Charge ordering in low dimensional organic compounds

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- charge ordering (CO) in quasi-one and quasi-two dimensional organic compounds induces a ferroelectric polarization on the basis of observation of a divergent increase of the dielectric susceptibility at the CO transition temperature.

- for two-dimensional organic salts of general formula \( \theta^- (\text{BEDT-TTF})_2X \), the geometrical frustration caused by the triangular lattice prevents long range order, but competition between domains with different charge ordering yields possibly a glass-like short range charge order state at low temperature.
In the case of half-filled band and strong Coulomb interactions between electrons (strong U) on neighboring sites, it is more favorable to localize the particles on the lattice sites to minimize the repulsion and the system is an insulator - the Mott transition.
The mean field approximation of the 1D Hubbard model shows that when $V$ exceeds a critical value, $V_c$, charge disproportionation occurs among sites with alternating « charge rich » and « charge poor » sites (Seo and Fukuyama 1997).

With $\Delta_D \neq 0$ numerical calculations on the plane $U$ and $V$ for a fixed $\Delta_D$ where the metallic phase at $\Delta_D = 0$ is replaced by the Mott insulating phase, and a phase with Wigner crystal-type CO is still present in the large U and V region.

Ground state phase diagram of the 1D extended Hubbard model at 1/4 filling on the plane of $U/t$ and $V/t$ for a fixed value of the dimerization gap $\Delta_D$

Quarter-filled without dimerization: DI-DCNQI)$_2$Ag  Wigner crystal type of charge ordering

Shibata et al. Tsuchiizu et al. 2001
Charge order and ferroelectricity in quasi-1D Fabre salts
Structure of Bechgaard-Fabre salts

\[ C = S, Se \]

\[ X = \text{AsF}_6, \text{PF}_6, \text{ClO}_4, \text{BF}_4, \ldots \]

parallel to the stacks (a-c plane)

perpendicular to the stacks (b-c plane)
Symmetry of anions

Centrosymmetric anions (CSA)
spherical: Br
octahedral: PF$_6$, AsF$_6$, SbF$_6$

Non-centrosymmetric anions (NCSA)
tetrahedral: ClO$_4$, BF$_4$, ReO$_4$, linear: SCN$^-$

C. Bourbonnais and D. Jérome 1990
• Ferroelectricity is defined by the appearance of a macroscopic electric polarization and its reversibility by applying an external field.

• For some ferroelectric materials, electron degrees of freedom and/or electronic interactions directly give rise to a macroscopic electric polarization and a ferroelectric transition $\Rightarrow$ electronic ferroelectricity.
- **Spin-driven ferroelectricity** where the ferroelectric transition is caused by magnetic interactions and magnetic ordering (primary order parameter) called multiferoics (cross-correlation between ferroelectricity and magnetism) Ex.: TbMnO$_3$ (for a review: T. Arima, J. Phys. Soc. Jpn 80, 052001, 2011)

- **Charge-ordered ferroelectricity** resulting from electronic charge degrees of freedom and charge ordering (CO). Electric polarization is associated to CO, this ferroelectricity is caused by electron correlation and/or electron-lattice interactions

Ex.: magnetite (Fe$_3$O$_4$), perovskite manganites (PrCa)MnO$_3$, 1D and 2D $\frac{1}{4}$ filled organic salts
Figure 1. (A) Example of a neutral one-dimensional chain exhibiting (B) site-centered charge ordering, (C) bond-centered charge ordering, and (D) a linear combination of these two that is ferroelectric. The arrows indicate the polarization, which is in total zero in (B) and (C), but develops a macroscopic moment, indicated by the red arrow in (D). The red dashed lines in (A), (B) and (C) indicate mirror planes of the system.
AC conductivity of (TMTTF)$_2$AsF$_6$

T dependence of the conductance


T dependence of the real part of the dielectric permittivity, $\varepsilon'$ at 100 et 300kHz, 1,3 and 10MHz
Real part of dielectric constant of \((\text{TMTTF})_2X\) salts

\[ \varepsilon' = \frac{\text{Im}G}{\omega} \]

1. For all anions: at \(T \approx T_{\rho}\), there is no anomaly.
2. For CSA and \(\text{ReO}_4\) anions, \(\varepsilon'\) diverges at \(T_{\text{CO}}\).

Huge magnitudes of \(\varepsilon'\): \(2 \times 10^6\) for \(\text{AsF}_6\), \(5 \times 10^5\) for \(\text{ReO}_4\).
C$^{13}$ NMR spectra for (TMTTF)$_2$AsF$_6$

NMR measurements in an external field of 9T (freq 96.4 MHz)

Below $T_{CO}$, doubling of the spectral line due to two inequivalent molecules with unequal electron densities - Charge disproportionation: 3:1 from $T_1^{-1}$ measurements

Spectral splitting (~charge disproportionation order parameter) versus temperature

At high temperatures the unit cell consists of two equivalent TMTTF molecules related by inversion about the counterion.

The breaking of the inversion symmetry within the unit cell below $T_{CO}$ and the spontaneous dipole moment associated with the charge imbalance on the two molecules yield the ferroelectric behaviour.

Vibrational modes in (TMTTF)$_2$X

a$_g$ stretching C=C mode: infrared active though electron-molecular (emv) coupling
Neutral TMTTF: \( \nu_3 = 1639 \text{ cm}^{-1} \) \text{Meneghetti et al.}
TMTTF$^+$: \( \nu_3 = 1567 \text{ cm}^{-1} \) \text{J.Chem. Phys. (1984)}
TMTTF$^{0.5+}$: \( \nu_3 = 1603 \text{ cm}^{-1} \)
Resonance frequency of emv coupled mode is a function of the charge (0.5 ±\( \rho \)) on the molecule

Temperature dependence of the \( \nu_3 \) mode

AsF$_6$  
\[ T = 20 \text{K} \] charge disproportionation: +0.63 and +0.37 (2\( \rho = 0.26 \))
\[ T = 10 \text{K} \] : +0.60 and +0.40 (2\( \rho = 0.20 \))

PF$_6$  
\[ T = 20 \text{K} \] : +0.56 and +0.44 (2\( \rho = 0.12 \))

M. Dumm and M. Dressel
Ferroelectric character

The ferroelectric state is triggered by the uniform shift of anions yielding a macroscopic ferroelectric polarization which is gigantically amplified by the charge disproportionation on the molecular stacks (S. Brazovski and T. Nattermann, Adv. in Phys. 53, 177)

CSA and ReO$_4$ salts show at $T_{CO}$ a second order phase transition described by the Curie law

\[
\varepsilon' = \frac{A}{|T - T_{CO}|}
\]

$1/\varepsilon'$ (T) is close to be linear

Ratio $A_L/A_H$ ($A_L$ at $T < T_{CO}$ $A_H$ at $T > T_{CO}$)

in CSA: $A_L/A_H \approx 2$

in ReO$_4$ $A_L/A_H \approx 1.5$

Phys. Rev. Lett. 86, 4081
2D Quarter-filled Conductors

$(ET)_2X$ compounds
(ET)$_2$X compounds
Structures of and $\theta$- $(\text{BEDT-TTF})_2\text{RbZn(SCN)}_4$ and $\alpha$-$(\text{BEDT-TTF})_2\text{I}_3$

4 (ET) molecules in the unit cell
- Stack 1: A and $A'$ combined by an inversion center
- Stack 2: B and C located on the inversion centers

Extended Hubbard model in a two-dimensional anisotropic triangular lattice

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

Different spatial patterns of stripe phases are stabilized depending on the anisotropy of the transfer integrals $t_c$ and $t_p$ and of the values of intersite Coulomb energies along the stacking direction $V_c$ and along the bonds in the transverse direction $V_p$.

- horizontal
- vertical
- diagonal
- 3fold

Above $T_{\text{CO}}$ diffuse rods of modulation vector: $q_1 = (1/3, k, 1/4)$ around Bragg reflections and diffuse planes connecting these diffuse rods were observed.

Below $T_{\text{CO}}$, all diffuse scatterings disappear and replaced by the superlattice reflections with the wavevector $q_2 = (0, k, 1/2)$ [Watanabe et al. J. Phys. Soc. Japan 73, 116]

Map of transfert integrals in the a-c plane at 220K

Ionicity of ET molecules determined from bonds lengths:
- Molecule A: quasi-neutral (0 to +0.2)
- Molecule B: quasi-ionic (+0.8 to 1.0)

⇒ Stripe ordering alternating along the c-axis (« horizontal Ordering »).
⇒ Uniform 1D spin chains: Bonner-Fisher susceptibility law - Spin-Peierls transition below 25K (dimerization of ET molecules in the 1D chain)
3 fold order

Origin of the triply periodic order indexed by $q_1 = (1/4, k, 1/3)$?

- Interplay between the Fermi surface nesting and the intersite Coulomb repulsion (Kuroki J. Phys. Soc. Jpn 75, 114716)

- $q_1$-type modulation comes from the intersite Coulomb repulsion and the $q_2$-type from the Fermi surface nesting (Odagawa and Motome Phys. Rev. Lett. 98, 206405)

Pin-ball liquid model (Hotta and Furukawa, Phys. Rev.B 74, 193107)
AC conductivity in θ- (BEDT-TTF)$_2$RbZn(SCN)$_4$

Dependences of the conductance $G$ (at a frequency of 1 kHz) of θ-(BEDT-TTF)RbZn(SCN)$_4$ for slow cooling (triangle) and heating (circles) at a rate of 0.1 K min$^{-1}$ normalized by its value $G_0$ at room temperature as a function of the inverse temperature.

The $\varepsilon'$ growth above $T_{CO}$ may indicate the polarizability of the charge disproportionation seen in NMR. The jump below $T_{CO}$ is associated with the 2c superstructure and the large charge gap: $T_{CO} = 1900$K

Temperature dependence of the real part of the dielectric permittivity $\varepsilon'$ of θ-(BEDT-TTF)RbZn(SCN)$_4$ at frequencies of 0.1 (triangles), 1 (circles) and 3 (crosses) MHz at a slow cooling rate 0.1 K min$^{-1}$ in the restricted temperature range in the vicinity of the charge-ordered phase transition.

Nad et al., J. Phys.:Condens. Matter 18, L509

Nad et al., J. Phys.:Condens. Matter 18, L509
Metal-insulating phase transition in $\alpha$-(BEDT-TTF)$_2$I$_3$

Conductivity

Abrupt phase transition at $T=135.1\,\text{K}$ of first order transition slightly hysteretic

Dimerization of stacks I along the a axis of Peierls type

Drop of $\varepsilon'$ below $T_{\text{MI}}$

Structural transition (dimerization)

Nad et al. Physica B
Charge disproportionation in $\alpha-(BEDT-TTF)_2I_3$

Horizontal stripe structure

CD already above CO transition

From infrared spectroscopy, NMR, and x-ray

At room temperature:
A=A'= 0.60  
B=0.68  
C=0.44

In the CO state:
A=0.81  
A'= 0.26  
B=0.74  
C=0.23

T. Kakiuchi et al.  
J. Phys. Soc. Jpn 76, 113702

T. Kakiuchi et al.  
J. Phys. Soc. Jpn 76, 113702
Optical second harmonic generation in $\alpha$-(BEDT-TTF)$_2$I$_3$

Activation of the even-order nonlinear optical phenomenon signifies the lack of inversion symmetry

SHG Images of $(TMTTF)_2X$ (X = SbF$_6$, AsF$_6$, and PF$_6$)

SbF$_6$ (as grown)

AsF$_6$ (Cleaved)

Transmission Image

T = RT

SHG Image

T = 5.7 K

K. Yamamoto et al. unpublished
SHG of (TMTTF)$_2$X (X = SbF$_6$, AsF$_6$, and PF$_6$)

K. Yamamoto et al. unpublished
1) conductivity

F. Nad, PM and H.M. Yamamoto
Phys. Rev. B76, 205101
2) Dielectric permittivity

FIG. 4. Variation of the real part of the dielectric permittivity $\varepsilon'$ of $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ normalized by its room-temperature value $\varepsilon'_0$ as a function of temperature on cooling with three cooling rates: slow cooling at 0.1 K/min, relaxed state (○); intermediate cooling at 4 K/min, intermediate state (△); and fast cooling at 9 K/min, quenched state (□).

FIG. 5. Variation of the real part of the dielectric permittivity $\varepsilon'$ of $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ normalized by its room-temperature value $\varepsilon'_0$ as a function of temperature on heating from the relaxed, intermediate, and quenched states obtained on cooling with different rates (Figs. 1 and 2). Heating rates: from the relaxed state, 0.1 K/min (○); from intermediate (△) and quenched states (□), 4–5 K/min.

F. Nad, PM and H.M. Yamamoto
Phys. Rev. B76, 205101

FIG. 6. Comparison of the temperature variation of the real part of the dielectric permittivity $\varepsilon'$ of $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ on cooling at the rate 4 K/min (●) and on heating at the rate 4–5 K/min (○).
Above $T_{CO} = 210 \text{K}$, diffuse rods of $q_1 = (1/3, k, 1/4)$

Below $T_{CO}$: **slow cooling:** diffuse rods disappear replaced by $q_2 = (0, k, 1/2)$

**fast cooling:** diffuse $q_1$ remains, but $q_2$ is disordered in the interlayer direction

similar to $\theta$- $(\text{BEDT-TTF})_2 \text{CsZn(SCN)}_4$ at low temperature

Inhomogeneous state composed of $q'_{1}$ and $q_2$ charge order
Charge cluster glass

Kagawa et al., Nature Phys. 9, 419
Glass-like state in $\theta$- (BEDT-TTF)$_2$CsZn(SCN)$_4$

**Figure 1.** Arrhenius plot of the conductance $G$, normalized by its room temperature value $G_0$, at frequency 1 kHz for slow cooling (0.1 K min$^{-1}$) of $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ ($\bigotimes$); same plots for $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ with slow cooling (0.1 K min$^{-1}$) ($\bigodot$) and fast cooling (9 K min$^{-1}$) ($\square$). The inset shows the frequency dependence of the conductance $G$ of $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ normalized by its value $G_0$ at two temperatures, 5 and 20 K.

F. Nad, PM and H.M. Yamamoto
J. Phys.: Condens. Matter 20, 485211
Both 3x3 and 1x2 period charge clusters are observed in $\theta$- (BEDT-TTF)$_2$CsZn(SCN)$_4$
$q_1 = (2/3, k, 1/3)$ and $q_2 = (0, k, 1/2)$
The size of the $q_1$ charge clusters grows at $T$ decreases but level off below 100K while the growth of the $q_2$ charge clusters continues to grow till much lower temperature
Figure 5. a) Temperature dependences of the real part of dielectric permittivity $\varepsilon'$ of $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ at different frequencies indicated near the curves in MHz. b) Temperature dependence [36] of the real part $\varepsilon'$ of (TMTSF)$_2$PF$_6$ at fixed frequencies (in kHz) top to bottom: 0.111, 0.5, 1.1, 2, 3, 5, 11, 30, 100, 300, 1000.
Comparison between CsZn and fast cooled RbZn

The low temperature of $\theta$- (BEDT-TTF)$_2$CsZn(SCN)$_4$ may indicate a combination of frustrated domains which, with decreasing temperature, are frozen into a glass-like short-range charge ordered state.

Figure 6. Comparison of the temperature dependence of $\varepsilon'$ measured at 1 MHz for $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ and fast cooled (9 K/min) $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$.

The low temperature of $\theta$- (BEDT-TTF)$_2$CsZn(SCN)$_4$ may indicate a combination of frustrated domains which, with decreasing temperature, are frozen into a glass-like short-range charge ordered state.
Nonlinear conductivity in $\alpha$-(BEDT-TTF)$_2$I$_3$

Voltage oscillations in the nonlinear state in the range up to 30kHz

FIG. 4. (Color online) Fast Fourier transformation spectra of the characteristic oscillation observed at 89 K for $J \parallel a$.

FIG. 2. (Color online) Current-voltage characteristics in $\alpha$-(BEDT-TTF)$_2$I$_3$, measured by applying regulated current pulses along (a) $J \parallel a$, (b) $J \parallel b$, and (c) $J \parallel c$. Oscillation appears in the shaded regions in (a) and (b) at 88 K.

Tamura et al. J. Applied Phys. 107, 103716
High field transport from the standpoint of hot electrons

\[ P = \sigma(T_e) E^2 \] for voltage-regulated scheme

\[ P = J^2 / \sigma(T_e) \] for current-regulated scheme

The \( P \) term gives rise to the energy gain of the electrons and increases electron temperature \( T_e \) (C: electron heat capacity)

K term gives the spatial distribution of \( T_e \) due to thermal conductivity \( K \).

Mori et al. PRB79, 115118
Non linear conduction in rapidly cooled \( \theta\) - \((ET)_2RbZn(SCN)_4\)

The activation energy \(\Delta\) decreases roughly linearly with \(J_{ext}\)

\[ \Rightarrow \text{Flow of carriers may reduce the energy gap order in a nonequilibrium state} \]

Inada et al. Phys. Rev. B79, 165102
Non linear conduction in rapidly cooled $\theta$- (ET)$_2$CsZn(SCN)$_4$

Fig. 1. Nonlinear resistivity of the \( \theta \)-type organic salt along the in-plane direction. (a) \( \theta \)-(BEDT-TTF)\(_2\)CsZn(SCN)\(_4\) \[26\] and (b) rapidly cooled \( \theta \)-(BEDT-TTF)\(_2\)RbZn(SCN)\(_4\) \[19\].
Similarity with superconductivity where the energy gap decreases with excess quasiparticle density

Flow of carriers injects extra holes and electrons to the charge-ordered domains and reduce the energy gap in order that the excess carriers are « thermally » activated (Ajisaka et al. Prog. Theor. Phys. 121, 1289)

Such a gap reduction is phenomenologically handled by setting an effective temperature $T^*$ higher than $T$ or by setting an effective chemical potential
A different approach for non-linearity

Nonlinear I-V is attributed to electric field induced unbinding of pairs of an electron and a hole that are thermally excited and attracted to each other due to the 2D long range Coulomb interaction.

Takahide et al. Phys. Rev. 81, 235110
Current-induced melting of the charge order in CsZn

M. Watanabe et al.

$q_1 = (2/3, k, 1/3)$
$q_2 = (0, k, 1/2)$

With external current, only the two-fold ordering melts

The nonlinear conduction is induced by the CO melting with charge flow
Sliding charge density wave

Electronic crystals: an experimental overview
-the combination of site-centered and bond-centered charge order yields ferroelectricity as seen in 1D organic salts

-in 2D (BEDT-T) salts, the stabilization of charge order takes place with the doubling of the unit cell in slow cooling process and with the tendency of the divergence of the dielectric permittivity

In \(\theta\)- (ET)\(_2\)RbZn(SCN)\(_4\), dimerization is suppressed by fast cooling

In \(\theta\)- (ET)\(_2\)CsZn(SCN)\(_4\), there is no long range charge order state but competition between two superstructures which induces glassy state at low temperature

-For nonlinearity, the energy gap of the charge order decreases with excess injected quasi particles which are thermally activated (thermal model)
Very surprisingly nonlineratity occurs with melting of the two-fold superstructure
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