Charge disproportionation in $\alpha$-(BEDT-TTF)$_2X$

K. Katono, K. Ichimura, T. Taniguchi, Y. Kawashima, K. Yamaya, and S. Tanda
Department of Applied physics, Hokkaido University, Sapporo, Japan.
STM observation of electronic states

3a x 3a commensurate Charge density wave

2H-TaSe$_2$

B. Giambattista et al.

4a×4a Charge stripe in hole doped cupper oxide

Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$

T. Hanaguri et al.

Inorganic materials

Abrikosov flux lattice (Superconductivity)

NbSe$_2$

H. F. Hess et al.

STM measurement has been applied for many electronic phases.
Outline

1. Introduction
2. Results and Discussion
   \( \alpha-(\text{BEDT-TTF})_2\text{I}_3 \)
   \( \alpha-(\text{BEDT-TTF})_2\text{KHg(SCN)}_4 \)
   \( \alpha-(\text{BEDT-TTF})_2\text{RbHg(SCN)}_4 \)
3. Conclusion
Charge order by inter-site Coulomb interaction

Extended Hubbard model with \( \frac{1}{4} \) filling band

\[
H = \sum_{\langle ij \rangle} \sum_{\sigma} (t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c.) + \sum_i U n_i n_{i\uparrow} + \sum_{\langle ij \rangle} V_{ij} n_i n_j
\]

\( U \): On-site Coulomb \hspace{1cm} \( V \): Off-site Coulomb

Experimental result

\( ^{13}\text{C}-\text{NMR} \)

\( \alpha-(\text{BEDT-TTF})_{2}I_{3} \)

Raman spectroscopy

\( 0-(\text{BEDT-TTF})_{2}\text{RbZn(SCN)}_{4} \)

- Two doublet (four peaks)
- Two different site (charge rich and poor)

\( T_{\text{CO}} = 135 \text{ K} \)

\( T_{\text{CO}} = 190 \text{ K} \)

Mode frequency depends on charge on the molecule.

The modes split into several bands.

- Charge order

Y. Takano et al. Synth. Met. 120, 1081 (2001)


Structure of charge order

Metallic state \hspace{1cm} Charge ordering state

\( V < V_C \)
\( \delta = 0 \)
\( +\delta \quad -\delta \quad +\delta \quad -\delta \)

\( V > V_C \)
\( \delta > 0 \)

The structure depends on anisotropy of off-site Coulomb interaction originated from site arrangement

Charge order is deeply related to off-site Coulomb interaction
Charge disproportionation ($\alpha$-(BEDT-TTF)$_2$I$_3$)

X-ray diffraction

Metallic state

(Charge order)

Molecular Charge

Density of States

Charge ordering transition

$T_{\text{CO}} = 135$ K

(1 bar)

Charge disproportionation (CD) even above $T_{\text{CO}}$.

Ratio of CD is increasing with lowering temperature.

How is CD related to Charge order?

STM observation of CD in real space at room temperature.
STM image of $\alpha$-(BEDT-TTF)$_2$I$_3$

Two-fold periodicity in columns indicated by arrows.

Assign B and C as brighter and darker spot in column II

Charge disproportionation in column II

B site > C site

Two fold periodicity develops in both column I and II. Amplitude of the charge modulation: column II > column I.
Charge distribution of $\alpha$-$(\text{BEDT-TTF})_2\text{I}_3$

Two fold periodicity forms horizontal stripe structure far above $T_{\text{CO}} = 135$ K.

Does stripe structure exist in other $\alpha$-type compound?

We study the charge distribution on $\alpha$-$(\text{BEDT-TTF})_2\text{MHg(SCN)}_4$ [$M = \text{K, Rb}$]
Charge distribution of $\alpha$-(BEDT-TTF)$_2$I$_3$

Two fold periodicity forms horizontal stripe structure far above $T_{CO} = 135$ K.

Does stripe structure exist in other $\alpha$-type compound?

We study the charge distribution on $\alpha$-(BEDT-TTF)$_2$MHg(SCN)$_4$ [$M = K, Rb$]
\(\alpha-(\text{BEDT-TTF})_2\text{MHg}((\text{SCN})_4 [M = \text{K, Rb}]\)

Temperature dependence of resistance (\(M = \text{K}\))


- Density wave transition \(T_{\text{DW}} = 8 \text{ K}\)
- NMR \(\Rightarrow\) No magnetic order
- X-ray diffraction
  \(\Rightarrow\) satellite peak far above \(T_{\text{DW}}\), whose wave vector corresponds to that of DW.
  (P. Foury-Leylekian et al., Synth. Met. 137, 1271(2003).)
STM image of $\alpha$-(BEDT-TTF)$_2$MHg(SCN)$_4$ (M = K, Rb) in metallic state

$M = K$

$I = 500 \text{ pA} \quad V = 15 \text{ mV}$

$a = 10.3 \text{ Å}, c = 10.3 \text{ Å}$ (determined by STM)

$4.4 \text{ nm} \times 3.7 \text{ nm}$ on $a$-$c$ plane $300 \text{ K}$

$M = Rb$

$I = 100 \text{ pA} \quad V = 15 \text{ mV}$

$a = 10.3 \text{ Å}, c = 10.5 \text{ Å}$ (determined by STM)

$4.3 \text{ nm} \times 4.2 \text{ nm}$ on $a$-$c$ plane $300 \text{ K}$

Images of K and Rb salts are quite different. Vertical stripe structure was observed in Rb salt.
Charge distribution of $\alpha-(\text{BEDT-TTF})_2\text{KHg(SCN)}_4$

- Horizontal stripe structure develops locally.
- Vertical stripe structure was not observed.

Horizontal stripe

Tunneling current [a.u.]
Distance [nm]

Upper side of the image
Charge distribution of $\alpha$-(BEDT-TTF)$_2$KHg(SCN)$_4$

- Horizontal stripe structure develops locally.
- Vertical stripe structure was not observed.

Red line: stripe structure with charge rich

Horizontal stripe

Tunneling current [a.u.]

Distance [nm]

Upper side of the image
Features of charge stripe structure

<table>
<thead>
<tr>
<th>X</th>
<th>(I_3)</th>
<th>(\text{KHg( SCN)}_4)</th>
<th>(\text{RbHg( SCN)}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge stripe at RT</td>
<td>Horizontal</td>
<td>Horizontal</td>
<td>Vertical</td>
</tr>
<tr>
<td>Ground state</td>
<td>Charge order (Horizontal stripe) (T_{\text{CO}} = 135 \text{ K})</td>
<td>Density wave (T_{\text{DW}} = 9 \text{ K})</td>
<td>Density wave (T_{\text{DW}} = 12 \text{ K})</td>
</tr>
</tbody>
</table>

The stripe structure at room temperature is similar to the structure of charge ordering state below \(T_{\text{CO}}\).

Stripe structures in metallic state are formed by off-site Coulomb interaction.
Charge stripe structure and off site Coulomb interaction

**Assumption**

Off-site coulomb interaction just depends on distance between molecules.

**Comparison**

Compare $D_1/D_2$ of the $\alpha$-type ET compound.

Distance
- Molecules on inter-columns: $D_1$
- Molecules on intra-columns: $D_2$

**Stripe structure**

- /$I_3$
  - $\rightarrow$ Horizontal stripe
- /$K$Hg(SCN)$_4$
  - $\rightarrow$ Horizontal stripe (at 300 K)
- /$Rb$Hg(SCN)$_4$
  - $\rightarrow$ Vertical stripe $\rightarrow$ Horizontal stripe (below 100 K) [K. Noda et al. Phys. Rev. B 87, 085105 (2013)]

**Graph**

Horizontal and vertical stripes are classified by $D_1/D_2$
Summary

Stripe structures were observed in three $\alpha$-type compounds.

⇒ Stripe structure essentially exists in $\alpha$-type BEDT-TTF compounds.

$\alpha$-(BEDT-TTF)$_2$I$_3$ : charge ordered state
$\alpha$-(BEDT-TTF)$_2$MHg(SCN)$_4$ [M = K, Rb] : Density wave

<table>
<thead>
<tr>
<th>X</th>
<th>I$_3$</th>
<th>KHg(SCN)$_4$</th>
<th>RbHg(SCN)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge stripe at RT</td>
<td>Horizontal</td>
<td>Horizontal</td>
<td>Vertical</td>
</tr>
<tr>
<td>Ground state</td>
<td>Charge order (Horizontal stripe) $T_{CO} = 135$ K</td>
<td>Density wave $T_{DW} = 9$ K</td>
<td>Density wave $T_{DW} = 12$ K</td>
</tr>
</tbody>
</table>

Stripe structures were classified by anisotropy of long range Coulomb interaction $D_1/D_2$. 
Future work

We are performing STM/STS of CD state at various temperature.

Thank you for your attention.
The region taking lien profiles

Diagonal stripe region.

The region shown in the presentation.
Local diagonal stripe structure of $\alpha$-(BEDT-TTF)$_2$I$_3$

The energy of diagonal stripe is higher than horizontal and vertical stripe in $\alpha$-type BEDT-TTF compounds. [H. Seo, J. Phys. Soc. Jpn. 69, 805 (2000).]

Diagonal stripe structure is exciting state
Domain structure of $\alpha$-(BEDT-TTF)$_2$I$_3$

- Diagonal stripe structure
- No two-fold charge modulation
- Region in which $A'$ is charge rich

Local excited state was observed.
STM current image at sample bias

The same periodic patterns were observed at sample bias.

These STM images correspond to the image of BEDT-TTF layer.
STM image of anion and BEDT-TTF layer of $\alpha$-(BEDT-TTF)$_2$KHg(SCN)$_4$

**BEDT-TTF layer**

**Anion layer**

FIG. 2. (a) Constant current image of a type I surface, scanned with a negative tip. The nominal unit cell dimensions, based on calibration of the STM piezos using highly oriented pyrolytic graphite as a standard, were 9.9 Å×9.7 Å for both scans. Alternating columns of all-α and β-γ ET molecules along the $a$ axis are evident. (b) The same area of the crystal, scanned at the same potential, but with reversed polarity. The same pattern of alternating columns is present, but the image shows slightly more disorder and reduced resolution. (c) 2D FFT of the larger raw scan which produced the filtered image in (a). All transforms were indexed to an orthogonal 2D lattice. (d) Similar 2D FFT of the larger raw scan which produced the filtered image in (b).

FIG. 3. (a) Constant current image of a type II surface scanned with a negative tip, after Fourier lattice filtering. This image is attributed to the K and Hg atoms shown in the model in Fig. 1(c). (b) The same area as in (a), scanned with a positive tip, indexed and filtered as before. This image is attributed to the SCN molecules shown in the model in Fig. 1(c). The nominal STM unit cell dimensions were 8.1 Å×8.0 Å for both scans. (c) 2D FFT of the larger original scan used to produce (a). (d) 2D FFT of the larger original scan used to produce (b).

Fig. 3. (Color online) STM image of $\alpha$-(BEDT-TTF)$_2$I$_3$ in $\approx 7.0 \times 6.5$ nm$^2$, where the thermal drift was corrected with the reported lattice parameters. The assigned $a$- and $b$-axes are indicated by the arrows.

Charge distribution of $\alpha$-($\text{BEDT-TTF}$)$_2\text{RbHg(SCN)}_4$

Vertical stripe develops in most of the observed area.
Scanning Tunneling Microscopy (STM)

STM current image of graphite

STM is a powerful tool to study the charge order.

$I(\mathbf{r}) \propto \int_0^{\epsilon V} \rho(E, \mathbf{r}) dE$

$\rho$: Electronic density of states

$I = 0.1 \, \text{nA}, \, V = 0.5 \, \text{V}$

$15 \, \text{nm} \times 15 \, \text{nm}$
ドナー分子に対する
アニオン分子の位置がわかる図

KHg,
RbHgのバイアス反転した像があれば
それを表示

溝口先生の論文

Si(1,1,1)面の構造相転移の論文があればそれも
### 格子パラメータ

<table>
<thead>
<tr>
<th></th>
<th>M=K,X=S</th>
<th></th>
<th>M=Rb,X=S</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300(K)</td>
<td>11(K)</td>
<td>300(K)</td>
<td>11(K)</td>
</tr>
<tr>
<td>a(Å)</td>
<td>10.018</td>
<td>9.914</td>
<td>10.061</td>
<td>9.941</td>
</tr>
<tr>
<td>b(Å)</td>
<td>20.586</td>
<td>20.420</td>
<td>20.602</td>
<td>20.403</td>
</tr>
<tr>
<td>c(Å)</td>
<td>9.921</td>
<td>9.778</td>
<td>9.976</td>
<td>9.844</td>
</tr>
<tr>
<td>α(°)</td>
<td>103.62</td>
<td>103.40</td>
<td>103.70</td>
<td>103.25</td>
</tr>
<tr>
<td>β(°)</td>
<td>90.45</td>
<td>90.50</td>
<td>90.58</td>
<td>90.54</td>
</tr>
<tr>
<td>γ(°)</td>
<td>93.31</td>
<td>92.84</td>
<td>93.19</td>
<td>92.59</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>1984.8</td>
<td>1923.7</td>
<td>2005.3</td>
<td>1941.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>RT</th>
<th>20 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>b(Å)</td>
<td>10.793</td>
<td>10.6695</td>
</tr>
<tr>
<td>c(Å)</td>
<td>17.400</td>
<td>17.324</td>
</tr>
<tr>
<td>a(Å)</td>
<td>17.400</td>
<td>16.975</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>1695.4</td>
<td>1639.5</td>
</tr>
</tbody>
</table>


$^{13}$C NMR

$\alpha$-(BEDT-TTF)$_2$I$_3$

Y. Takano et al.

**Two doublet** (four peaks)

$\downarrow$

Two different site (charge rich and poor)

Raman spectroscopy

$\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$

K. Yamamoto et al.

The modes split into several bands.

$T_{\text{CO}}=135$ K

$T_{\text{CO}}=190$ K

Mode frequency depends on charge on the molecule.

Charge disproportionation

$T_{\text{C}}=135$ K

$T_{\text{C}}=190$ K
Organic donor molecules

Large unit cell

\[(TMTSF)_{2}\text{PF}_6\]

\[
\begin{align*}
a &= 0.7297 \text{ (nm)} & a &= 83.39 \text{ (deg)} \\
b &= 0.7711 \\c &= 1.3522 & g &= 71.01 \\
V &= 714.3 \text{ (Å}^3\text{)} \text{ (Z=1)}
\end{align*}
\]

\[a-(\text{BEDT-TTF})_2\text{I}_3\text{ P -1}\]

\[
\begin{align*}
a &= 0.9211 \text{ (nm)} & a &= 96.95 \text{ (deg)} \\
b &= 1.0850 \\c &= 1.7488 & g &= 90.75 \\
V &= 1717 \text{ (Å}^3\text{)} \text{ (Z=2)}
\end{align*}
\]

Carrier density is quite lower than simple metal.

Less screening
\[\Rightarrow\text{ Coulomb repulsion cannot be screened.}\]

Electron correlation plays an important role.
Charge order by inter-site Coulomb interaction

Extended Hubbard model

\[ H = \sum_{\langle ij \rangle} \sum_{\sigma} (t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \text{h.c.}) + \sum_i U n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij \rangle} V_{ij} n_{i\uparrow} n_{j\downarrow} \]

\( U \): on-site Coulomb + \( V \): off-site (long range) Coulomb

\[ U < U_C \quad \Rightarrow \quad \delta = 0 \]
\[ U > U_C \quad \Rightarrow \quad \delta > 0 \]

Charge order (disproportionation) to gain long range Coulomb repulsion

\( \delta \): charge disproportionation

Off-site Coulomb \( V \) plays an important role.
Charge order in $\alpha$ and $\theta$-(BEDT-TTF)$_2X$

- Vertical stripe
- Donor stacking

- Horizontal stripe

$^{13}$C-NMR (R. Chiba et al.)
Reflection spectroscopy (H. Tajima et al.)
IR and Raman spectroscopy (K. Yamamoto et al.)

Purpose of the present study:
Direct observation of charge order in real space
α-(BEDT-TTF)$_2$I$_3$

$b$-$c$ plane

Fermi surface

- P -1
- $a$=0.9211 (nm)
- $b$=1.0850
- $c$=1.7488
- $\alpha$=96.95 (deg)
- $\beta$=97.97
- $\gamma$=90.75
- $V$=1717 (Å$^3$) (Z=2)

Resistance

- Metal-insulator transition (Bulk) charge order
- $T_{CO} = 135$ K

13C-NMR

- Two doublet (four peaks)
- Two different site (charge rich and poor)

R. Kondo et al.

N. Tajima et al.

Y. Takano et al.
Synth. Met. 120, 1081 (2001)
Organic donor molecules

Large unit cell

(TMTSF)$_2$PF$_6$

\[ a=0.7297 \text{ (nm)} \quad \alpha=83.39 \text{ (deg)} \]
\[ b=0.7711 \quad \beta=86.27 \]
\[ c=1.3522 \quad \gamma=71.01 \]
\[ V=714.3 \text{ (Å}^3\text{)} \text{ (Z=1)} \]

\[ \alpha-(\text{BEDT-TTF})_2\text{I}_3 \]

\[ a=0.9211 \text{ (nm)} \quad \alpha=96.95 \text{ (deg)} \]
\[ b=1.0850 \quad \beta=97.97 \]
\[ c=1.7488 \quad \gamma=90.75 \]
\[ V=1717 \text{ (Å}^3\text{)} \text{ (Z=2)} \]

Carrier density is quite lower than simple metal.

Less screening \Rightarrow Coulomb repulsion cannot be screened.

Electron correlation plays an important role.
Organic conductors

Charge transfer salt \((D^{+0.5})_2X^{-1}\) 2:1 salt
1/4 or 1/2 filled \(\pi\)-band

Electronic states extend on a donor molecule ⇒ Molecular Orbital (MO)
Conduction by overlap of \(\pi\) orbital
Donor arrangement determines shape of Fermi surface

Low dimensional conduction

1D \((\text{TMTSF})_2X\) SDW, (triplet) SC
2D \((\text{BEDT-TTF})_2X\) SC vs AFM, SC vs CO

Various electronic phases

Molecular degree of freedom
Donor arrangement and band structure

Various electronic phases
Molecular degree of freedom

Phase diagram of $\kappa$-(BEDT-TTF)$_2$X
Phase diagram of $\theta$-(BEDT-TTF)$_2$X
Charge order in organic conductors

$^{13}$C NMR

$\alpha$-(BEDT-TTF)$_2$I$_3$

Y. Takano et al.
Synth. Met. 120, 1081 (2001)

Two doublet (four peaks)

↓

Two different site (charge rich and poor)

Raman spectroscopy

$\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$

K. Yamamoto et al.

Mode frequency depends on charge on the molecule.

$T_{CO}=135$ K

$T_{CO}=190$ K

The modes split into several bands.

Charge disproportionation
実効的な off-site Coulomb相互作用の異方性からの考察

- $I_3$塩、$K$塩：horizontal stripe
  (電荷不均化の振幅：$I_3$塩＞$K$塩)
- Rb塩：vertical stripe

オフサイトクーロン相互作用の異方性$V_p/V_c$
$I_3$塩＜$K$塩＜0.96＜Rb塩

<table>
<thead>
<tr>
<th>温度</th>
<th>塩</th>
<th>$a$</th>
<th>$c$</th>
<th>$p$</th>
<th>$C(1/2c)$</th>
<th>$p/C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>K</td>
<td>10.018</td>
<td>9.921</td>
<td>5.589429</td>
<td>4.9605</td>
<td>1.126788</td>
</tr>
<tr>
<td></td>
<td>Rb</td>
<td>10.061</td>
<td>9.976</td>
<td>5.614799</td>
<td>4.988</td>
<td>1.125661</td>
</tr>
<tr>
<td></td>
<td>$I_3$</td>
<td>10.793</td>
<td>9.187</td>
<td>5.864919</td>
<td>4.5935</td>
<td>1.276787</td>
</tr>
<tr>
<td></td>
<td>Rb</td>
<td>9.941</td>
<td>9.844</td>
<td>5.546385</td>
<td>4.922</td>
<td>1.126856</td>
</tr>
<tr>
<td>20 K</td>
<td>$I_3$</td>
<td>10.6695</td>
<td>9.0162</td>
<td>5.791399</td>
<td>4.5081</td>
<td>1.284665</td>
</tr>
</tbody>
</table>

Organic conductors

Charge transfer salt $\left(\text{D}^{+0.5}\right)_2\text{X}^{-1}$ 2:1 salt
1/4 or 1/2 filled p-band

Electronic states extend on a donor molecule $\Rightarrow$ Molecular Orbital ($\pi$-orbital)
Conduction by overlap of $p$ orbital

Donor molecules

Crystal structure of $\alpha$-(BEDT-TTF)$_2$I$_3$

- $a=0.9211$ (nm)  $\alpha = 96.95$ (deg)
- $b=1.0850$  $\beta = 97.97$
- $c=1.7488$  $\gamma = 90.75$
- $V=1717$ (Å$^3$)  (Z=2)  P -1

Large unit cell

Carrier density is quite lower than simple metal.

Coulomb repulsion cannot be screened.