Anomalous dielectric response in the dimer Mott insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

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We have measured and analyzed the dielectric constant of the dimer Mott insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, which is known as a playground for a spin-liquid state. Most unexpectedly, this particular organic salt has nontrivial charge degrees of freedom, being characterized by a relaxor-like dielectric relaxation below around 60 K. This is ascribed to the charge disproportionation within the dimer due to the intersite Coulomb repulsion. A possible microscopic model is suggested and discussed.

I. INTRODUCTION

The electric dipole is a fundamental concept in describing the response of a material to an electric field.[1] Spontaneously emerging electric dipoles are of particular importance in the field of modern electronics. Ferroelectric materials that show spontaneous electric dipoles below a transition temperature T_c have been used in applications such as high-density, nonvolatile memories.[2] In conventional ferroelectric materials, two kinds of electric dipoles are recognized. One is a displacement type, in which cations shift relative to anions below T_c. The other is an order-disorder type, in which polar molecules are randomly oriented above T_c, and align below T_c. BaTiO$_3$ and NaNO$_2$ are typical examples of the former and the latter types, respectively.[1] Recently, a third type of ferroelectricity was noted in the layered iron oxide LuFe$_2$O$_4$, in which the electric dipole comes from the ordering of the Fe^{2+} and Fe^{3+} ions on a double-layered triangular lattice.[3] These dipoles are understood in terms of atomic positions in the crystal of interest.

Here we show a truly electronic type of electric dipole in the organic salt κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, where BEDT-TTF stands for bis(ethylenedithio)-tetrathiafulvalene. κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is known as a dimer Mott insulator,[4] and has been investigated as an ideal candidate for a spin-liquid state.[5–7] This organic salt is a layered compound in which the BEDT-TTF and Cu$_2$(CN)$_3$ layers are alternately stacked along the a axis. The BEDT-TTF layer is responsible for the electrical and magnetic response while the Cu$_2$(CN)$_3$ layer only acts to electrostatically stabilize the crystal. The Greek letter κ specifies a packing pattern of the BEDT-TTF molecules, which is schematically shown in Fig. 1(a). In this pattern, hole exists per two dimerized molecules as indicated by the dotted ellipsoids. Thus, if one regards the two molecules as a sort of "atom" represented by the closed circles in Fig. 1(b), one can identify this BEDT-TTF layer with a "half-filled" system in which one hole is localized on each site.[8] This system meets the definition of a Mott insulator, hence the name "dimer Mott insulator." The spin degrees of free-
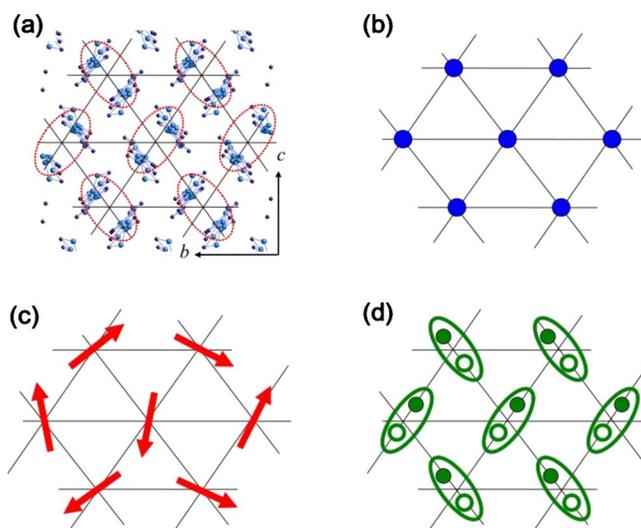

FIG. 1. (Color online) (a) Schematic of the BEDT-TTF layer in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. The dotted ellipsoids represent dimerized molecules. (b) A triangular lattice of dimers, where closed circles represent identified with the dimerized molecules. (c) A triangular lattice of magnetic dipoles (spins). (d) A triangular lattice of electric dipoles, where open and closed circles represent positive and negative point charges, respectively. This is identical to Fig. 5(f).

dom on each localized hole acts as a magnetic dipole as shown in Fig. 1(c). The magnetic dipoles interact via a superexchange interaction $J/k_B \sim 250$ K, but an antiferromagnetic transition does not take place above 32 mK, owing to the frustration coming from the geometry of the triangular lattice based on dimers. To be more precise, recent *ab initio* calculations reveal that the dimer network cannot be regarded as a regular triangle in which the anisotropy of the transfer integral reaches 0.8 but still the spin system is in the frustrated region.[9,10] This lack of long-range order of the magnetic dipoles defines a spin liquid.[5]

We have found that κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ exhibits dielectric relaxation below around 60 K, which is not expected from the charge excitations in conventional Mott insulators. Based on the extended Hubbard model, we ascribe this to the charge disproportionation within the dimer driven by the intersite Coulomb interaction.

II. EXPERIMENTAL

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ was grown by an electrochemical method. Dielectric constant (ε) and resistivity (ρ) measurements were carried out using an HP4284A impedance analyzer along with cooling down in a liquid-helium cryostat. Electric displacement-electric field curves were measured with a homemade apparatus based on the Sawyer-Tower circuit[11] with a maximum electrical field of 1000 V. The measurement direction was set to be perpendicular to the BEDT-TTF layer (along the *a* axis) because a dielectric constant cannot be measured precisely for conductive media.[12] The cross-plane resistivity is much higher than the in-plane one and the contact resistance was safely neglected. We should note that the temperature and frequency dependence of ε is similar between the in- and cross-plane directions of layered materials so that the ac response of a two-dimensional dielectric material can be discussed from the cross-plane measurement at least qualitatively.[13] The magnitudes of ε are even close in some materials such as LuFe$_2$O$_4$.[14]

III. RESULTS AND DISCUSSION

Figure 2(a) shows the dielectric constant with respect to various frequencies plotted as a function of temperature. The dielectric constant increases with decreasing temperature below 60 K and simultaneously begins to show frequency dependence. As temperature is lowered, the dielectric constant goes through a broad maximum at a temperature T_{max} depending on the measurement frequency f, then decreases toward 2.1–2.5. T_{max} corresponds to a crossover temperature below which the response to the changing electric field begins to lag. The ac conductivity also shows frequency dependence as shown in Fig. 2(b). In this case, the frequency dependence becomes significant below around 40 K, which is lower than that for the dielectric constant. Roughly speaking, we see that the ac conductivity bends around T_{max} and remains higher than the conductivities at lower frequencies.

The dielectric relaxation we observe is indeed unconventional. First, the charge degrees of freedom is believed to be
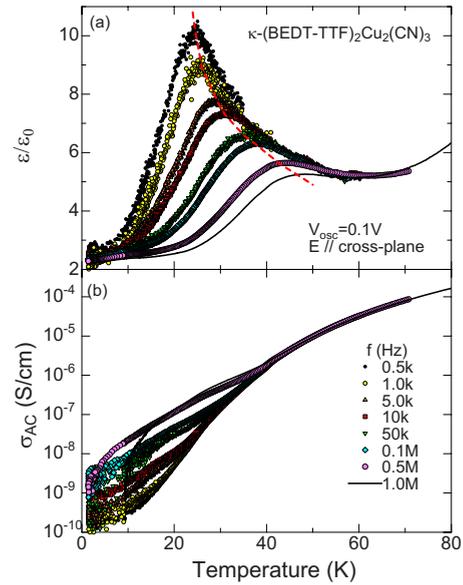

FIG. 2. (Color online) (a) The dielectric constant of a single crystal of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ along the *a* axis (cross-plane) direction at various frequencies as a function of temperature. The randomly oriented electric dipoles appear below 60 K. The dotted curve indicates the peak temperature T_{max}. (b) The ac electrical conductivity of the same crystal.

insubstantial in the Mott insulator but the increasing dielectric constant below 60 K indicates the existence of randomly oriented electric dipoles as shown in Fig. 1(d). Second, the dielectric relaxation implies collective motion of the electric dipoles. If all the dipoles were independent, the response would be independent of f, because $k_B T \gg hf$.

Similar relaxation behavior is widely observed in disordered systems such as glass-forming liquids, spin-/cluster-glasses, and relaxor ferroelectrics. The measurement frequency is plotted as a function of $1/(T_{max}-T_c)$ in Fig. 3. T_c is the transition temperature, which we assume to be 6 K be-
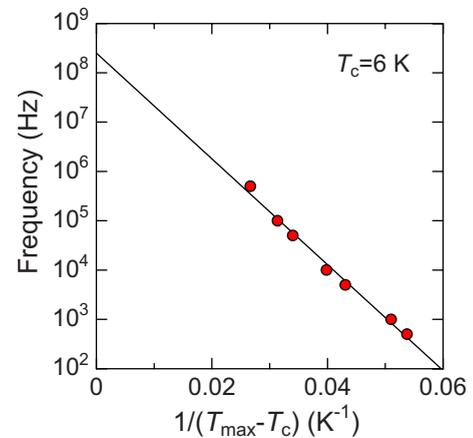

FIG. 3. (Color online) The measurement frequency f plotted as a function of $1/(T_{max}-T_c)$. T_{max} is the peak temperature at which the dielectric constant goes through a broad maximum, and T_c is assumed to be 6 K. The solid line corresponds to the fitting curve, where f_0 and E_g/k_B are evaluated to be 2.5×10^8 Hz and 250 K, respectively.

cause the specific heat,[6] the thermal conductivity,[7] and the thermal-expansion coefficient[15] show anomaly at this temperature. The data are roughly linear, which suggests that the Vogel-Fulcher law $f=f_0 \exp[-E_0/k_B(T_{max}-T_c)]$ consistently explains the frequency dependence of T_{max}. Since the Vogel-Fulcher law is widely observed in glass-forming liquid,[16] spin-/cluster-glasses,[17,18] and relaxor ferroelectrics,[19,20] it is natural to conclude that the dielectric relaxation comes from disordered arrangements of the electric dipoles.

The values of f_0 and E_0/k_B are evaluated to be 2.5 $\times 10^8$ Hz and 250 K, respectively. We should emphasize that f_0 is significantly smaller than a typical value of f_0 $\sim 10^{12}$ Hz for relaxor ferroelectric materials.[20] The physical meaning of $1/f_0$ is a typical time scale for ac response in the high-temperature limit, which should be longer in domain motions than in individual motions. It is known for magnetic systems that cluster glass materials (where ferromagnetic domains are randomly oriented) tend to show smaller values of f_0 than spin-glass materials (where individual spins are randomly oriented).[18] In this respect, we think that the polar domains are disordered rather than the individual electric dipoles. Similar disorder is reported in magnetic resonance experiments[21,22] and may be related to the suppression of the long-range order of magnetic moments.

It is well known that disorder in the terminal ethylene group seriously affects the physical properties in some (BEDT-TTF)-type organic salts. Some physical quantities such as superconducting T_c significantly depend on the cooling rate.[23] Theoretically, this type of disorder can be a pair breaker of superconductivity,[24] and modifies the intradimer Coulomb interaction.[25] We performed dielectric measurements with different cooling rates ranging from 0.5 to 10 K/min, and found that the data were essentially the same as in Fig. 2 (not shown). We further measured the dielectric response for a deuterated sample and found that the data were again essentially the same (not shown). These results indicate that the observed dielectric relaxation does not come from the disordered arrangements of the hydrogen bonding in the terminal ethylene group. In this context, we can say that the single crystal used here contains no substantial lattice defects or disorder, as pure as crystals of other organic salts. In relaxor ferroelectric materials, in contrast, more than a few percents of the host atoms are replaced by different atoms, which can be seeds for the inhomogeneity.[19,26]

Although no clear phase transition is observed in the thermodynamic quantities of this material, one may find a trace of a transition temperature. Figure 4(a) shows the inverse dielectric constant as a function of temperature. These data are plotted after subtracting the dielectric constant at 1.2 K as the temperature-independent part. The dielectric constant below 60 K obeys the Curie-Weiss law, i.e., it is roughly inversely proportional to $T-T_c$ with $T_c=6$ K. As shown in Fig. 4(b), around T_c, the dielectric constant has an anomaly that is almost independent of frequency. As shown in the inset of Fig. 4(b), the electric displacement D shows no remnant polarization below 6 K, indicating that the ordering of the electric dipoles is of antiferroelectric type.

We propose a microscopic origin of this antiferroelectric response. The extended Hubbard model based on the BEDT-TTF molecular orbitals is a widely accepted model for this
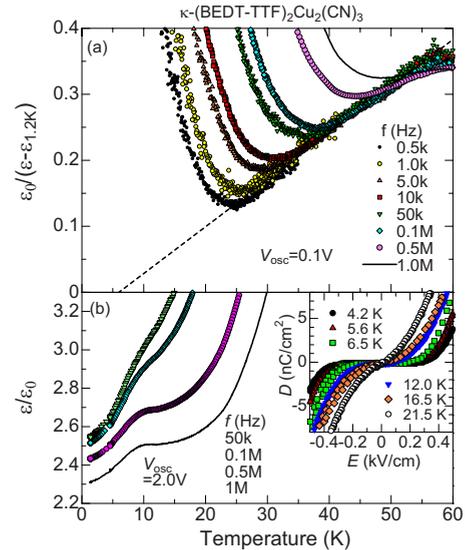

FIG. 4. (Color online) (a) The inverse dielectric constant plotted as a function of temperature. The temperature-independent part (the dielectric constant at 1.2 K) has been subtracted. The dotted line indicates that the dielectric constant obeys the Curie-Weiss law with a Curie temperature $T_c=6$ K. (b) The low-temperature part of the dielectric constant. A frequency-independent cusp is observed near T_c. The inset shows the electric displacement D plotted as a function of external electric field E.

family of organic materials, which consists of transfer integral, on-site Coulomb repulsion, and intersite Coulomb repulsion terms.[27] Owing to the large transfer integrals and Coulomb repulsion between the dimerized molecules, an electron on a dimer is described by the superposition of two quantum states expressed by $\psi_{dimer}=a_A\phi_A+a_B\phi_B$ with the coefficients $a_A=a_B=1/\sqrt{2}$ as shown in Fig. 5(a). Here, ϕ_A and ϕ_B represent the wave functions of the dimerized A and B molecules. The electron on the dimer thus fluctuates between A and B, rather than staying statically at the center of the dimer. On the other hand, the interdimer Coulomb repulsion polarizes the dimers (i.e., unequalizes a_A and a_B) such that the electrons on neighboring dimers stay apart as far as possible. When these two electrons come close [Figs. 5(b) and 5(c)], the repulsion is higher than when they are far apart [Figs. 5(d) and 5(e)]. In this way, the intradimer quantum fluctuation and the dipole-dipole interaction compete. In related organic conductors of one dimension, the same sort of interaction induces a ferroelectric transition.[28] Owing to the zigzag packing of BEDT-TTF molecules, the dipole-dipole interaction becomes relatively small, and concomitantly the intradimer quantum fluctuation is dominant, allowing the effects of dipole-dipole interaction to remain as short range correlations. As a result, the system goes back and forth between two configurations; Figs. 5(f) and 5(g) show two snapshots of the quantum fluctuation coupled with the inversion symmetry.

Our model suggests that the charge ordering instability survives in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. This is reasonable; depending on the degree of dimerization, the ground state of the quarter-filled organic salts can be continuously changed from the charge ordered insulator to the dimer Mott
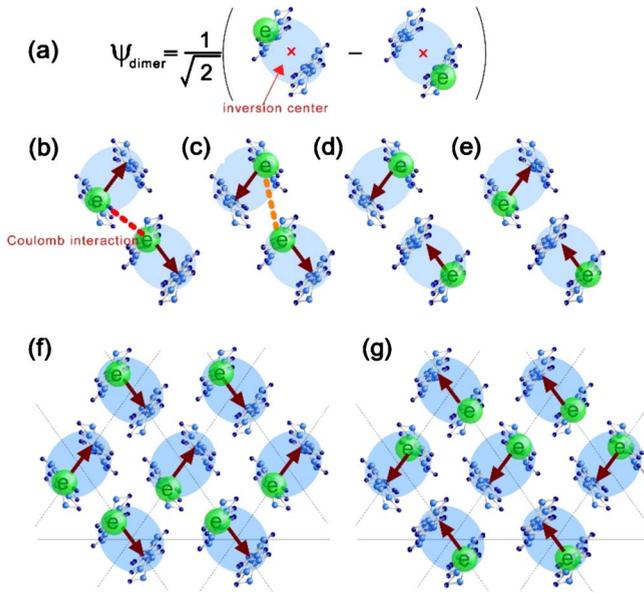
FIG. 5. (Color online) (a) Schematic of a quantum electric dipole. [(b)–(e)] Schematics of two neighboring quantum electric dipoles. The arrows represent the electric dipoles. (b) and (c) represent the cases when two electrons are come close to one another, whereas (d) and (e) represent the cases when the two electrons are far apart. [(f) and (g)] Possible short-range domains of the electric dipoles fluctuating collectively.

insulator.[27,29] These two pictures are extreme limits and real materials lie in between. Detailed theoretical study on this picture is written separately,[30] based on the model including the transverse Ising term which accounts for the charge degrees of freedom, and the Kugel-Khomskii term describing the couplings of spin and charges. Motivated by our experiment, Naka and Ishihara,[31] in parallel with Ref. 30, also calculated the mean-field phase diagram on the similar model, and successfully explained a possible existence of a ferroelectric charge order. It should be noted that before our experimental study, Clay *et al.*[32] have discussed the physical properties of the organic salts in terms of electron-paired crystal and already predicted that the charge ordering pattern is hidden in the title compound. Actually, their predicted pattern is similar to Figs. 5(f) and 5(g).

We can understand the dielectric response qualitatively using the above concept. This electric dipole is tightly bound to the molecular arrangement, fluctuating collectively within a certain length scale. When an external electric field is applied, such collective dynamical domains easily obey the external field, retaining an inhomogeneous nature. Thus a mean square value of $\sqrt{\langle q^2 \rangle} L$ is induced by the external field, where

q is proportional to the difference of the electron densities $n_A = |a_A|^2$ and $n_B = |a_B|^2$ and L is the distance between the A and B molecules. From the slope in Fig. 4(a), $\sqrt{\langle q^2 \rangle}$ is evaluated to be $0.1e$. Of course, the above estimate of L and $\sqrt{\langle q^2 \rangle}$ came from the oversimplified picture. In the present experiment, the dipole moments tend to align perpendicular to the BEDT-TTF layer, and the charge should be polarized along the BEDT-TTF molecule. We should note that the charge distribution of the π electrons on the molecule is about 5–10 Å, which is the same length scale as the intermolecular distance. Thus we believe that the estimated charge disproportionation of $0.1e$ will not be off the mark.

Finally, we briefly add some notes on the nature of this dielectric relaxation. (i) The dielectric constant at 1 MHz above 10 K is independent of dc bias up to 2 kV/cm. This makes a remarkable contrast to relaxor ferroelectric materials[33] or internal barrier-layer capacitors[34] and excludes a possibility for extrinsic origins.[35] (ii) The dielectric response is also independent of magnetic field up to 15 T and represents a remarkable contrast to multiglass or multiferroic materials.[36,37] (iii) We observed similar dielectric relaxation in β'-(BEDT-TTF)$_2$ICl$_2$.[38] This clearly indicates that this type of electric dipoles widely exists in dimerized BEDT-TTF molecules and reveals the importance of the charge degrees of freedom in such systems.

IV. SUMMARY

In summary, we have measured the dielectric constant of the dimer Mott insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, and have found anomalous dielectric relaxation below around 60 K. This relaxation resembles that of relaxor ferroelectric materials, which strongly suggests the existence of interacting electric dipoles. This electric dipole is ascribed to the charge disproportionation within the BEDT-TTF dimers driven by the intermolecular Coulomb interaction. We have evaluated the charge disproportionation to be $0.1e$ from the temperature dependence of the dielectric constant. The present results indicate that nontrivial charge degrees of freedom survive in the dimer Mott insulator, which may be related to the characteristic properties of this family such as pressure-induced superconductivity.

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