Anion size and isotope effects in (EDO-TTF)$_2$XF$_6$

Yoshiaki Nakano$^{1,2}$, Hideki Yamochi$^{2,5}$, Gunzi Saito$^3$, Mikio Uruichi$^4$ and Kyuya Yakushi$^4$

$^1$Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan  
$^2$Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan  
$^3$Research Institute, Meijo University, Tempaku-ku, Nagoya 468-8502, Japan  
$^4$Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan  
$^5$ERATO “Non-equilibrium Dynamics Project”, JST

E-mail: nakano@kuchem.kyoto-u.ac.jp (Y. Nakano); yamochi@kuchem.kyoto-u.ac.jp (H. Yamochi)

Abstract. (EDO-TTF)$_2$PF$_6$ is a quasi one-dimensional molecular conductor and undergoes a peculiar metal-insulator (MI) transition. The phase transition mechanism is cooperative among Peierls, charge ordering, and anion ordering transitions, which is accompanied with a distinct molecular deformation. (EDO-TTF)$_2$XF$_6$ (X = P (1h), As (2h), Sb (3h)) showed that the transition temperature ($T_{MI}$) and the width of thermal hysteresis ($\Delta T_{MI}$) were systematically changed depending on the anion size, i.e., the $T_{MI}$ decreased in order of 279.0 K (1h), 270.8 K (2h), and 242 K (3h) and the $\Delta T_{MI}$ increased in order of 1.0 K (1h), 5.5 K (2h), and 14 K (3h). The deuterated salts, (EDO-TTF-$d_2$)$_2$XF$_6$ (X = P (1d) and As (2d)), showed higher $T_{MI}$ of 282.0 K (1d) and 274.0 K (2d) and narrower $\Delta T_{MI}$ of 0.0 K (1d) and 5.0 K (2d) than the undeuterated 1h and 2h, respectively. X-ray analysis revealed the anisotropic thermal expansion of unit cell. The linear relationship between $\Delta T_{MI}$ and volume change at $T_{MI}$ was found.

1. Introduction
Molecular conductors have provided the variety of phases due to interplay between electron-electron, electron-phonon and so on. Among them, (EDO-TTF)$_2$PF$_6$ is known as the peculiar metal-insulator (MI) transition system accompanied with distinct molecular deformation. In the high temperature (HT) metallic phase, weakly dimerized columns consist of slightly bent EDO-TTF molecules, and the quasi-one-dimensional Fermi surface is formed. In the low temperature (LT) insulating phase, the column drastically changes the periodicity to the tetramerized one, and the lattice undergoes the nesting of the Fermi surface. As for EDO-TTF molecule, the half of EDO-TTF molecules become the boat shape (B) and the other half exhibit the more flatten shape (F) than that in the HT phase, in which the tetramer of [B,F,F,B] is formed. The charge ordering pattern is a [0,1,1,0] type corresponding to the [B,F,F,B] tetramer. The PF$_6$ anion exhibits the rotational disorder in the HT phase, while the freedom of rotation is suppressed in the LT phase. Therefore, this MI transition is cooperatively driven by Peierls, charge ordering, and anion ordering mechanisms [1].

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In addition, the photo-induced phase transition (PIPT) with ultrafast speed and high efficiency [2] is demonstrated in (EDO-TTF)$_2$PF$_6$. This phenomenon indicates the domino effect, and is completely different from the local photochemical reaction. The strong and coherent coupling between the electronic state and the lattice deformation (and/or the molecular vibrations) is crucial in the thermal and photo-induced phase transitions. It is indispensable to investigate a feature of thermal equilibrium state in order to understand the difference between the thermal and photo-induced states and elucidate the true nature of PIPT phenomenon.

Here, the transition temperatures and hysteresis widths of undeuterated (EDO-TTF)$_2$XF$_6$ (X = P (1h), As (2h), and Sb (3h)) and deuterated (EDO-TTF-d$_2$)$_2$XF$_6$ (X = P (1d), As (2d)) are reported. The structural parameters of isostructural (EDO-TTF)$_2$XF$_6$ are compared for the better understanding of the thermal equilibrium states. The relationship between the transition feature and the structure are discussed as the anion effect.

2. Results and discussion

2.1. Transition temperature

The magnetic susceptibility ($\chi$) of 1h, 2h, 3h, 1d, and 2d at 300 K were 2.8~3.0 × 10$^{-4}$ emu mol$^{-1}$. The $\chi$ values of these salts slightly decreased on lowering temperature as commonly observed for the Pauli paramagnetism of metallic molecular conductors, and the thermal hysteresis loops were observed, indicating the first-order phase transition. For example, at the first thermal cycle, the $\chi$ value of 3h sharply decreased at 229 K on cooling process and completely disappeared. The sudden recovery was observed at 251 K on heating, getting back to Pauli paramagnetic state. When $T_{MI}^{\uparrow}$ ($T_{MI}^{\downarrow}$) is defined as the temperature at which the populations of HT and LT phases are the same in the heating (cooling) process, the transition temperature ($T_{MI}$), and the width of thermal hysteresis loop ($\Delta T_{MI}$) are simultaneously determined as $T_{MI} = (T_{MI}^{\downarrow} + T_{MI}^{\uparrow})/2$ and $\Delta T_{MI} = T_{MI}^{\uparrow} - T_{MI}^{\downarrow}$.

The hysteresis loops were measured on the successive thermal cycles. After the second cycle, the temperatures, $T_{MI}^{\downarrow}$ and $T_{MI}^{\uparrow}$, were slightly shifted to high and low temperatures, respectively, and $T_{MI}$ was converged into a constant value within an experimental error through several thermal cycles. As a consequence, the $\Delta T_{MI}$ also decreased through successive thermal cycles to give a converged value. This is likely due to degradation of the crystal size and quality since the crystals are easily broken into pieces through the transition. The converged $T_{MI}$ ($\Delta T_{MI}$) were 279.0 (1.0) for 1h, 270.8 (5.5) for 2h, 242 (14) for 3h, 282.0 (0.0) for 1d, and 274.0 K (5.0 K) for 2d. The converged $\Delta T_{MI}$ of 1d was very narrow but still finite. The $T_{MI}$ was suppressed as the anion size became larger, PF$_6$ < AsF$_6$ < SbF$_6$, and enhanced by the deuteration. It was also found that the salt with the larger anion show the wider $\Delta T_{MI}$.

2.2. Crystal structure

In the HT phase, 1h, 2h, and 3h belong to the triclinic system with space group $P\overline{1}$. One EDO-TTF molecule and a half of XF$_6$ anion are crystallographically independent and the unit cell contains two EDO-TTF molecules on the general positions and one anion on a center of inversion ($Z = 1$). EDO-TTF molecules showed a slightly bent shape, and were stacked in a head-to-tail manner along the $b$-axis, forming a slightly dimerized column. The stacking columns were connected to each other by sulfur-to-sulfur interatomic contacts along the $a$-axis. As a result, the organic conducting layer was formed parallel to the $ab$ plane.

In the LT phase, these crystals also belong to the triclinic system with space group $P\overline{1}$, while the unit cell is doubled along the diagonal direction of the $ab$ plane in the HT phase. The doubling direction corresponds to the nesting of the Fermi surface. Two EDO-TTF molecules and one XF$_6$ anion are crystallographically independent and the unit cell contains four EDO-TTF molecules and two XF$_6$ anions ($Z = 2$). The organic layers in the HT and LT phases are shown in figures 1(a) and (b), where the crystallographic axes in the HT phase ($a_{HT}$, $b_{HT}$, and $c_{HT}$) are transformed into those in the LT phase ($a_{LT}$, $b_{LT}$, and $c_{LT}$) as $a_{LT} = a_{HT} + b_{HT}$, $b_{LT} = a_{HT} - b_{HT}$, and $c_{LT} = -c_{HT}$.
The relationship between the crystal appearance and the crystallographic axes in the HT phase are shown in figure 1(c). The \(a'\)-, \(b\)-, and \(c^*\)-axes are normal to each other (i.e., the \(a'\)-axis is perpendicular to \(bc^*\) plane). Previously, Sakata et al. reported the effect of uniaxial strains along the \(a'\)-, \(b\)-, and \(c^*\)-axes on the electrical resistivity [3]. They found that the \(c^*\)-axial strain most effectively enhanced the \(T_{MI}\) in the small strain region of 2~4 kbar, while the \(a'\)- and \(b\)-axial strains made the \(T_{MI}\) nearly unchanged. They conjectured that the \(c^*\)-axial strain enhances \(T_{MI}\) since the strain along this axis brings the structure in the HT phase closer to that in the LT phase, and pointed out the important role of electrostatic interaction between the positive charge on EDO-TTF molecule and the negative charge on PF\(_6\) anion. Therefore, it is intriguing to examine the anisotropic aspect of crystal structure at variable temperature and under strain toward a better understanding of the thermal equilibrium state. As a reference, Kondo et al. applied uniaxial strain to \(\theta\)-(BEDT-TTF)\(_2\)CsZn(SCN)\(_4\) and \(\theta\)-(BEDT-TTF)\(_2\)Ag(CN)\(_2\), and carried out electrical resistivity measurement and structural analysis to clarify the relationship between the charge ordered and the superconducting phases [4]. The thermal lattice deformations of (EDO-TTF)\(_2\)XF\(_6\) under the strain-free condition are described below.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{The comparison between the organic layers of 1h at (a) 300 K (HT phase) and (b) 150 K (LT phase). In (b), red lines indicate the axes in the HT phase. (c) The schematic diagram for the relationship between the crystal appearance and the crystallographic axes in the HT phase. (d) Temperature dependence of lattice constants of (EDO-TTF)\(_2\)XF\(_6\) (X = P (red), As (blue), and Sb (green)).}
\end{figure}
Since the crystallographic axes in the HT and LT phases have the above relationship, the axes in the LT phase is easily transformed into those in the HT phase by using cosine formula and the $c^*$ and $a'$ are also given to divide the unit cell volume by the areas of $ab$ and $bc^*$ planes as $b_{\mathrm{HT}} = [(a_{\mathrm{LT}}^2 + b_{\mathrm{LT}}^2 - 2a_{\mathrm{LT}}b_{\mathrm{LT}}\cos\gamma_{\mathrm{LT}})]^{1/2}$, $c^* = V/(absiny)$, and $a' = (V/Z)/(bc^*)$.

The temperature dependence of $a'$, $b$, $c^*$, and $V$ are shown in figure 1(d). Since the area of $ab$ plane in the LT phase ($Z = 2$) is twice as large as that in the HT phase ($Z = 1$), all structural parameters are converted into those in the HT phase. The discontinuous changes of structural parameters at $T_{\mathrm{MI}}$ were observed as previously reported [5]. The magnitudes of discontinuous changes are estimated by linearly interpolating and extrapolating the experimental data and listed in table 1. Noting the magnitudes of discontinuous changes at $T_{\mathrm{MI}}$, the change of $b$-axis ($\Delta b$) at $T_{\mathrm{MI}}$ was nearly the same among 1h, 2h, and 3h, while the changes of $a'$- and $c^*$-axes ($\Delta a'$ and $\Delta c^*$) became larger as the anion size increased. The largest change was $\Delta c^*$ (or normalized $\Delta c^*/c^*_{\mathrm{HT}}$) along the interlayer direction. It was found that the structural change at $T_{\mathrm{MI}}$ is fairly anisotropic and the salt with the larger anion shows the larger volume change ($\Delta V$) at $T_{\mathrm{MI}}$ and the wider $\Delta T_{\mathrm{MI}}$. In this phase transition, discontinuous structural changes $\Delta x$ at $T_{\mathrm{MI}}$ ($x = a'$, $b$, $c^*$, $V$) are required, which must be a major origin of a large energy barrier between the HT and LT phases like spin crossover (e.g., [Fe(2-pic)3]Br2·EtOH [6] and [Fe(ptz)6](BF4)2 [7]) and valence-change (e.g., (npBifc)(F1TCNQ)) [8]) systems. The larger $\Delta x$ seems to connect with the wider $\Delta T_{\mathrm{MI}}$, and intriguingly, the linear relationship between $\Delta V$ and $\Delta T_{\mathrm{MI}}$ was found as $\Delta T_{\mathrm{MI}} = 2.19 \times |\Delta V| - 4.91$.

| Table 1 | Changes of lattice constants ($\Delta x^*$) of (EDO-TTF)$_2XF_6$ (X = P, As, Sb) at $T_{\mathrm{MI}}$ |
|---|---|---|
| X | P | As | Sb |
| $\Delta a'$ (Å) | 0.156 | 0.209 | 0.251 |
| $\Delta b$ (Å) | 0.086 | 0.088 | 0.087 |
| $\Delta c^*$ (Å) | -0.437 | -0.551 | -0.682 |
| $\Delta V$ (Å$^3$) | -2.7 | -4.7 | -8.6 |
| $\Delta a'/a'_{\mathrm{HT}}$ | $2.18 \times 10^{-2}$ | $2.92 \times 10^{-2}$ | $3.48 \times 10^{-2}$ |
| $\Delta b/b_{\mathrm{HT}}$ | $1.18 \times 10^{-2}$ | $1.20 \times 10^{-2}$ | $1.18 \times 10^{-2}$ |
| $\Delta c^*/c^*_{\mathrm{HT}}$ | $-3.79 \times 10^{-2}$ | $-4.73 \times 10^{-2}$ | $-5.80 \times 10^{-2}$ |
| $\Delta V/V_{\mathrm{HT}}$ | $-4.48 \times 10^{-3}$ | $-7.72 \times 10^{-3}$ | $-13.9 \times 10^{-3}$ |

$^a\Delta x = x_{\mathrm{LT}} - x_{\mathrm{HT}}$ ($x = a'$, $b$, $c^*$, and $V$)

3. Conclusion
We experimentally demonstrated the anion size and isotope effects on $T_{\mathrm{MI}}$ and $\Delta T_{\mathrm{MI}}$. The discontinuous changes of lattice parameters in (EDO-TTF)$_2XF_6$ (X = P, As, Sb) during thermally induced phase transition were estimated. The linear relationship between $\Delta V$ and $\Delta T_{\mathrm{MI}}$ was found. The structural studies under strains and photo-induced dynamic states are thirsted as the future work.

Acknowledgement
This work was partly supported by Creative Scientific Research (18GS0208) from JSPS.

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