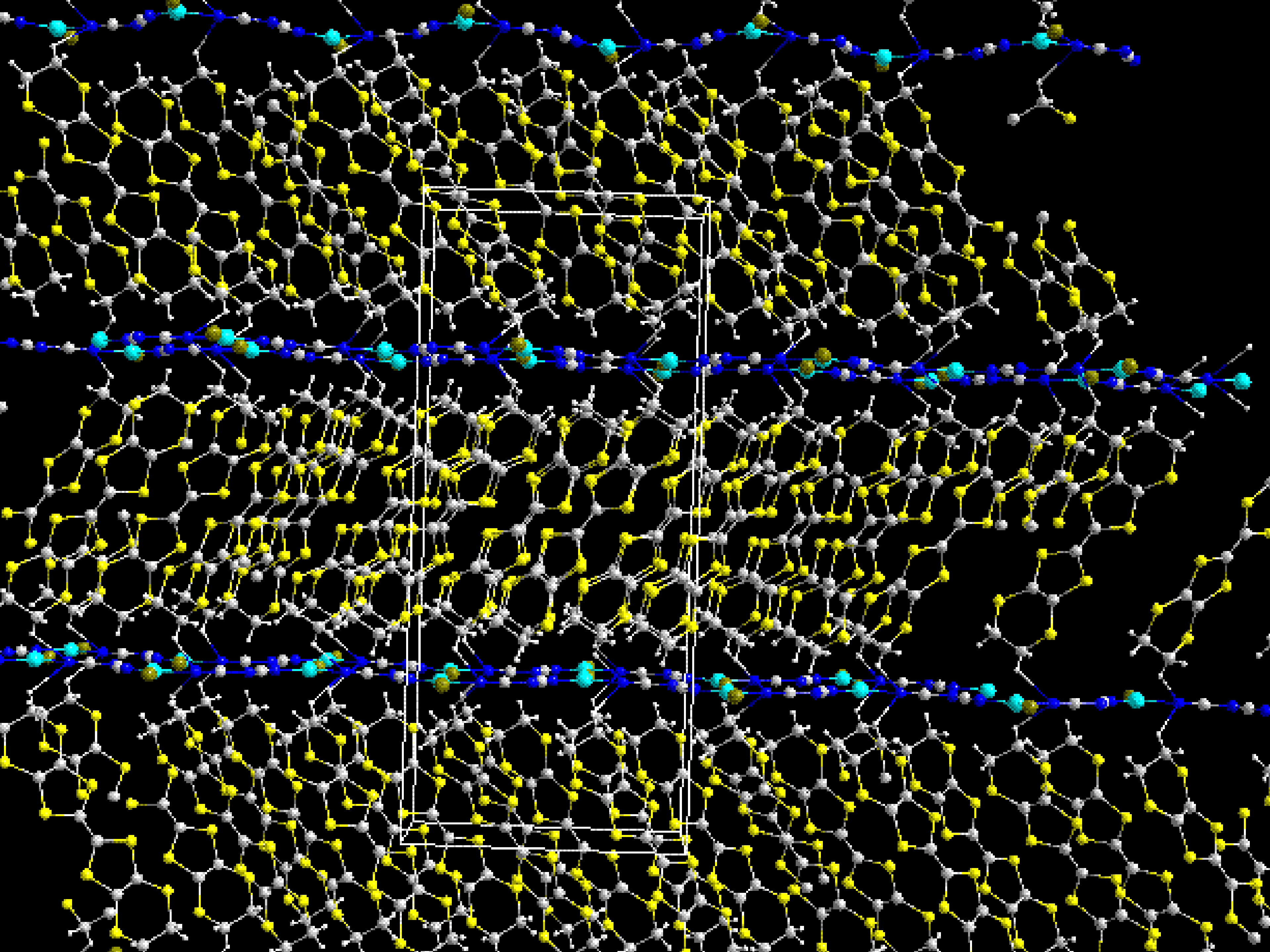

Unconventional Charge Dynamics in Low-Dimensional Organic Conductors

Martin Dressel
1. Physikalisches Institut der Universität Stuttgart

Outline

1. **Introduction**
   to molecular conductors
2. **Mott-Insulator-Intransition**
   κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$
   afm insulator to superconductor
3. **Mott-Insulator:**
   Disorder and Frustration
   κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$
   charge dynamics of a spin liquid
4. **Summary and Outlook**

A. Pustogow, T. Ivek,
S. Elsässer, D. Faltermeier,
K. Sedlmeier, S. Yasin,
N. Drichko, M. Dumm
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Moscow Institute of Physics and Technology

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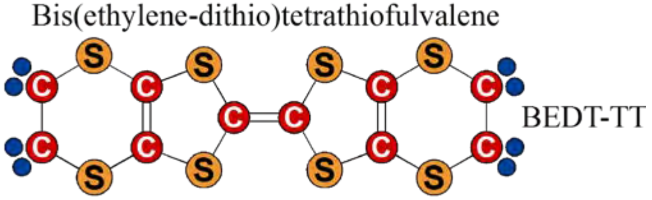
J. Schlueter
Argonne National Laboratory, U.S.A.

J. Merino
Universidad Autonoma, Madrid, Spain
R. McKenzie
Univ. Queensland, Brisbane, Australia

Quasi-Two-Dimensional Organic Conductors

charge transfer salts

(BEDT-TTF)$_2X$

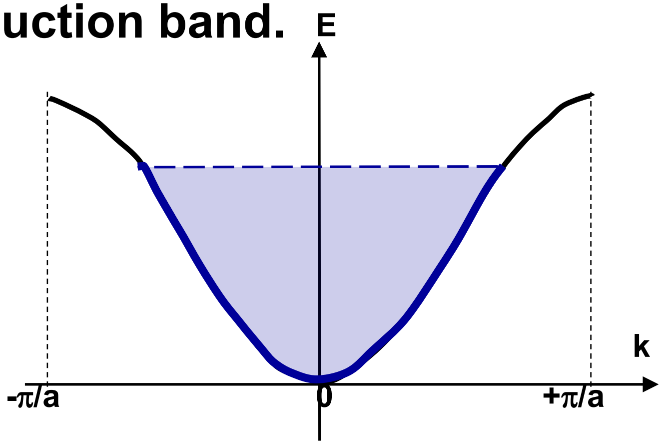


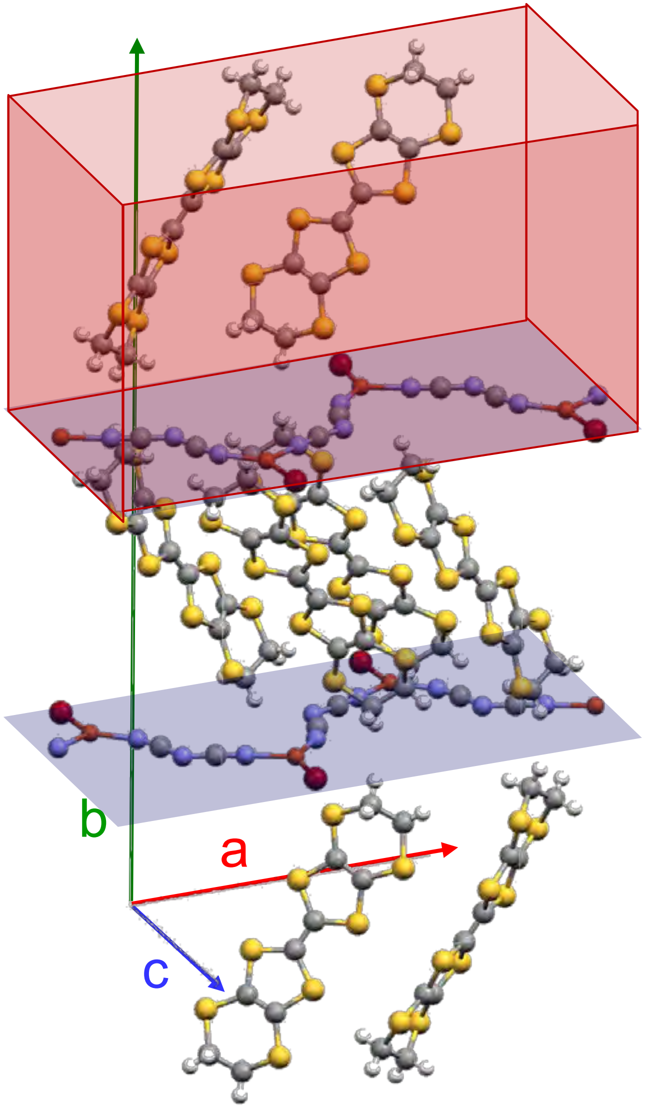
The structure consists of BEDT-TTF layers as electron **donors**, separated by sheets of inorganic **acceptors**.

- **Two dimensional electron system.**

The **bandfilling** depends on the stoichiometry: typically A_2B

- **¾ - filled conduction band.**

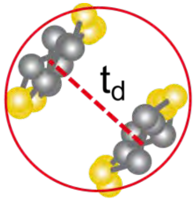




Quasi-Two-Dimensional Organic Conductors

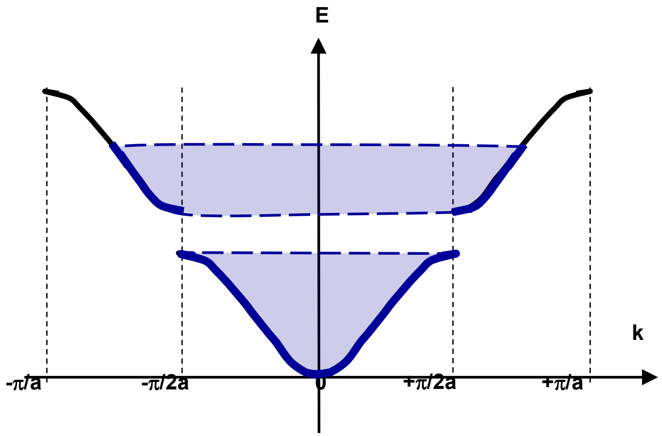
dimerized Mott insulators

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$



In the κ-phase, **dimers** are formed with a rather strong coupling $t_d \approx 0.2$ eV;
based on the dimer site, the system is half-filled.

- The onsite Coulomb repulsion ***U*** **$\approx$ 0.4 eV.**
  With an effective $U/W = 1.8$,
  the system is a **Mott insulator**.



Quasi-Two-Dimensional Organic Conductors

dimerized Mott insulators

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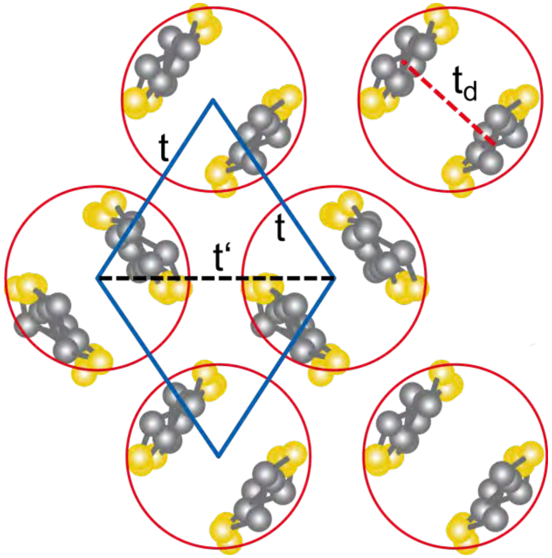

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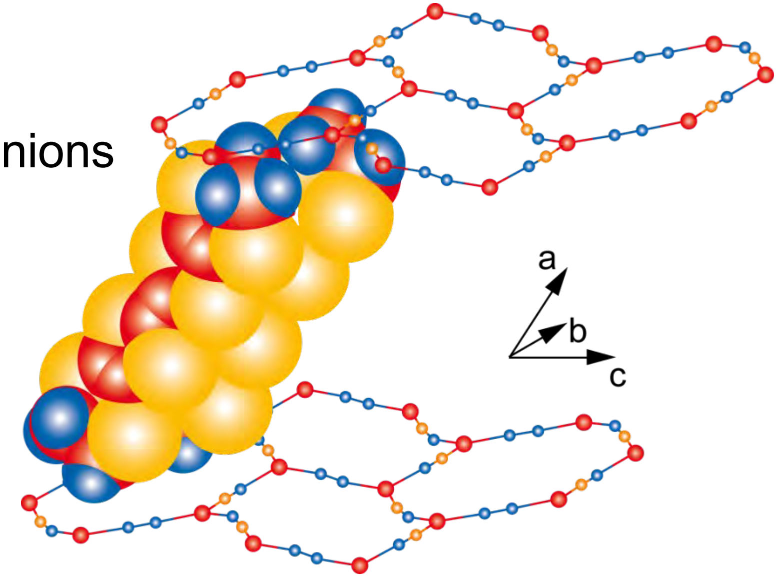
- The onsite Coulomb repulsion $\boldsymbol{U} \approx$ **0.4 eV.**
  With an effective $U/W = 1.8$,
  the system is a **Mott insulator**.

The dimers are arranged on a triangular lattice,

- close to **frustration** $\boldsymbol{t' \approx t}$.

The BEDT-TTF molecules are coupled to the anions via the terminal ethylene groups.

- **Disorder** in the anion sheets acts on the organic layers.

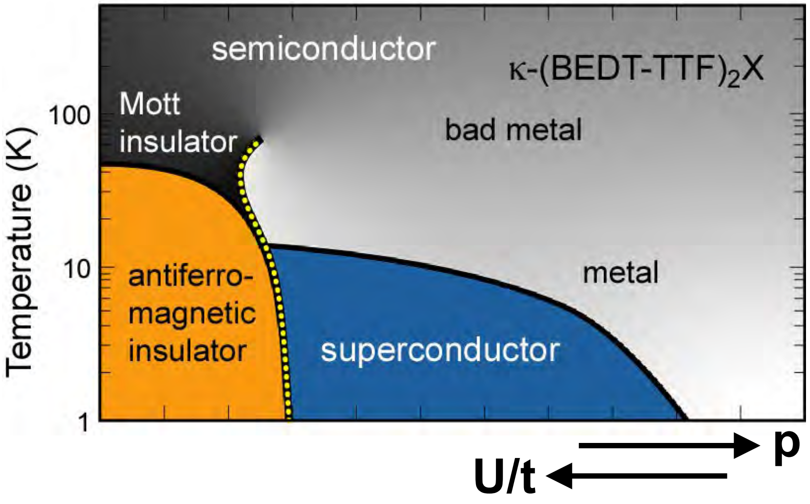


Metal-Insulator Transition

bandwidth control

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X

- two-dimensional half-filled electron system
- strong correlations, close to Mott transition
- tuning of bandwidth W = 4t
  by physical or chemical pressure



$$\frac{\textbf{electronic correlations (on-site U)}}{\textbf{bandwidth W}}$$

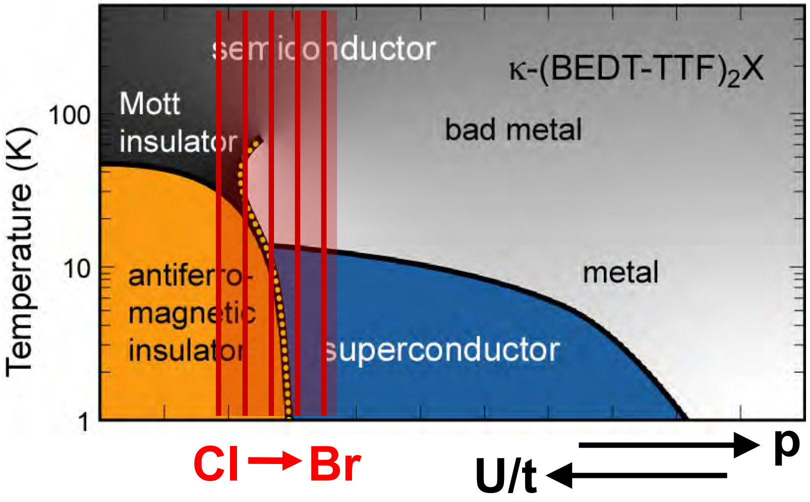
S. Yasin, M. Dumm, B. Salameh, P. Batail, C.Meziere, and M. Dressel, Eur. Phys. J. B **79**, 383 (2011)

Metal-Insulator Transition

bandwidth control

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$
with
x = 0%, 20%, 40%, 73%, 85%, and 90%.

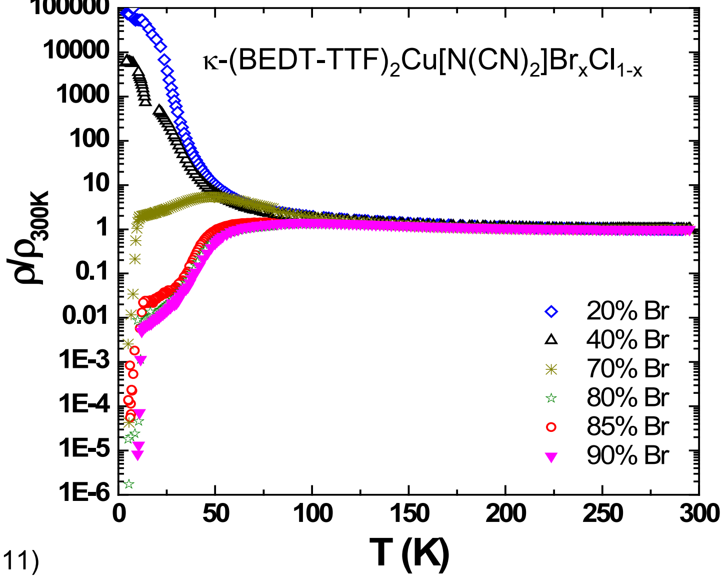
Changing size of the anions modifies the overlap integral ***t*** : **'chemical pressure'**



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

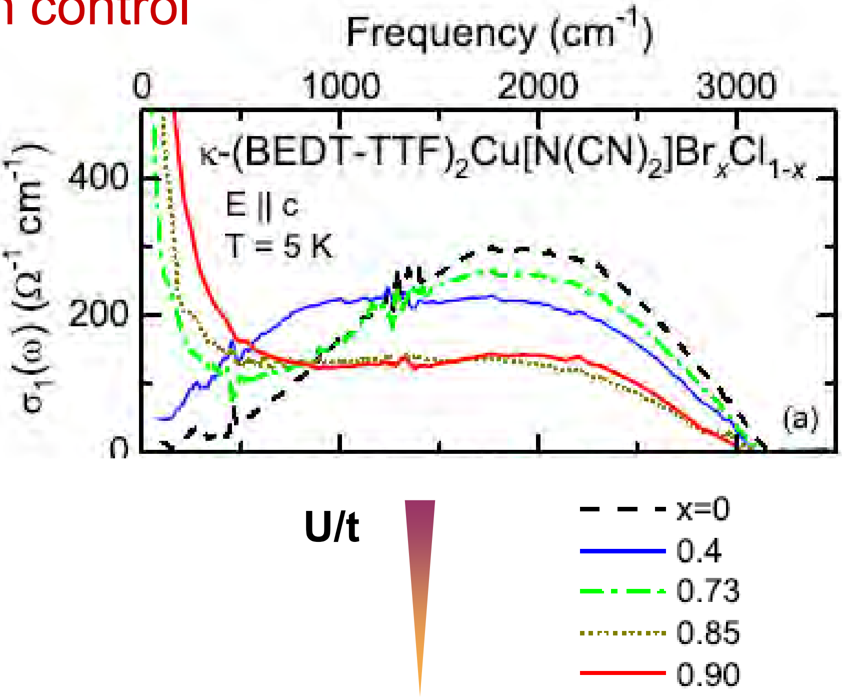


S. Yasin, M. Dumm, B. Salameh, P. Batail, C.Meziere, and M. Dressel, Eur. Phys. J. B **79**, 383 (2011)

Metal-Insulator Transition

bandwidth control

On the metallic side of the Mott transition a **coherent carrier response** develops for low temperatures.



From the extended Drude analysis, we find

- an **increase of the effective mass m*** when approaching MIT.
- a **rise in the scattering rate 1/τ.**

These findings agree with predictions by dynamical mean field theory **(DMFT)**.

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

Metal-Insulator Transition

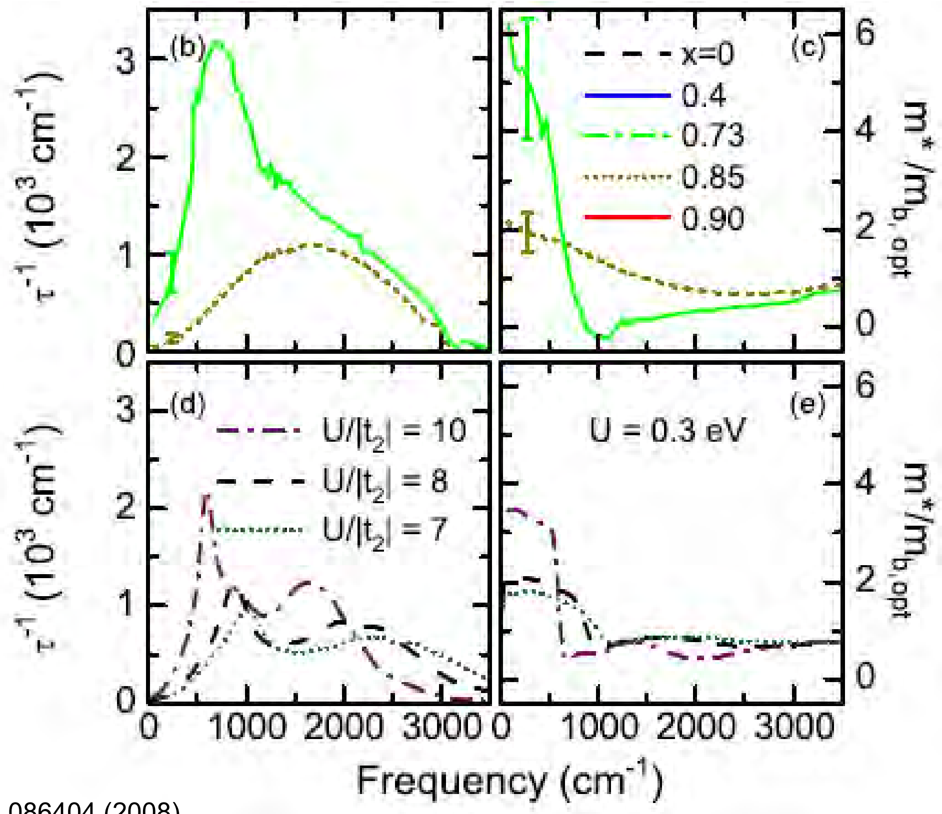
bandwidth control

Brinkman-Rice

Approaching the metal-insulator transition from the metallic side,
the **effective mass increases**,
because correlations become stronger.

Kadowaki-Woods

The slope of the scattering rate
$1/\tau(T)$ or $1/\tau(\omega)$
becomes larger
when correlations increase.



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

Dynamics of Correlated Charge Carriers

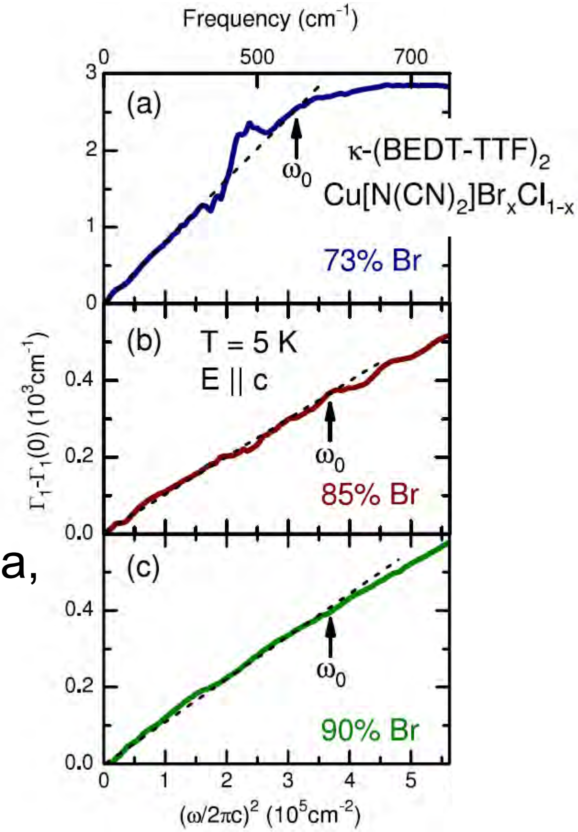
Fermi liquid behavior

At low temperatures T < 30 K
Fermi liquid behavior $\tau^{-1} \propto \omega^2$ is expected
up to a frequency $\omega^* \approx 500\ \mathrm{cm}^{-1}$.

The dc resistivity exhibits a
$\rho \propto \tau^{-1} \propto T^2$ behavior up to 30 K.

Comparing the slope for the two kind of data,
we obtain A/B = 56.
Landau predicted a prefactor of
$(2\pi)^2 \approx 40$ for a **Fermi liquid**.

$$\frac{1}{\tau} = \qquad B(\hbar\omega)^2$$



- The vicinity of the **Mott insulator** strongly influences the **metallic state**.
- Superconductivity evolves out of a Fermi liquid state.
- The presence of the Mott state is more important to **superconductivity** than antiferromagnetic fluctuations.

M. Dressel, J. Phys.: Cond. Matter **23**, 293201 (2011)
S. Yasin, M. Dumm, B. Salameh, P. Batail, C.Meziere, and M. Dressel, Eur. Phys. J. B **79**, 383 (2011)

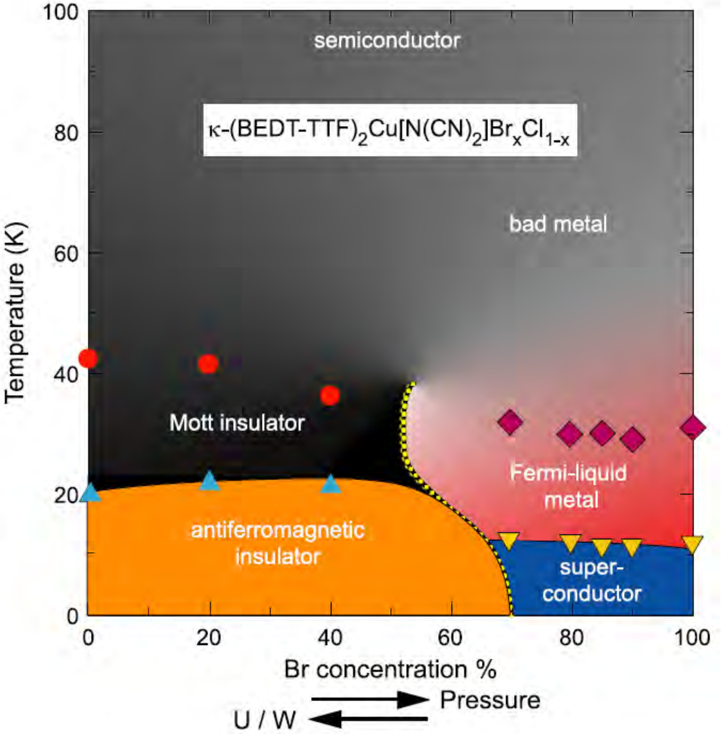
Metal-Insulator Transition on Triangular Lattice

first summary

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

- half-filled conduction band
- strong Coulomb repulsion U

- semiconductor / bad metal
- **Mott insulator**
  antiferromagnetic order
- **Fermi liquid**
  superconductor



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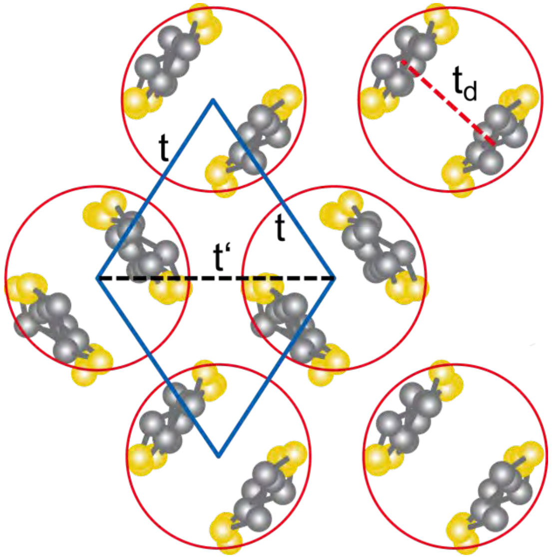
Mott Insulators on Triangular Lattice

correlation and frustration

Variation of correlation and frustration

κ-(BEDT-TTF)$_2X$ X =	t’/t	U/t	t_d (mev)	t (mev)	t’ (meV)
Hg(SCN)$_2$Cl	0.80	5.2	129	50.2	40.2
Cu[N(CN)$_2$]Br	0.42	5.1	200	78	33
Cu[N(CN)$_2$]Cl	0.44	5.5	200	73	32
Cu$_2$(CN)$_3$	0.83	7.3	200	55	45
Ag$_2$(CN)$_3$	0.95	4.2	200		



H.C. Kandpal et al., Phys. Rev. Lett. **103**, 067004 (2009); H.O Jeschke et al.; G. Saito et al., unpublished

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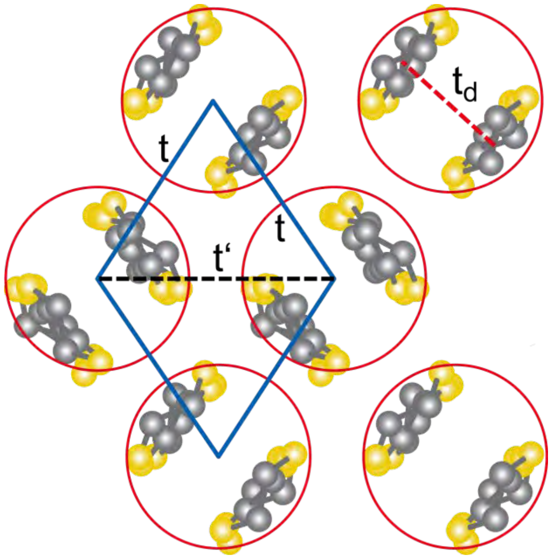
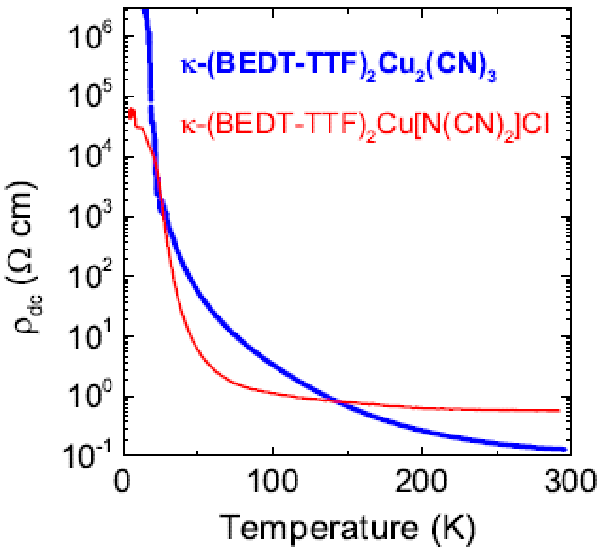


κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

- $T_M \approx 40$ K Mott insulator
  strong increase in ρ(T)
- $T_N = 25$ K afm order

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- gradual increase of ρ(T)
  with no sharp kink indicates the opening of a gap



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S. Elsässer, Dan Wu, M. Dressel, and J. A. Schlueter, Phys. Rev. B **86,** 155150 (2012)

Mott Insulators on Triangular Lattice

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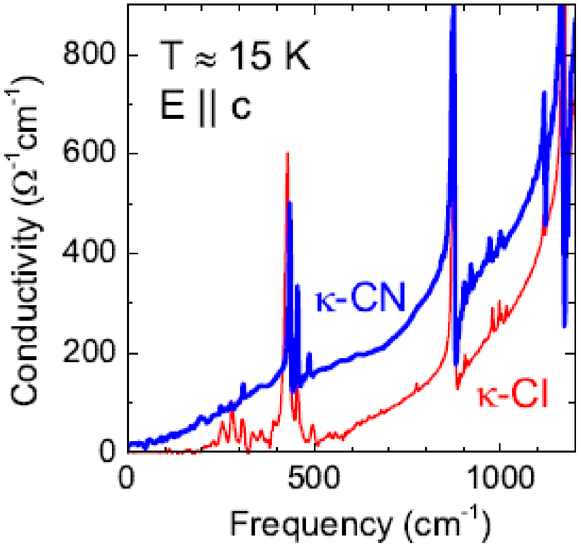

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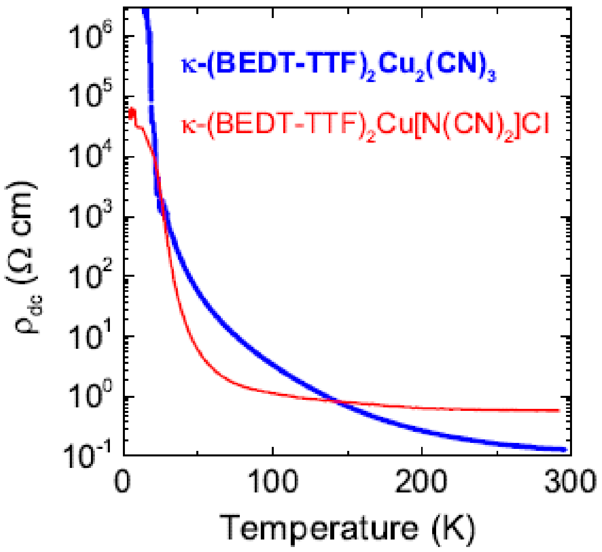

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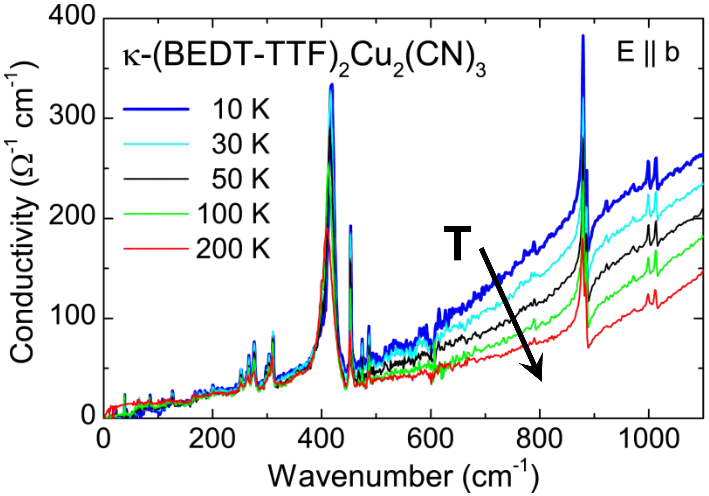
Mott Insulators on Triangular Lattice

correlation and frustration

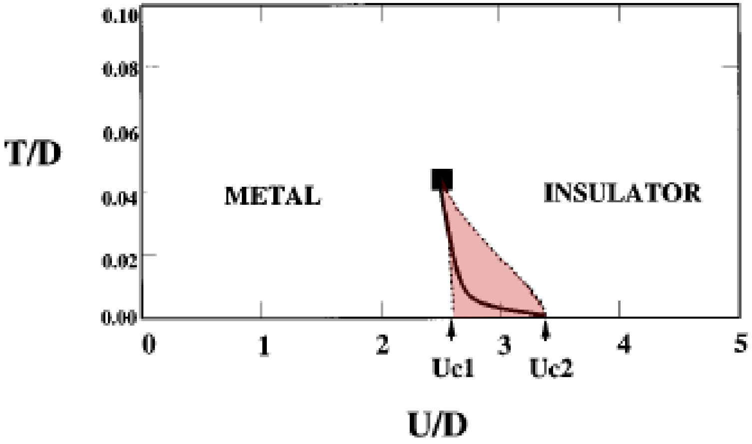
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- strong in-gap absorption
- $\sigma_1(\omega)$ increases upon cooling
- finite conductivity down to $\omega = 0$ that becomes larger as T decreases.
- $\sigma(\omega \to 0) = 0$ in accord with the high resistivity.



DMFT with full frustration at half filling: coexistence between paramagnetic metallic and insulating state.

However, κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ remains insulating at all temperatures.



M.J. Rozenberg, G. Kotliar, and X.Y. Zhang, Phys. Rev. B **49**, 10481 (1994)
A. Georges, G. Kotliar, W. Krauth, and M.J. Rozenberg, Rev. Mod. Phys. Rev. **68**, 13 (1996)

A. Pustogow et al., unpublished

S. Elsässer, Dan Wu, M. Dressel, and J. A. Schlueter, Phys. Rev. B **86**, 155150 (2012)

Mott Insulators on Triangular Lattice

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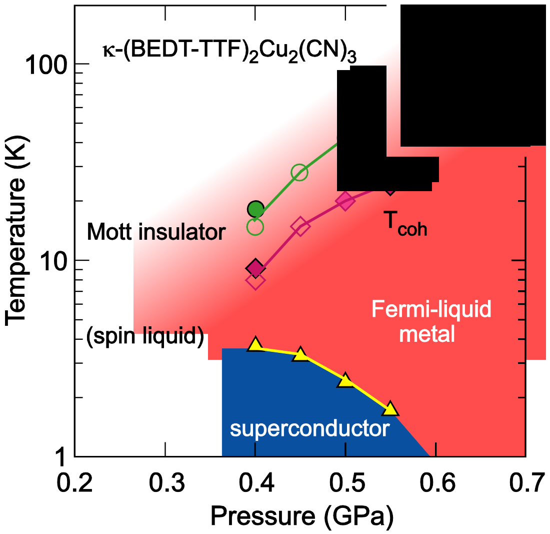
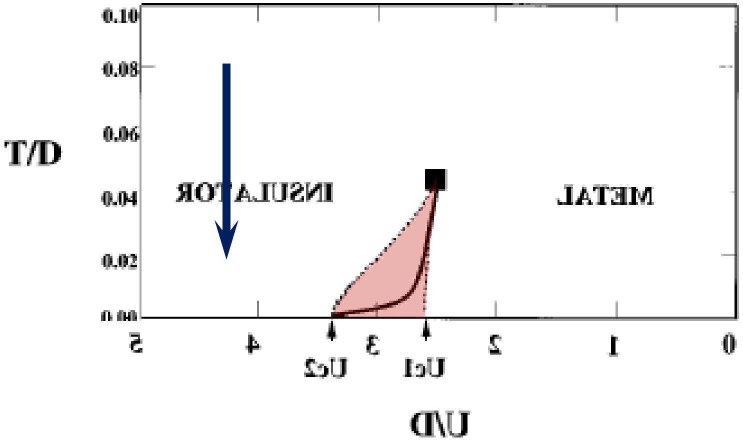


[redacted]

We are well into the insulating side: κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is a Mott insulator at all temperatures.



A. Georges, G. Kotliar, W. Krauth, and M.J. Rozenberg, Rev. Mod. Phys. Rev. **68**, 13 (1996)

Y. Kurosaki, Y. Shimizu, K, Miyagawa, K. Kanoda and G. Saito, Phys. Rev. Lett. **95**, 177001 (2005)

Mott Insulators on Triangular Lattice

correlation and frustration

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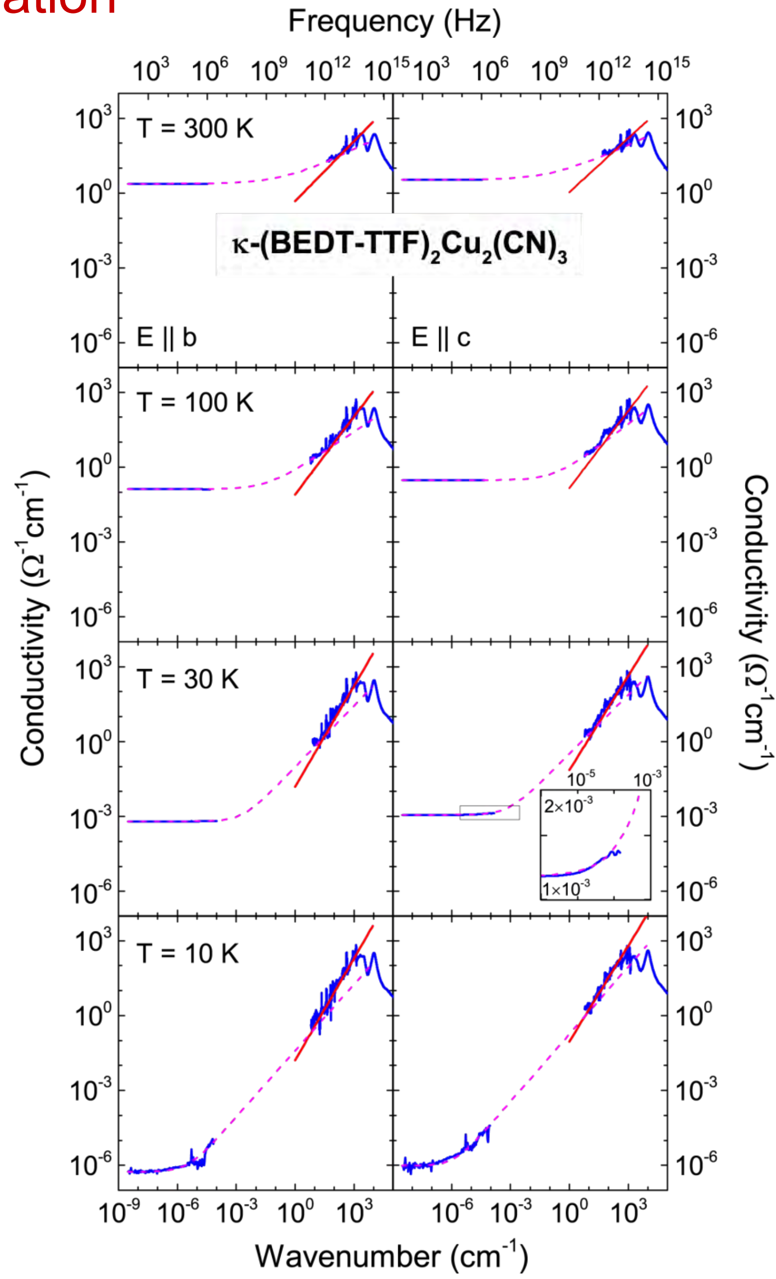

A. Pustogow et al., unpublished

Mott Insulators on Triangular Lattice

correlation and frustration

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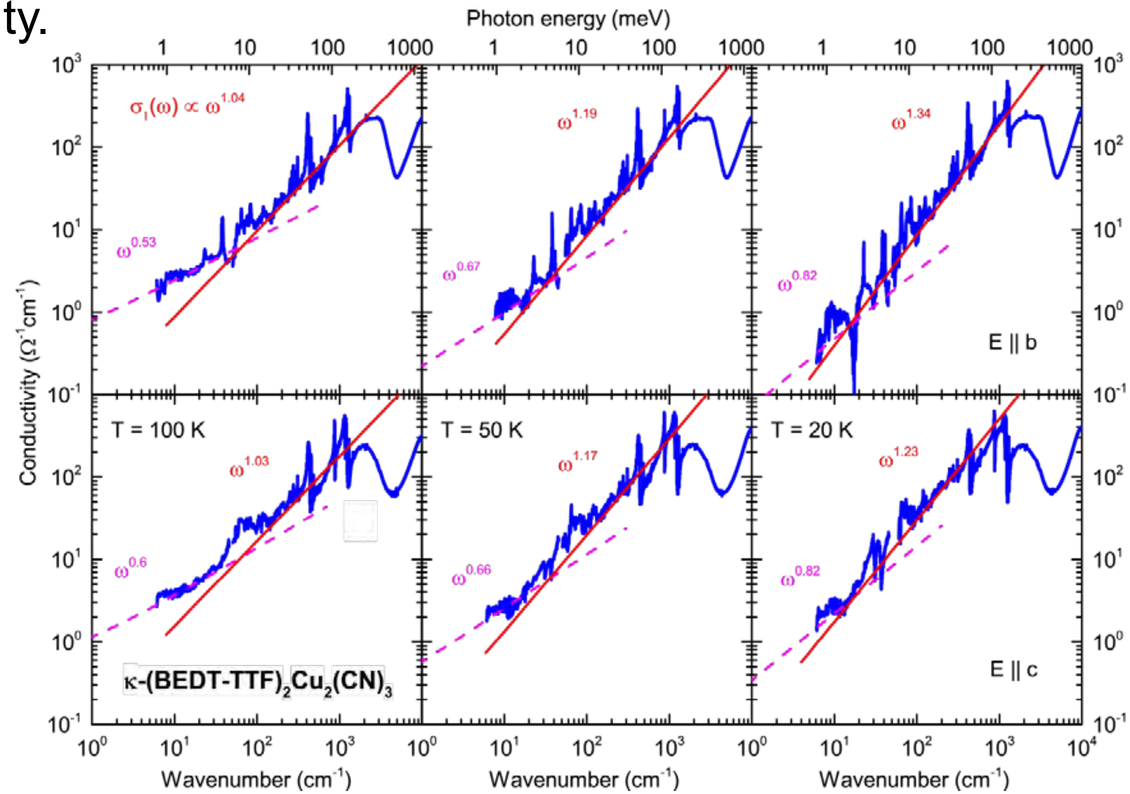
- $\sigma_1(\omega)$ increases upon cooling
- finite conductivity down to $\omega = 0$
  that becomes larger as T decreases.
- $\sigma(\omega \to 0) = 0$
  in accord with the high resistivity.
- **power-law behavior**
  $\sigma(\omega) \propto \omega^n$
  with crossover at $\hbar\omega = k_B T$
  due to spinon excitations.



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Mott Insulators on Triangular Lattice

correlation and frustration

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- $\sigma(\omega\rightarrow 0) = 0$
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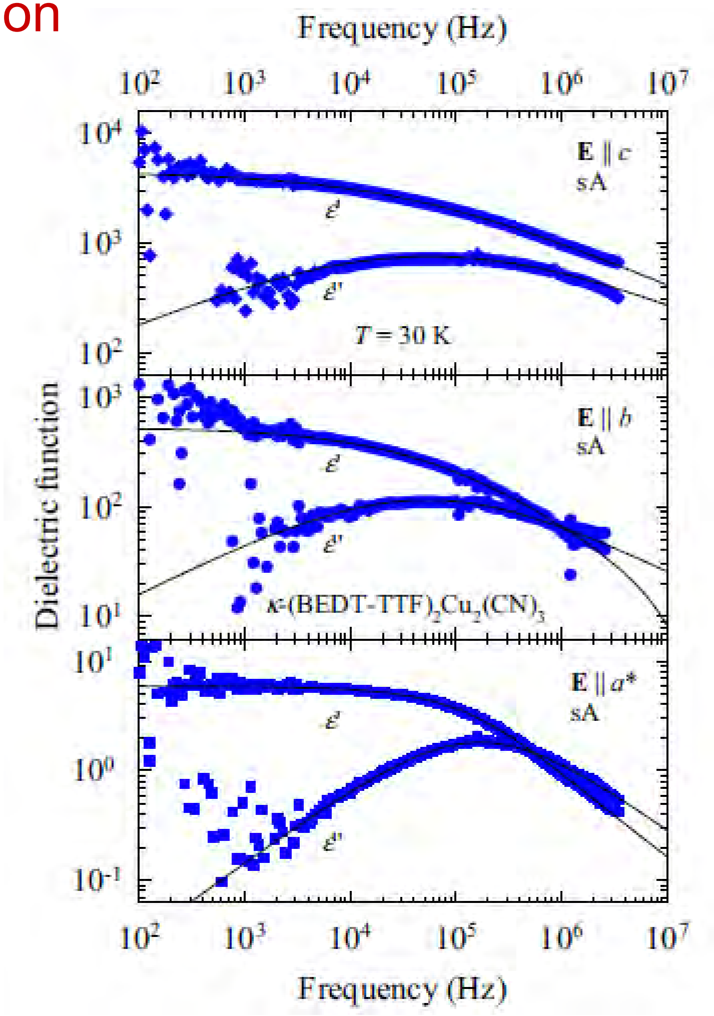
- **intense dielectric response**
  that becomes stronger at low temperatures
  and is present in all three directions.

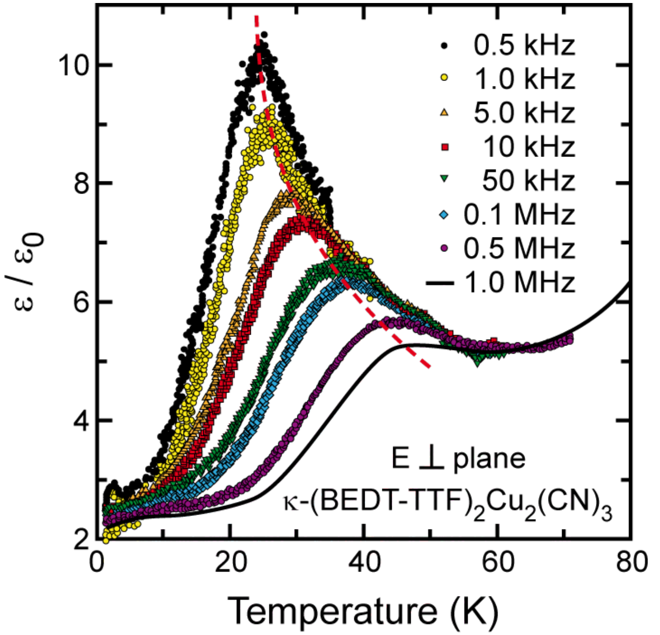


M. Pinterić et al., Phys. Rev. B **90**, 195139 (2014)

Mott Insulators on Triangular Lattice

correlation, frustration and disorder

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$



- **intense dielectric response** that becomes stronger at low temperatures and is present in all three directions.
- strongly **resembles relaxor ferroelectrics**

Where does disorder come from?
Where are the dipoles?

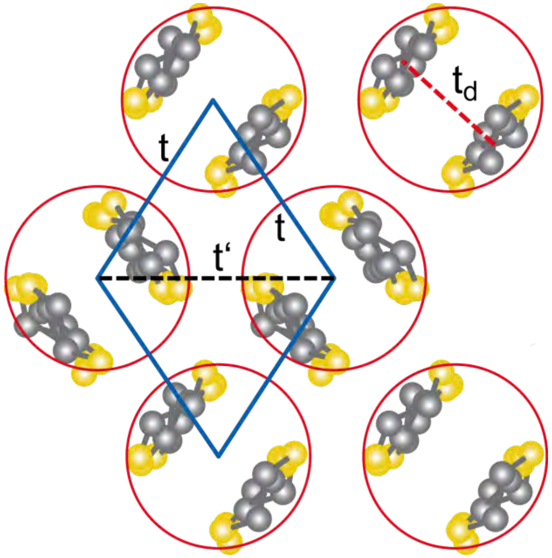
M. Abdel-Jawad et al., Phys. Rev. B **82**, 125119 (2010)
M. Pinterić et al., Phys. Rev. B **90**, 195139 (2014)

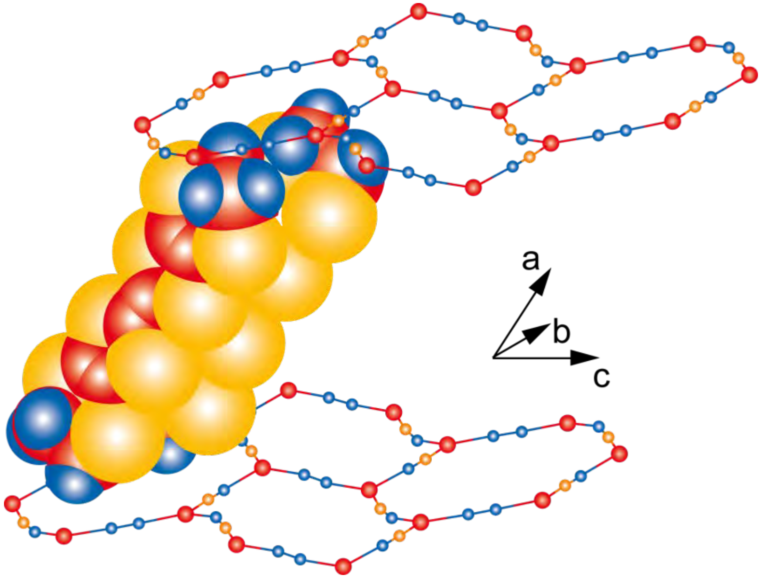
Mott Insulators on Triangular Lattice

correlation, frustration and disorder

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- electrodynamics takes place in BEDT-TTF layers
- coupled to anion network via ethylene endgroups



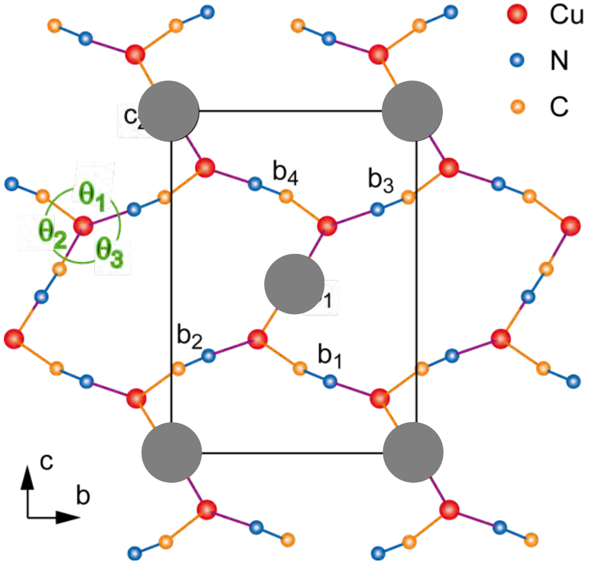


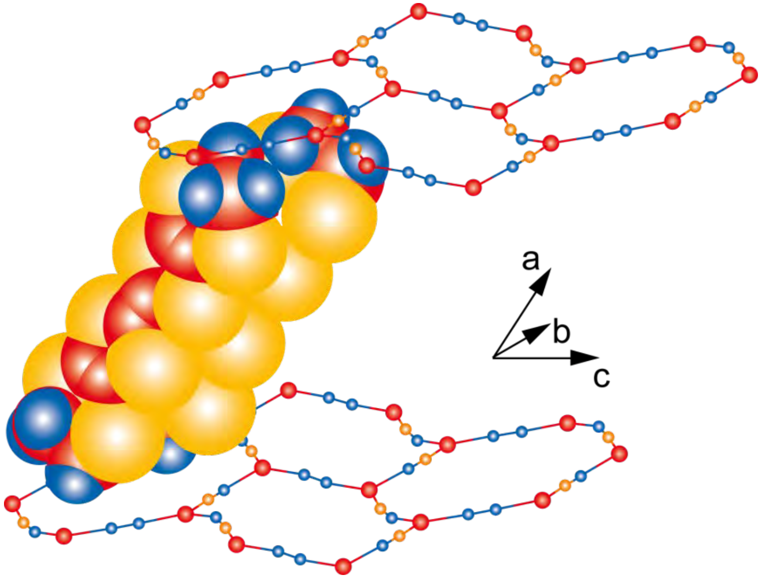
Mott Insulators on Triangular Lattice

correlation, frustration and disorder

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- electrodynamics takes place in BEDT-TTF layers
- coupled to anion network via ethylene endgroups
- symmetry group P2$_1$ with **inversion centers**





Mott Insulators on Triangular Lattice

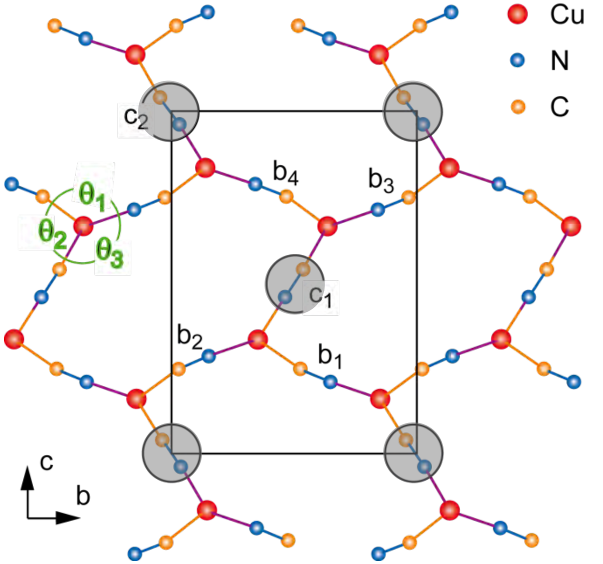
correlation, frustration and disorder

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- electrodynamics takes place in BEDT-TTF layers
- coupled to anion network via ethylene endgroups
- reduce symmetry locally to **P1**
- cyanide groups link each copper to three neighbors

Cu – CN – Cu   **Cu – NC – Cu**

- cyanide isomorphism causes **disorder**



Mott Insulators on Triangular Lattice

correlation, frustration and disorder

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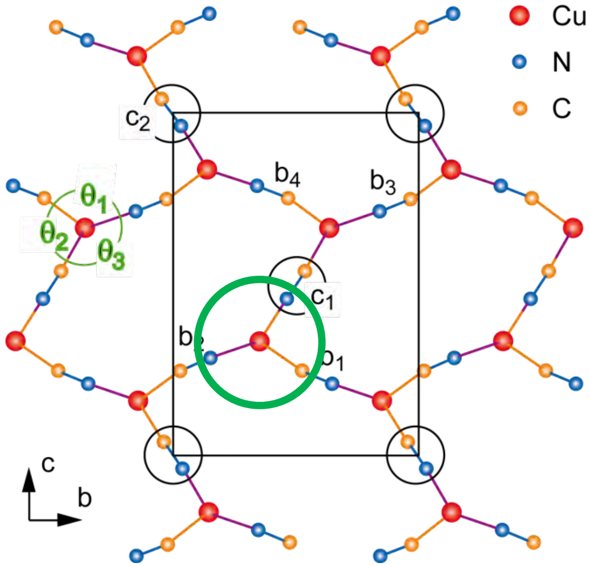
- cyanide groups link each copper to three neighbors



$\theta_1 \approx \theta_2 \approx \theta_3 \approx 120°$

Cu – CN – Cu **Cu – NC – Cu**

- cyanide isomorphism causes **disorder**

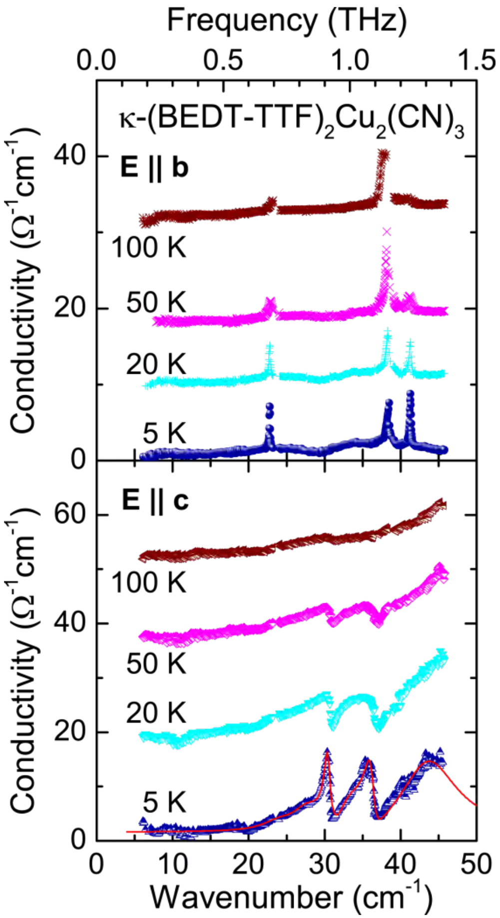
- copper linkages are **frustrated**

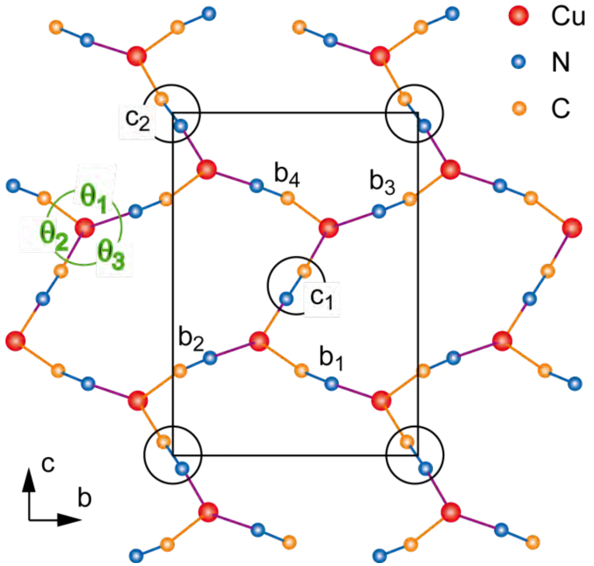
Mott Insulators on Triangular Lattice

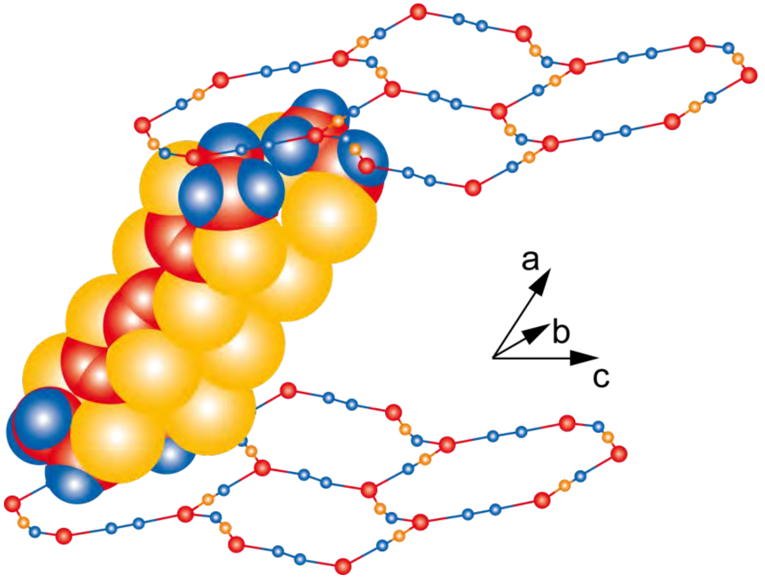
lattice dynamics

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- strong dipole moment of cyanide
- low-frequency lattice vibrations of cations coupled to anions







Mott Insulators on Triangular Lattice

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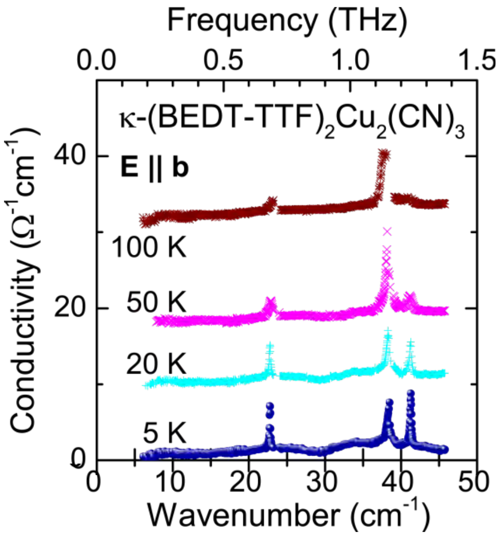
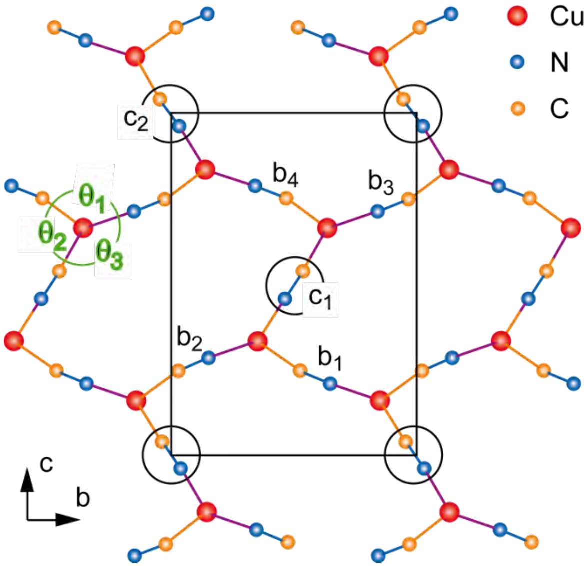
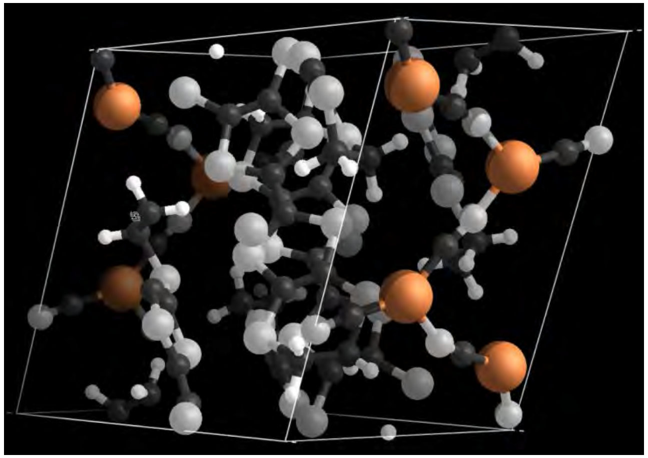




***Ab-initio* phonon calculations**
based on density-functional-theory (DFT).



Mott Insulators on Triangular Lattice

lattice dynamics

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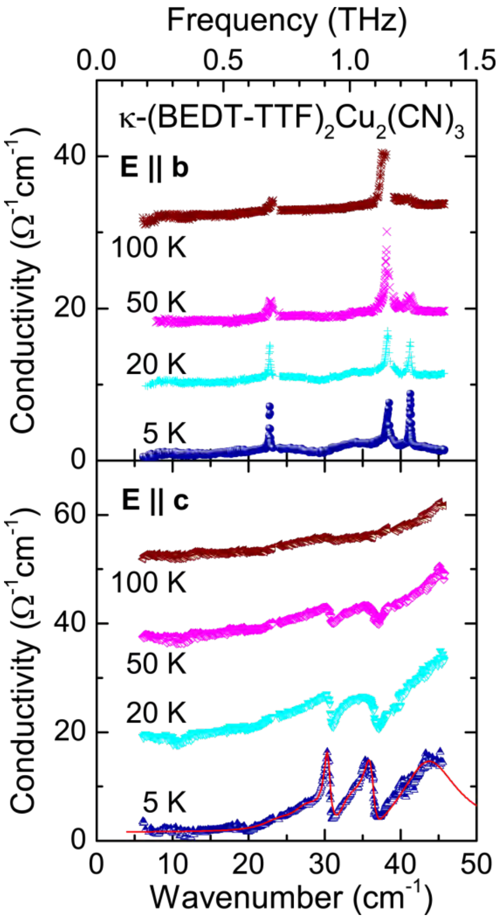
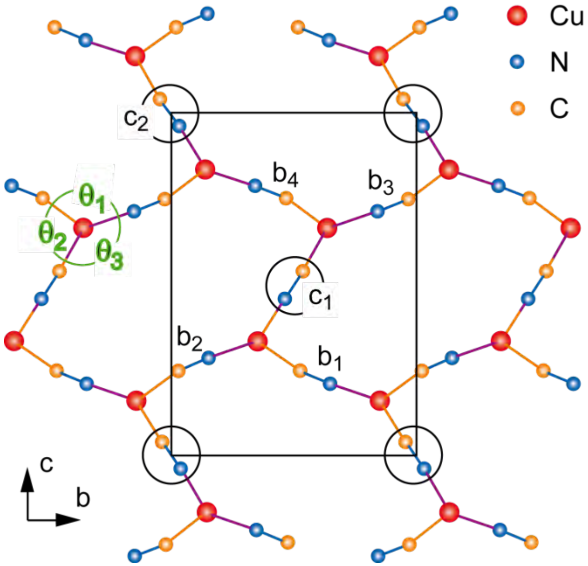




Mode	E || b		E || c	
#	calc.	exp.	calc.	exp.
4	24.3	22.7		
5			33.3	31.2
8			37.8	37.0
9	38.2	38.4		
12	41.0	41.3		

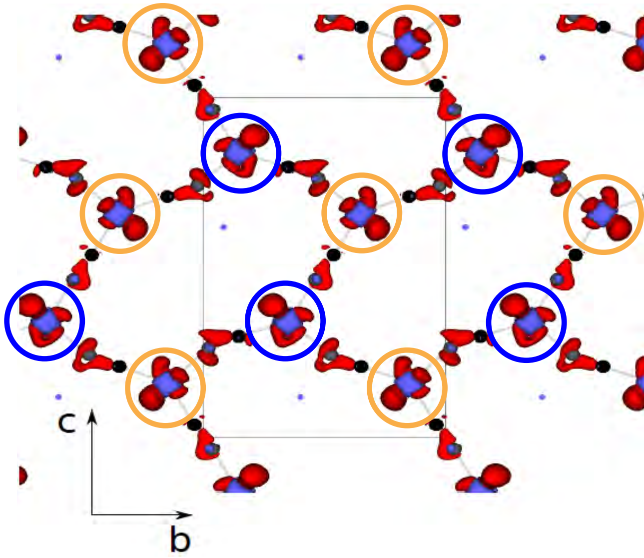
Mott Insulators on Triangular Lattice

frustration and disorder

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

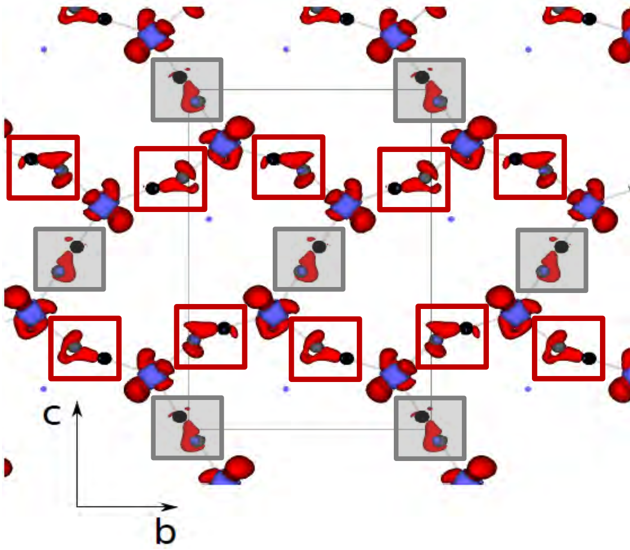
- strong dipole moment of cyanide
- low-frequency lattice vibrations of cations coupled to anions

- **DFT calculations**: charge distribution induced by cation-anion interaction
- different electron concentration at Cu sites:



Mott Insulators on Triangular Lattice

frustration and disorder



κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- strong dipole moment of cyanide
- low-frequency lattice vibrations of cations coupled to anions

- **DFT calculations**: charge distribution induced by cation-anion interaction
- different electron concentration at Cu sites:

- different electron concentration at cyanide sites:
  CN along b-direction
  CN along c-direction

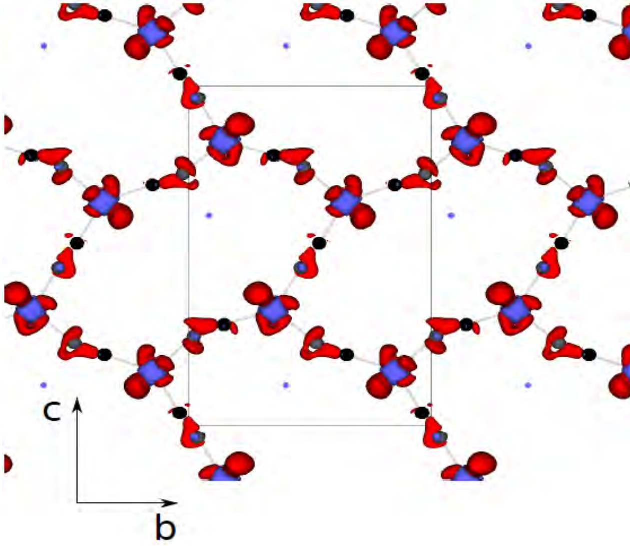
Mott Insulators on Triangular Lattice

frustration and disorder

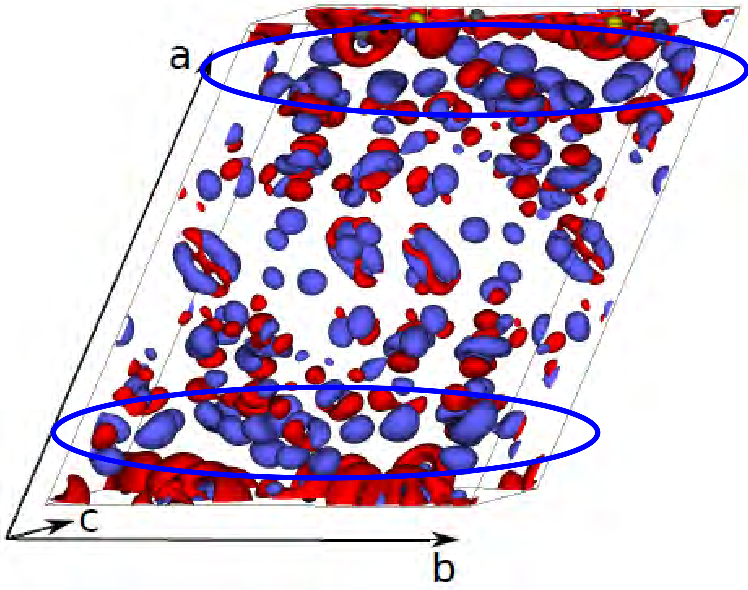
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- strong dipole moment of cyanide
- low-frequency lattice vibrations of cations coupled to anions

- **DFT calculations**: charge distribution induced by cation-anion interaction



- BEDT-TTF molecules donate electrons via the hydrogen bonds to anion sheets



Metal-Insulator Transition on Triangular Lattice

summary

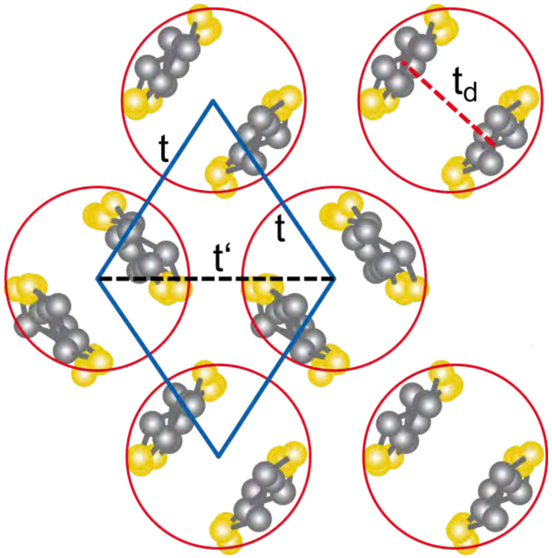
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

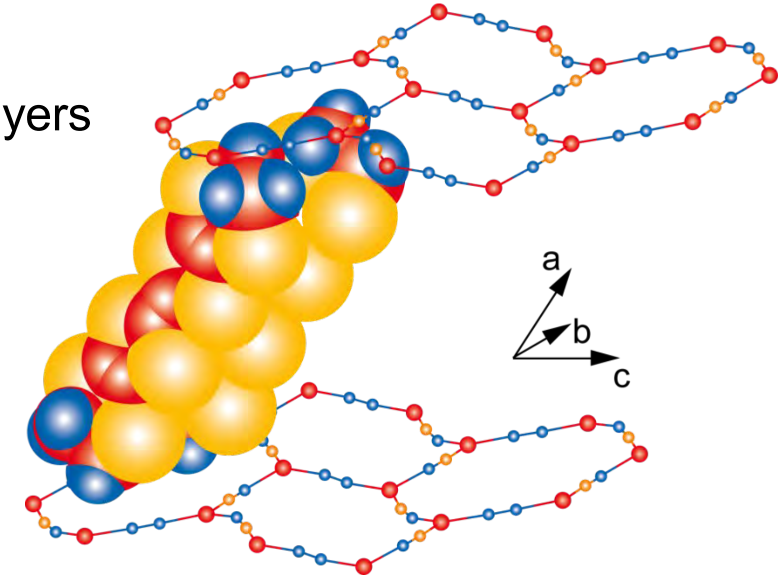
- Mott insualtor with half-filled conduction band
- highly frustrated lattice
- no magnetic order

- relaxor ferroelectric like dielectric response
- no charge disproportionation and dipole on the dimers

- strong lattice vibrations

- disorder and frustratioon in anion network with dipole moments
- coupling of anion sheets to the BEDT-TTF layers sceening by charges on organic molecules





M. Dressel, J. Phys.: Cond. Matter **23**, 293201 (2011)