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Dielectric ordering and colossal magnetodielectricity in the antiferromagnetic insulating state of λ-(BEDT-TSF)$_2$FeCl$_4$

E. Negishi,[1] T. Kuwabara,[1] S. Komiyama,[2] M. Watanabe,[2] Y. Noda,[2] T. Mori,[3] H. Matsui,[1] and N. Toyota[1]
[1]*Physics Department, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*
[2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[3]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*
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We report on the temperature and magnetic-field dependence of dielectric constant ε_1^c and conductivity σ_1^c along the *c* axis in the antiferromagnetic insulating (AFM-I) state of λ-(BEDT-TSF)$_2$FeCl$_4$, which indicate some dielectric ordering in coexistence with AFM-I. There appears a sharp upturn of saturated electric polarizations and a colossal magnetodielectricity (CMD) in magnetic fields. On a basis of the π-d superexchange interaction we propose a charge ordering-induced polarization model leading to two candidates of ferroelectric or antiferroelectric orderings, and discuss the prominent magnetoelectric effects associated with CMD in terms of the field-induced unlocking or melting charge ordering.

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There have been long-term studies of ferroelectromagnets in which magnetic and electric orders coexist.[1] Recently, extensive work has been devoted with a renewed interest in rare-earth manganites,[2–4] since a reciprocal control using a magnetoelectric (ME) effect that a magnetic (electric) field controls dielectric (magnetic) properties, is highly expected for an application to a multifunctional electronic device. In a perovskite $TbMnO_3$, for example, an application of magnetic field causes the prominent ME effect on the ferroelectric polarizations via a magnetoelastic coupling in the commensurate antiferromagnetic state.[3] Here we describe a ME effect in a π-d coupled-charge transfer salt λ-(BEDT-TSF)$_2$FeCl$_4$ which is a quasi-two-dimensional (Q2D) paramagnetic metal (PM) containing Fe^{3+} ions with the high spin $S_d=5/2$; where BEDT-TSF is an abbreviation of bis(ethylenedithio)tetraselenafulvalene, simply denoted as BETS.[5]

The material takes a triclinic structure of the space group $P\overline{1}$ with an inversion symmetry. Four independent BEDT-TSF donors form a columnar structure along the *a* axis via a face-to-face overlap, and each column is coupled via a side-by-side overlap along the *c* axis (see Fig. 5). The metallic state with paramagnetic spins S_d turns into an antiferromagnetic insulating (AFM-I) state at the metal-insulator (MI) transition temperature $T_{MI}=8.3$ K. Below T_{MI}, the in-plane resistance increases drastically more than six orders of magnitude. On the other hand, the magnetic susceptibility χ shows a discontinuous change at T_{MI}, which evidences an appearance of quantum spins $S_\pi=1/2$ of localized π electrons to form the S_π-S_d coupled antiferromagnetic (AFM) ordering at T_{MI}.[6] At a critical magnetic field H_{MI}, however, AFM-I becomes unstable against forming the reentrant metallic states with a field-forced alignment of S_d, leaving π electrons to be mobile again.[7] Recently, there have been disclosed phenomena both in the high-temperature PM and in the low-temperature AFM-I. The former is an anomalous metallic state coexistent with dielectric anomalies revealed by microwave conductivity measurements,[8] and then supported by successive observations of structure-related anomalies by specific-heat,[9] proton NMR,[10] and x-ray diffraction measurements.[11] An origin of the extraordinary dielectricity in PM has been discussed in terms of a spontaneous electronic phase separation into normal metallic and relaxor ferroelectric domains.[12] The latter is a nonlinear transport phenomenon associated with a negative resistance (NR) and switching effects in AFM-I (Ref. 13) which systematically depend on magnetic fields.[14] These results both in PM and AFM-I have disclosed that some charge instabilities as well as magnetic interactions are of intrinsic importance in the present magnetic conductor. This paper presents evidence for a dielectric ordering coexisting with AFM-I, and the ME effect associated with a colossal magnetodielectricity (CMD).

The capacitance $C=\varepsilon_1 S/d$ and conductance $G=\sigma_1 S/d$, where d is a distance of about 0.5 mm apart between electrical contacts and S the cross section of an order of 10^{-3} mm^2, were measured by a three-terminal method using acapacitance bridge at the excitation frequency $f(=\omega/2\pi)$ of 10^1–10^4 Hz and the excitation voltage v_{ac} fixed at 10 or 100 mV. Our measurements were unable to be made near the H_{MI}-T phase boundary [see the inset of Fig. 4(a)], where the huge recovery of G higher than 10^2 μS became too large to measure C and G. The dc bias (E_{bias}) dependence of C and G along the c axis was measured in order to evaluate the polarization curve ΔP-E and the current-voltage ($I-V$) characteristics, the latter of which were *in situ* measured also on the same sample immersed in liquid helium to avoid a self-heating effect.[13] Magnetic fields were applied to the b^* axis perpendicular to the ac conducting plane.

Figure 1 shows the temperature dependence of ε_1^c along the c axis at 1 kHz. With increasing temperature ε_1^c becomes very large, amounting to the order of 10^4 in magnitude, although the data are not available near T_{MI} due to a huge recovery of conductivity. For comparison we also plot ε_1^c measured at 44.5 GHz by a microwave cavity perturbation method.[12] Here ε_1^c starts to increase above 6 K, takes a peak just below T_{MI}, and remains constant above T_{MI}. (For the anomalous dielectricity in PM, refer to Ref. 12. In comparison to $\varepsilon_1^{a*,b*}$ along other directions shown in the inset, the magnitude of the dielectric response is found to be tremendously anisotropic with respect to the orientation of the ac

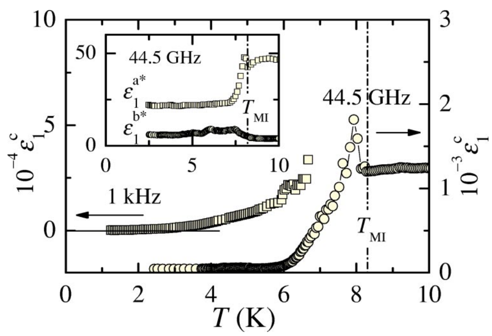

FIG. 1. The c-axis dielectric constant ε_1^c at 1 kHz and 44.5 GHz[12] as a function of temperature. The inset shows the dielectric constants ε_1^{a*} and ε_1^{b*} along $a*$ and $b*$ at 44.5 GHz.

electric field to the crystallographic axis in AFM-I as well as in PM.

Figure 2 shows the E_{bias} dependence of ε_1^c and $\Delta\sigma_1^c$. First of all, we discuss the data at $H=0$. At low E_{bias}, $\Delta\sigma_1^c$ sharply increases with E_{bias}. This is compared with J-E curves in the inset. These curves at higher E (not shown here) reproduce our previous data exhibiting nonlinear transports with NR and switching effects.[13,14] The closed squares in Fig. 2 are the differential conductivity $\sigma_{\text{diff}}=dJ/dE$ calculated from the J-E curve at $H=0$. An overall agreement between $\Delta\sigma_1^c$ and σ_{diff} proves that σ_1^c exclusively detects a response of π electrons responsible for steady, nonlinear J-E characteristics. On the other hand, ε_1^c decreases drastically by a factor of 10 with increasing E_{bias} and diminishes at higher E_{bias} than 110–120 V/cm. This behavior is reversible with respect to E_{bias}. The polarization curves $P(E_{\text{bias}})$ evaluated by $\int_0^{E_{\text{bias}}}\varepsilon_1^c dE$ are shown in Fig. 3. ΔP at $H=0$ increases rather sharply at low E_{bias}, and then tends to saturate at high E_{bias}. To note, these polarizations should exhibit a negligibly small dielectric loss as mentioned above.

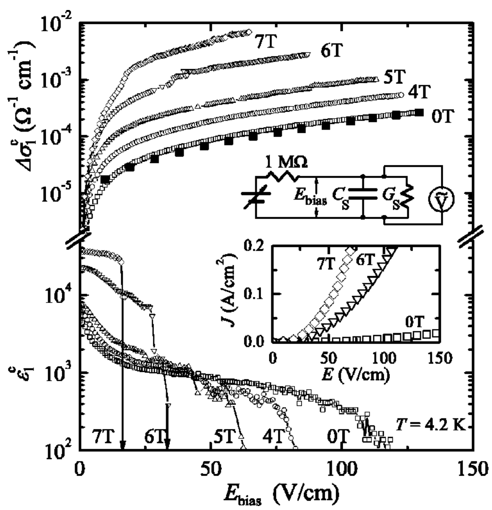

FIG. 2. E_{bias} dependence of ε_1^c and $\Delta\sigma_1^c$ at $T=4.2$ K and $H=0$–7 T. The measuring circuit with sample capacitance C_s, conductance G_s, and the road resistor of 1 MΩ is illustrated. To note, only the relative change can be reliably obtained for σ_1^c due to the internal resistance of the voltage source to which the magnitude of G_s^{-1} can be comparable. The inset shows J-E curves at 4.2 K.

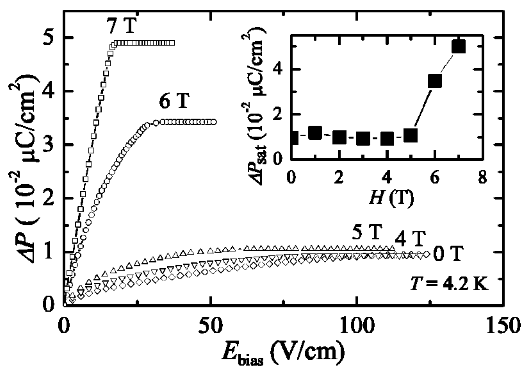

FIG. 3. The relative change of polarization ΔP as a function of E_{bias} at $T=4.2$ K and $H=0$–7 T. To note, only ΔP can be obtained due to the uncertain integration constant. The inset shows the magnetic-field dependence of the saturation value ΔP_{sat}.

Magnetic-field effects already displayed in Fig. 2 are as follows. The E_{bias} dependence of σ_1^c becomes much enhanced monotonously with H, being consistent with a rapid growth of nonlinearity in the J-E curves. From the steady conductivity point of view, it indicates that a magnetic field acts as a breaker to the highly insulating state to bring the system into more conducting states. On the other hand, the magnetic-field effect on ε_1^c is quite different at H below and above 5 T, as shown in Fig. 3. In $H \leqslant 5$ T, the saturated polarization ΔP_{sat} is almost independent on H as shown in the inset, while E_{bias} giving the saturation decreases with H. At $H=6$ and 7 T, however, there is a sharp increase of ΔP at low E_{bias}, and ΔP_{sat} takes a sharp upturn as shown in the inset. Thus H of about 5–6 T is found to be a certain threshold magnetic field separating dielectrically different states. It indicates that a magnetic field acts as a promoter to the state with higher dielectric response. To note, this threshold magnetic field agrees with H* giving a crossover from highly resistive AFM-I of $\sim 10^{-2}$ nS to highly conductive AFM-I of 10^3–10^4 nS as observed in the nonlinear transport. (See Fig. 1 in Ref. 14.)

Figure 4(a) shows the magnetic-field dependence of ε_1^c and σ_1^c at 4.2 K, where open and closed triangles indicate data taken with increasing and decreasing H, respectively. The solid line in the inset of Fig. 4(a) shows $H_{\text{MI}}(T)$ which separates AFM-I from the reentrant PM. Figure 4(a) reveals a huge increase of ε_1^c with H as well as σ_1^c; $[\varepsilon_1^c(7.5\text{ T})-\varepsilon_1^c(0)]/\varepsilon_1^c(0)\sim 10^2$ and $[\sigma_1^c(7.5\text{ T})-\sigma_1^c(0)]/\sigma_1^c(0)\sim 10^4$. Figure 4(b) shows the magnetic-field dependence of ε_1^c and σ_1^c at 2.5 K $\leqslant T \leqslant$ 6.5 K. The divergent increase of ε_1^c observed just above 7 T at 4.2 K [Fig. 4(a)] shifts systematically to lower fields with increasing temperature. This divergence is clearly seen in the vicinity of upper limiting H which is close both to the threshold magnetic field for ΔP_{sat} (Fig. 3) and to H*.[14] [See the dotted curve in the inset of Fig. 4(a).]

As described so far, a certain dielectric ordering is reasonably expected to exist in AFM-I and relevant electric dipoles may exhibit CMD. Here fundamental questions arise: Where and why can such electric dipoles emerge? We propose a model for the dielectric ordering based on charge ordering (CO) of π electrons as follows. Figure 5 illustrates the crys-

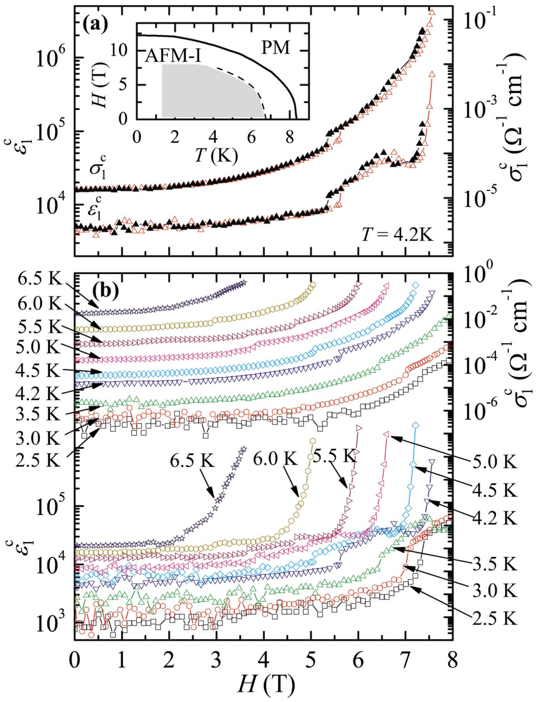

FIG. 4. (Color) Magnetic-field dependence of ε_1^c and σ_1^c; (a) at 4.2 K and (b) at 2.5–6.5 K, where $G\ (=\sigma_1^c S/d) < 10^2 \mu$S and $C(=\varepsilon_1^c S/d) < 10^2$ pF. The inset shows the H-T phase diagram. The solid and dotted lines show a phase boundary H_{MI} and upper limits in our measurements, respectively. The shaded region represents the measurable regime. Note the appearance of several jumps and their hysteresis (Ref. 15) both in ε_1^c and σ_1^c (for example, around H =5.5–7.0 T at 4.2 K).

tal structure projected along the c axis, featuring two columns running along the a axis with three independent transfer integrals, t_A, t_B, and t_C. Molecular-orbital calculations based on an extended Hükel method indicate a strong dimerization for pairs B'–A and B–A' as shown in the figure. Therefore π electrons are expected to be most stably localized within a dimer and furnished with $S_\pi = 1/2$. Mori and Katsuhara[16] calculated magnetic exchange interactions and spin polarizations, which have been consistent so far with experiments such as the antiferromagnetic resonance[17,18] and field-induced superconductivity.[19] The most important result is that the strongest superexchange interaction $J_{\pi d}$ of 3d orbitals via Cl is found to be with π orbitals at selective Se sites of BETS donors labeled B' and B. [We call this interaction as $J_{\pi d}(6)$ after Fig. 2 and Table 6 in Ref. 16.] This superexchange interaction of about −14 K in magnitude is stronger by a factor of 10 than those with other six π orbitals at S sites. Due to this exclusively large superexchange interaction, the charge as well as the spin of π electrons is expected to be localized at these Se sites of B' and B as shown in the figure. The AFM order between S_π and S_d is thus realized by the energy gain of this magnetic ordering which may overcompensate the intersite repulsive Coulomb interaction between localized π electrons at B' and B. Therefore CO should be the primary origin to induce the PM-to-AFM-I transition.

Accordingly, thus localized π electrons (holes) can form

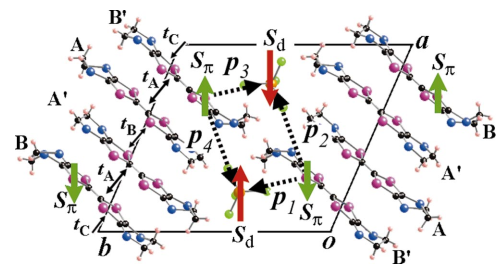

FIG. 5. (Color) Crystal structure projected along the c axis with possible electric dipoles p_i (i=1–4) and AFM spin arrangement. BEDT-TSF molecules stack along the a axis and two $FeCl_4$ anions with Fe^{3+} spin S_d are illustrated. The transfer integrals are t_A =33.55 (in a unit of 10^{-3}), t_B=18.27, and t_C=14.83. Each column is coupled by side-by-side transfer integrals, t_p=−2.80, t_q=−9.30, t_r =13.00, t_s=17.11, and t_t==2.56 (see Fig. 2 in Ref. 16).

an electric dipole moment with a negative charge in the center of $FeCl_4$ anions. Figure 5 illustrates the arrangement of four possible dipoles $\boldsymbol{p_i}$ (i=1–4). We call this model a charge ordering-induced polarization (COP) model. Here $\boldsymbol{p}_1$ and $\boldsymbol{p}_3$ are directly concerned with $J_{\pi d}(6)$, while $\boldsymbol{p}_2$ and $\boldsymbol{p}_4$ are other possible dipoles. To note, the total polarization $\boldsymbol{P}_t \equiv \Sigma_{i=1}^4 \boldsymbol{p_i}$ =0, since $\boldsymbol{p}_1+\boldsymbol{p}_3=\boldsymbol{p}_2+\boldsymbol{p}_4=0$ due to the inversion symmetry. Recently, the first-order structural phase transition was observed at T_{MI}.[11] Since the structural analysis is not made yet for AFM-I, two possibilities may arise at present. One is a uniform transformation to $P1$ which is a unique subgroup of $P\bar{1}$ for the high-temperature PM phase. Here, $P1$ is the most primitive space group in which only translation symmetry remains to hold with losing the inversion symmetry in $P\bar{1}$. An alternative candidate is a nonuniform transformation to form some superlattice. In the former case, a ferroelectric arrangement with $\boldsymbol{P}_t \neq 0$ could be expected; while, in the latter case, there could be expected a variety of dielectric arrangements which might induce an antiferroelectric ordering or some polarization waves.

As already mentioned, dielectric anomalies occur at $T_{\mathrm{MI}} < T < T_{\mathrm{FM}} \simeq 70$ K in PM. It was found quite recently that the width of (007) Bragg reflection becomes broader around T_{FM} and the peak gets split.[20] This structural anomaly in PM is ascribed to an appearance of a possible heterogeneous structure with dielectric relaxor domains of about 0.4 μm in size. If we assume that the inversion symmetry is locally broken in the domain, we may expect a ferroelectric ordering responsible for the extraordinary dielectric response of microwave electric fields, in particular, along the c axis (Fig. 1). This picture, in which some relaxor ferroelectrics appears as a precursory phenomenon to the low-temperature structural phase transition, naturally leads us that a ferroelectric ordering could be induced below T_{MI}. Since the E_{bias} dependence of ΔP (Fig. 3) is reminiscent of ferroelectricity, it is important to study whether a spontaneous polarization and/or characteristic hysteresis occur or not. It is noted that the ferroelectric order is clearly observed in $TbMnO_3$.[3]

In this COP model, the localized π electrons, which are *locked* at the Se sites at low H and T in order to keep $J_{\pi d}(6)$ as effectively as possible, are considered to tend to be *unlocked* or *melted* around H*. Both the sharp upturn of ΔP_{sat}

and the rapid increase of ε_1^c and σ_1^c seems to be induced in this unstable CO states, leading to quite a sensitive response of the polarization to $E_{\mathrm{bias}} \| v_{\mathrm{ac}} \| c$. Eventually, at $H \geqslant H_{\mathrm{MI}}$, the unlocked CO collapses to let π electrons free in the reentrant PM. In conclusion, the present λ-$(BETD\text{-}TSF)_2FeCl_4$ provides ME and CMD effects that can be attributed to unlocking or melting CO induced by magnetic fields. The present CMD effect on a basis of the COP model, the mechanism of which is quite different from that of $TbMnO_3$,[3] may provide an intriguing opportunity to explore ME effects in other magnetic molecular systems.

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