conductivity \( \sigma' \) for field directions \( \mathbf{E} \perp \mathbf{b} \) and \( \mathbf{E} \parallel \mathbf{b} \), measured at low frequencies, providing a good estimate of the d.c. conductivity \( \sigma_{dc} \) (see Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86159 Augsburg, Germany, 2Institute of Physics, Goethe-University Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt(M), Germany, 3Department of Physics, Faculty of Science, Kyoto Sangyo University, Kyoto 603-8555, Japan, 4Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA. 5Present address: IGCE, Unesp—Univ Estadual Paulista, Departamento de Física, Cx. Postal 178, CEP 13506-900 Rio Claro (SP), Brazil. *e-mail: peter.lunkenheimer@physik.uni-augsburg.de.

Supplementary Information). Besides the known overall semiconducting characteristics of \( \sigma_{dc}(T) \) (refs 14–16), including the abrupt increase of the charge gap below about \( 50 \) K (refs 15,16), some interesting and hitherto unreported behaviour is observed: whereas at elevated temperatures \( (T > 50 \) K) the conductivity within the planes exceeds the out-of-plane conductivity by a constant factor of more than 200, the anisotropy becomes significantly reduced on cooling to 4.2 K, with an overall reduction of the conductivity by about 6 ( \( \mathbf{E} \parallel \mathbf{b} \)), respectively 9 ( \( \mathbf{E} \perp \mathbf{b} \)) orders of magnitude. Of particular interest here is the jump-like drop in the conductivity by two decades at around \( 27 \) K, about the same temperature where long-range antiferromagnetic ordering of hole spins occurs, followed by weak ferromagnetic canting below \( 23 \) K (refs 12,13). Below \( T_N \approx 27 \) K, intralayer antiferromagnetic and interlayer ferromagnetic ordering of hole spins occurs, followed by weak ferromagnetic canting below \( 23 \) K (refs 12,13). κ-Cl becomes superconducting below \( 12.8 \) K, when applying pressures of 300 bar (ref. 14).

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An anomaly, although less clearly pronounced, is visible also for the field directed parallel to the ET planes \((\mathbf{E} \perp b)\) in the data for crystal 3 in Fig. 1. A less clear signature is not surprising given the strong overall reduction of \(\sigma_{\text{dc}} (\mathbf{E} \perp b)\) below 50 K being much stronger than for \(\mathbf{E} \parallel b\). A corresponding jump in the out-of-plane conductivity was also found in sample 2 (see Supplementary Information). A distinct drop in \(\sigma_{\text{dc}}\) has not been observed in most a.c. and d.c. studies reported so far (except in ref. 16), which may be ascribed to the higher precision of dielectric measurements at high resistances, compared with standard d.c. set-ups. This abrupt reduction of the conductivity within the Mott insulating state is a first hint to a charge-order transition, that is, a collective localization of charge carriers.

Figure 2 shows the dielectric constant \(\varepsilon'(T)\) of sample 1 for various frequencies. Pronounced peaks reaching absolute values of up to several hundred are revealed. Whereas the peak positions are nearly frequency independent, their amplitudes become strongly suppressed with increasing frequency. The overall behaviour is typical for order–disorder-type ferroelectrics, where the electric dipoles that are disordered at high temperatures order with net overall polarization below a phase-transition temperature \(T_{\text{FE}}\) (ref. 17). Identifying the dipoles with the holes fluctuating within the dimers at \(T > T_{\text{FE}}\) and cooperatively locking in to one of the two ET molecules at \(T < T_{\text{FE}}\) provides a plausible scenario for the present material (see Fig. 1 insets). Similar behaviour as observed in Fig. 2 was also found for other ferroelectric charge-transfer salts18,19. The peaks are superposed to a rather high background contribution \(\varepsilon_0\) of about 120, partly arising from stray-capacitance contributions due to the small sample dimensions. The dashed line in Fig. 2 demonstrates that the high-temperature flanks of \(\varepsilon'(T)\) at low frequencies (that is, the static dielectric constant \(\varepsilon_0(T)\)) are consistent with a Curie–Weiss behaviour, \(\varepsilon_0 = C/(T - T_{\text{CW}}) + \varepsilon_0\), with a Curie–Weiss temperature \(T_{\text{CW}} = 25\,\text{K} \approx T_{\text{FE}}\) and a background term \(\varepsilon_0\). This temperature agrees reasonably with the Néel temperatures between about 25 and 30 K reported in the literature (see Supplementary Information for a detailed discussion) and with \(T_{\text{CW}} \approx 27\,\text{K}\) deduced from thermal expansion measurements (Supplementary Fig. S7). Sample 2 showed a similar dielectric response to that seen in Fig. 2 (see Supplementary Information), despite having a significantly different geometry and a different contact material—clear evidence for the intrinsic nature of the observed behaviour. In a previous dielectric investigation of \(\kappa\)-Cl (ref. 20), relaxational behaviour was deduced from frequency-dependent dielectric measurements below 30 K, consistent with the notion of order–disorder ferroelectricity17. Owing to the restricted temperature range in that work, no \(\varepsilon'(T)\) peaks were detected20.

Further evidence for ferroelectric ordering in \(\kappa\)-Cl is provided by so-called positive-up-negative-down (PUND) measurements, where a sequence of trapezoid pulses (Fig. 3a) is applied to the sample. The resulting current response (Fig. 3b) shows strong peak-like features occurring when the electric field \(|E|\) exceeds about 10 kV cm\(^{-1}\) for the first and third pulse. Obviously, here the macroscopic polarization of the sample is switched, that is, the dipoles within the ferroelectric domains reorient along the field, implying a motion of charges and, thus, a peak in \(I(t)\). As expected for ferroelectrics, at the second and forth pulse, no corresponding features show up because the polarization was already switched by the preceding pulse. (The horizontal sections in \(I(t)\) represent the trivial charging and discharging currents of the sample capacitor.) The typical PUND response was clearest for low frequencies, \(\nu < 100\,\text{Hz}\).

Stimulated by these results, we have also performed field-dependent polarization measurements, \(P(E)\). Typical results are shown in Fig. 3c. Above \(T_{\text{FE}}\), elliptical curves are observed (crosses), typical for linear polarization response (parallellectricity) with loss contributions from charge transport17. However, at lower temperatures, a clear onset of nonlinearity above about 8.5 kV cm\(^{-1}\) occurs and saturation at the highest fields is observed (circles), as expected for ferroelectrics. The saturation polarization of several tenths of a microcoulomb per square centimetre compares well to that of the ferroelectric charge-transfer salt tetraethylvalenep-bromalanil (0.2 µC cm\(^{-2}\); ref. 21) and the electronic ferroelectric and multiferroic magnetite (0.5 µC cm\(^{-2}\); ref. 22). In the electronic ferroelectric Pr\(_{1-x}\)Ca\(_x\)MnO\(_3\) (44 µC cm\(^{-2}\); ref. 23), higher values are found. Interestingly, at higher fields, \(|E| > 12\,\text{kV cm}^{-1}\), breakdown effects were observed. This may indicate that the sample resistance has become too low and that interplane charge transport sets in. Thus, there is a rather restricted range of roughly 9–12 kV cm\(^{-1}\) for nonlinear polarization response in \(\kappa\)-Cl.

Overall, the results presented in Figs 2 and 3 provide strong evidence for ferroelectricity in \(\kappa\)-Cl. Coinciding with the occurrence of magnetic ordering, the appearance of simultaneous electrical and magnetic order is a well-understood phenomenon in multiferroic systems with spiral spin order1–3. Thereon the onset of helical spin order breaks inversion symmetry and, owing to the Dzyaloshinskii–Moriya interaction, triggers the formation of displacive ferroelectric order through the electro-magnetic coupling \(P \propto \mathbf{e} \times \mathbf{Q}\). Here \(\mathbf{Q}\) denotes the propagation vector of spin order and \(\mathbf{e} = \mathbf{S} \times \mathbf{S}\), a cross product between adjacent spins \(\mathbf{S}\) and \(\mathbf{S}\), gives the spiral axis3–4. Thus, these systems are regarded as spin-driven ferroelectrics. Could this be the mechanism generating multiferroicity in \(\kappa\)-Cl? Indeed, it has been pointed out that a finite Dzyaloshinskii–Moriya interaction is present in \(\kappa\)-Cl (refs 8, 13). However, to our knowledge no experimental evidence for a helical magnetic structure in this material has been found until now.

To check for a spin-driven mechanism, we have performed magnetic field-dependent dielectric measurements. Usually, spin-driven multiferroics show a strong dependence of the dielectric properties on externally applied magnetic fields (so-called magnetocapacitive effects)1,2,24. Moreover, in \(\kappa\)-Cl a spin-flop transition at 0.25 T into a direction perpendicular to the field has been found below 23 K (refs 12, 13). In the spin-driven scenario, the spin-flop transition would affect the dielectric properties through \(P \propto \mathbf{Q} \times (\mathbf{S} \times \mathbf{S})\). Remarkably, no variation of the dielectric properties in fields up to 9 T was found (see Supplementary Information), ruling out a spin-driven mechanism for multiferroicity in \(\kappa\)-Cl.

This suggests that for \(\kappa\)-Cl a purely electronic, charge-order-driven ferroelectric state, as also considered for other ferroelectric charge-transfer salts6,9,18,25,26, is realized. In fact, in a review article on this mechanism8, charge-transfer salts were considered as good candidates for multiferroics with a ferroelectric state driven by...
charge order. The mechanism discussed in that work is based on a combination of bond- and site-centred charge order leading to the breaking of inversion symmetry. This provides a plausible scenario for \(k\)-Cl just as in the structurally related \((ET)_{2}Cu_{3}(CN)_{5}\), at high temperatures each hole can be assumed to be delocalized on an ET dimer\(^{10-11}\). This corresponds to pure bond centring (see Fig. 1c of ref. 6). Below \(T_{N_{b}}\), the holes lock in to one of the two molecules of the dimers, additionally establishing site centring (Fig. 1d in ref. 6). This will primarily lead to a polarization parallel to the planes, but, owing to the inclined spatial orientation of the ET molecules\(^{6}\), a polarization along \(b\) is also induced.

The results presented so far were obtained with \(E \parallel b\) to exclude problems arising from the high in-plane conductivity of \(k\)-Cl, which considerably exceeds the out-of-plane conductivity, at least at elevated temperatures (Fig. 1). Below \(T_{N_{b}}\), which coincides with the charge-order transition, the conductivities come rather close to each other and the out-of-plane conductivity exceeds the in-plane behaviour only by about one order of magnitude. This indicates that dielectric experiments, aiming at a detection of the polar ground state, should be possible. In general, measurements of the dielectric properties of highly conducting samples are difficult to perform owing to dominant charge-transport and inductance contributions as well as Maxwell–Wagner relaxations\(^{27}\), making the interpretation of those results difficult. However, in light of the distinct anomalies seen for \(E \parallel b\), some signatures of the ferroelectric polarization parallel to the planes (\(E \perp b\)) can be expected. Figure 4 shows such results for sample 3. At \(T > 30\ K\), a peak shows up that strongly shifts with frequency, thus showing the typical signature of a relaxation process. Most likely it is of Maxwell–Wagner type and can be ascribed to electrode polarization arising from the formation of the depletion layers of Schottky diodes that form at the electrode–sample interfaces\(^{27}\). However, at lower temperatures and partly superimposed by this non-intrinsic contribution, another peak is revealed. It occurs close to \(T_{N_{b}}\) and its position does not, or only weakly, depend on frequency (the apparent weak shift at frequencies beyond several kilohertz can be ascribed to the contribution of the Maxwell–Wagner peak, which dominates at high frequencies). Just as for \(E \parallel b\), the maximum becomes strongly suppressed for high frequencies. The observation of a peak in \(\varepsilon'(T)\) for \(E \perp b\), despite its significant rounding, which is probably due to partial shielding by mobile charge carriers, is a clear indication for an in-plane component of the ferroelectric polarization. The measurements of the in-plane dielectric properties of \(k\)-Cl reported in ref. 28, which were restricted to temperatures below 25 K and a narrow frequency range, showed similar behaviour as in Fig. 4. Interestingly, close to the upper temperature limit of 25 K of this investigation, just the onset of a peak was observed, in good agreement with the present results. Owing to the high conductivity for \(E \perp b\), meaningful \(P(E)\) results could not be obtained. PUND experiments for \(E \perp b\) also suffer from the high conductivity, which, moreover, is revealed to be highly nonlinear\(^{28}\). Nevertheless, the obtained results (see Supplementary Information) are consistent with a ferroelectric polarization for \(E \perp b\).

In contrast to the spin-driven systems, for charge-order multiferroics the ferroelectric and magnetic transition temperatures can differ significantly\(^{6,22}\). How can the nearly identical transition temperatures in \(k\)-Cl be explained within the above framework? The magnetism in \(k\)-Cl arises from the spins of the holes, which, at \(T > T_{N_{b}}\), are already located on a single dimer. As the holes fluctuate within the dimers, their spins—on average—sit at the centres of the dimers, forming an anisotropic triangular lattice within the \(ac\) planes (indicated by lines in the schematic drawing in the right inset of Fig. 1), giving rise to geometrical frustration. Indeed, in \((ET)_{2}Cu_{3}(CN)_{5}\), where frustration is even stronger, a spin-liquid state is formed\(^{29}\). There, dielectric measurements\(^{9}\) have revealed relaxor ferroelectricity, that is, short-range cluster-like ferroelectric order. However, in \(k\)-Cl, we find long-range ferroelectricity, which we assume to be caused by charge order, which implies the collective off-centre positioning of holes within

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**Figure 3** | Electric polarization switching. **a**, Time-dependent excitation signal \(E \parallel b\) of the PUND measurements performed at 25 K with waiting time \(\delta\) and pulse width \(p\). **b**, Resulting time-dependent current of sample 2. The spikes in response to pulses I and III provide evidence for polarization switching. **c**, Polarization-field hysteresis curves at temperatures below and above the ferroelectric phase transition.

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**Figure 4** | Temperature-dependence of the dielectric constant. \(\varepsilon'(T)\) for sample 3, for selected frequencies and \(E \perp b\). The lines are guides for the eyes.
the dimers below $T_{\text{fg}}$. Consequently, the spins no longer reside on a highly frustrated triangular lattice (left inset of Fig. 1). The frustration should therefore be reduced and magnetic order sets in (see Supplementary Information).

The observed conductivity, dielectric and polarization properties of $\kappa$-Cl provide evidence for ferroelectricity, making this material the first example of a multiferroic charge-transfer salt. We propose charge-order-driven electronic ferroelectricity as the most plausible scenario at present to explain the observed polar order in this material. Our measurements indicate that ferroelectric order drives the magnetic order, in marked contrast to the well-known spin-driven mechanism in the helical magnets. Thus, $\kappa$-Cl not only stands for a new class of multiferroics but also represents a candidate for the realization of a new coupling mechanism of magnetic and ferroelectric ordering.

Methods

Crystal growth. Crystals of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl were grown according to literature methods.

Dielectric measurements. For the dielectric measurements, contacts of graphite paste (samples 1 and 3) or evaporated gold (sample 2) were applied at opposite sides of the crystals, ensuring an electrical field direction parallel (samples 1 and 2) and for sample 3 parallel to the ET planes. The dielectric constant and conductivity were determined using a frequency-response analyser (Novocontrol Alpha-Analyser) and an autobalance bridge (Hewlett-Packard HP4284).

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References


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Author contributions

M.L., A.L., P.L. and J.M. conceived and supervised the project. J.M. grew the high-quality single crystals. B.H., J.M. and R.R. prepared the samples for the experiments. S.K., P.L. and M.d.S. performed the dielectric measurements and analysed the data. P.L. together with M.L. and J.M., wrote the paper with contributions from C.H., A.L., J.A.S. and M.d.S. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to P.L.

Competing financial interests

The authors declare no competing financial interests.