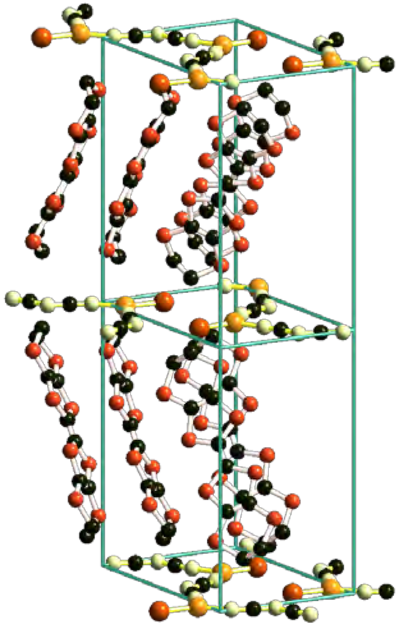
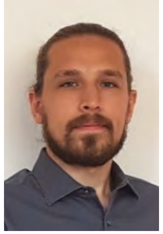
Molecular metals – test ground for correlated electrons in a compressible lattice



Michael Lang
Goethe-Universität Frankfurt

Collaborators







E. Gati*, B. Wolf, U. Tutsch, H. Schubert, J. Müller
Physikalisches Institut, Goethe-Universität Frankfurt, SFB TR49
*Ames Lab, Iowa State University, USA

M. Garst
Institut für Theoretische Physik, Universität zu Köln und TU Dresden
Institut für Theoretische Physik, Universität Karlsruhe

J. Fischer, P. Lunkenheimer, H.-A. Krug von Nidda, F. Kolb,
Exp. Phys. V, Augsburg University

M. Matsuura, A. Nakao
Neutron Science and Technology Center, Tokai, Japan

T. Sasaki, S. Iguchi
IMR, Tohoku University, Sendai, Japan

O. Stockert
MPI CPfS Dresden, Germany

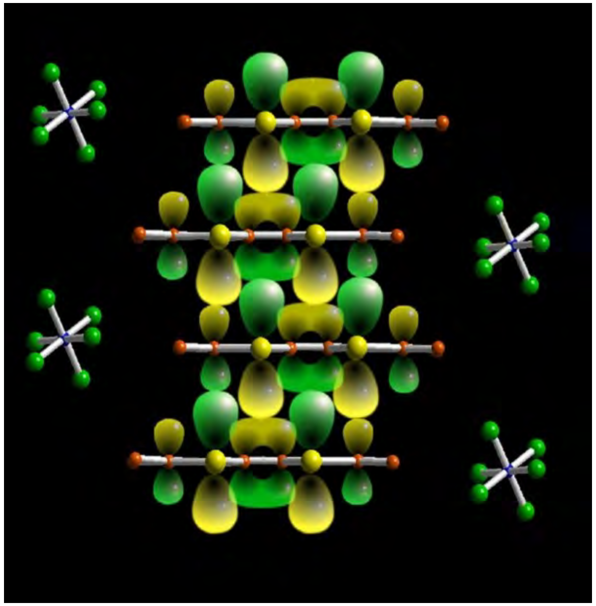
R. Valentí, S. Winter, S. Biswas
Institut für Theoretische Physik, Goethe-Universität Frankfurt

H. Jeschke
Institut für Theoretische Physik, Goethe-Universität Frankfurt and
Research Inst. for Interdiscipl. Science, Okayama University, Japan

J.A. Schlueter
Materials Science Division, Argonne National Laboratory, USA

Building blocks

e.g. $(TMTSF)_2PF_6$



- Weak intermolecular overlap: small *W* (~ ***U***)

- Low dimensionality
- Small charge carrier concentration

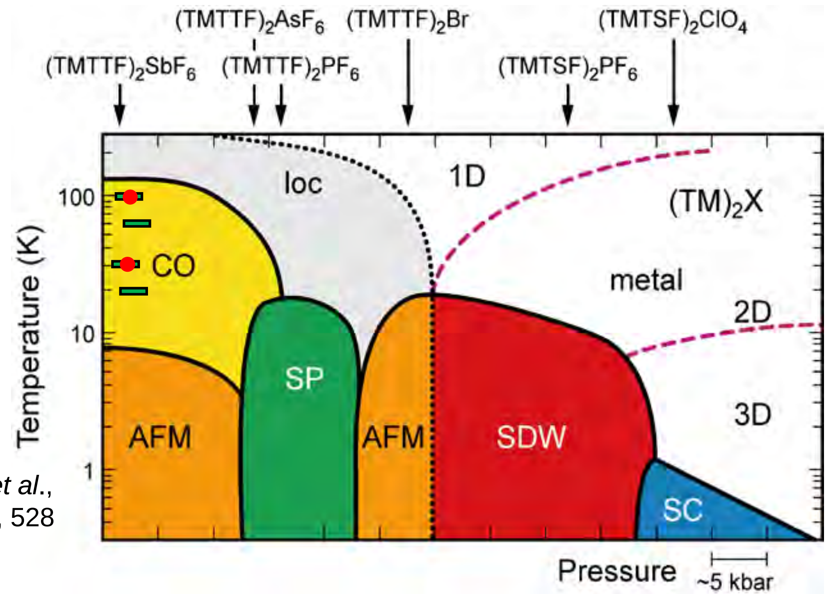
} favourable for long-range Coulomb interactions (~ ***V***)

$\Rightarrow$ strongly correlated (*U* + *V*) π-electrons

$\Rightarrow$ soft lattice (compressibility $> 10 \cdot \kappa_T^{Cu}$)

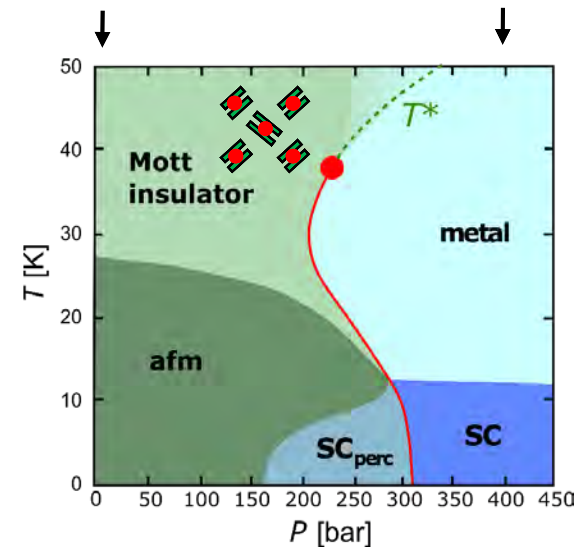
Phase diagrams

$(TM)_2X$



Dressel *et al.*, Crystal **2**, 528 (2012)

κ-(BEDT-TTF)$_2$X ("κ-X")



Kanoda, Physica C **287**, 299 (1997)

⇒ Test grounds for studying correlated electrons under well-controlled conditions

⇒ Systematic investigations on fundamental aspects of correlation physics

Outline

1) Fundamental aspects of the Mott transition in κ-$(ET)_2Cu[N(CN)_2]Cl$
   – involvement of lattice degrees of freedom

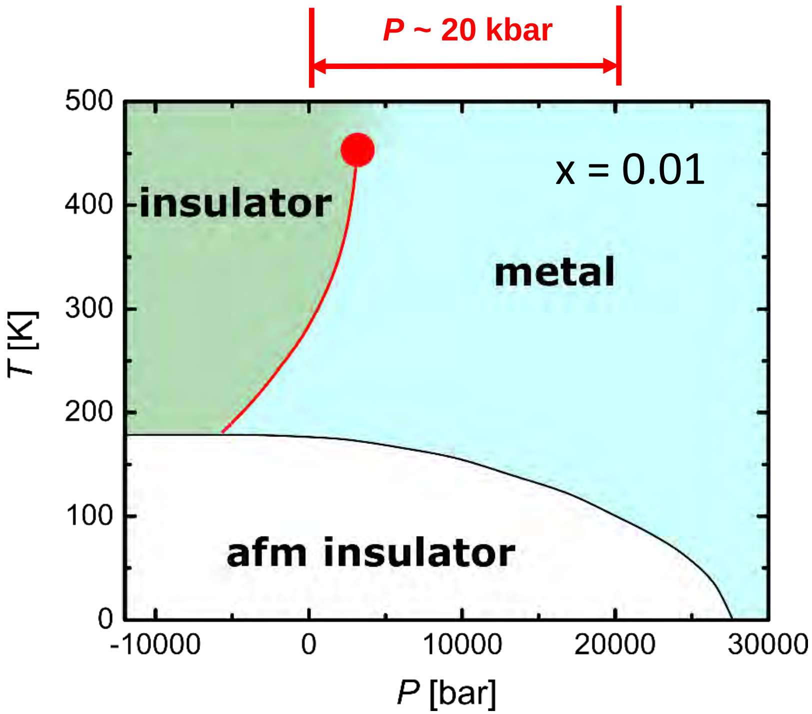
2) Signatures of ferroelectricity/multiferroicity in κ-$(ET)_2Cu[N(CN)_2]Cl$
   – open issues

3) The case of κ-$(ET)_2Hg(SCN)_2Cl$
   – a proof-of-principle demonstration for ferroelectricity in dimerized $(ET)_2X$

4) Phonon anomalies in κ-$(ET)_2Cu[N(CN)_2]Cl$
   – coupling to intra-dimer electronic degrees of freedom

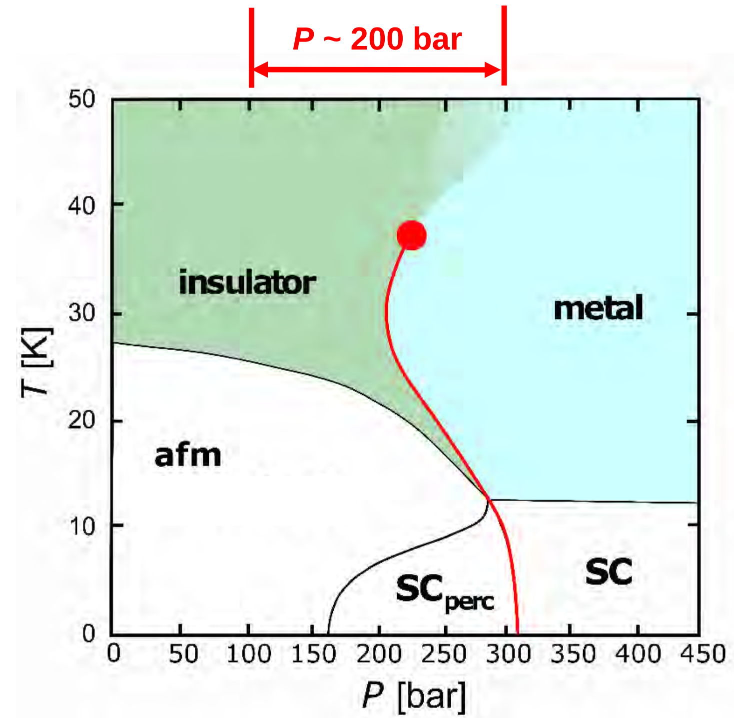
Materials on the verge of the Mott transition

$(V_{1-x}Cr_x)_2O_3$



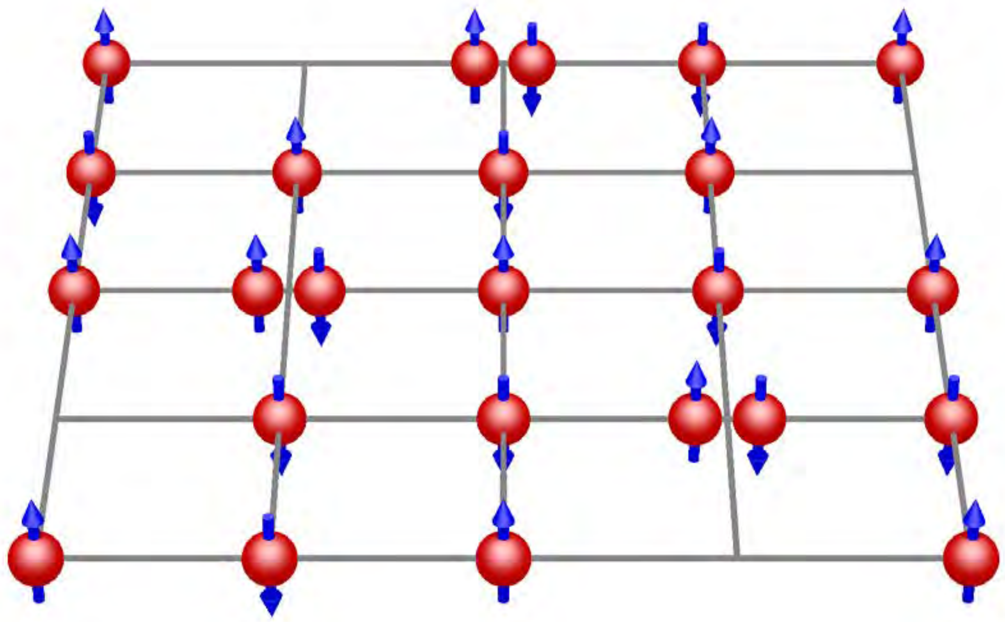
Cf. McWham *et al.*, PRB **7**, 1920 (73)
Limelette *et al.*, Science **302**, 89 (03)
Georges *et al.*, J. Phys. **114**, 165 (04)

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl ("κ-Cl")



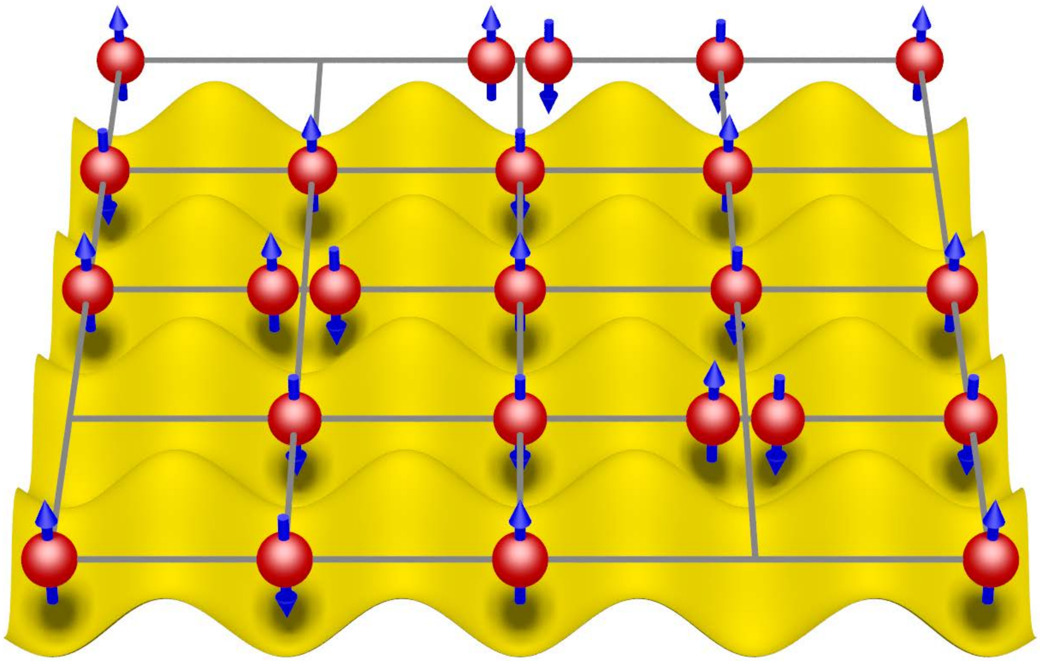
Cf. Lefebvre *et al.*, PRL **85**, 5420 (00)
Limelette *et al.*, PRL **91**, 016401 (03)
Fournier *et al.*, PRL **90**, 127002 (03)
Kagawa *et al.*, PRB **69**, 064511 (04)

The Mott transition



Purely electronic picture sufficient for real materials?

The Mott transition

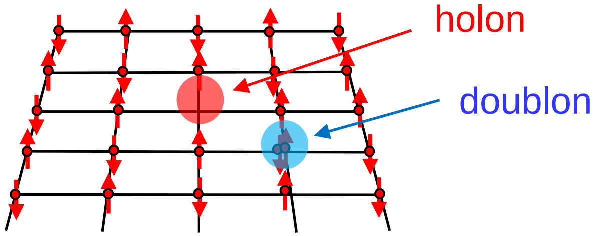


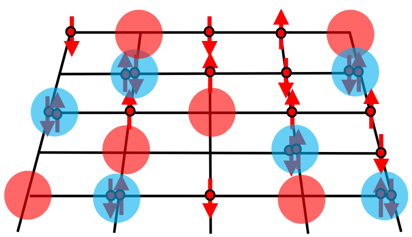
Role of a compressible lattice? (cf. pressure dependence!)

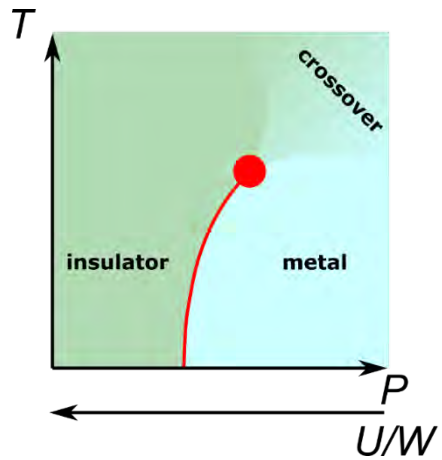
Universal properties?

The Mott transition

Mott metal-insulator transition



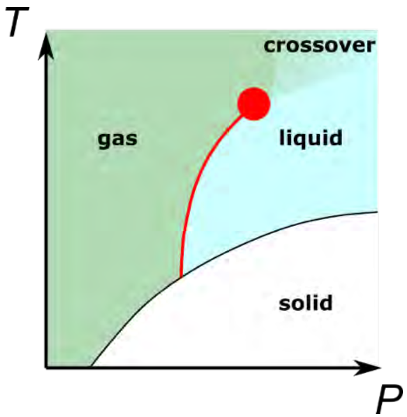




order parameter?

C. Castellani *et al.*, PRL **43**, 1957 (79)
G. Kotliar et al., PRL **84**, 5180 (2000)

Liquid-gas transition

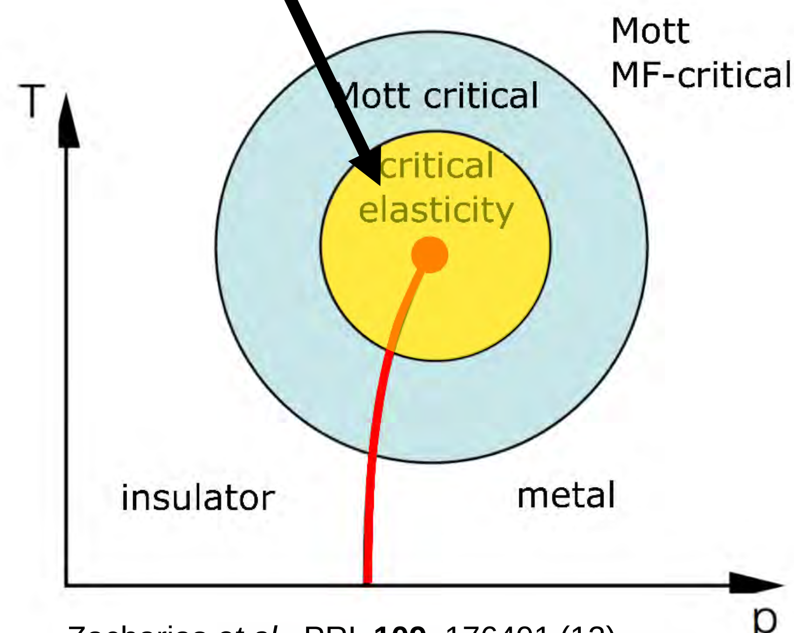


order parameter: ρ

→ **Ising** universality class! (for purely electronic systems)

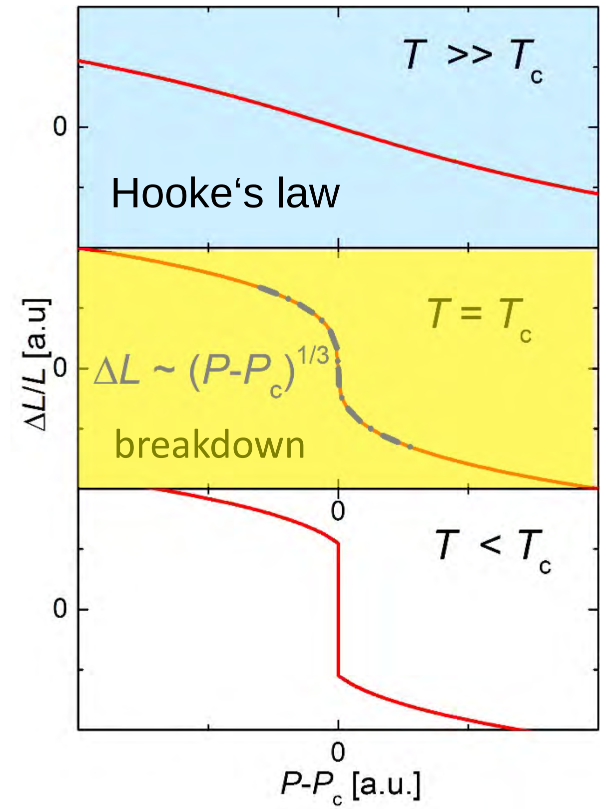
Role of electron-phonon coupling

Non-perturbative electron-phonon-coupling



Zacharias *et al.*, PRL **109**, 176401 (12)
Zacharias *et al.*, Eur. Phys. J. Special Topics 224, 1021 (15)

Breakdown of Hooke's law



long-range shear forces: suppression of microscopic fluctuations
Ising criticality → **Mean-field** criticality

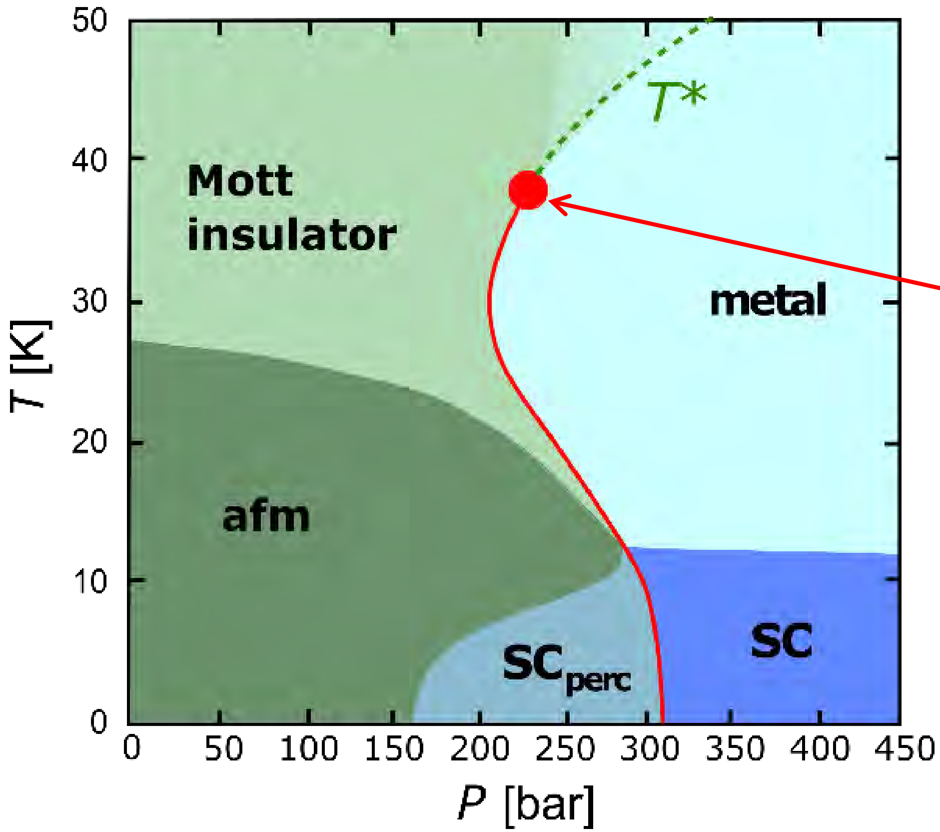
Experimental test

$\Rightarrow$ explore lattice effects $\Delta L/L$ around the Mott transition under control of *T* and *p*!

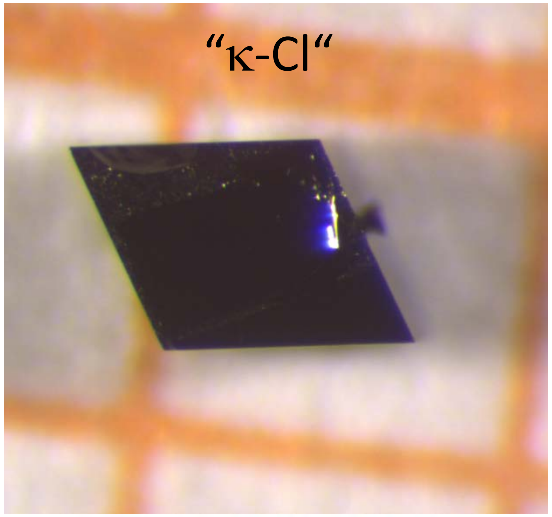
$\Rightarrow$ combine high-resolution dilatometry with He-gas pressure

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl - "κ-Cl"

κ-Cl

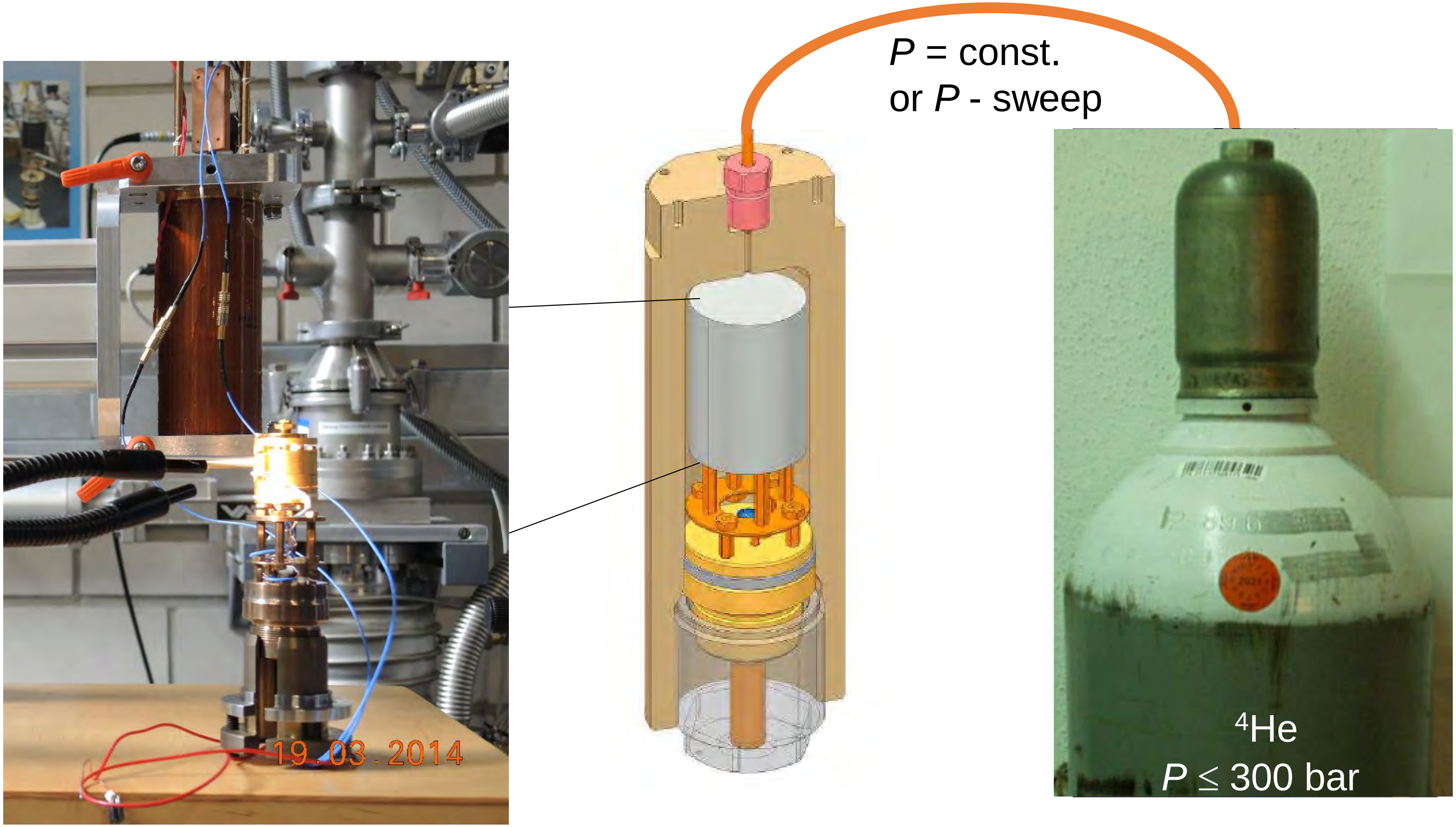


P_c ~ 235 bar
T_c ~ 37 K



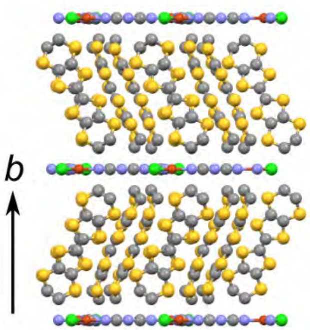
Kanoda, Physica C **287**, 299 ('97)
Lefebvre *et al.*, PRL **85**, 5420 (00)
Limelette *et al.*, PRL **91**, 016401 (03)
Fournier *et al.*, PRL **90**, 127002 (03)
Kagawa *et al.*, PRB **69**, 064511 (04)

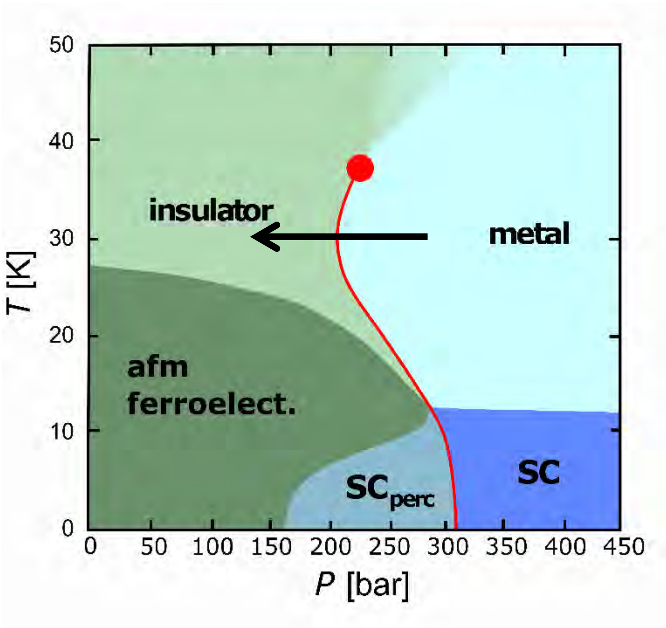
Thermal expansion under He-gas pressure

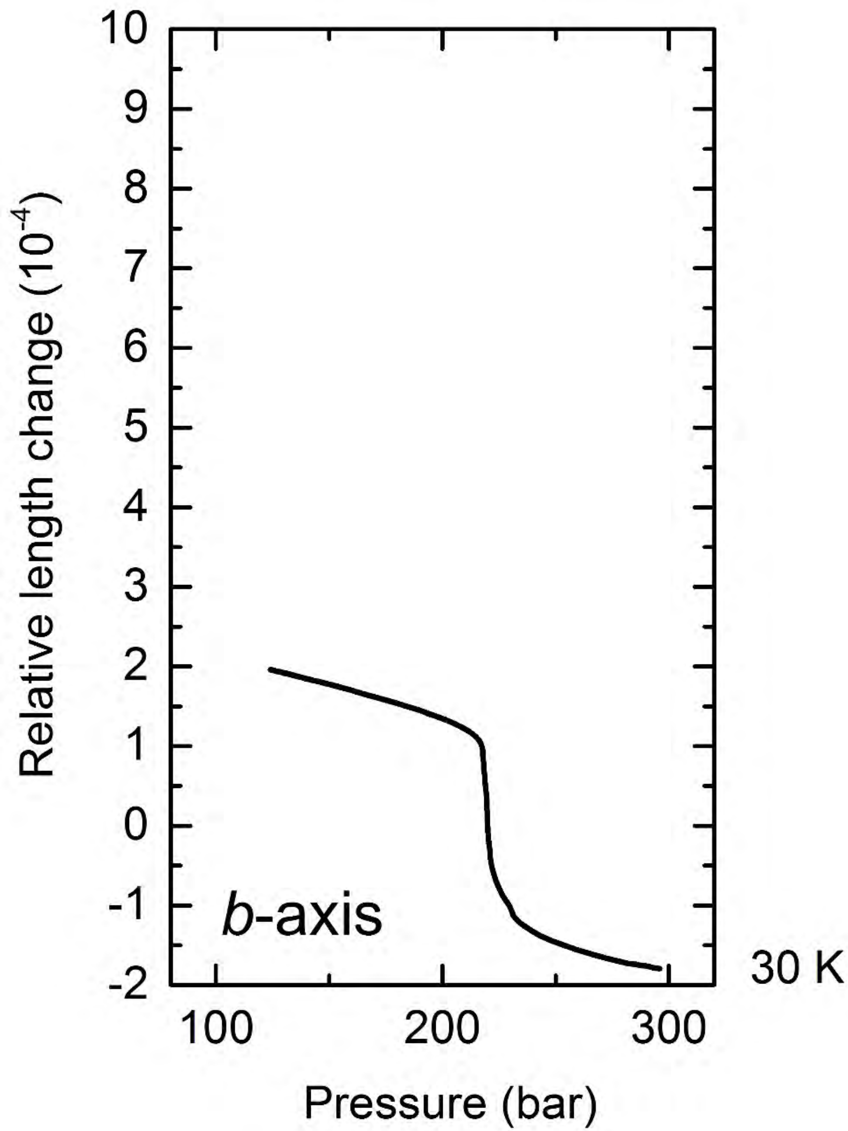


Manna *et al.*, Rev. Sci. Instrum. **83**, 085111 (12)

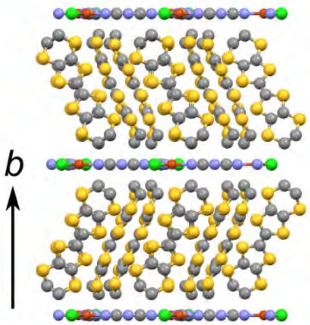
Length change at the Mott transition

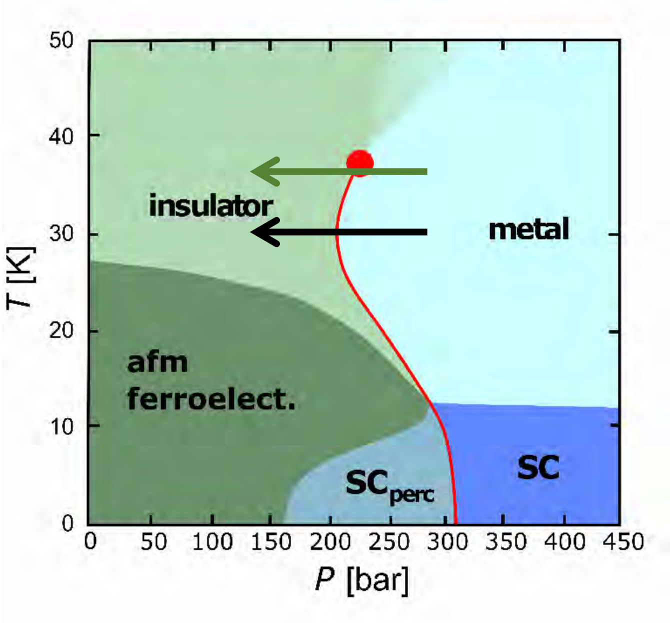


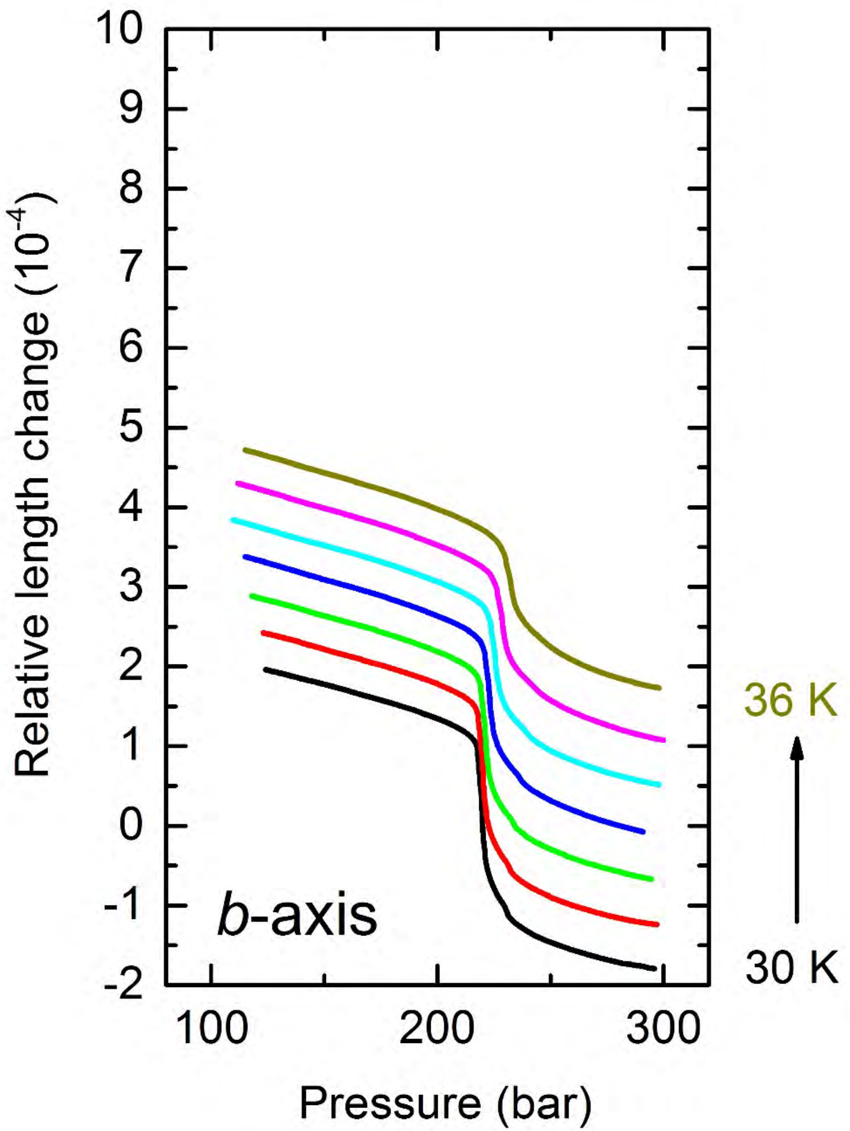




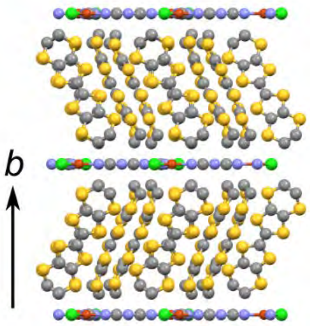
Length change at the Mott transition

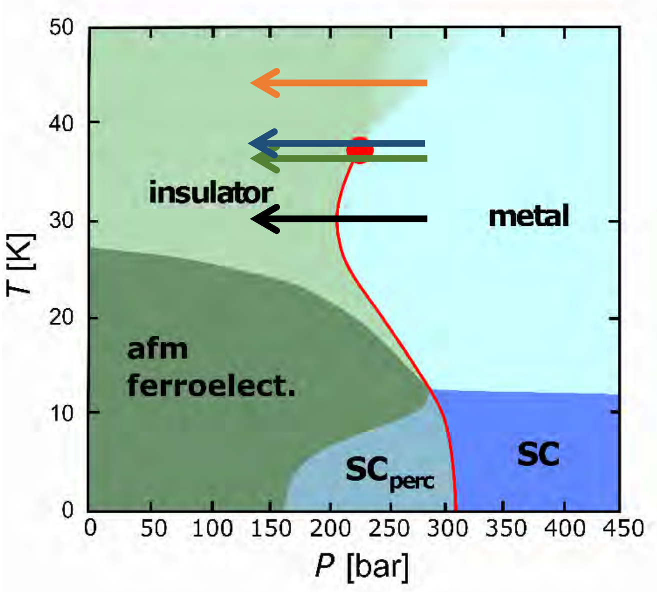


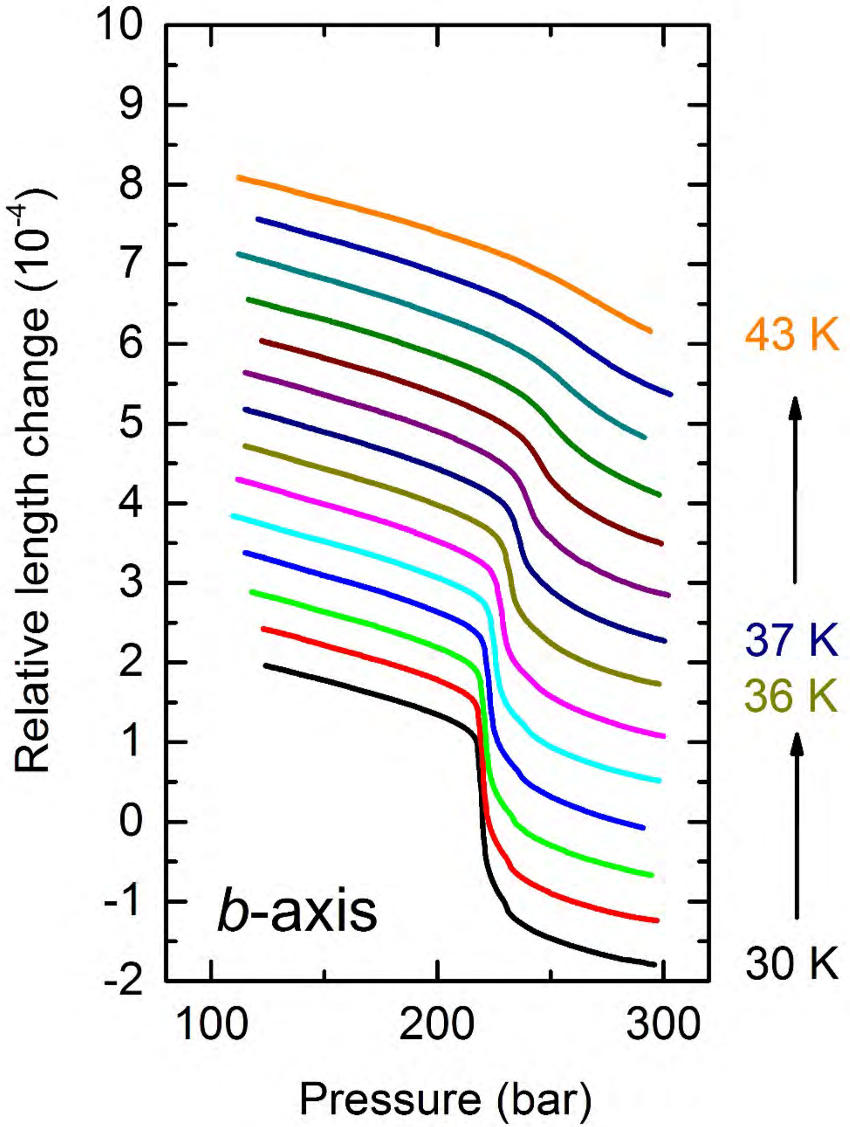




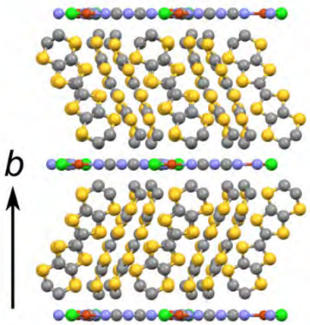
Length change at the Mott transition

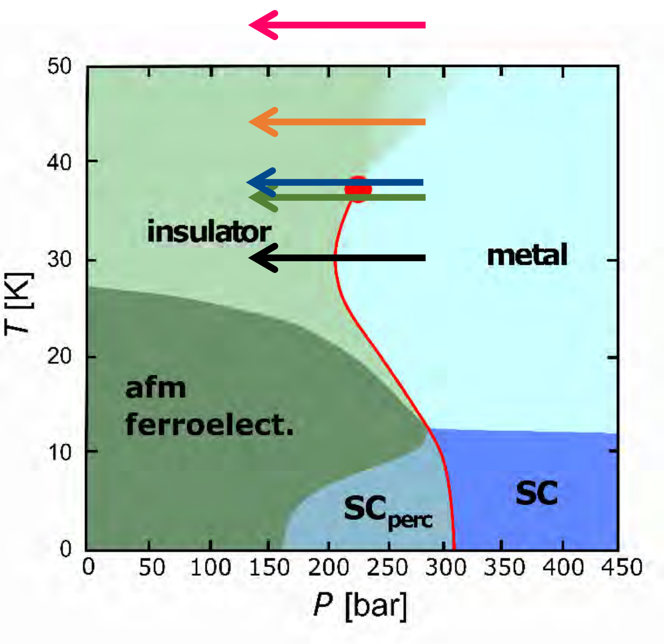


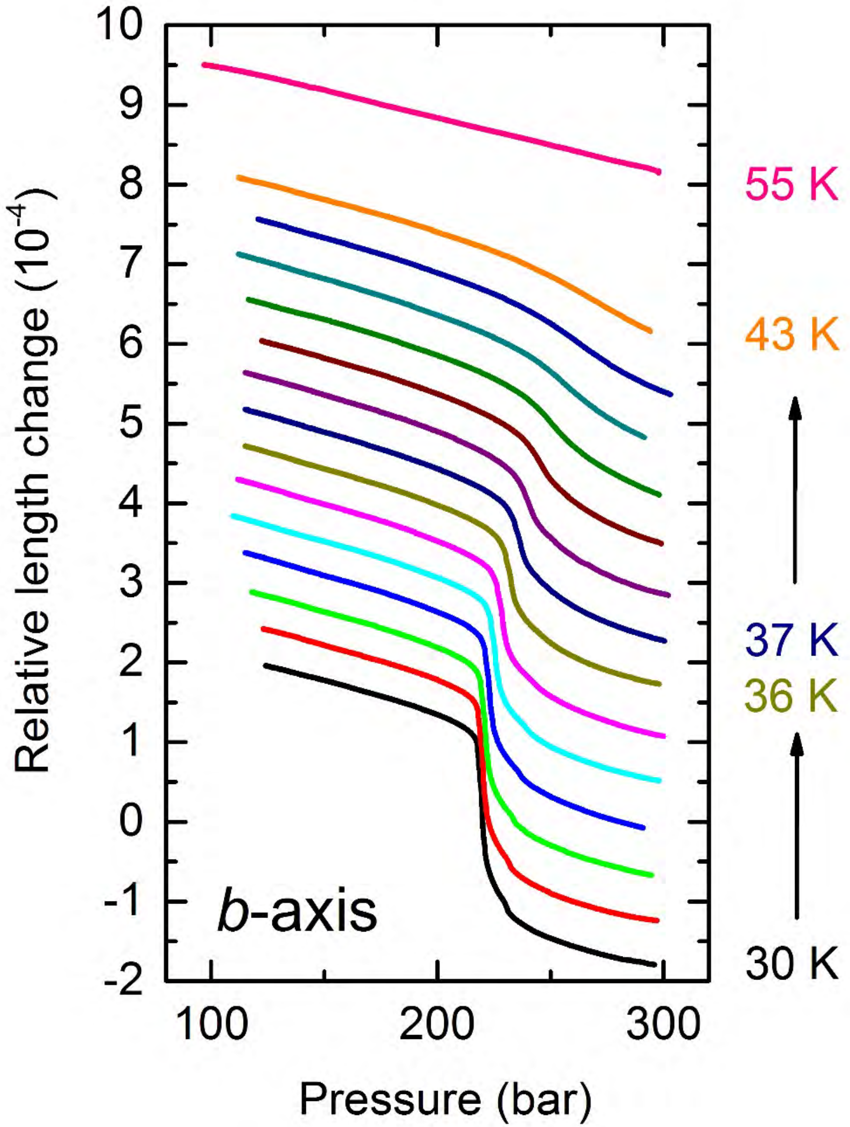




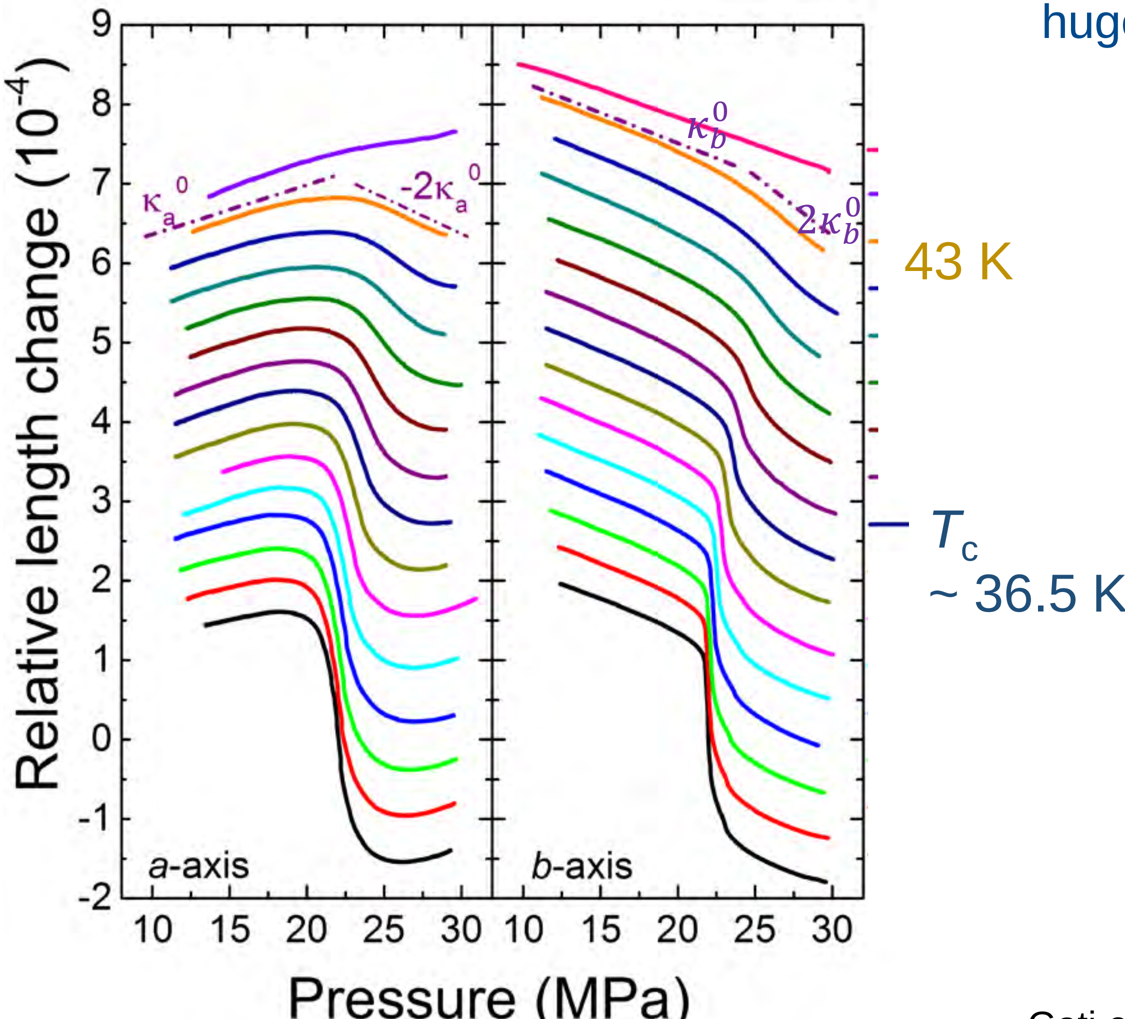
Length change at the Mott transition







Breakdown of Hooke‘s law



huge changes of compressibility

$$\kappa = -\frac{1}{L} \cdot \frac{dL}{dp}$$

over

$$\frac{\Delta T}{T_c} \leq 20\ \%$$

$$\frac{\Delta p}{p_c} \leq 10\ \%$$

Cf. Ultrasonic measurements:
Fournier et al., PRL **90**, 127002 (03)

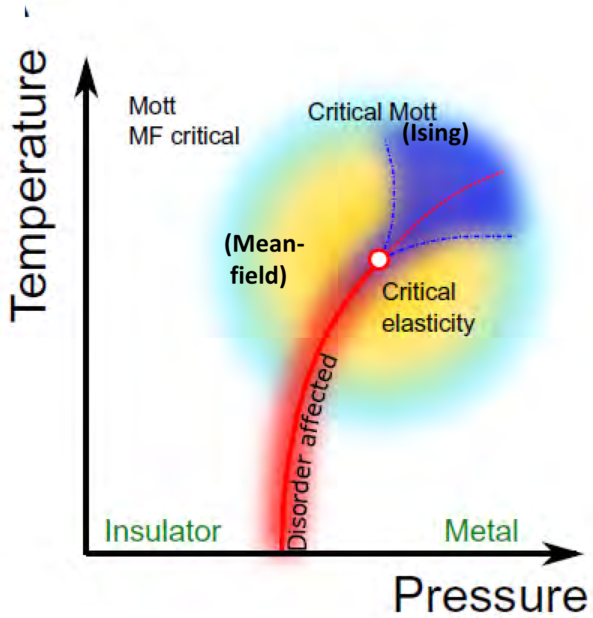
Gati *et al.*, Science Advances **2**, e1601646 (16)

Implications

$\Rightarrow$ Observations ($|\Delta\kappa| \sim \kappa$) consistent with

"critical elasticity"

i.e., a strong coupling of
electrons $\Leftrightarrow$ compressible lattice



$\Rightarrow$ Suggesting

$\rightarrow$ intriguing cross-correlations
$\rightarrow$ new functionalities !?

$\Rightarrow$ Relevant for any pressure-tuneable Mott system
$\rightarrow$ κ-(BEDT-TTF)$_2X$, Et$_x$Me$_{4x}Z$[Pd(dmit)$_2$]$_2$, …
$\rightarrow$ $(V_{1-x}M_x)_2O_3$, NiO, PbCrO$_3$, …

Outline

1) Fundamental aspects of the Mott transition in κ-$(ET)_2Cu[N(CN)_2]Cl$
– involvement of lattice degrees of freedom

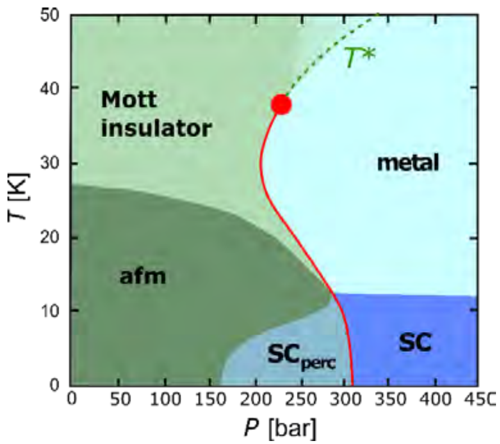
2) Signatures of ferroelectricity/multiferroicity in κ-$(ET)_2Cu[N(CN)_2]Cl$
– open issues

3) The case of κ-$(ET)_2Hg(SCN)_2Cl$
– a proof-of-principle demonstration for ferroelectricity in dimerized $(ET)_2X$

4) Phonon anomalies in κ-$(ET)_2Cu[N(CN)_2]Cl$
– coupling to intra-dimer electronic degrees of freedom

Ferroelectricity in κ-$(ET)_2Cu[N(CN)_2]Cl$

"κ-Cl"



~ 60 K

$T_\sigma \approx T_N$

See also

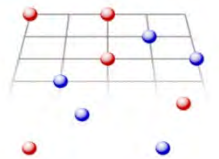
H. Ito *et al.*, JPSJ **65**, 2987 (1996)

M. Dressel *et al.*, Synth. Met. **70**, 927 (1995)

P. Lunkenheimer *et al.*, Nature Mater. **11**, 755 (2012)

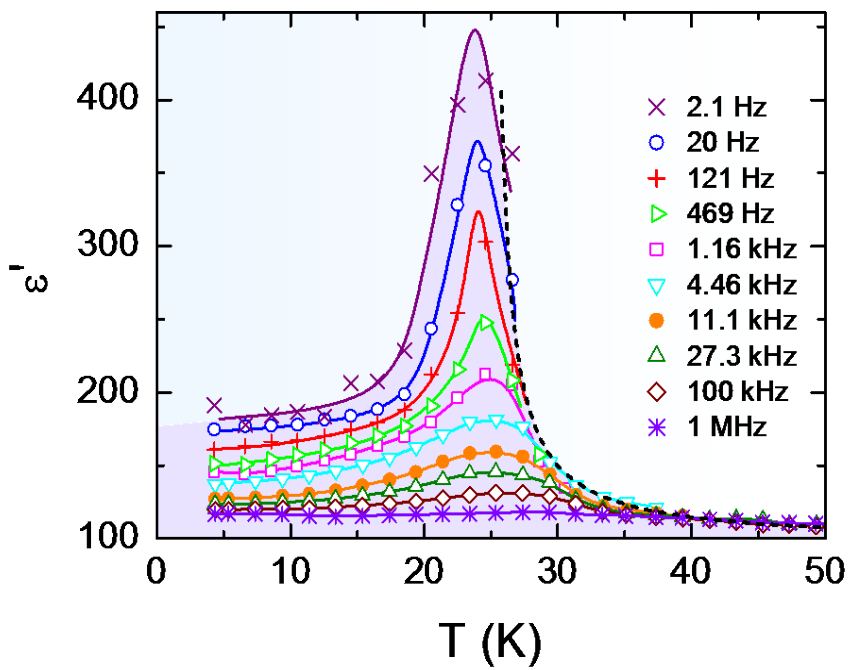
Drop in σ' around 26 K:

- partial charge localization (charge-order) !?
- coinciding with T_N



Ferroelectricity in κ-$(ET)_2Cu[N(CN)_2]Cl$

GOETHE UNIVERSITÄT
FRANKFURT AM MAIN

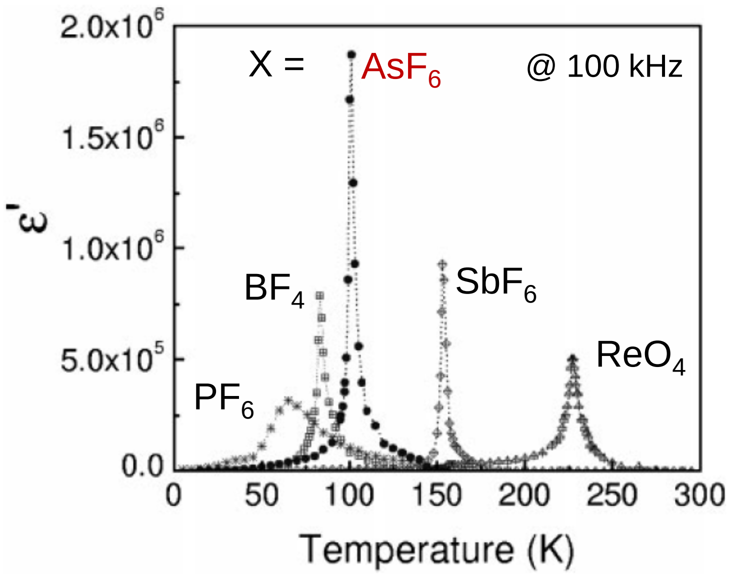


P. Lunkenheimer *et al.*,
Nature Mater. **11**, 755 (2012)

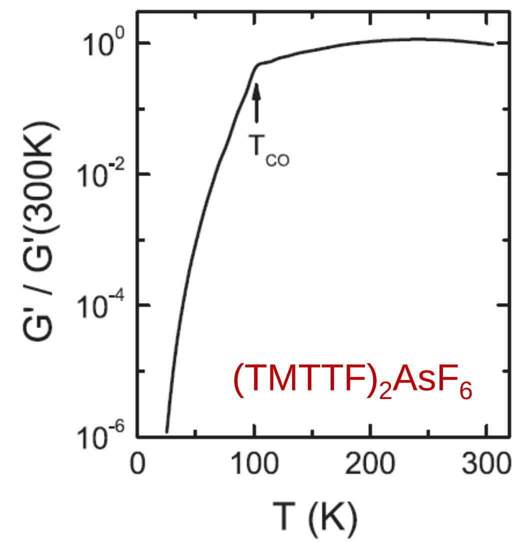
⇒ order-disorder type ferroelectric order coinciding with T_N !

⇒ multiferroic !

Ferroelectricity in quasi-1D $(TMTTF)_2X$



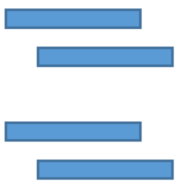
Nad *et al.*, J. Phys. Condens. Matt. **12**, L435 (2000)



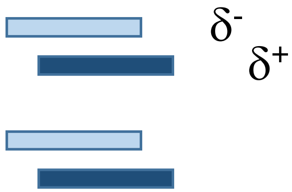
Nad, Monceau, JPSJ **75**, 051005 (2006)

charge-order transition at T_{co} : $U + V$

$T > T_{CO}$



$T < T_{CO}$



Theor. prediction:

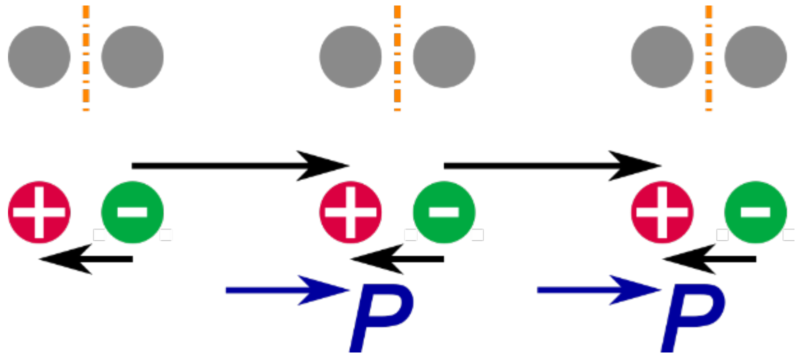
Seo, Fukuyama
JPSJ **66**, 1249 (1997)

Experiment:

Chow *et al.*,
PRL **85**, 1698 (2000)

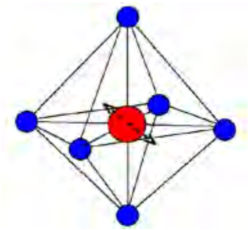
CO-driven ferroelectricity

Van den Brink, Khomskii
J. Phys. Cond. Matt.
20, 434217 (2008)

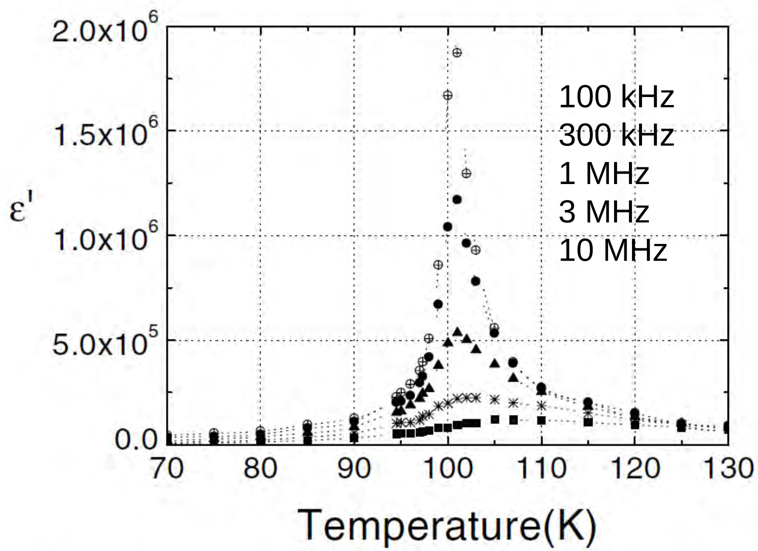


$\Rightarrow$ electronic ferroelectricity

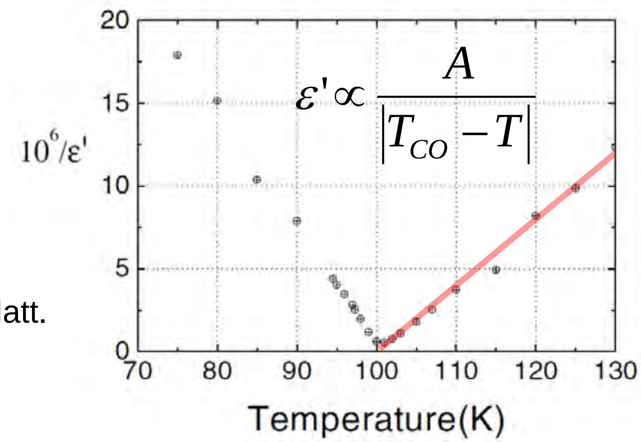
Cf. displacive ferroelectrics:

off-center motion of ions in  e.g., Ti in $BaTiO_3$

Dielectric response in $(TMTTF)_2AsF_6$



F. Nad *et al.*,
J. Phys. Cond. Matt.
12, L435 (2000)

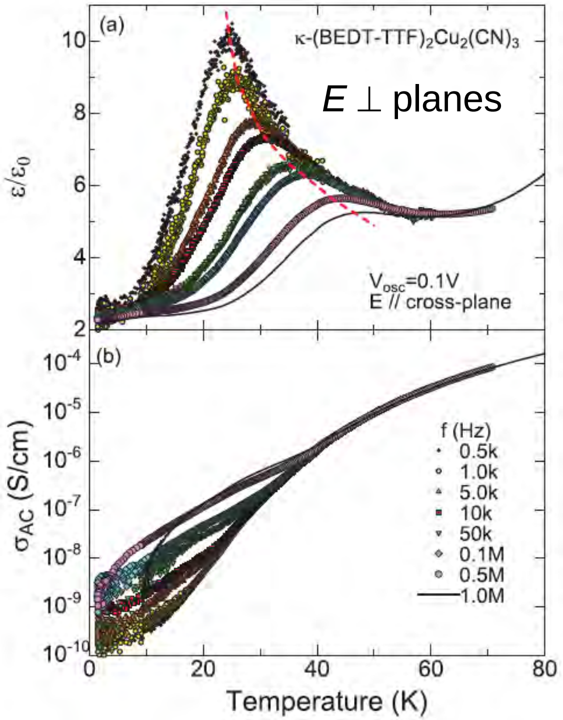


→ same phenomenology found for κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$!

Order-disorder-type ferroelectricity

↑ ↑ ↑ ↑ ← *cooling* ↗ ↖ ↘ ↗

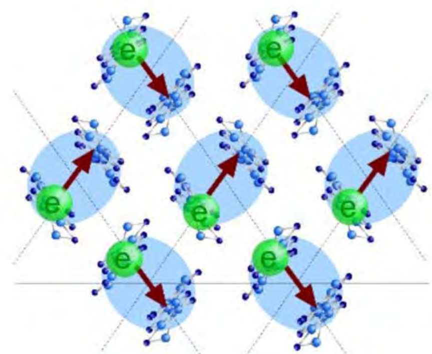
Dielectric anomalies in κ-$(ET)_2Cu_2(CN)_3$



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

relaxor ferroelectricity

Assigned to “*intra*-dimer degrees of freedom“



C. Hotta, Phys. Rev. B **82**, 241104(R)(2010)

M. Naka, S. Ishihara, J. Phys. Soc. Jpn. **79**, 063707 (2010)

T. Clay *et al*., Physica B **405**, S253 (2010)

H. Gomi *et al*., Phys. Rev. B **87**, 195126 (2013)

Problem: no spectroscopic evidence for charge disproportionation $\delta > 0.005\ e$!

K. Sedlmeier *et al*., PRB **86**, 245103 (2012)

Dielectric anomalies in dimerized $(ET)_2X$

GOETHE UNIVERSITÄT FRANKFURT AM MAIN

κ-$(ET)_2Cu_2(CN)_3$
κ-$(ET)_2Ag_2(CN)_3$
ß'-$(ET)_2ICl_2$
α-$(ET)_2I_3$
• • •

relaxor type

κ-$(ET)_2Cu[N(CN)_2]Cl$ order-disorder type CO: ?

Cf. $(TM)_2X$ order-disorder type $CO \rightarrow FE$: ✓

$\rightarrow$ Calls for a test case in dimerized $(ET)_2X$!?

Outline

1) Fundamental aspects of the Mott transition in κ-$(ET)_2Cu[N(CN)_2]Cl$
– involvement of lattice degrees of freedom

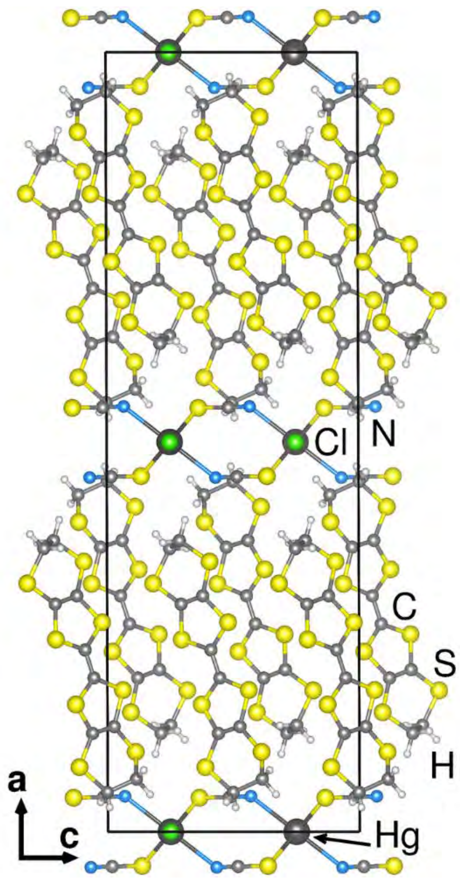
2) Signatures of ferroelectricity/multiferroicity in κ-$(ET)_2Cu[N(CN)_2]Cl$
– open issues

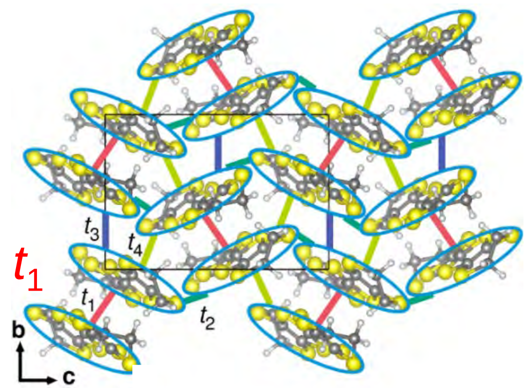
3) The case of κ-$(ET)_2Hg(SCN)_2Cl$
– a proof-of-principle demonstration for ferroelectricity in dimerized $(ET)_2X$

4) Phonon anomalies in κ-$(ET)_2Cu[N(CN)_2]Cl$
– coupling to intra-dimer electronic degrees of freedom

The case of κ-$(ET)_2Hg(SCN)_2Cl$

"κ-HgCl"





H. Jeschke, R. Valentí

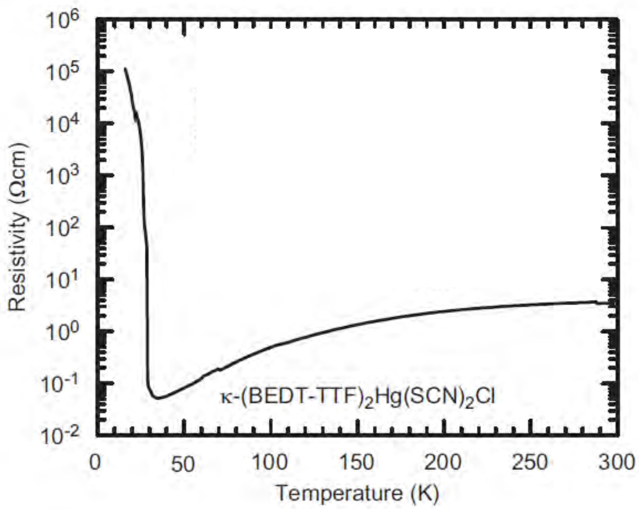
X	t_1 (meV)
$Hg(SCN)_2Cl$	126
$Cu_2(CN)_3$	167
$Cu[N(CN)_2]Cl$	185

Konovalikhin *et al.*,
Bull. of Russ. Acad. Sci.,
Div. Chem. Scien. 41, 1819 (1992)

- moderate dimerization

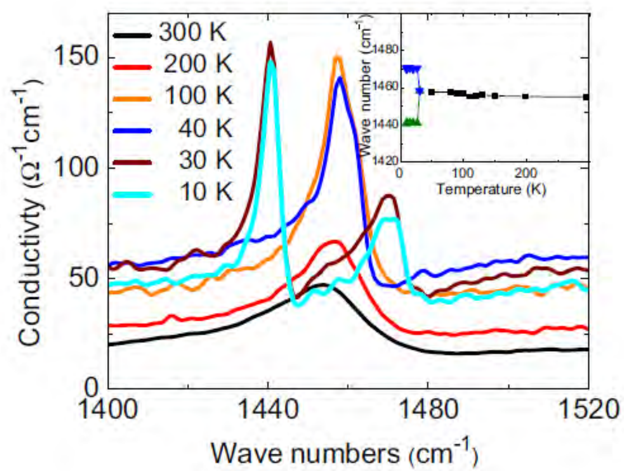
The case of κ-$(ET)_2Hg(SCN)_2Cl$

T_{MI} = 30 K

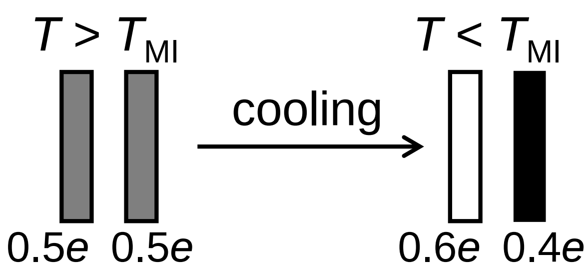


Yasin *et al*., Physica B: Condens. Matter **407**, 1689 (2012)

CO @ T_{MI}



Drichko *et al*., Phys. Rev. B **89**, 075133 (2014)

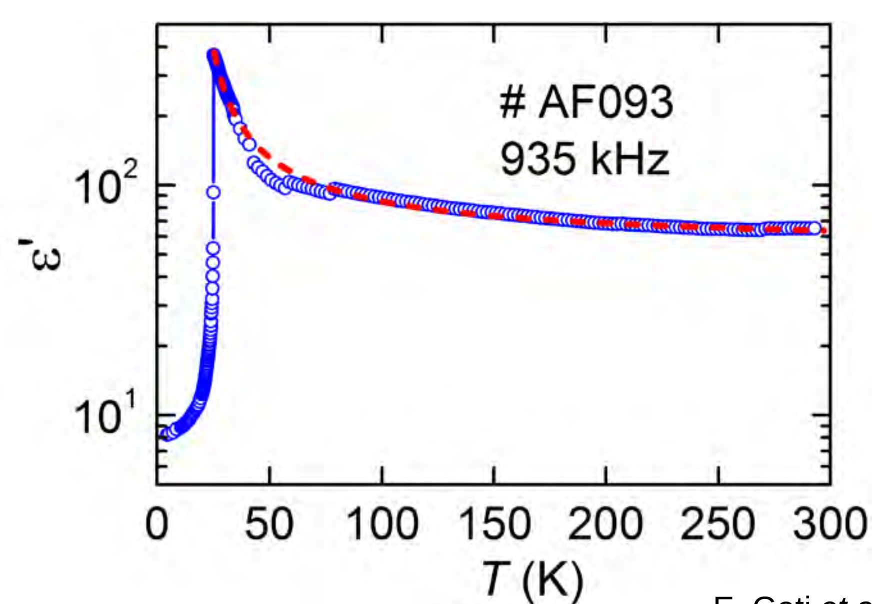


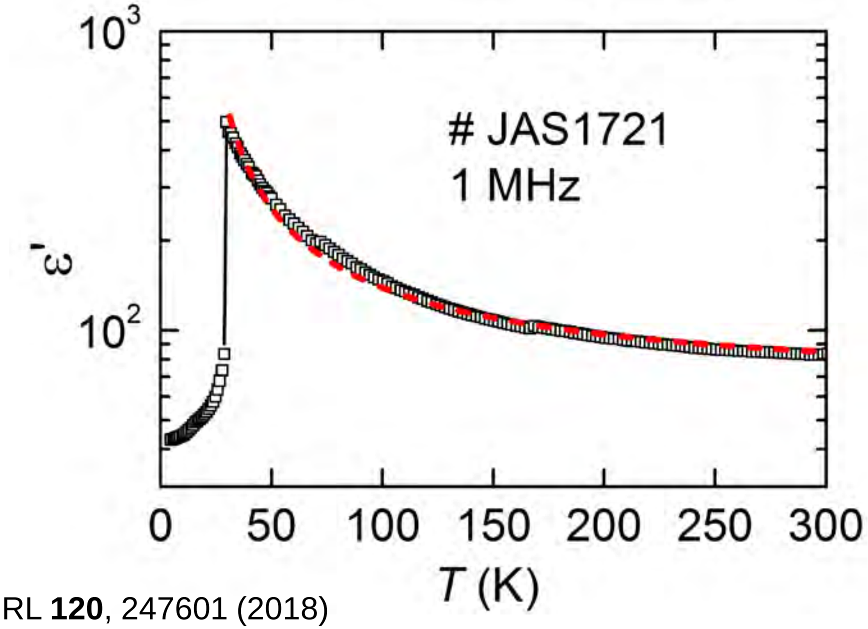
⇒ charge disproportionation

$\delta = \pm\, 0.1\, e$

The case of κ-$(ET)_2Hg(SCN)_2Cl$

E ⊥ *bc* planes





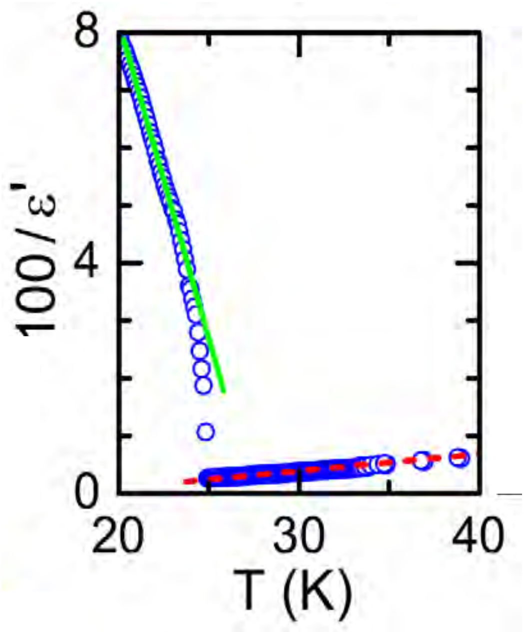
E. Gati *et al.*, PRL **120**, 247601 (2018)

- sharp peak at $T \approx T_{CO}$
- $\varepsilon'(T) \propto C/(T - \theta_{CW})$
- no significant frequency dependence below about 1 MHz

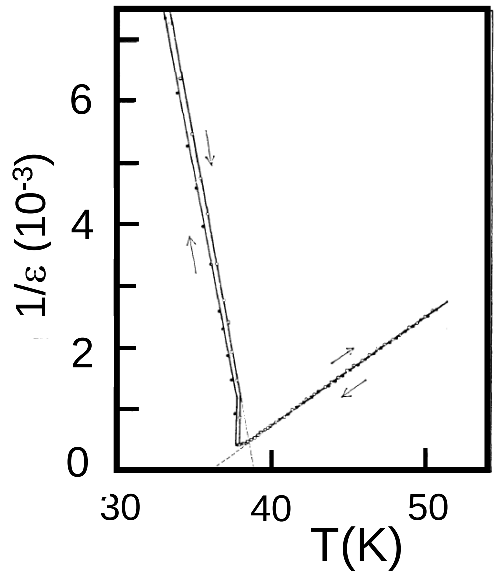
$\Rightarrow$ ferroelectric transition

The case of κ-$(ET)_2Hg(SCN)_2Cl$

κ-$(ET)_2Hg(SCN)_2Cl$



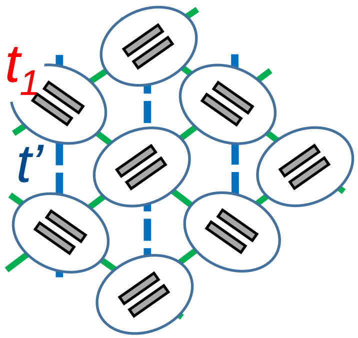
$AgNa(NO_2)_2$

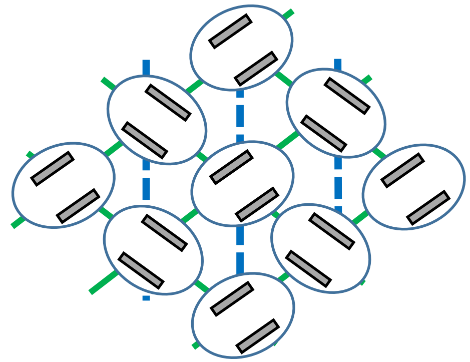


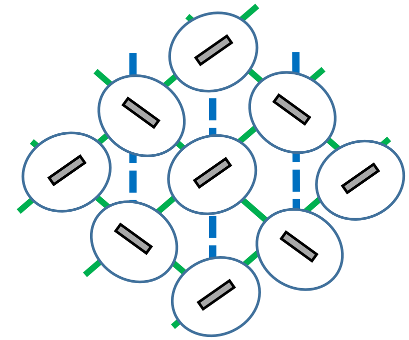
K. Gesi, J. Phys. Soc. Jpn. 28, 395 (1970)

indicative of 1st-order *order-disorder* type ferroelectric transition at T_{CO}

Implications for dimerized $(ET)_2X$







strong — *dimerization strength* t_1/t' — *weak* (*no*)

κ-$(ET)_2Cu[N(CN)_2]Cl$ $t_1/t' \sim 5$	κ-$(ET)_2Hg(SCN)_2Cl$ $t_1/t' \sim 3$	θ-$(ET)_2M'M(SCN)_4$ $t_1/t' \sim 1$

Proof-of-principle demonstration:

Relevance of intra-dimer degrees of freedom for ferroelectric signatures in dimerized $(ET)_2X$

Outline

1) Fundamental aspects of the Mott transition in κ-$(ET)_2Cu[N(CN)_2]Cl$
– involvement of lattice degrees of freedom

2) Signatures of ferroelectricity/multiferroicity in κ-$(ET)_2Cu[N(CN)_2]Cl$
– open issues

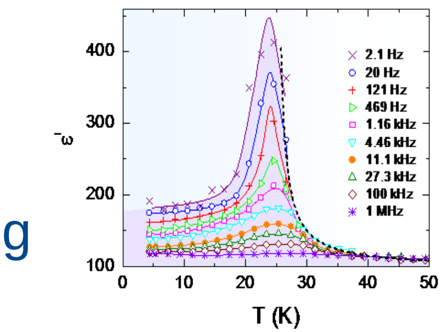
3) The case of κ-$(ET)_2Hg(SCN)_2Cl$
– a proof-of-principle demonstration for ferroelectricity in dimerized $(ET)_2X$

4) Phonon anomalies in κ-$(ET)_2Cu[N(CN)_2]Cl$
– coupling to intra-dimer electronic degrees of freedom

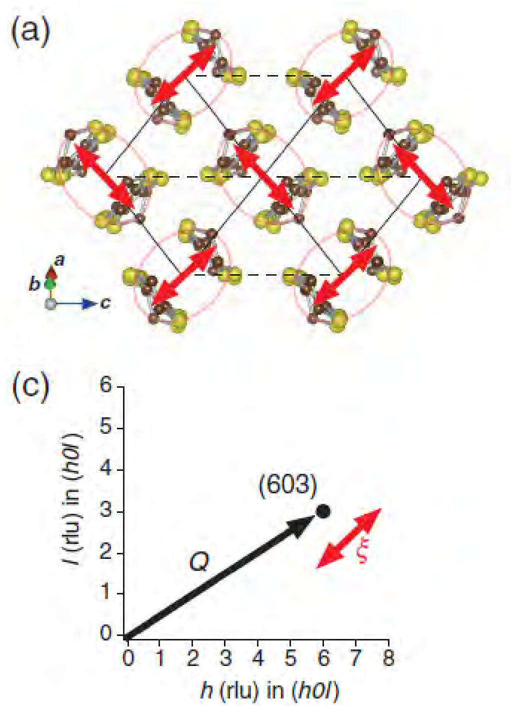
Phonon anomalies in κ-$(ET)_2Cu[N(CN)_2]Cl$

Inelastic neutron scattering on κ-$(d8\text{-}ET)_2Cu[N(CN)_2]Cl$

Masato Matsuura *et al*., Phys. Rev. Lett. **123**, 027601 (2019)



Idea: intra-dimer charge d.o.f. ⇔ dimer breathing/shearing modes



$$I \propto (\boldsymbol{Q} \cdot \boldsymbol{\xi})^2$$

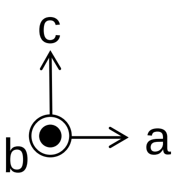
momentum transfer

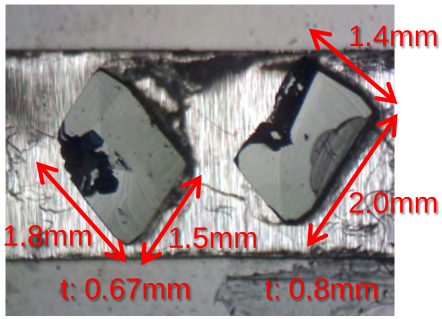
polarization vector of phonon mode

⇒ Q = (603) selected

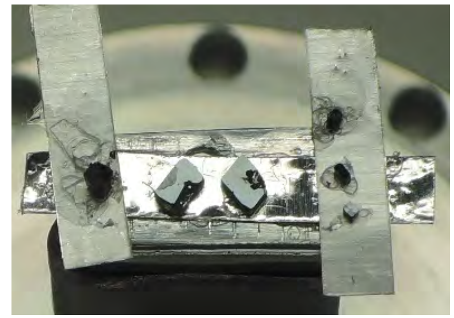
Phonon anomalies in κ-$(ET)_2Cu[N(CN)_2]Cl$

Single crystals κ-(d8-ET)$_2$Cu[N(CN)$_2$]Cl ($T_N = 27K$)



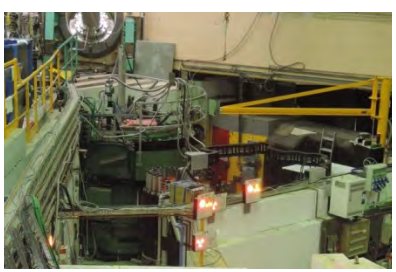


ILL
2 crystals (~7 mg, ~4 mm^3)



FRM2
6 crystals (~9 mg, ~5 mm^3)

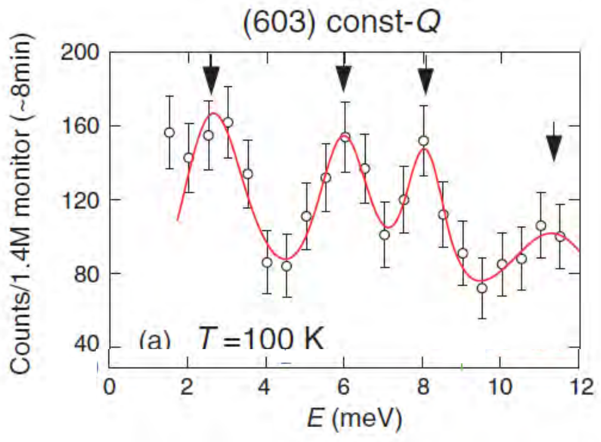
Triple-axis spectrometers



IN8@ILL France, 2×10^8/cm^{-2}s^{-1}

PUMA@FRM2 Germany, ~10^8/cm^{-2}s^{-1}

T dependence of Q = const. scans

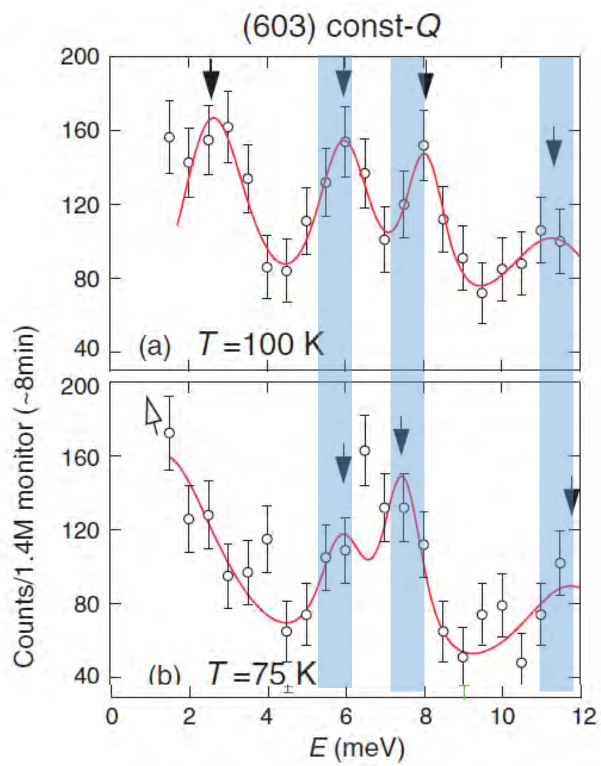


- phonon peaks at E = 2.6, 6, 8 and 11 meV
- peak widths $\Delta E_{\mathrm{FWHM}} \approx$ 2.3 meV >> $\Delta E_{\mathrm{res}} \approx$ 0.5 meV

  $\Rightarrow$ finite lifetime $\tau_q \sim \Gamma_q^{-1}$
  $\Rightarrow$ Γ_q from fits (damped harmonic oscillators)

M. Matsuura et al., Phys. Rev. Lett. **123**, 027601 (2019)

T dependence of Q = const. scans



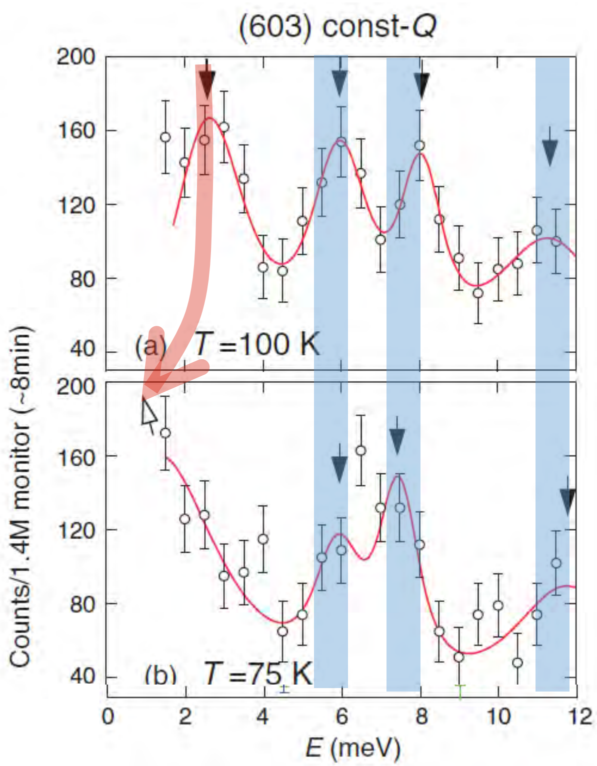
- phonon peaks at E = 2.6, 6, 8 and 11 meV
- peak widths $\Delta E_{\mathrm{FWHM}} \approx 2.3$ meV >> $\Delta E_{\mathrm{res}} \approx 0.5$ meV

  $\Rightarrow$ finite lifetime $\tau_q \sim \Gamma_q^{-1}$
  $\Rightarrow$ Γ_q from fits (damped harmonic oscillators)

- modes at E = 6, 8 and 11 meV almost independent on cooling to 75 K

M. Matsuura et al., Phys. Rev. Lett. **123**, 027601 (2019)

T dependence of Q = const. scans



- phonon peaks at *E* = 2.6, 6, 8 and 11 meV
- peak widths $\Delta E_{\mathrm{FWHM}} \approx 2.3$ meV >> $\Delta E_{\mathrm{res}} \approx 0.5$ meV

  $\Rightarrow$ finite lifetime $\tau_q \sim \Gamma_q^{-1}$
  $\Rightarrow$ Γ_q from fits (damped harmonic oscillators)

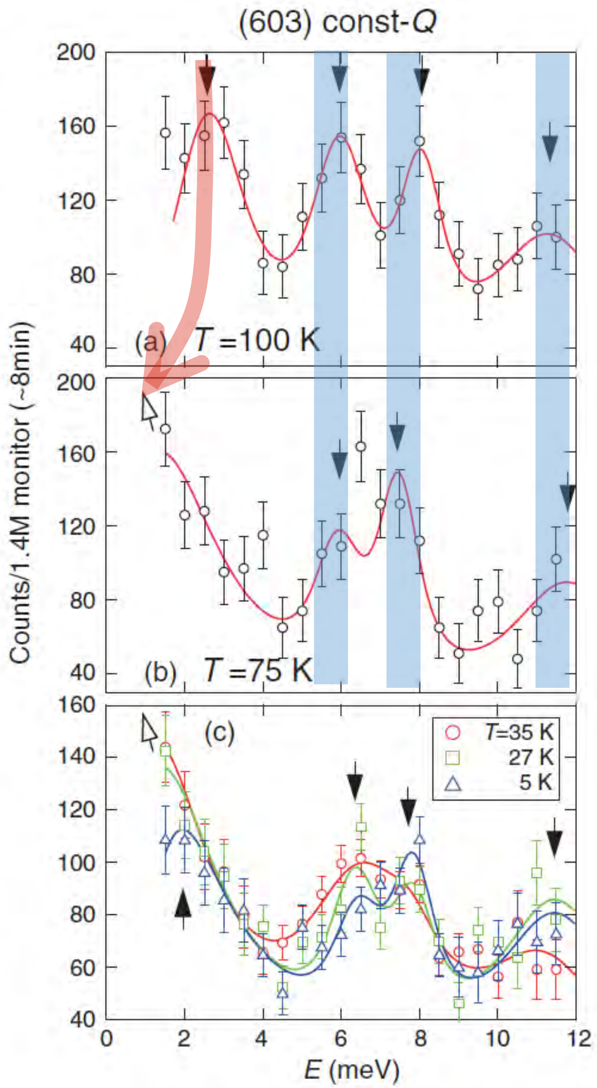
- modes at *E* = 6, 8 and 11 meV almost independent on cooling to 75 K

- strong renormalization of mode at 2.6 meV

  $\Rightarrow \omega_q \approx \Gamma_q$

M. Matsuura et al., Phys. Rev. Lett. **123**, 027601 (2019)

T dependence of Q = const. scans



- phonon peaks at E = 2.6, 6, 8 and 11 meV
- peak widths $\Delta E_{\mathrm{FWHM}} \approx 2.3$ meV >> $\Delta E_{\mathrm{res}} \approx 0.5$ meV

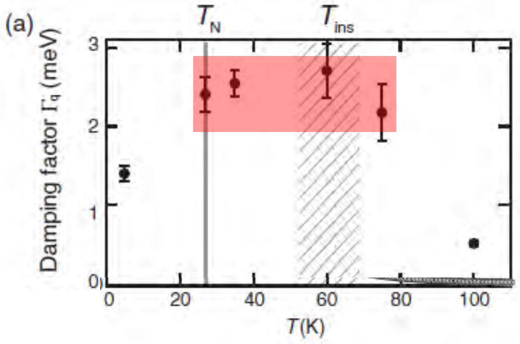
  $\Rightarrow$ finite lifetime $\tau_q \sim \Gamma_q^{-1}$
  $\Rightarrow$ Γ_q from fits (damped harmonic oscillators)

- modes at E = 6, 8 and 11 meV almost independent on cooling to 75 K

- strong renormalization of mode at 2.6 meV

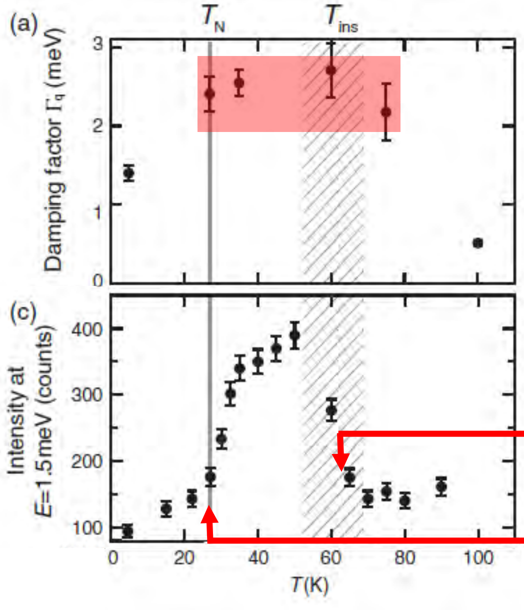
  $\Rightarrow \omega_q \approx \Gamma_q$
  $\Rightarrow$ T dependent

T dependence of Q = const. scans



- Overdamped modes ($\omega_q \approx \Gamma_q$) for a wide range of temperatures

T dependence of Q = const. scans



- Overdamped modes ($\omega_q \approx \Gamma_q$) for a wide range of temperatures

- Strong enhancement of scattering intensity at E = 1.5 meV for $T_{N,FE} \leq T \leq$ 60-65 K

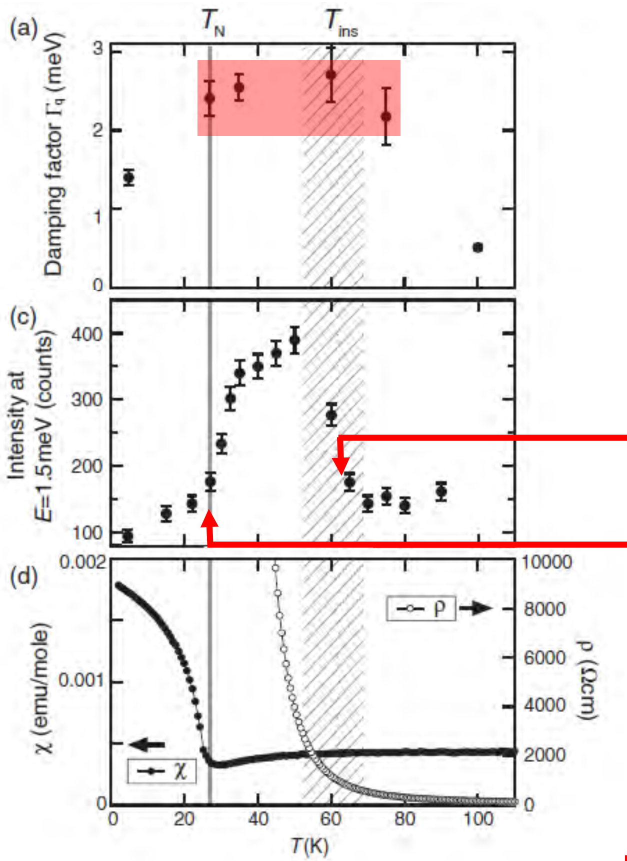
opening of Δ_{charge}

K. Kornelsen *et al.*,
Solid State Commun. 81, 343 (1992)

$T_N \approx T_{FE}$: “freezing“ of spin- (and charge) fluctuations

T dependence of Q = const. scans

GOETHE UNIVERSITÄT FRANKFURT AM MAIN



- Overdamped modes ($\omega_q \approx \Gamma_q$) for a wide range of temperatures

- Strong enhancement of scattering intensity at E = 1.5 meV for $T_{\mathrm{N,FE}} \leq T \leq$ 60-65 K

opening of Δ_{charge}

K. Kornelsen *et al.*,
Solid State Commun. 81, 343 (1992)

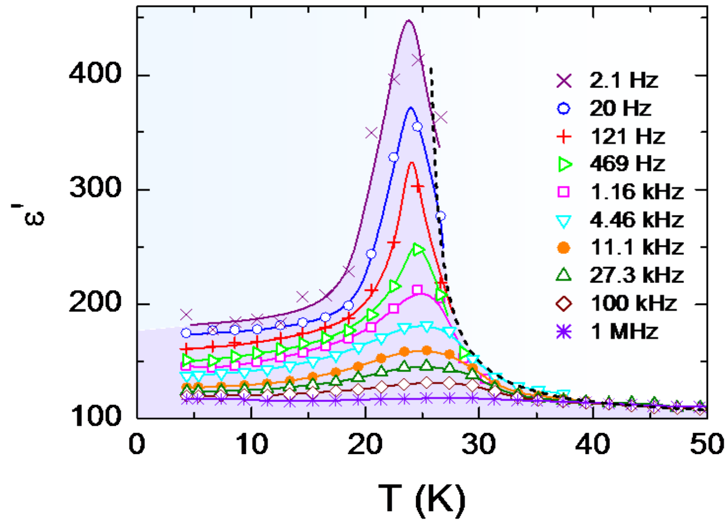
$T_{\mathrm{N}} \approx T_{\mathrm{FE}}$: “freezing“ of spin- (and charge) fluctuations

$\Rightarrow$ phonon anomaly $\Leftrightarrow$ fluctuating intra-dimer d.o.f.
charge fluctuations $\omega_{\mathrm{ch}} \sim$ 1-2 meV

Discussion

Intra-dimer charge fluctuations (ω_{ch} ~ 1-2 meV)

$\overset{?}{\Leftrightarrow}$ dielectric anomaly (static CO)



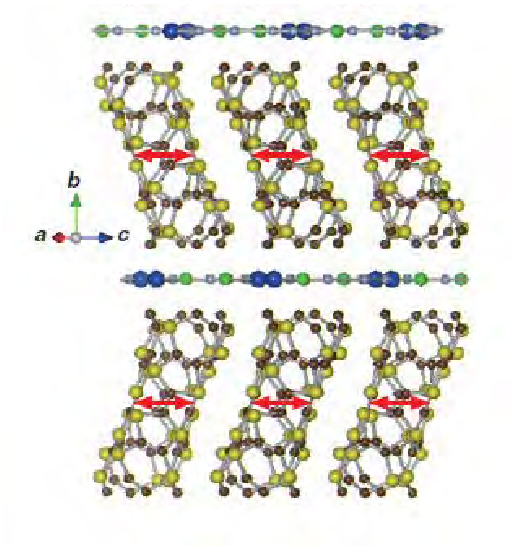
in the presence of a finite E-field!

κ-$(ET)_2Cu[N(CN)_2]Cl$

⇒ Fluctuating dipoles at the brink of static charge order !?

Attempt to identify the low-lying mode

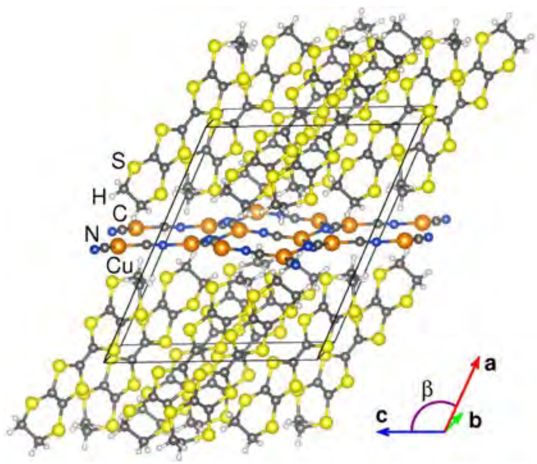
κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl



phonon calculations:

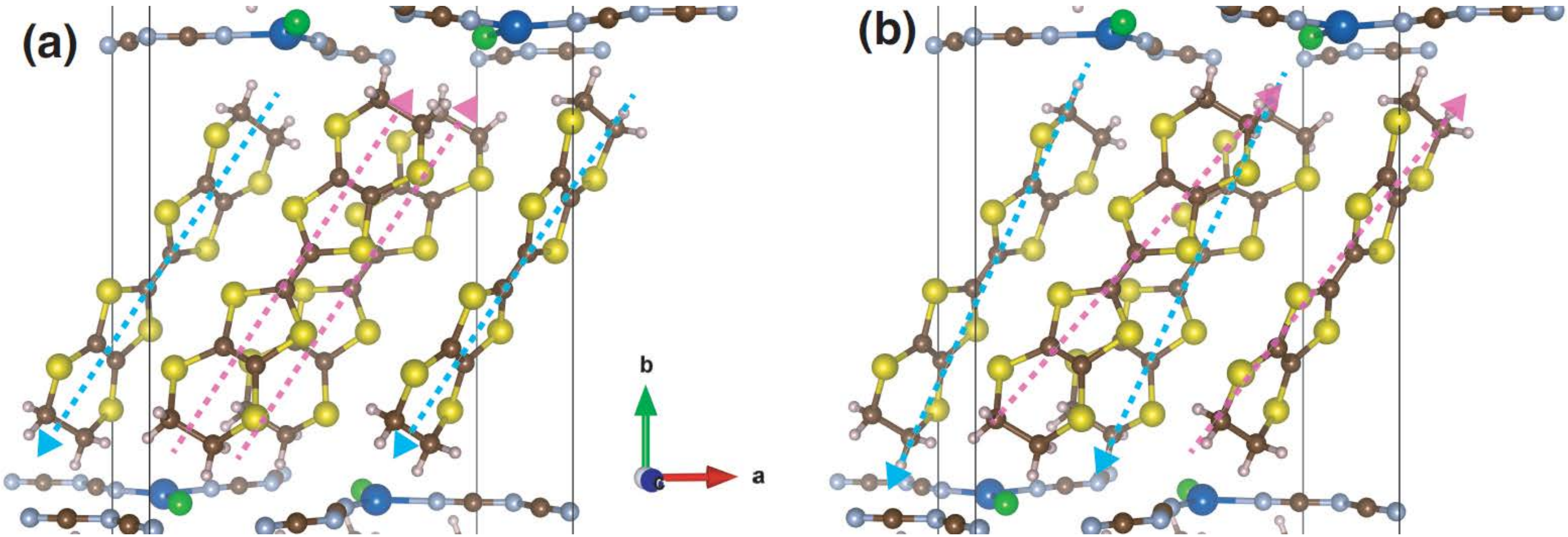
in progress

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$



Dressel *et al.*,
PRB **93**, 081201 (R) (2016)

Attempt to identify the low-lying mode



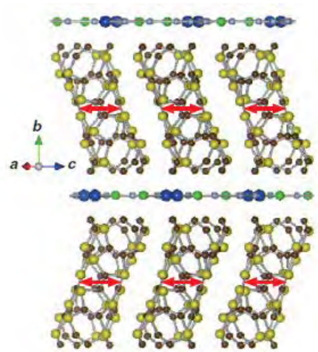
κ-$Cu_2(CN)_3$ 3.1 meV

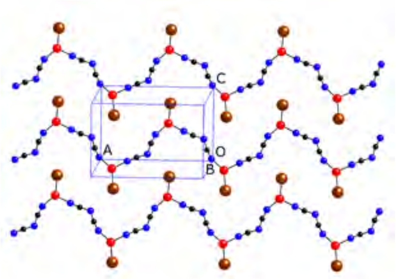
4.1 meV

(cf. E = 2.6 meV for κ-Cl)

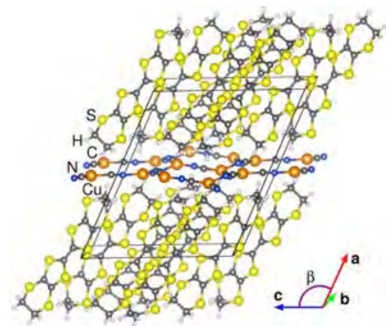
Attempt to identify the low-lying mode

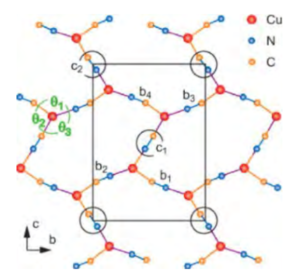
κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$





κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$





- less dense out-of plane packing
- less rigid anion network

⇒ Softer spring constants expected for κ-Cl as compared to κ-CN

Summary

κ-$(ET)_2X$:

correlated electrons coupled to a compressible lattice

$X = Cu[N(CN)_2]Cl$

Mott physics (@ p = 230 bar)

Hugh changes of the compressibility around the Mott transition

$\Rightarrow$ indicating *critical elasticity*

Beyond Mott (p = 0)

Signatures for electronic ferroelectricity/multiferroicity

accompanied by strong phonon renormalization effects

$\Rightarrow$ fluctuating dipoles at the brink of static ferroelectricity !?