Tailoring Matter on the Molecular Level: organic solids as models to study physics in reduced dimensions
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Outline

1. Organic Conductors
   basics and development

2. Competing Interactions
   charge order
   charge fluctuations, superconductivity

3. Electronic Correlations
   localization
   Mott transition, charge dynamics

4. Outlook

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Organic Conductors basics

Organic materials:
19 Mio. compounds containing carbon

Aromatic rings:
delocalized $\pi$-orbitals
e.g. benzene

aspirin

TNT

naphthalene
...
Organic Conductors
basics

Organic solids

are in general insulators because the bonds are saturated, the electronic bands are filled

Requirements for electrical conductivity:

- overlap of orbitals: band formation
- add or extract electrons: partially filled bands
  - electrical field effect
  - charge transfer salts
Organic Conductors
charge transfer salts

TTF-TCNQ

The structure consists of TTF and TCNQ stacks.
TTF is a strong electron donor,
TCNQ is an electron acceptor.

Along the stacks the $\pi$-orbitals overlap
leading to one-dimensional conductivity.
Organic Conductors
charge transfer salts

$\text{(TMTTF)}_2\text{PF}_6$

The structure consists of TMTTF stacks as electron donors, separated by inorganic acceptors.

Along the stacks the $\pi$-orbitals overlap leading to one-dimensional conductivity.
Organic Conductors
crystal growth

Growth of single crystals
by electro-crystallization from solution.

typical size: 1 to 5 mm

(TMTSF)$_2$PF$_6$
Organic Conductors
development

Starting point:

1964 W.A. Little predicts excitonic superconductivity in organic polymer chains

1973 F. Wudl, A. Heeger
1dim organic conductor
TTF-TCNQ

1979 K. Bechgaard, D. Jerome
1dim organic superconductor
(TMTSF)$_2$ClO$_4$

1984 E.B. Yagubskii
2dim organic superconductor
(BEDT-TTF)$_2$X

Ishiguro, Yamaji, Saito, 1998
**Organic Conductors**

radical cation salts

\[(\text{BEDT-TTF})_2X\]

Bis(ethylene-dithio)tetrathiofulvalene

The structure consists of BEDT-TTF layers as electron **donors**, separated by sheets of inorganic **acceptors**.

anisotropy within the plane perpendicular to the plane

\[\frac{\sigma_c}{\sigma_a} \approx 0.5\]

\[\frac{\sigma_b}{\sigma_a} \approx 10000\]
Organic Conductors
radical cation salts

\((\text{BEDT-TTF})_2X\)

The layered arrangement of the organic molecules, separated by anions, leads to a **two-dimensional electronic system**.

- The **bandwidth** depends on the overlap integral between neighboring molecules \(W = 8t \approx 1\) eV for these compounds.

- The **band-filling** depends on the stoichiometry.

- The **on-site** \((U)\) and **inter-site** \((V)\) Coulomb interactions depend on the molecule 
  \(U_{\text{eff}} = 0.5\) eV

**strong influence of electron-electron correlations**
Ordering Phenomena
low-dimensional systems

Competing interactions:

- lattice degree of freedom
- charge degree of freedom
- spin degree of freedom
- orbital degree of freedom
- electron-electron interaction
- electron-phonon interaction
- spin-phonon interaction
- spin-spin interaction

Localization, metal-insulator transition, antiferromagnetic ordering, …

Ordering patterns in low-dimensional systems

**k-space phenomena:**

- Fermi-surface instabilities: CDW, SDW

**real space phenomena:**

- spin-Peierls, spin order, charge order, Wigner crystal
Ordering Phenomena
low-dimensional systems

Charge order in two dimensions
1/4-filled systems

homogeneous charge distribution
horizontal stripes
vertical stripes
diagonal stripes checker board
Ordering Phenomena
low-dimensional systems

Charge order in two dimensions
1/4-filled systems

- homogeneous charge distribution
- horizontal stripes
- vertical stripes
- diagonal stripes
- checker board
Optical Reflection Measurements
experimental setup

Fourier transform infrared spectrometer
  Bruker IFS 113v
  Bruker IFS 66v

Infrared microscope
  Bruker Hyperion

Frequency range:
  15 cm\(^{-1}\) – 25 000 cm\(^{-1}\)
  (2 meV – 3 eV)

Temperature range:
  1 K ≤ T ≤ 300 K

Magnetic field:  Hydrostatic pressure:
  B ≤ 12 Tesla  p < 7 GPa

Absolute values of reflectivity by Au evaporation method.

size of the surfaces:  (0.5 – 1 mm\(^2\))
with IR microscope:  (150 \(\mu\)m\(^2\))
Small in-plane anisotropy:
reflectivity is higher
in the direction of larger overlap.

Deviations from a simple metallic behavior.

The spectral weight is defined as
\[ I_\sigma = \int_0^\infty \sigma_1(\omega) d\omega = \frac{\omega_p^2}{8} \]
where the plasma is given by
\[ \omega_p^2 = \frac{16te^2}{h V_m} \sin \left\{ \frac{\pi}{2} \rho \right\} \]

The width of the conductance band is
typically 0.8-1 eV
(overlap integrals \( t \) about 0.1 eV).
This is comparable to Coulomb interaction \( U \).

Molecular Vibrations
in BEDT-TTF salts

The **intra-molecular vibrations** are a measure of the localized charge.

\[ \nu_3 (A_g) \]

\[ \nu_2 = 1554.2 \text{ cm}^{-1} \]

The phonon frequency shifts down when electrons are taken off.

**Raman shift** in \( \alpha-(\text{BEDT-TTF})_2\text{NH}_4\text{Hg(SCN)}_4 \) three vibrational peaks indicates three different sites.
The **intra-molecular vibrations** are a measure of the localized charge.

IR active molecular vibrations are intense only for polarization $E \perp$ conducting layers

**IR mode** in $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ splitting below 150 K indicates charge order $\Delta \rho = 0.2e$
Collective Modes
in charged ordered systems

The inter-molecular vibrations are lattice vibrations, which become IR active due to charge order: collective excitations.

Collective CO mode in $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ appears below 150 K.

S. Kaiser et al., arXiv:0812.3732
Quasi-Two-Dimensional Organic Conductors

electronic correlations

• $\alpha$-(BEDT-TTF)$_2X$
  2:1 stoichiometry: insulator, metal, superconductor
  1/4-filled system: hole carriers

• $\kappa$-(BEDT-TTF)$_2X$
  2:1 stoichiometry, dimerized: metal, superconductor
  1/2-filled upper band: hole carriers
Quasi-Two-Dimensional Organic Conductors
(BEDT-TTF)$_2$X salts

Proposed Phase Diagrams

¼ filled compounds

½ filled compounds

Tuning parameters:

- electronic correlations (on-site $U$, inter-site $V$)
- bandwidth $W$
Metal-Insulator Transition
bandwidth control by anion substitution

What are the dynamical properties close to the metal-insulator transition?
We investigated the temperature dependent optical conductivity of \( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Br_xCl_{1-x} \) with \( x = 0\%, 40\%, 73\%, 85\%, \) and \( 90\% \).

Changing size of the anions changes the overlap integral \( t \): ‘chemical pressure’

\( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Cl \) is a semiconductor at room temperature which becomes a Mott insulator below 100 K. At low temperature it orders magnetically, under slight pressure it superconducts.

\( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Br \) is metallic for \( T \leq T^* \approx 50 \) K. Organic superconductor with maximum \( T_c = 12 \) K.

Optical Properties
of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$
Metal-Insulator Transition in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$

When the **temperature rises**, the gap shifts to lower frequencies, like a mean-field behavior.

When **Br content increases**, i.e. $U/t$ decreases, spectral weight starts to fill the gap, finally a Drude-like component develops.

The optical conductivity contains different contributions which can be disentangled:

**Intra-molecular vibrations:**

\[ \nu_4 \]

emv coupling

**Electronic Excitations**

- Intra-dimer excitations
- Inter-dimer excitations

Optical Properties
itinerant charge carriers

Inter-dimer excitations

localized charge carriers
due to the on-site (dimer) Coulomb repulsion;
excitations across a Mott-Hubbard gap
delocalized charge carriers

Hubbard model on frustrated square lattice

\[ H = -t_2 \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) - t_1 \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} - \mu \sum_i c_{i\sigma}^\dagger c_{i\sigma} \]

- \( t_2 \): nearest neighbor hopping amplitude
- \( t_1 = 0.8t_2 \): next-nearest neighbour hopping amplitude
- \( U \): on-dimer Coulomb repulsion

\( U \approx 0.3 \text{ eV} \)
\( t_2 \approx 0.03 \text{ eV} \)

Metal-Insulator Transition
bandwidth control U/t

Metallic state

- Drude-like feature due to the coherent quasiparticles (Fermi liquid)
- band of width $W$ centered around $U/2$
- broad band at $U$ of width $2W$.

Insulating state

- gap of $\Delta_{\text{Mott}} = U-W$
- broad band of width $2W$ centered around $U$

Dynamics of Correlated Charge Carriers

Temperature dependent optical conductivity

DMFT calculations for the Hubbard model

- Number of holes per dimer
  \[ N_{\text{eff}}(\omega) = \frac{m_b}{e^2} \frac{2}{\pi} \int_0^\omega \sigma_1(\omega')d\omega' \]
- Band at U/2 suppressed in experimental data
- Gradual destruction of quasiparticles above T*

\[ \kappa-(ET)_2\text{Cu[N(CN)]Br}_{0.73}\text{Cl}_{0.27} \]

\[ \sigma_1(\Omega^{-1}\text{cm}^{-1}) \]

\[ \nu(\text{cm}^{-1}) \]

Dynamics of Correlated Charge Carriers

effective charge carrier number

Effective carrier number per BEDT-TTF dimer

With increasing correlations U/t:
- spectral weight is transferred to higher frequencies
- effective charge-carrier number is suppressed

Dynamics of Correlated Charge Carriers
frequency dependent scattering rate and mass

Extended Drude analysis

\[
\frac{1}{\tau(\omega)} = \frac{ne^2}{m} \frac{\sigma_1(\omega)}{\left[\sigma_1(\omega)\right]^2 + \left[\sigma_2(\omega)\right]^2}
\]

\[
m^*(\omega) = \frac{ne^2}{m\omega} \frac{\sigma_2(\omega)}{\left[\sigma_1(\omega)\right]^2 + \left[\sigma_2(\omega)\right]^2}
\]

from DMFT calculations

The scattering rate indicates a Fermi-liquid behavior:

\[
\frac{1}{\tau} = A \left[ (2\pi k_B T)^2 + (\hbar \omega)^2 \right]
\]

The prefactor \( A \) becomes larger as the metal-insulator transition is approached, because correlations increase. (Kadowaki-Woods-plot)

from experiments

When approaching the metal-insulator transition from the metallic side, the effective mass increases, because correlations increase. (Brinkman-Rice)

Drude Weight at the Metal-Insulator Transition
density of states

The Mott transition can be visualized as a reduction in the density of states at the Fermi energy.

At the transition $D(E_F)$ is zero.

Since the metal-insulator transition is first order, there is an abrupt jump with $(D_c/D_0) = 0.1 \ldots 0.3$.

For large $x > 70\%$ we find a dramatic increase of the spectral weight as the temperature is reduced below $T^* = 50 \text{ K}$.

This clearly separates the Mott insulating from the metallic state at $x_c \approx 70\%$. 

**Diagram:**
- The figure shows the evolution of the spectral weight $D(E)$ and $D/D_0$ with Br concentration and temperature.
- A dramatic increase in spectral weight is observed for $x > 70\%$ at temperatures below $T^* = 50 \text{ K}$.
The two-dimensional organic conductor \( \kappa-(BEDT-TTF)_{2}\text{Cu}[\text{N(CN)}_{2}]\text{Br}_{x}\text{Cl}_{1-x} \) is a half-filled correlated electron system which serves as a model of a **bandwidth controlled Mott insulator**.

- For the metallic compounds a coherent carrier response appears below 90 K.
- When the Mott transition is approached by increasing \( U/t \), the Drude spectral weight decreases.
- The Drude response disappears on crossing the phase border to the Mott insulator.

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Summary
two-dimensional organic conductors

- In the half-filled compounds $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$ a bandwidth-controlled Mott transition was explored.
- The dependence of coherent carriers response for different band-fillings was studied; it increases on doping from 1/2 filling.
- For metallic compounds with the same U/t ratio, a coherent carriers response is present only at low temperatures for 1/2-filled compound, - it increases slightly on cooling for 1/4-filled compound - it stays constant for 1/5-filled compound.
