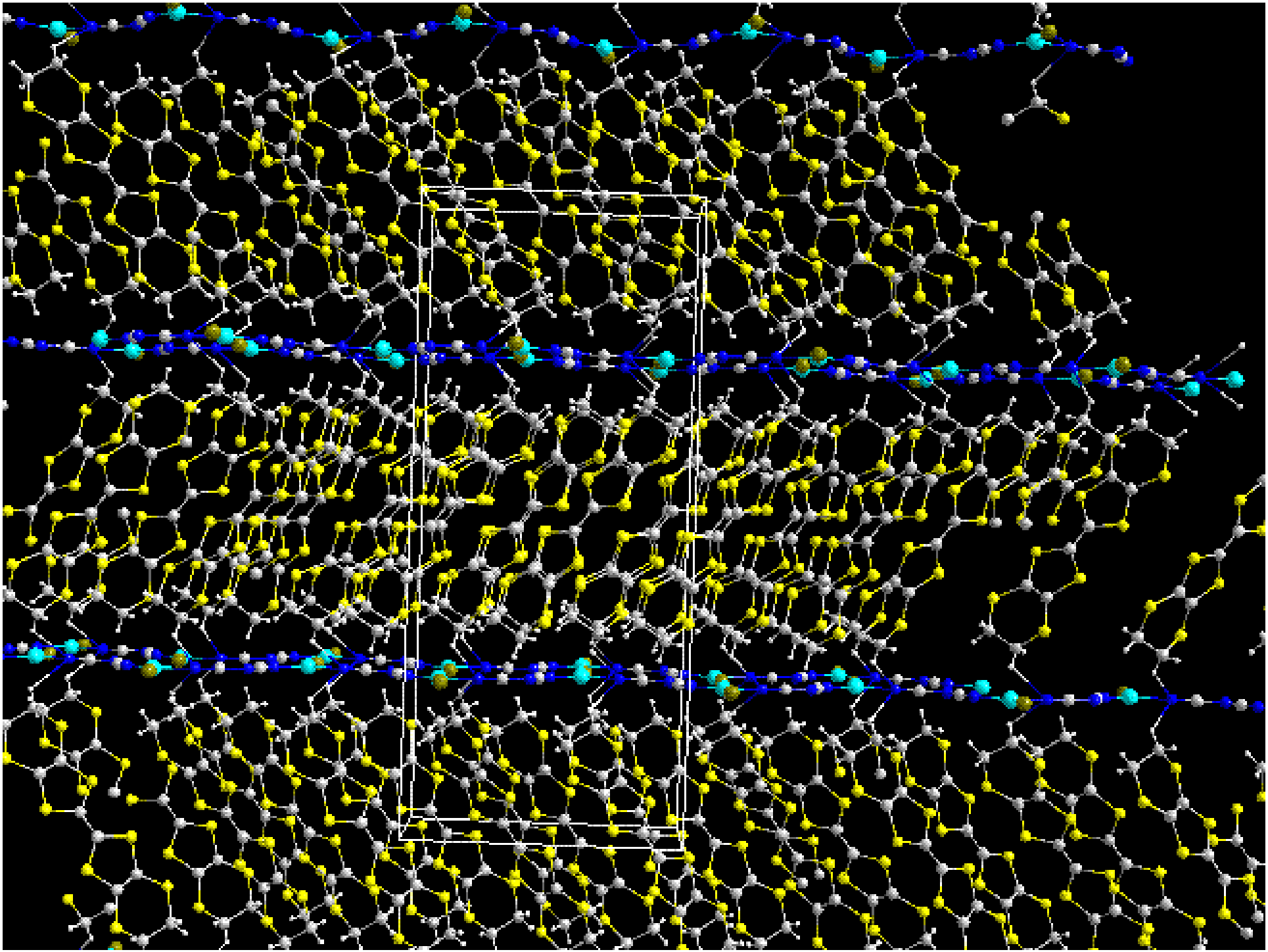

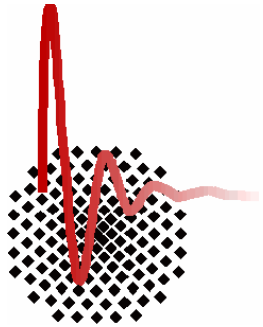

Tailoring Matter on the Molecular Level:

organic solids as models to study physics in reduced dimensions

Martin Dressel
1. Physikalisches Institut der Universität Stuttgart, Germany

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

N. Drichko, M. Dumm,
D. Faltermeier, S. Kaiser,
Y. Sun, S. Yasin
Universität Stuttgart, Germany

C. Meziere, P. Batail
CNRS, Universite d'Angers, France

J. Schlueter
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R. Lyubovskaya
RUS, Chernogolovka, Russia

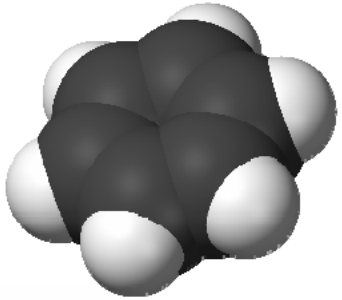
J. Merino
Universidad Autonoma, Madrid, Spain

R. McKenzie
UQ, Brisbane, Australia

A. Greco
Rosario, Argentina

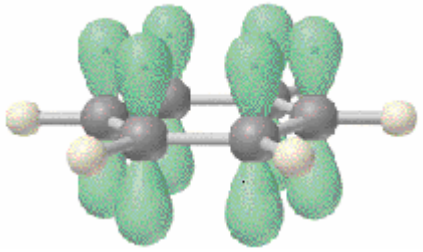
Organic Conductors

basics



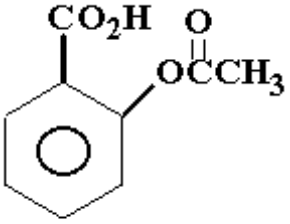
Organic materials:

19 Mio. compounds containing carbon

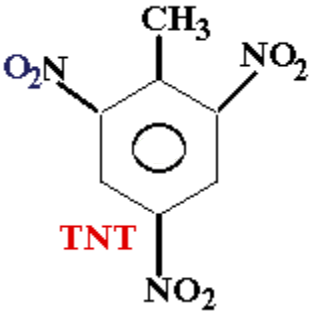


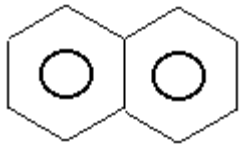
Aromatic rings:

delocalized π-orbitals
e.g. benzene



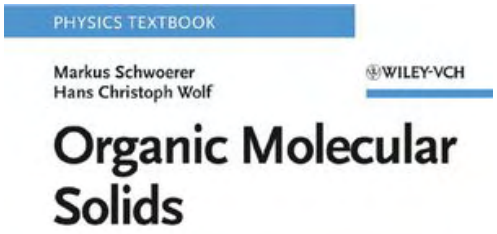
aspirin

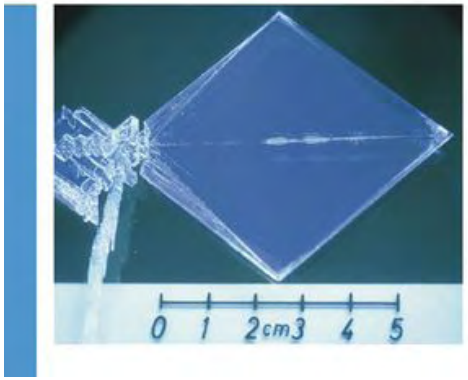




naphthalene

. . .

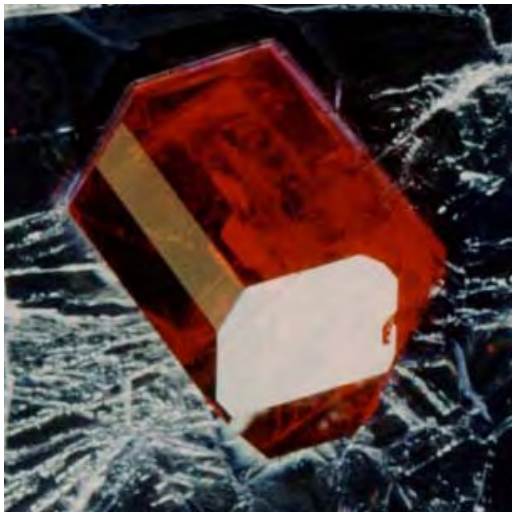




Organic Conductors
basics

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

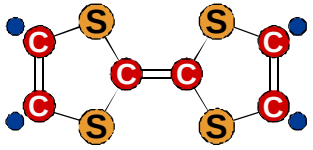
Organic Conductors

charge transfer salts

TTF-TCNQ

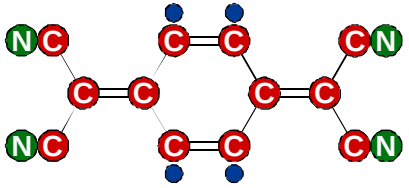
The structure consists of TTF and TCNQ stacks.
TTF is a strong electron donor,
TCNQ is an electron acceptor.

Tetrathiofulvalene

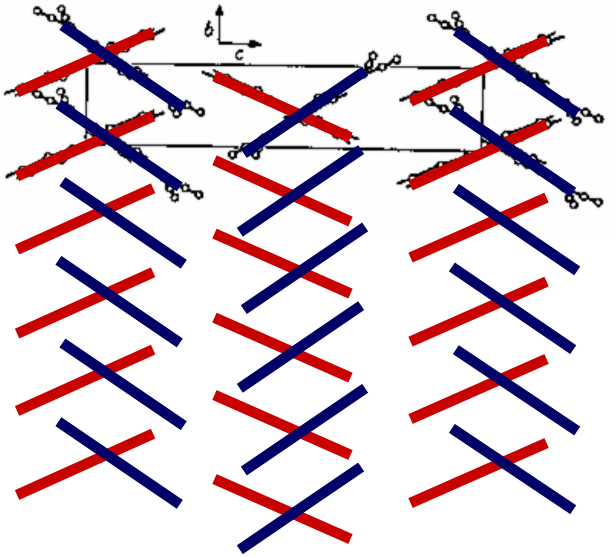


TTF

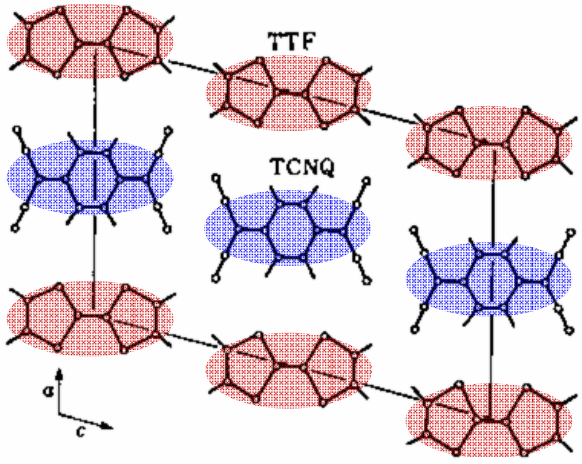
Tetracyanoquinodimethane

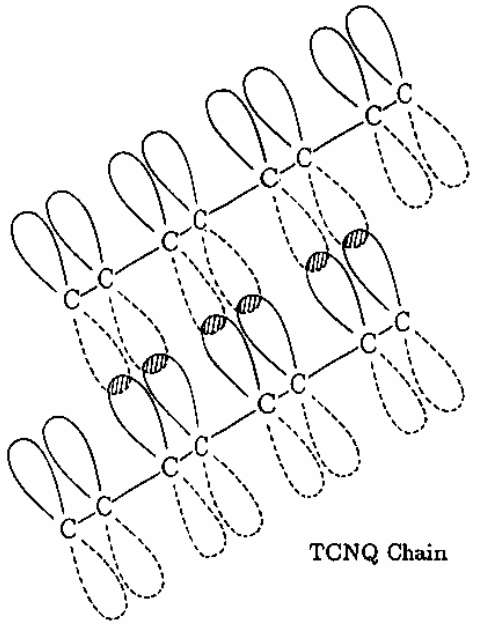


TCNQ



Along the stacks the π-orbitals overlap
leading to one-dimensional conductivity.





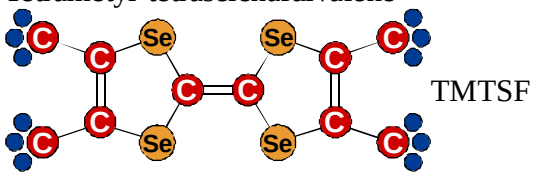
Organic Conductors

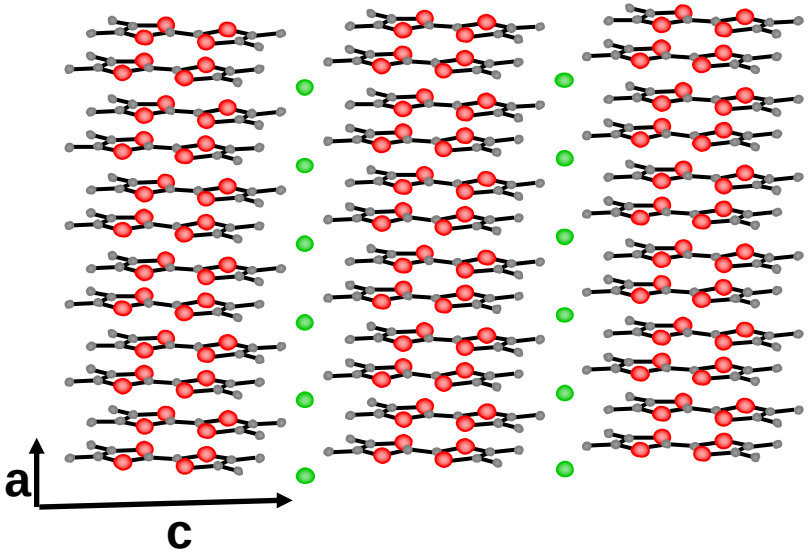
charge transfer salts

$(TMTTF)_2PF_6$

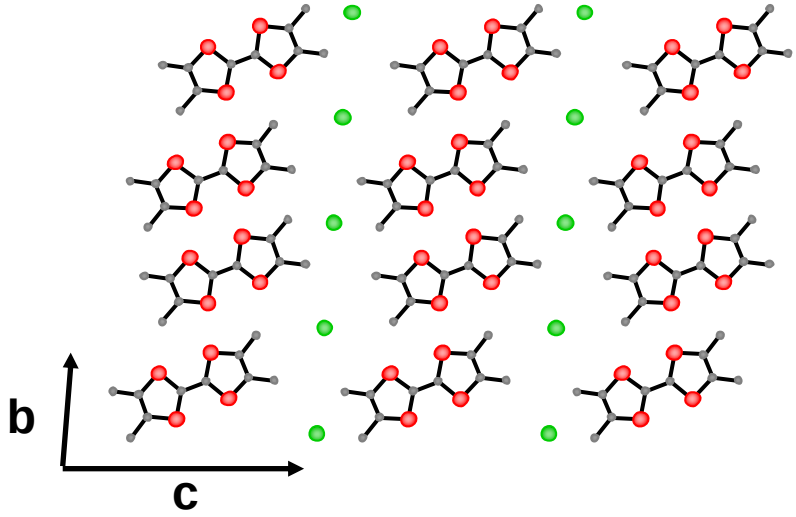
The structure consists of TMTTF stacks as electron donors, separated by inorganic acceptors.

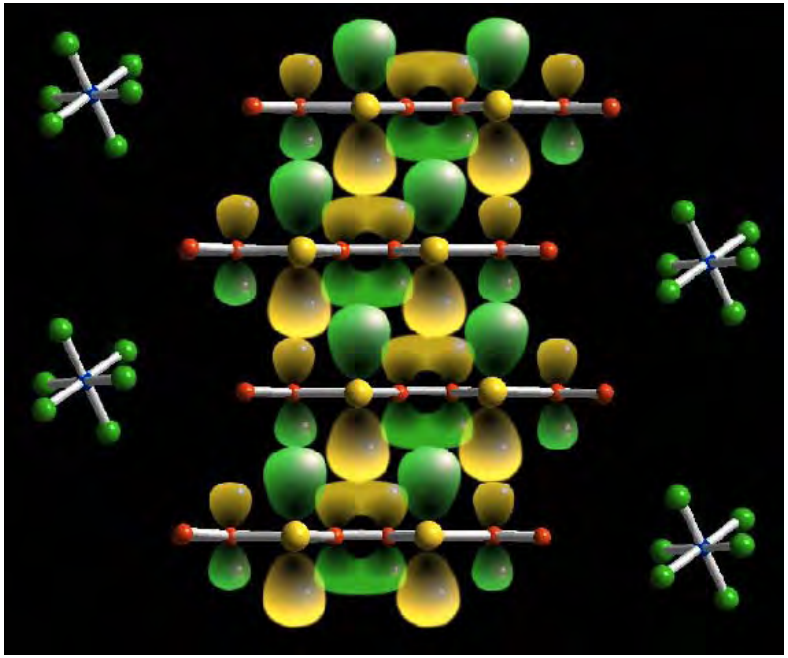
Tetrametyl-tetraselenafulvalene





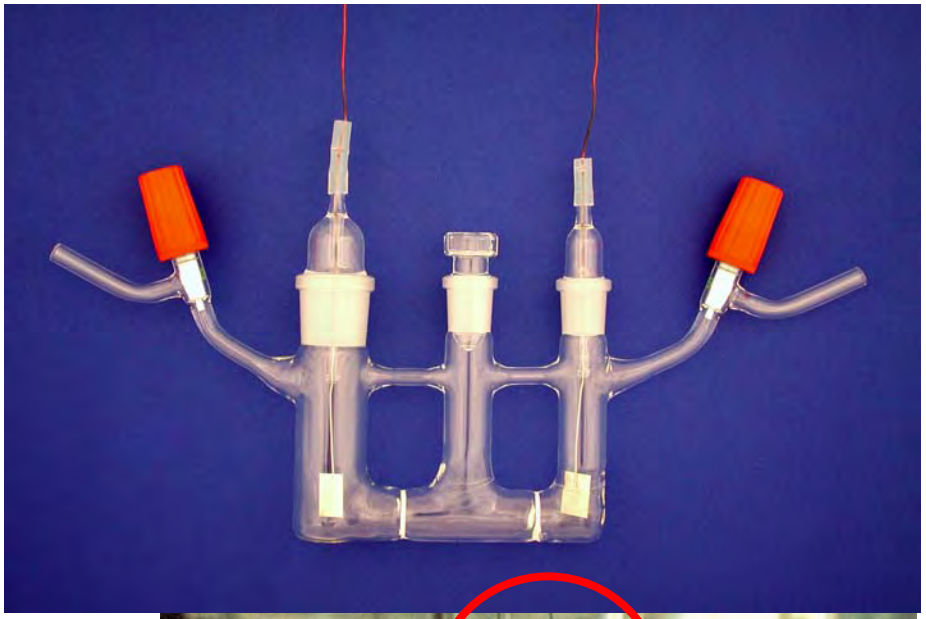
Along the stacks the π-orbitals overlap leading to one-dimensional conductivity.





Organic Conductors

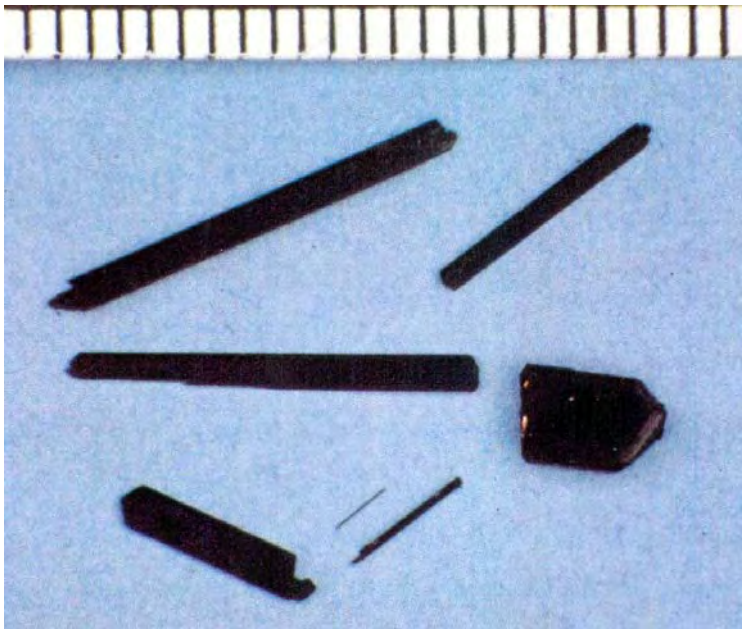
crystal growth



Growth of single crystals
by electro-crystallization from solution.

typical size: 1 to 5 mm

$(TMTSF)_2PF_6$ 5 mm

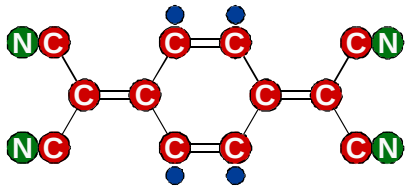


Organic Conductors
development

Starting point:

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

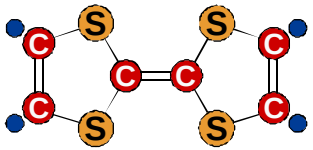
Tetracyanoquinodimethane



TCNQ

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

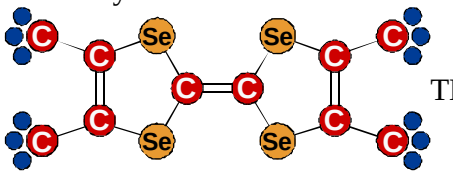
Tetrathiofulvalene



TTF

1979 K. Bechgaard, D. Jerome
1 dim organic superconductor
$(TMTSF)_2ClO_4$

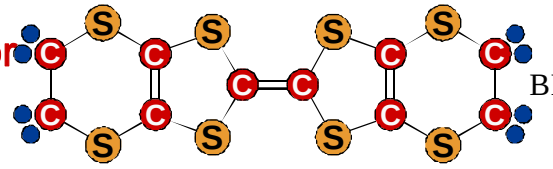
Tetrametyl-tetraselenafulvalene



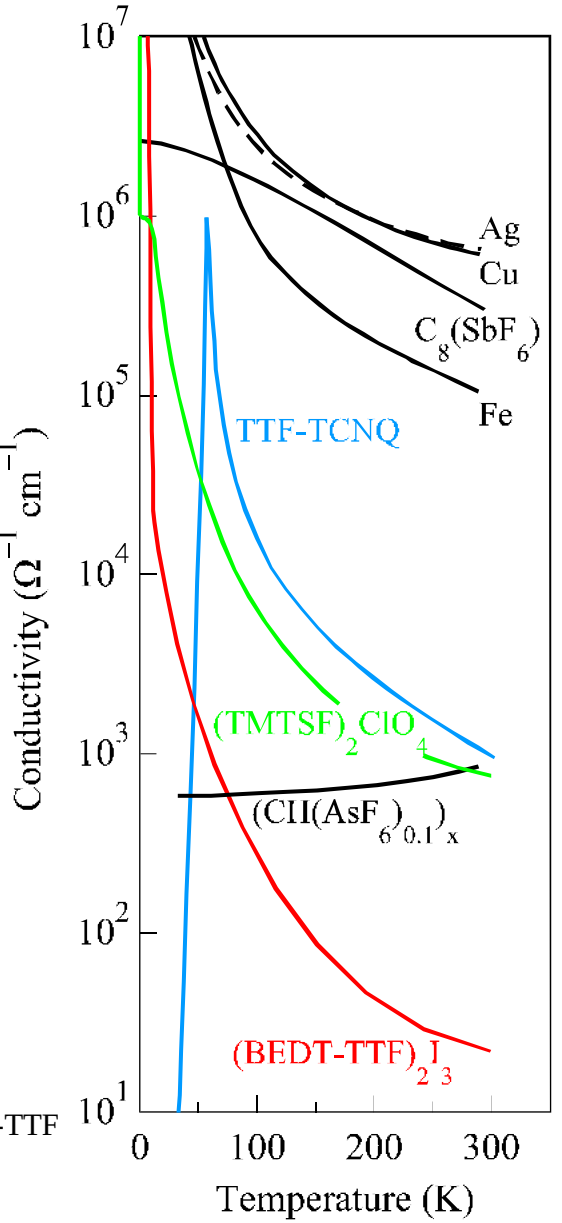
TMTSF

1984 E.B. Yagubskii
2 dim organic superconductor
$(BEDT\text{-}TTF)_2X$

Bis(ethylene-dithio)tetrathiofulvalene



BEDT-TTF

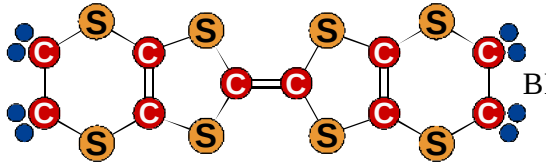


Ishiguro, Yamaji, Saito, 1998

Organic Conductors
radical cation salts

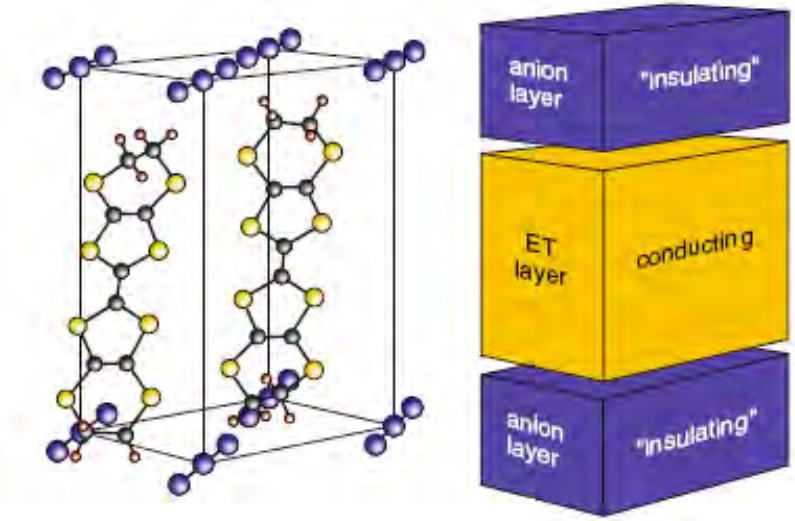
$(BEDT\text{-}TTF)_2X$

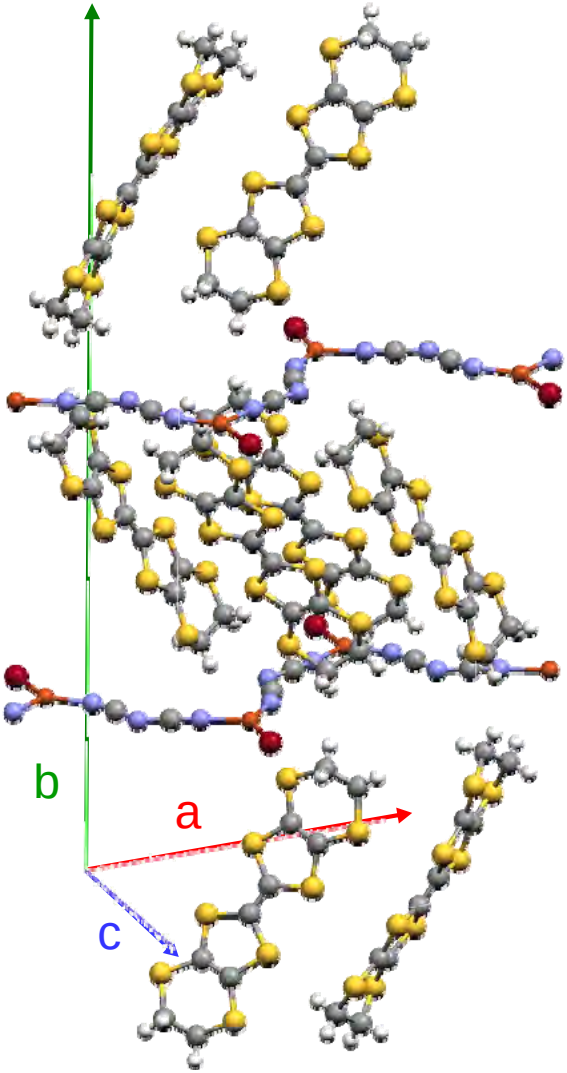
Bis(ethylene-dithio)tetrathiofulvalene



BEDT-TTF

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





anisotropy within the plane $\sigma_c / \sigma_a \sim 0.5$

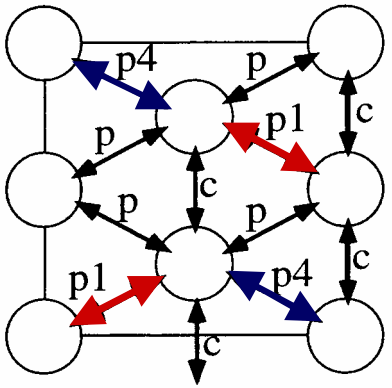
perpendicular to the plane $\sigma_b / \sigma_a \sim 10000$

Organic Conductors

radical cation salts

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

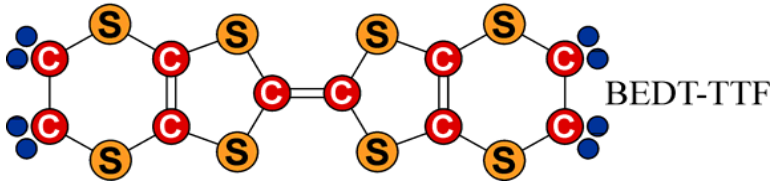
The layered arrangement of the organic molecules,
separated by anions, leads to a **two-dimensional electronic system**.



- 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
$U_{eff} = 0.5$ eV



strong influence of
electron-electron correlations

Ordering Phenomena

low-dimensional systems

Competing interactions:

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

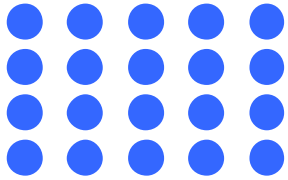
spin-Peierls, spin order, charge order, Wigner crystal

Ordering Phenomena

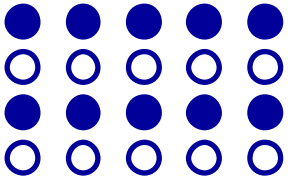
low-dimensional systems

Charge order in two dimensions

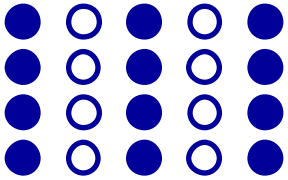
1/4-filled systems



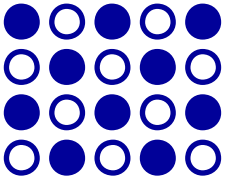
homogeneous
charge distribution



horizontal stripes



vertical stripes



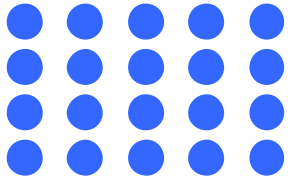
diagonal stripes
checker board

Ordering Phenomena

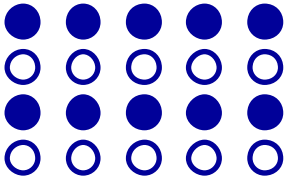
low-dimensional systems

Charge order in two dimensions

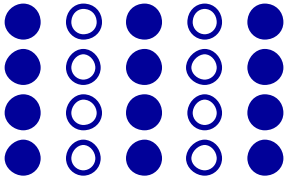
1/4-filled systems



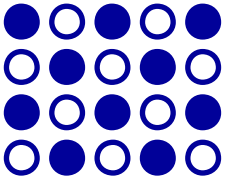
homogeneous
charge distribution



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:

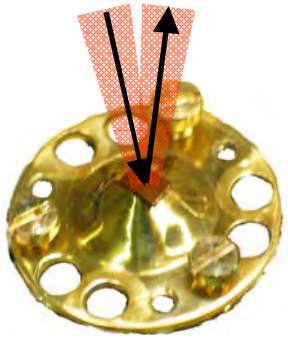
1 K ≤ T ≤ 300 K

Magnetic field:

B ≤ 12 Tesla

Hydrostatic pressure:

p < 7 GPa



Absolute values of reflectivity by Au evaporation method.

size of the surfaces: (0.5 – 1 mm)^2

with IR microscope: (150 μm)^2

Quasi-Two-Dimensional Organic Conductors

optical properties

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

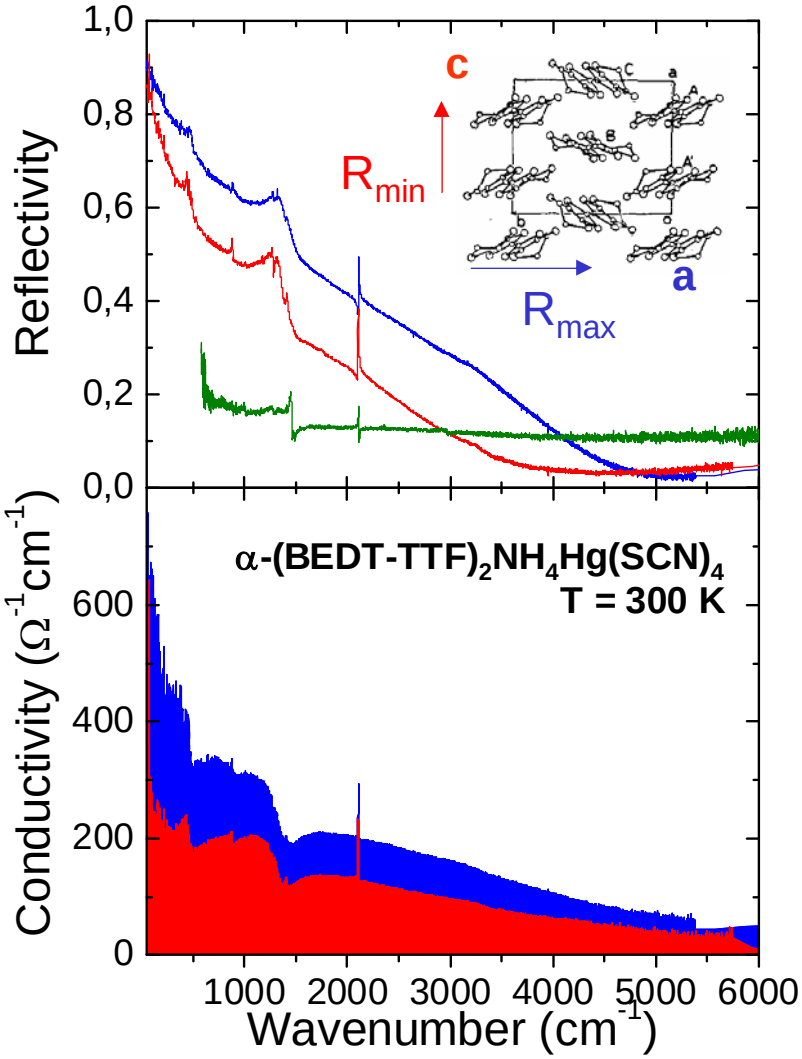
$$I_\sigma = \int_0^\infty \sigma_1(\omega) d\omega = \frac{\omega_p^2}{8}$$

where the plasma is given by

$$\omega_p^2 = \frac{16 t d^2 e^2}{\hbar V_m} \sin\left\{\frac{\pi}{2}\rho\right\}$$

The width of the conductance band is
typically 0.8-1 eV
(overlap integrals t about 0.1 eV).

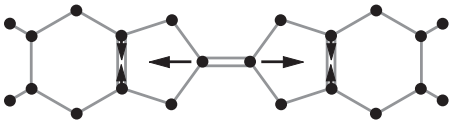
This is comparable to Coulomb interaction U.



M. Dressel and N. Drichko, Chem. Rev. **104**, 5689 (2004)
N. Drichko et al., Phys. Rev. B **74**, 235121 (2006)

Molecular Vibtrations
in BEDT-TTF salts

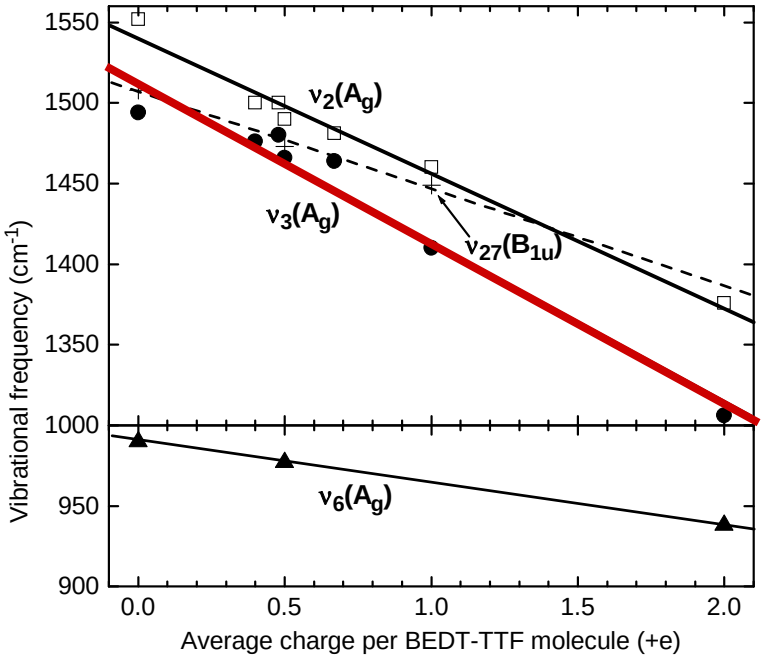
The **intra-molecular vibrations** are a measure of the localized charge.



$\nu_3\,(A_g)$

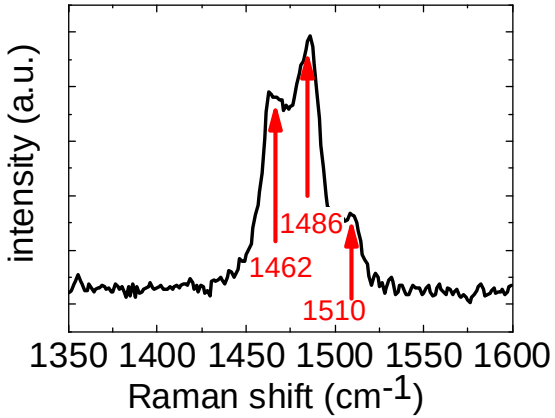
$\nu_2 = 1554.2\ cm^{-1}$

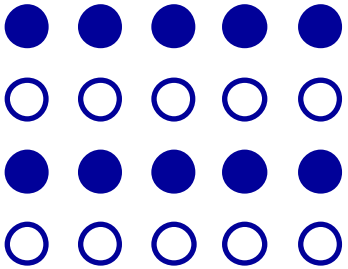
The phonon frequency shifts down when electrons are taken off.



electrons on molecule

Raman shift in α-$(BEDT\text{-}TTF)_2NH_4Hg(SCN)_4$ three vibrational peaks indicates three different sites.

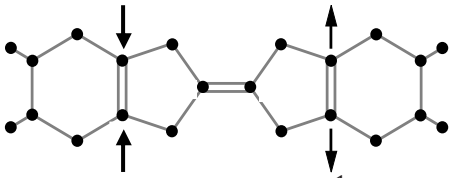




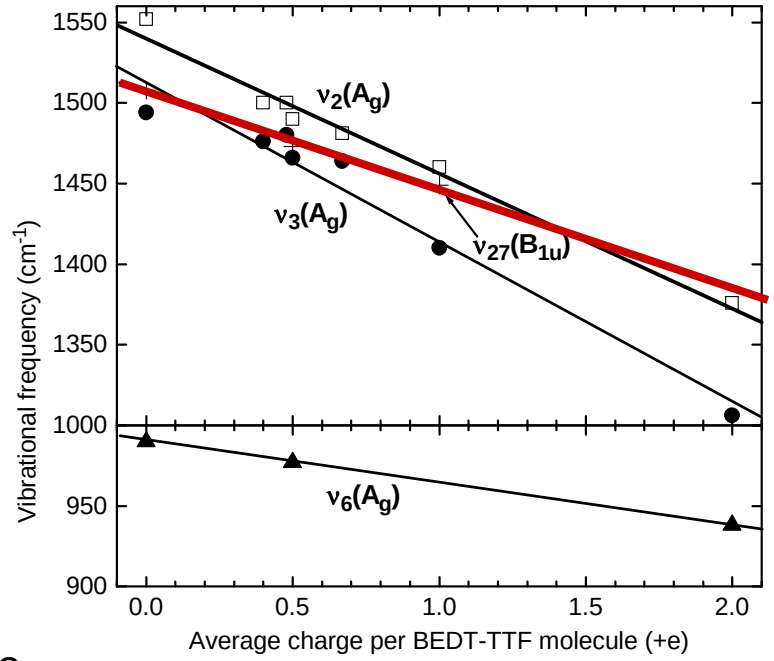
horizontal stripes

Molecular Vibtrations
in BEDT-TTF salts

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

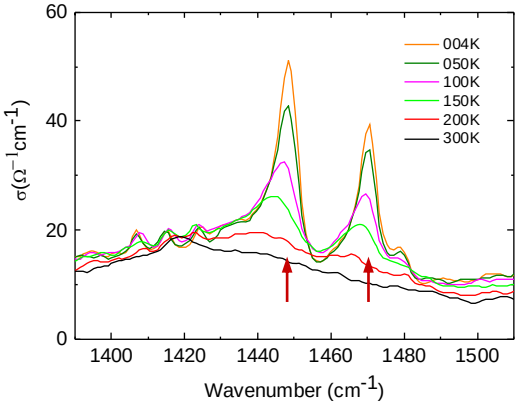


$\nu_{27}\,(B_{1u})$

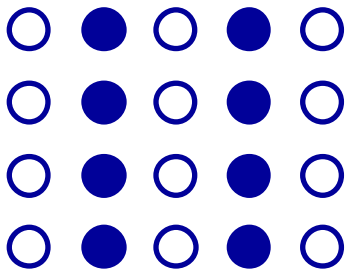


IR active molecular vibrations are intense only for polarization E ⊥ conducting layers

IR mode in β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ splitting below 150 K indicates charge order $\Delta\rho$ = 0.2e



electrons on molecule



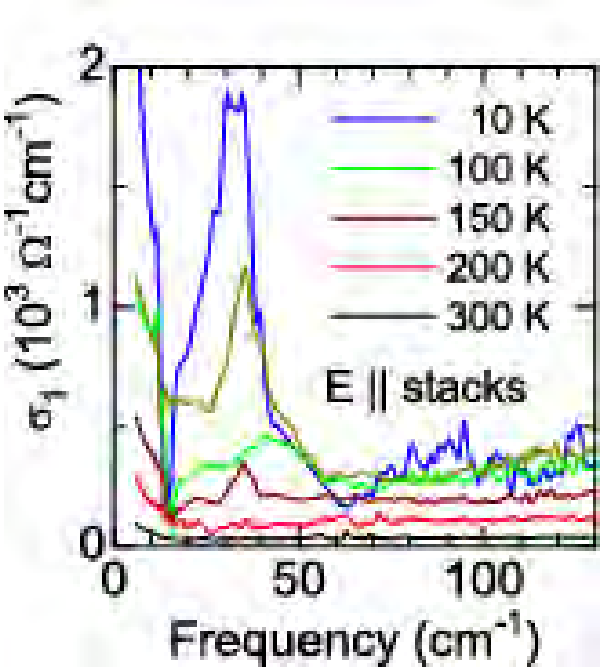
vertical stripes

S. Kaiser et al., arXiv:0812.3732

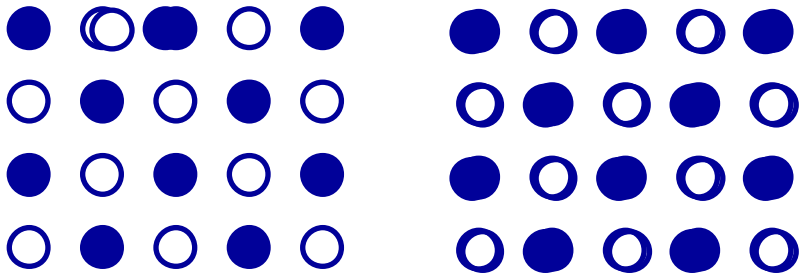
Collective Modes
in charged ordered systems

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

collective excitations.



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

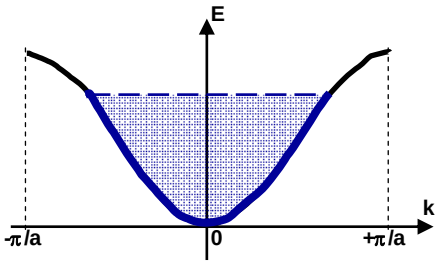


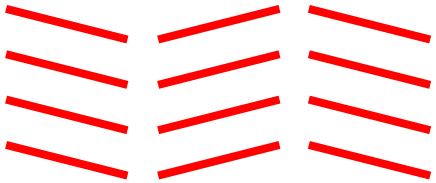
S. Kaiser et al., arXiv:0812.3732

Quasi-Two-Dimensional Organic Conductors

electronic correlations

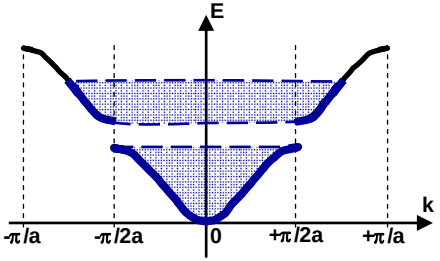
- α-(BEDT-TTF)$_2X$
  2:1 stoichiometry: insulator, metal, superconductor
  1/4-filled system: hole carriers

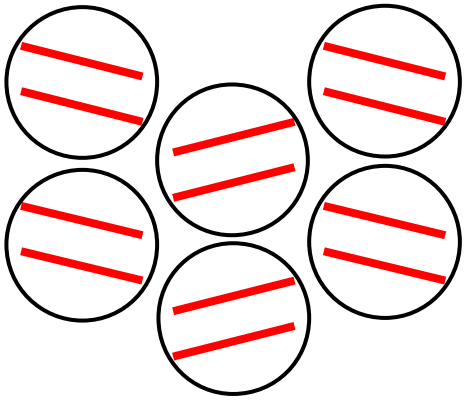




- κ-(BEDT-TTF)$_2X$

2:1 stoichiometry, dimerized: metal, superconductor
1/2-filled upper band: hole carriers





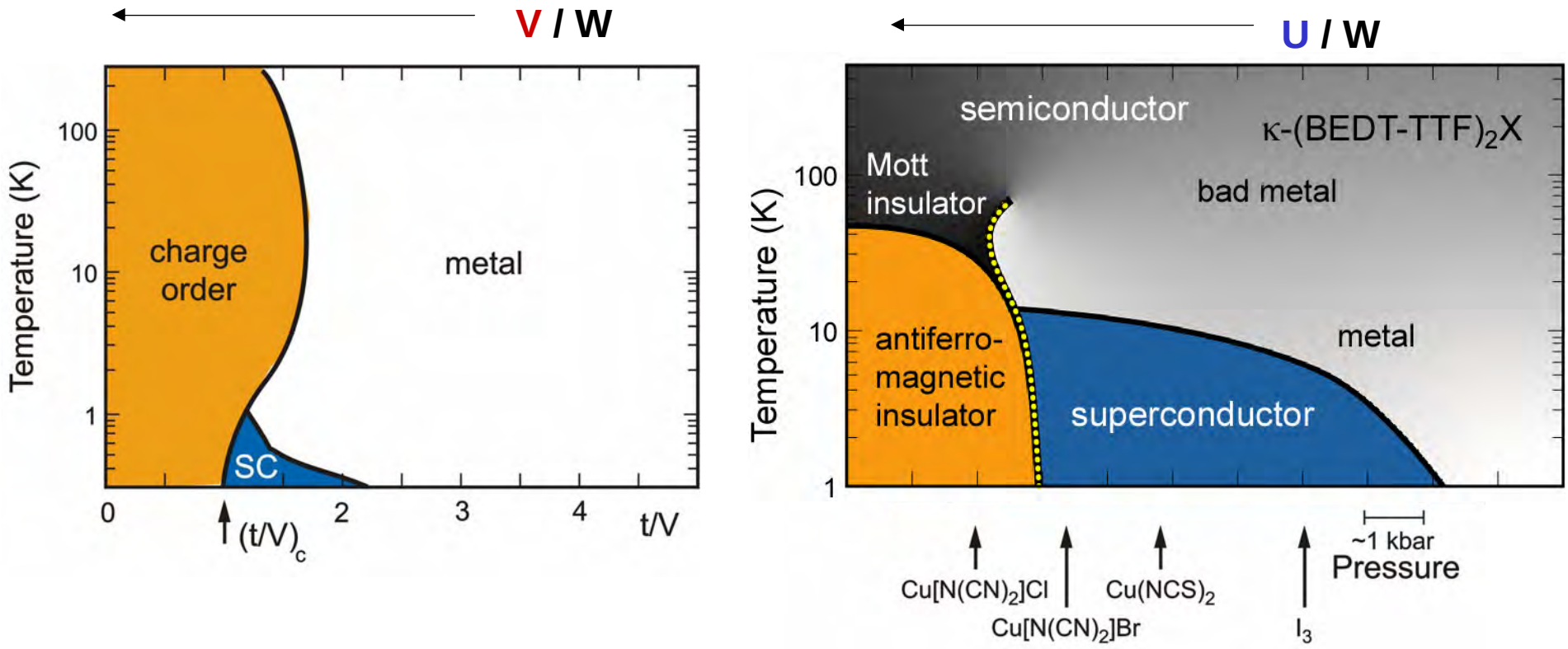
Quasi-Two-Dimensional Organic Conductors

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

Proposed Phase Diagrams

¼ filled compounds

½ filled compounds



Tuning parameters: **electronic correlations (on-site U, inter-site V)** / **bandwidth W**

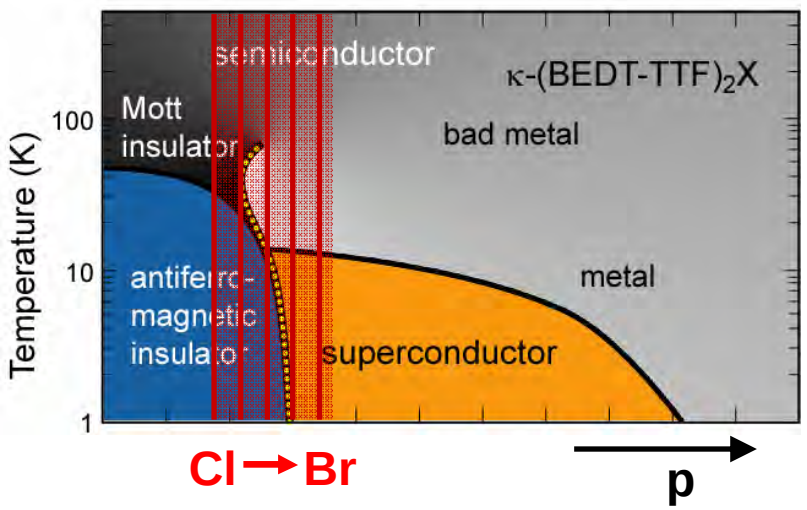
Metal-Insulator Transition

bandwidth control by anion substitution

What are the dynamical properties close to the metal-insulator transition?

We investigated the temperature dependent **optical conductivity of** **κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$** with x = 0%, 40%, 73%, 85%, and 90%.

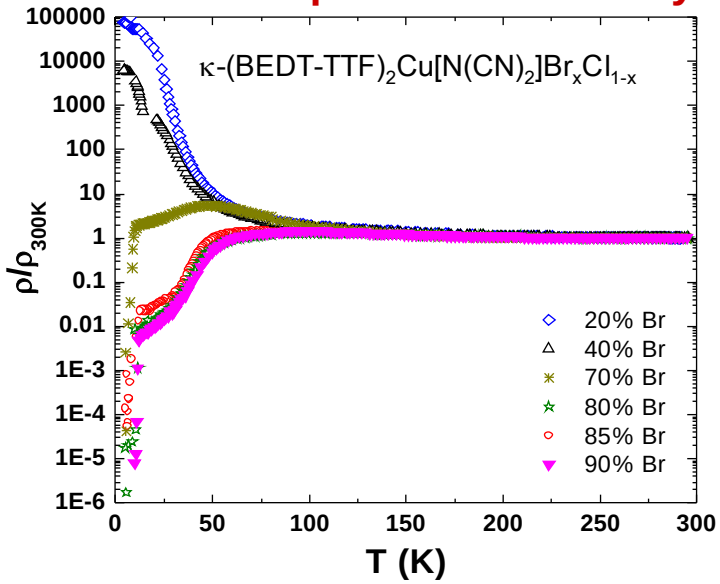
Changing size of the anions changes the overlap integral ***t*** : **'chemical pressure'**



κ-(BEDT-TTF)$_2$Cu[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.

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is
metallic for T ≤ T* ≈ 50 K.
Organic superconductor with maximum T$_c$ = 12 K.

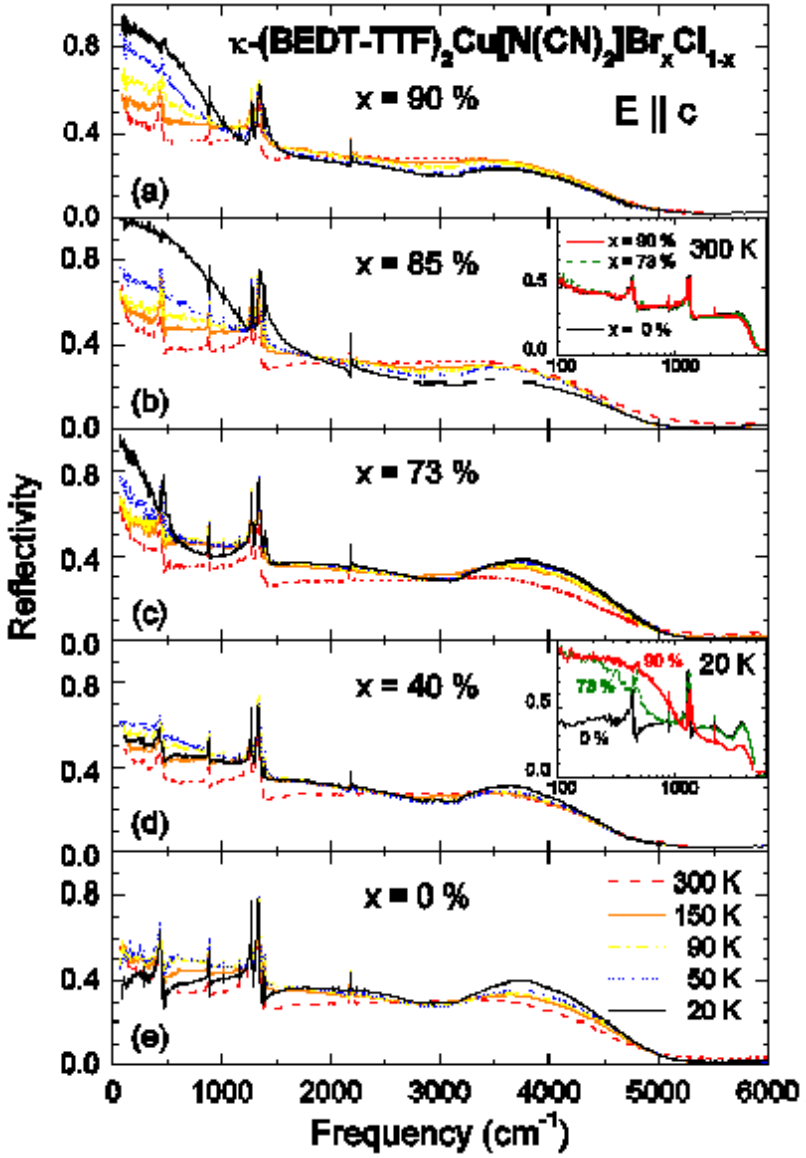
in-plane dc resistivity



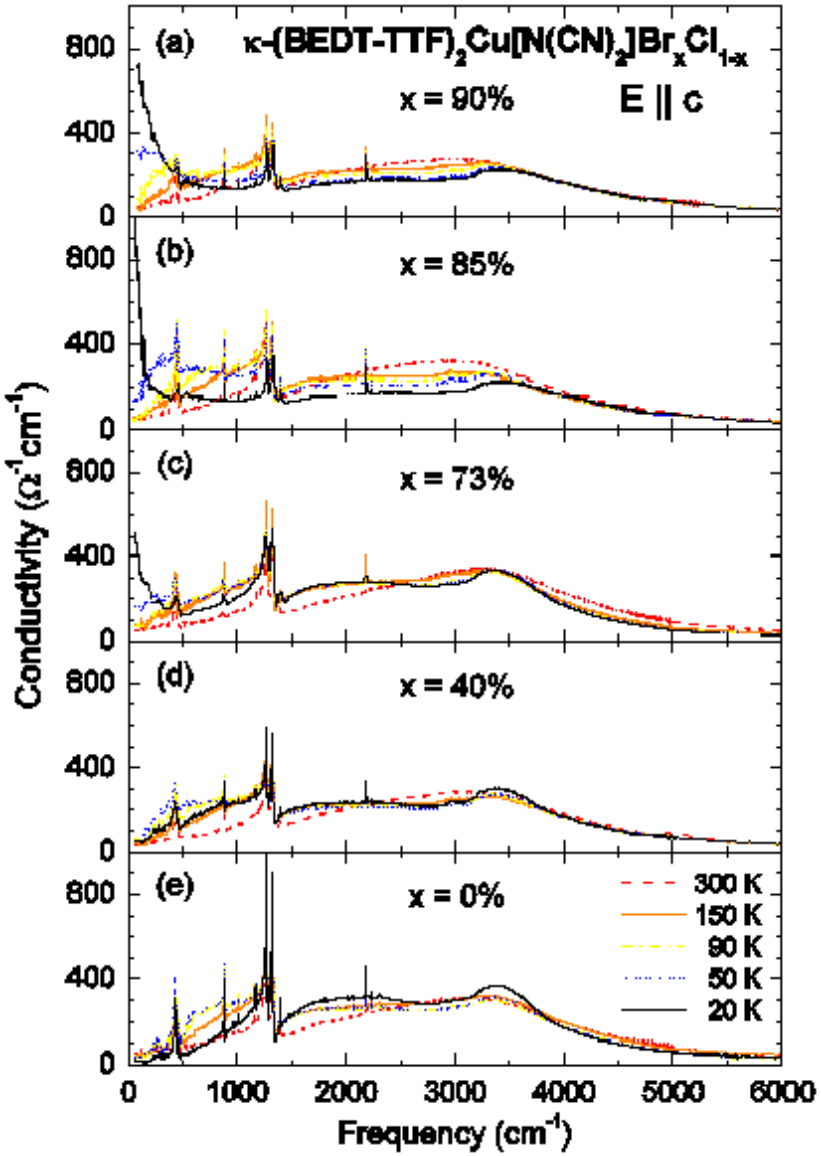
D. Faltermeier et al., Phys. Rev. B **76**, 165113 (2007); M. Dumm et al. Phys. Rev B (2009)

Optical Properties

of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$



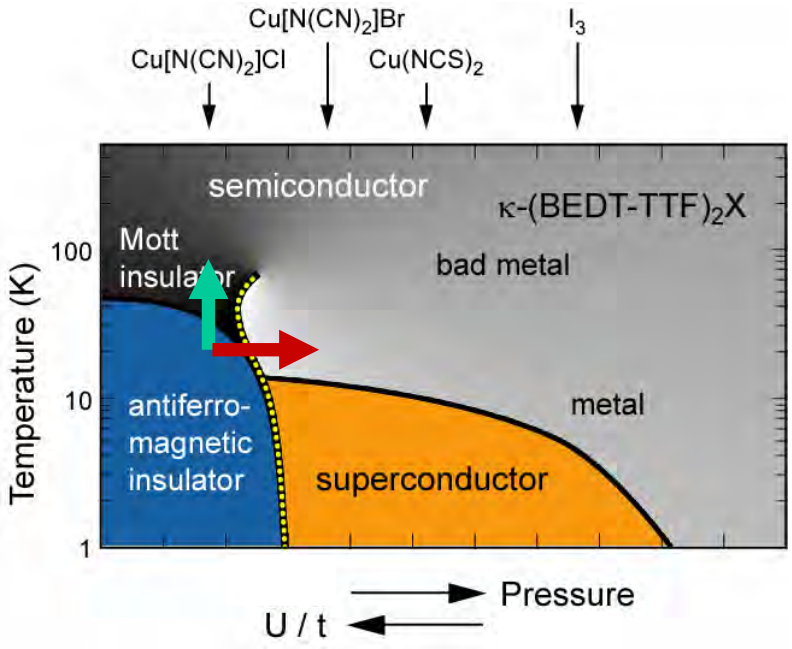
Br content

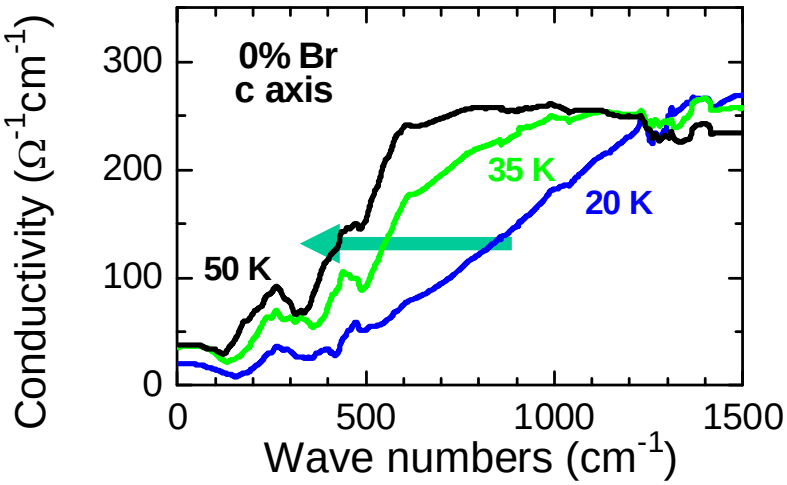


Metal-Insulator Transition

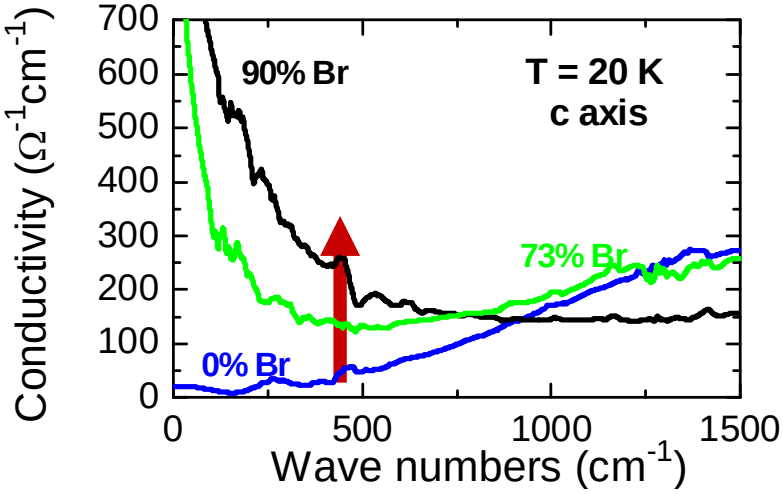
in κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br_xCl_{1-x}$

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.

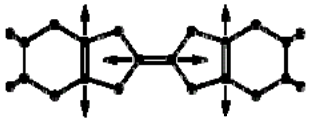


M. Dumm et al., Phys. Rev. B (2009)

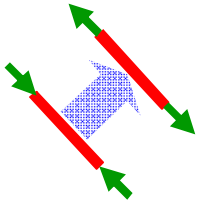
Optical Properties
different contributions

The optical conductivity contains
different contributions
which can be disentangled:

Intra-molecular vibrations:



ν_4

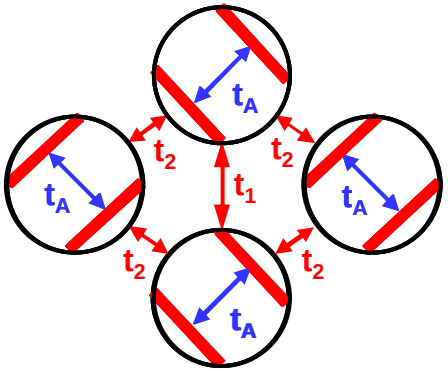


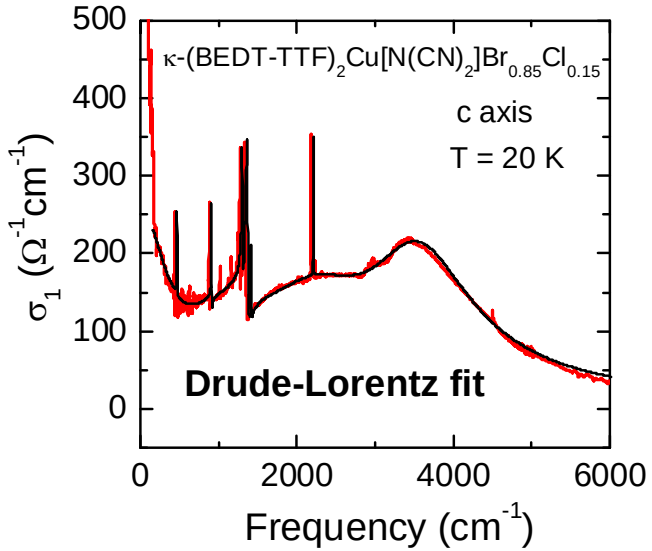
emv coupling

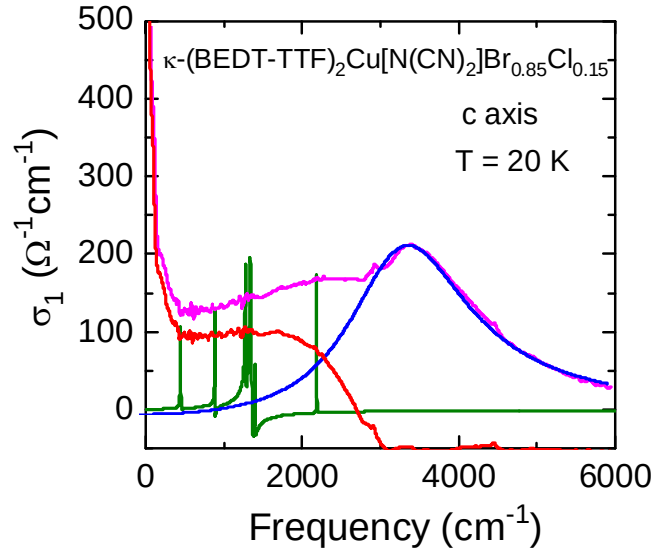
Electronic Excitations

Intra-dimer excitations

Inter-dimer excitations







M. Dressel, et al., Physica B (2008)

Optical Properties

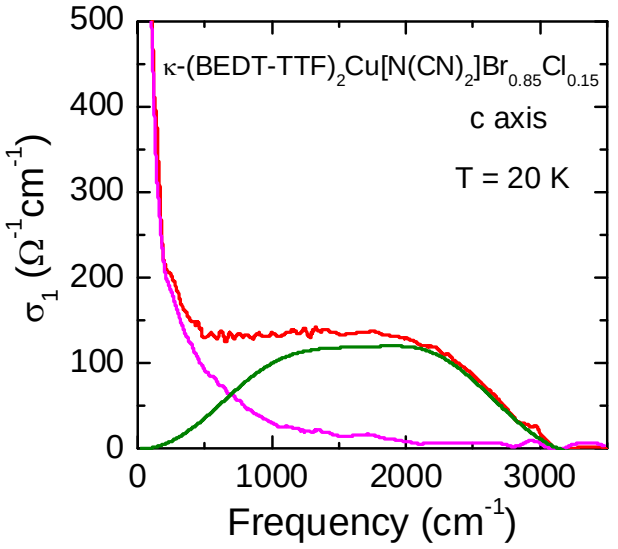
itinerant charge carriers

Inter-dimer excitations

localized charge carriers

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

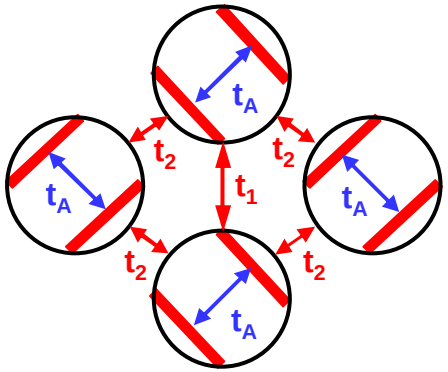
delocalized charge carriers



Hubbard model on frustrated square lattice

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

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



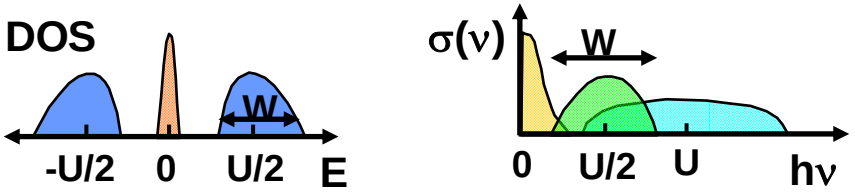
U ≈ 0.3 eV
t_2 ≈ 0.03 eV

M. Dressel, et al., Physica B (2008)

Metal-Insulator Transition

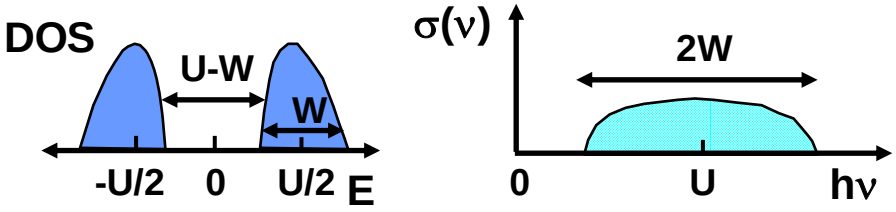
bandwidth control U/t

Metallic state

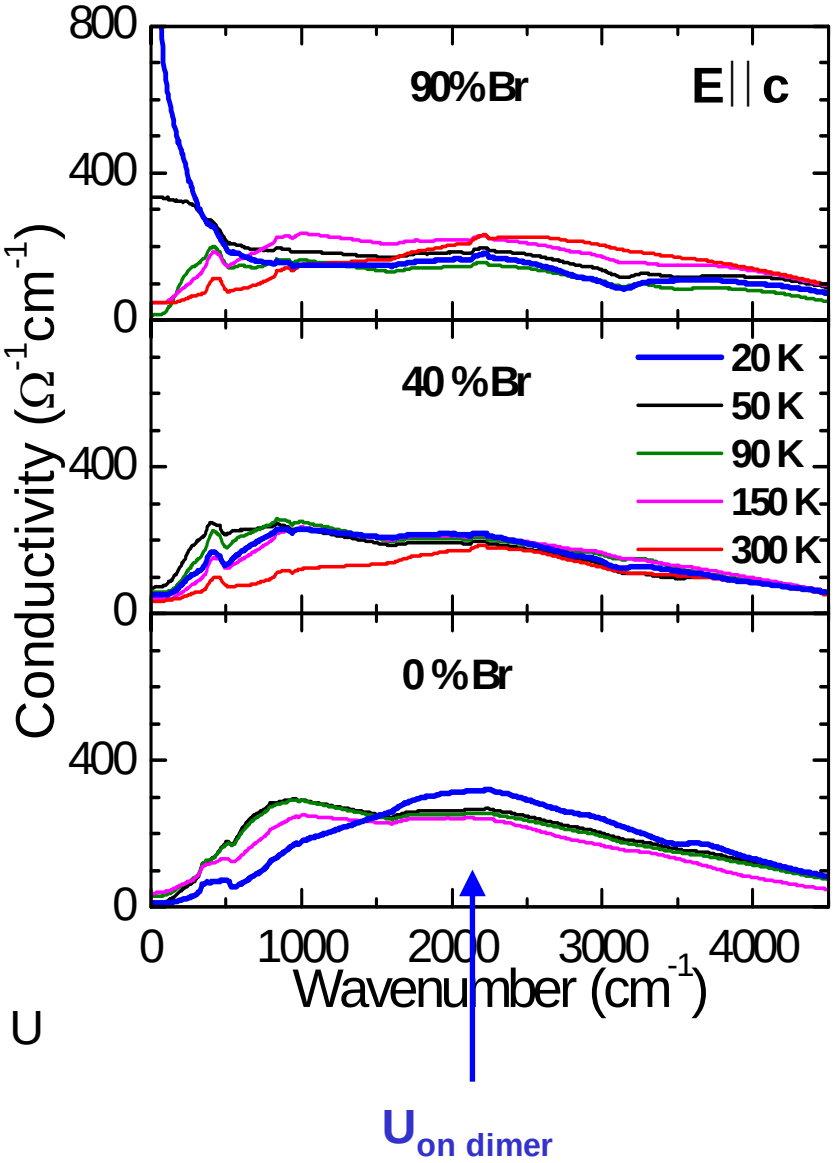


- **Drude-like feature** due to the coherent quasiparticles (Fermi liquid)
- **band** of width W centered **around U/2**
- **broad band at U** of width 2W.

Insulating state



- **gap of Δ_{Mott} = U-W**
- **broad band of width 2W** centered around U



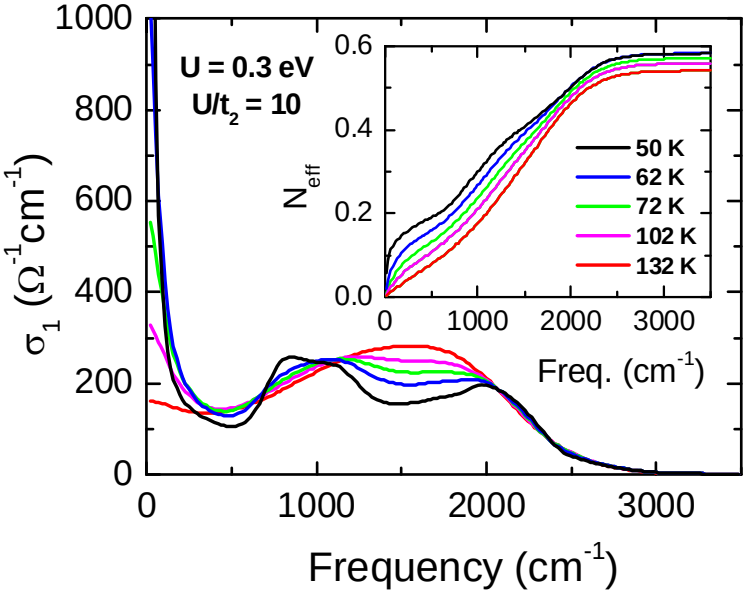
M. Rozenberg, G. Kotliar and H. Kajueter, Phys. Rev. B **54**, 8452 (1996); M. Dumm et al. Phys. Rev. B (2009)

Dynamics of Correlated Charge Carriers

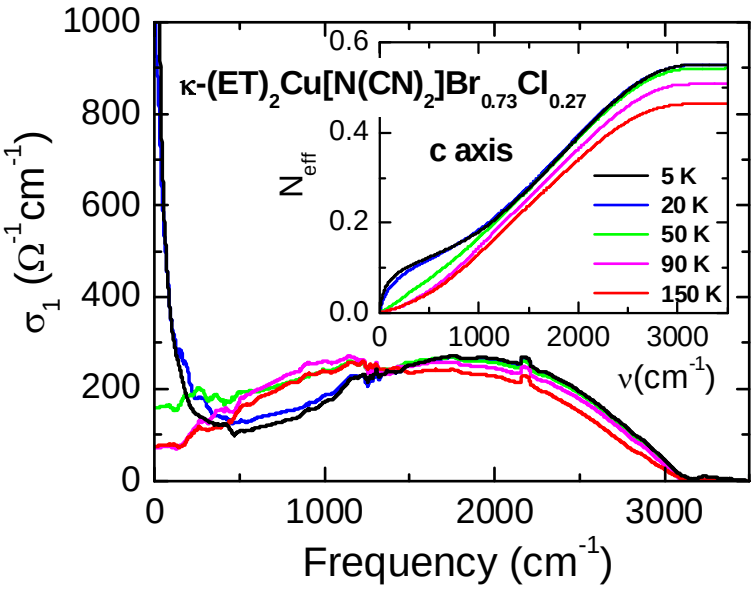
optical conductivity

Temperature dependent optical conductivity

DMFT calculations for the Hubbard model



optical conductivity of correlated charge carriers for E||c



- Number of holes per dimer $N_{\mathrm{eff}}(\omega) = \Omega \frac{m_b}{e^2} \frac{2}{\pi} \int_0^{\omega} \sigma_1(\omega') \mathrm{d}\omega'$ Ω = 3300 Å^3 m_b = 2.5 m_e
- Band at U/2 suppressed in experimental data
- Gradual destruction of quasiparticles above T*

J. Merino, M. Dumm, N. Drichko, M. Dressel, R. McKenzie, Phys. Rev. Lett. **100**, 086404 (2008).

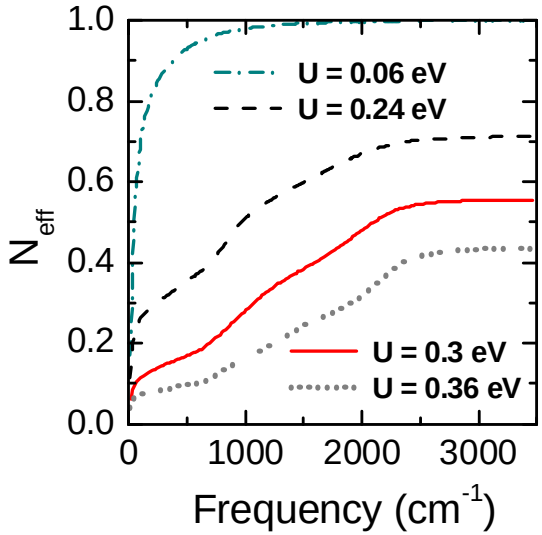
Dynamics of Correlated Charge Carriers

effective charge carrier number

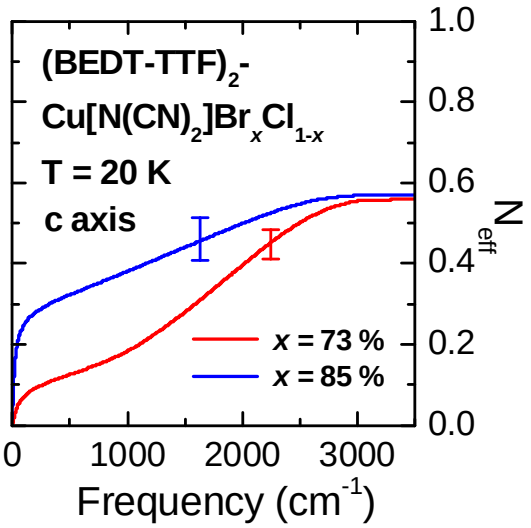
Effective carrier number per BEDT-TTF dimer

$$N_{\mathrm{eff}}(\omega) = \frac{2D}{\pi}\frac{\Omega \mathrm{h}^2 M}{e^2 d^2 \langle -E_{\mathrm{kin}} \rangle}\int_0^{\omega}\sigma_1(\omega')\mathrm{d}\omega'$$

t_2 = 0.03 eV



$$N_{\mathrm{eff}}(\omega) = \frac{2}{\pi}\frac{\Omega m_b}{e^2}\int_0^{\omega}\sigma_1(\omega')\mathrm{d}\omega'$$



With increasing correlations U/t:

- spectral weight is transferred to higher frequencies
- effective charge-carrier number is supressed

J. Merino, M. Dumm, N. Drichko, M. Dressel, R. McKenzie, Phys. Rev. Lett. **100**, 086404 (2008).

Dynamics of Correlated Charge Carriers

frequency dependent scattering rate and mass

Extended Drude analysis

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

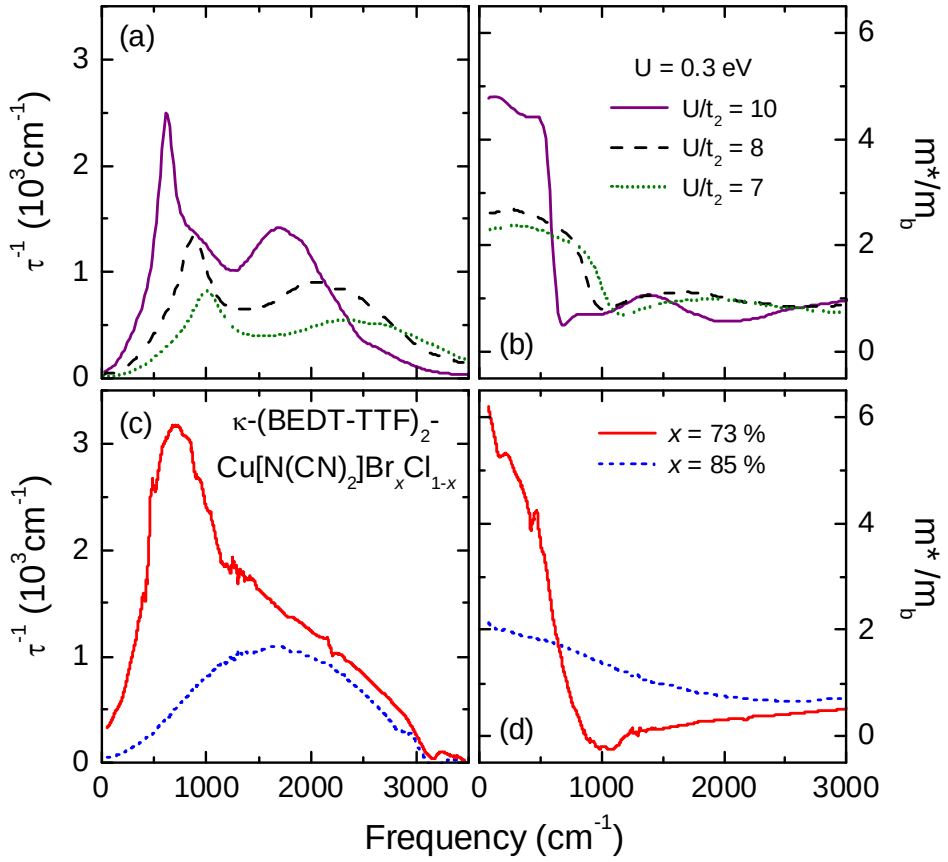
from DMFT calculations

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



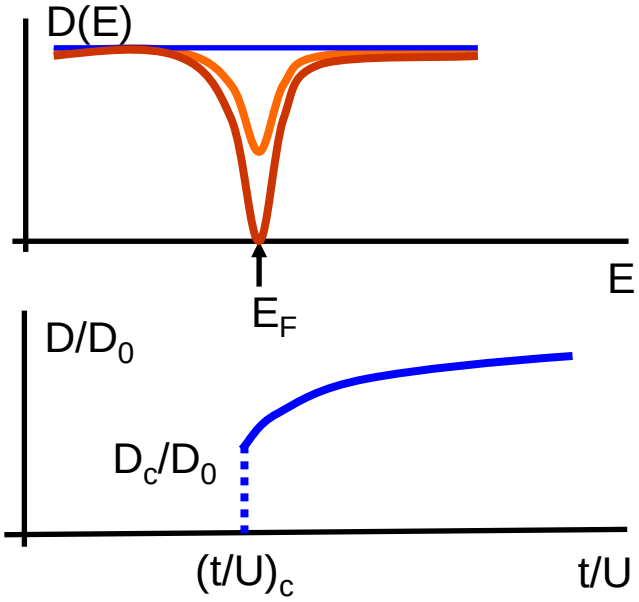
When approaching the metal-insulator transition from the metallic side, the effective mass increases, because correlations increase.
(Brinkman-Rice)

J. Merino, M. Dumm, N. Drichko, M. Dressel, R. McKenzie, Phys. Rev. Lett. **100**, 086404 (2008).

Drude Weight at the Metal-Insulator Transition

density of states

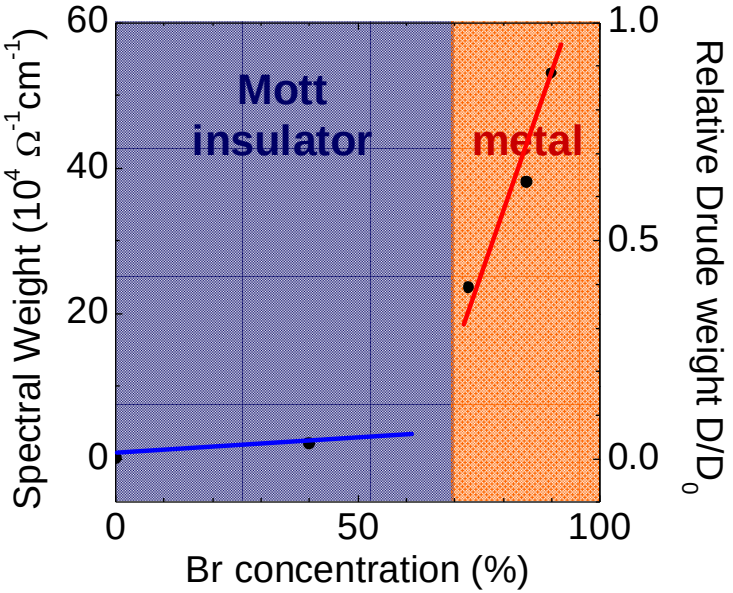
The Mott transition can be visualized as
a **reduction in the density of states**
at the Fermi energy.
At the transition $D(E_F)$ is zero.



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 K.

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

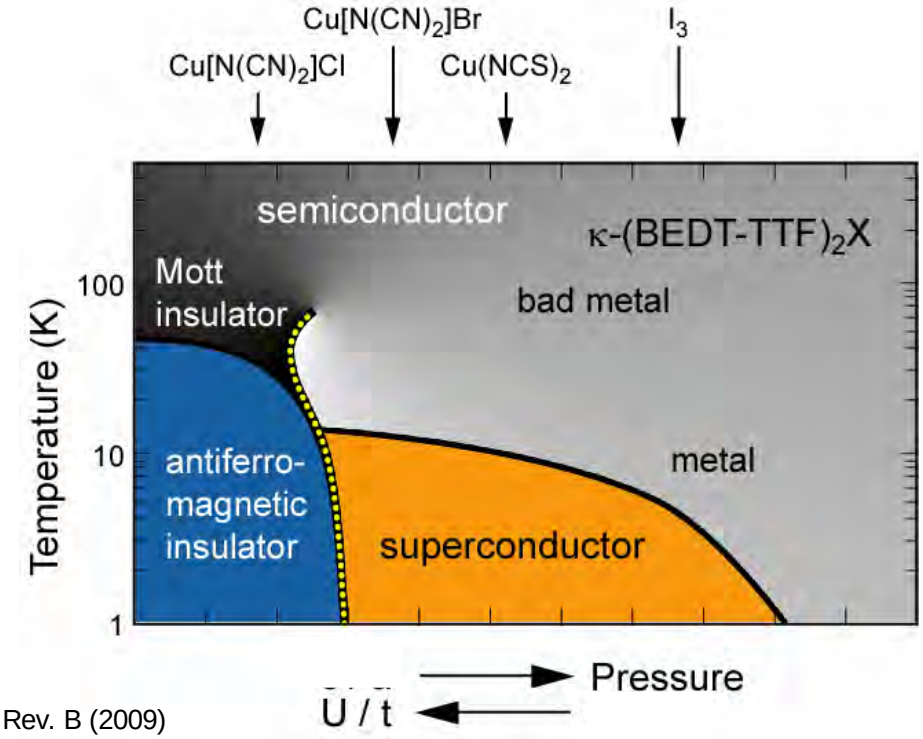


Summary: ½ Filling

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$

The two-dimensional organic conductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$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.

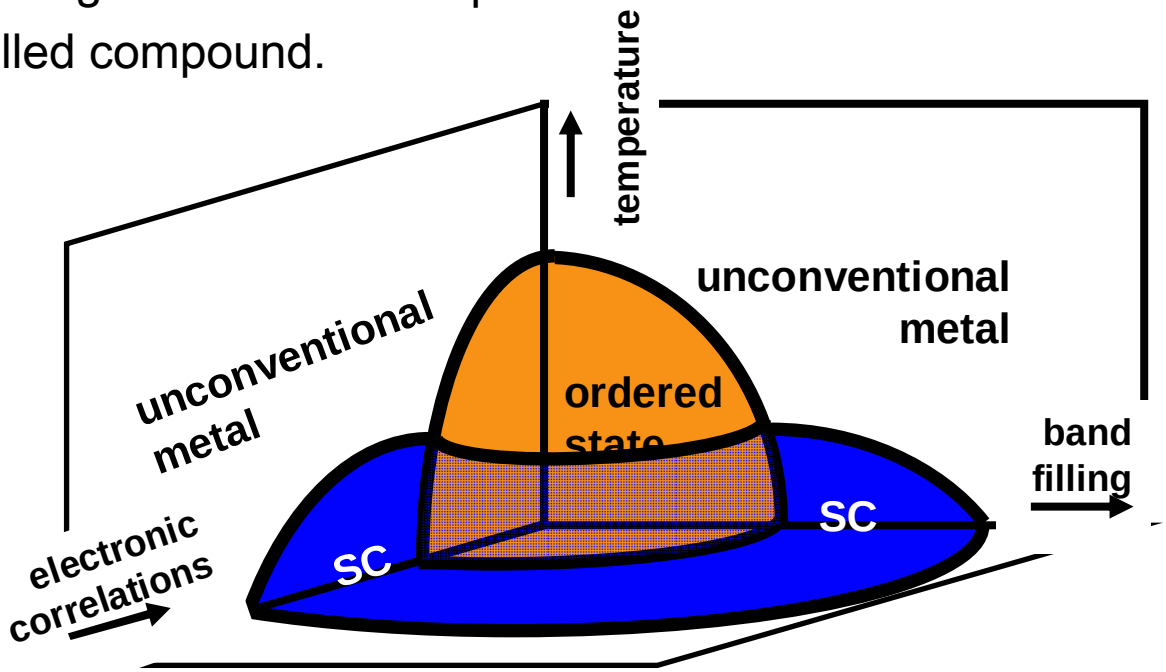


D. Faltermeier et al., Phys. Rev. B **76**, 165113 (2007); M. Dumm et al. Phys. Rev. B (2009)

Summary

two-dimensional organic conductors

- In the half-filled compounds κ-(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.



Dressel and Drichko, Chem. Rev. **104**, 5689 (2004)