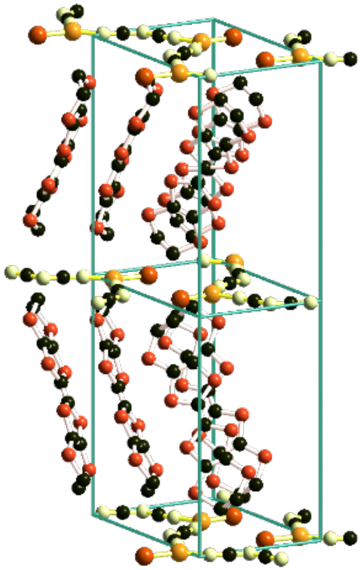
Probing lattice effects in molecular spin-liquid-candidate systems



Michael Lang
Goethe-Universität Frankfurt

SFB-TRR 288

Elastic Tuning and Response of Electronic Quantum Phases of Matter

Frankfurt-Karlsruhe-Mainz

Collaborators



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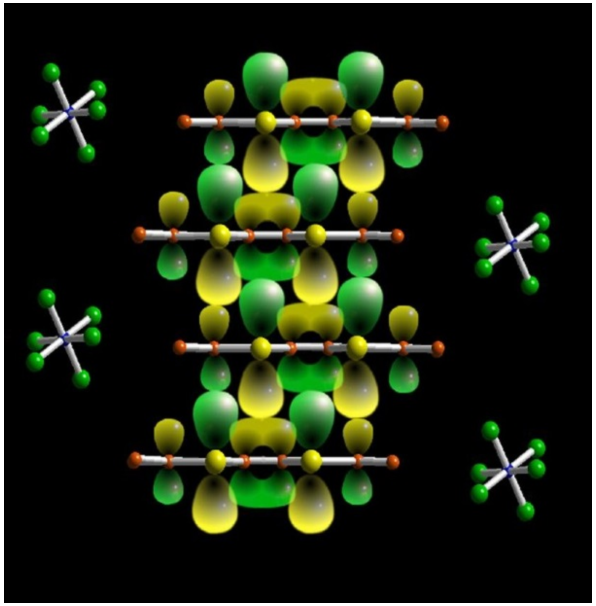
Molecular materials – charge transfer salts

e.g. $(TMTSF)_2PF_6$



- Weak intermolecular overlap: small *W* (~ ***U*** ~ 0.5 eV)

- Low dimensionality
- Small charge carrier concentration

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

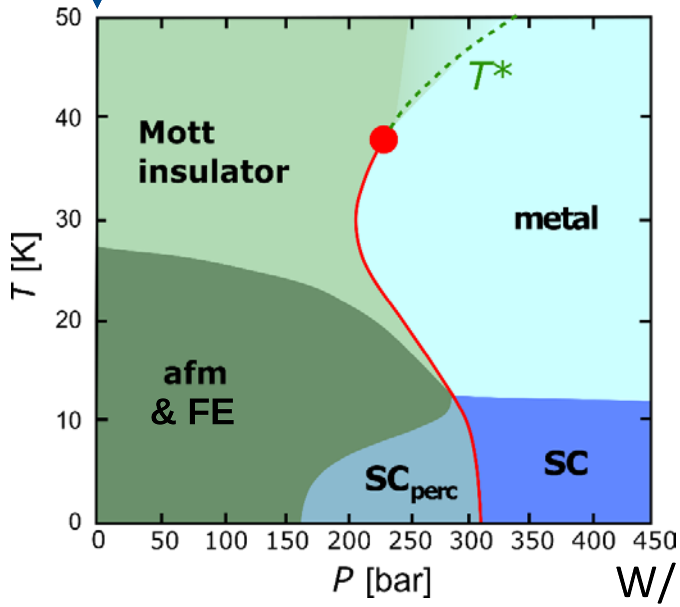
$\Rightarrow$ strongly correlated (*U* + *V*) π-electrons

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

κ-(BEDT-TTF)$_2$X

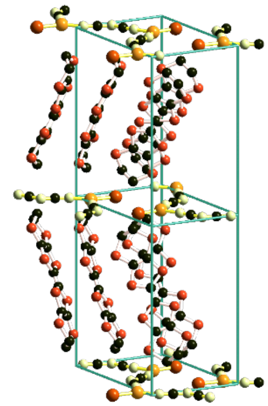
X = Cu[N(CN)$_2$]Cl

κ-Cl



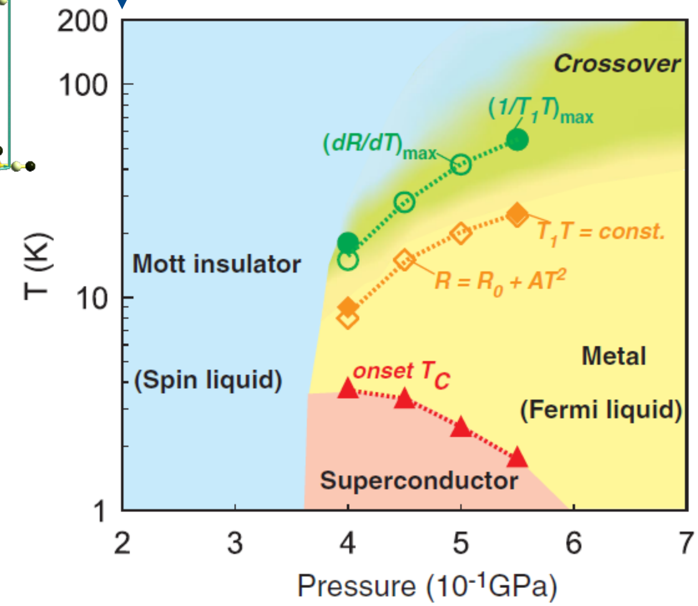
W/U

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



X = Cu$_2$(CN)$_3$

κ-CN



Y. Shimizu *et al.*, Phys. Rev. Lett. **91**, 107001 (2003)
Y. Kurosaki *et al.*, Phys. Rev. Lett. **95**, 177001 (2005)

- weak Mott insulators
- varying degree of frustration depending on X
- κ-CN: candidate for QSL

Outline

1) κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

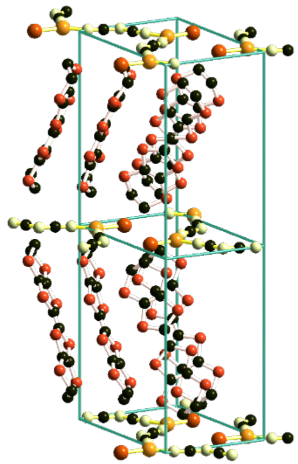
Recap on experimental observations incl. lattice effects

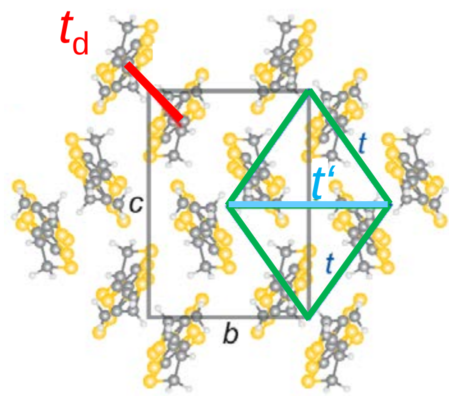
Phonon renormalization studied by inelastic neutron scattering

2) κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$

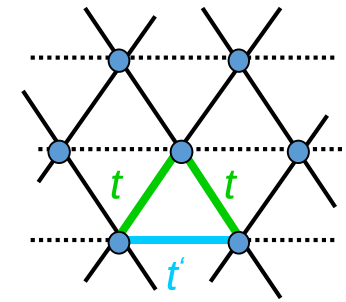
Any differences?

1) κ-(BEDT-TTF)$_2$X – electronic structure





effective-dimer model

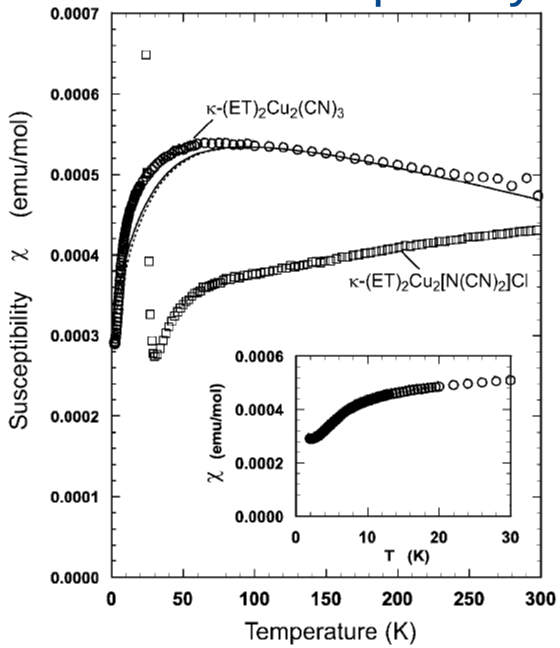


1 hole/dimer

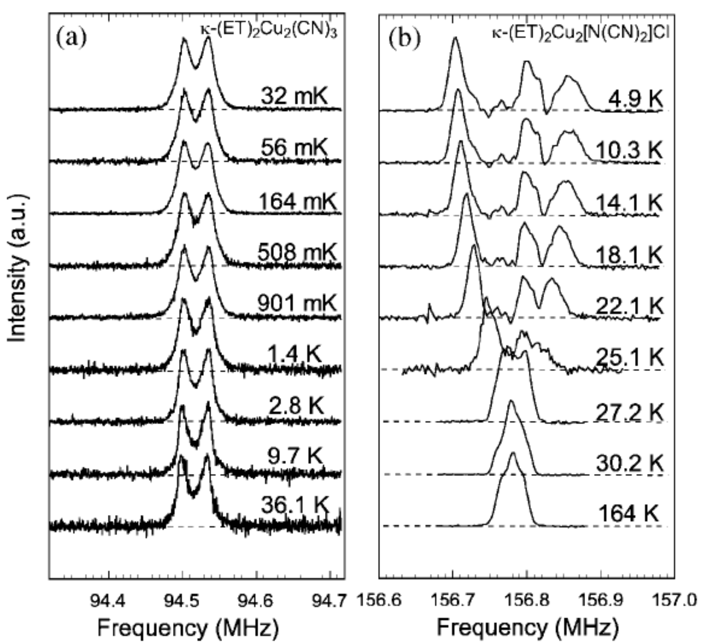
X =	Cu[N(CN)$_2$]Cl	$Cu_2(CN)_3$	Hg(SCN)$_2$Cl
t_d/t' =	5	4.2	3
t'/t =	0.44	0.86	0.79
	H. C. Kandpal *et al.*, PRL 103, 067004 (2009)	H. O. Jeschke *et al.*, PRB **85**, 035125 (2012)	E. Gati *et al.*, PRL 120, 247601 (2018)

Magnetic properties of X = $Cu_2(CN)_3$

DC-Susceptibility



^{1}H-NMR



Y. Shimizu *et al*., Phys. Rev. Lett. **91**, 107001 (2003)
Y. Shimizu *et al*., Phys. Rev. B. **73**, 140407(R) (2006)

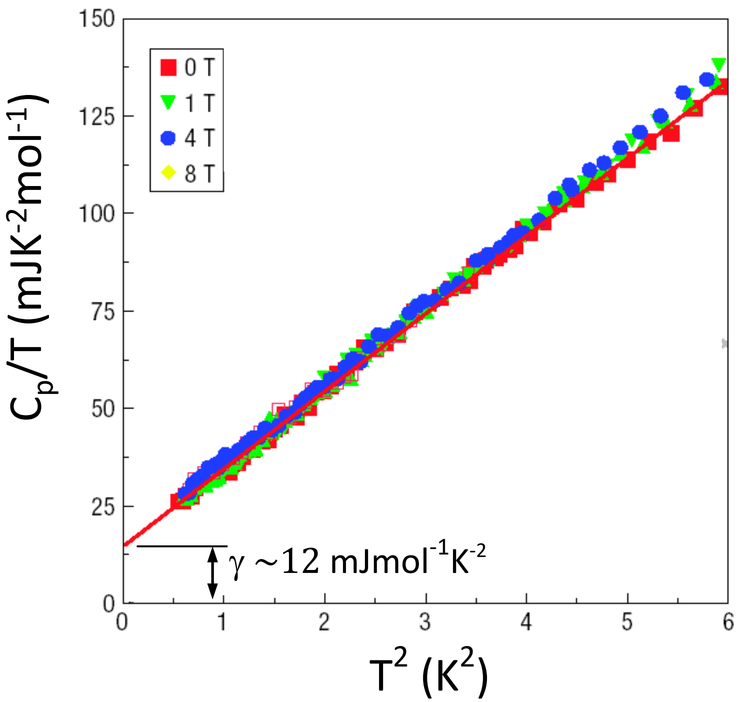
- S = ½ triangular-lattice Heisenberg afm with *J* ~ 250 K
- no long-range magnetic order down to 30 mK

⇒ "*quantum spin liquid candidate*"

Low-energy excitations of X = $Cu_2(CN)_3$

Specific heat

after subtraction of C_{nucl}

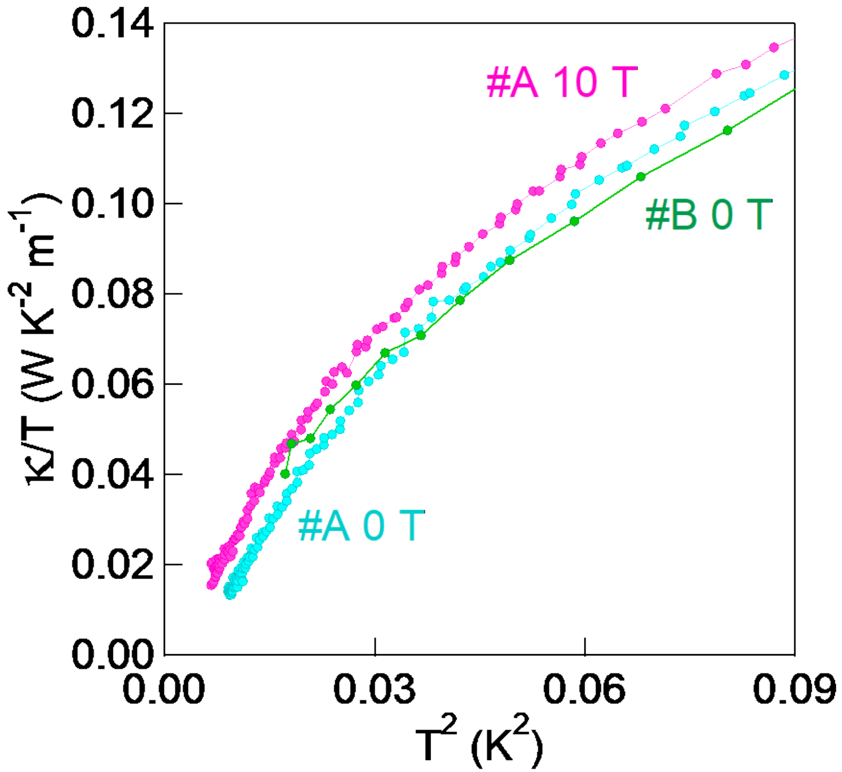


S. Yamashita et al., Nature Physics **4**, 459 (2008)

$$\left({}^{C}/_{T}\right)_{T\to 0} = \gamma$$

"gapless spinons with Fermi surface"

Thermal conductivity



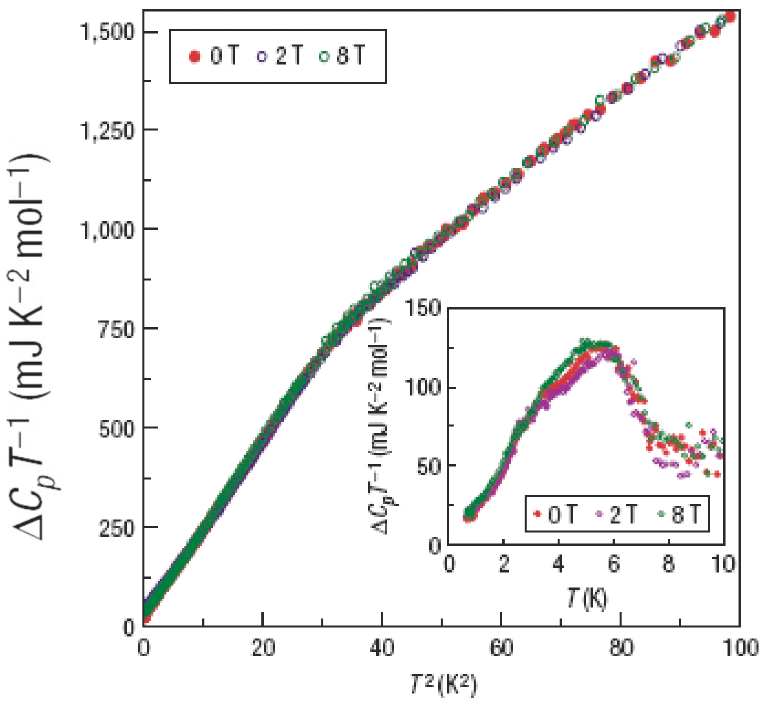
M. Yamashita et al., Nature Physics **5**, 44 (2009)

$$\left({}^{\kappa}/_{T}\right)_{T\to 0} \approx 0$$

"spin gap $\Delta \leq 0.46$ K ~ J/500"

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

Specific heat

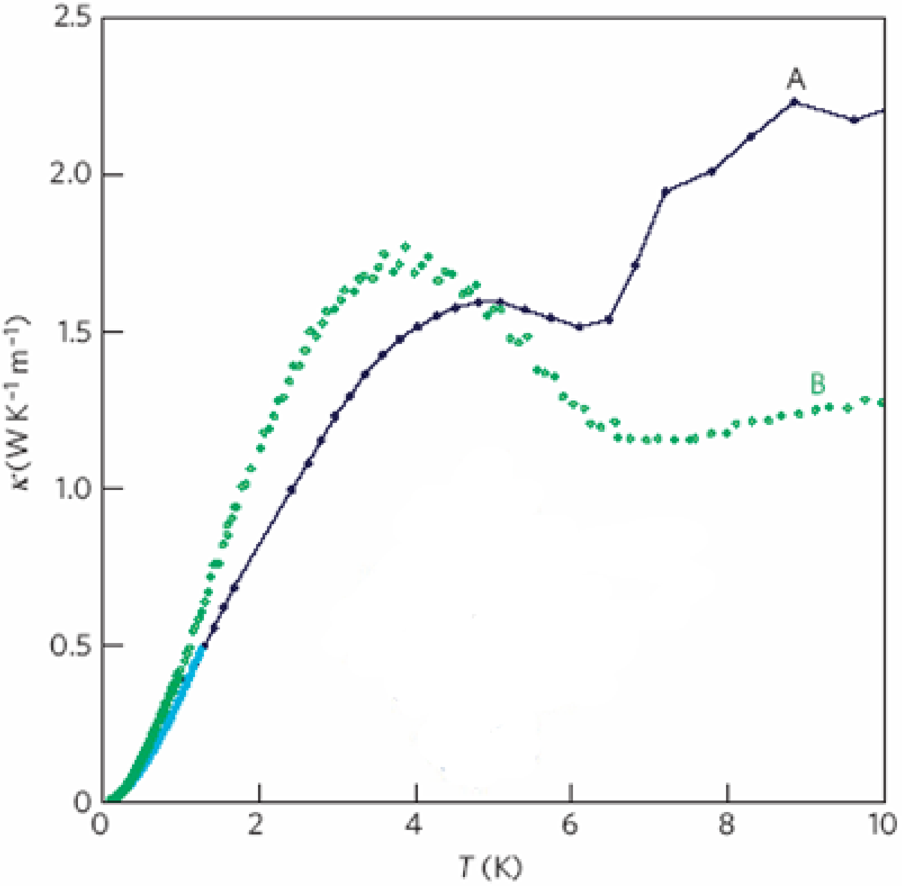


S. Yamashita *et al*.,
Nature Physics **4**, 459 (2008)

⇒“*crossover to a quantum spin liquid*“

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

Thermal conductivity

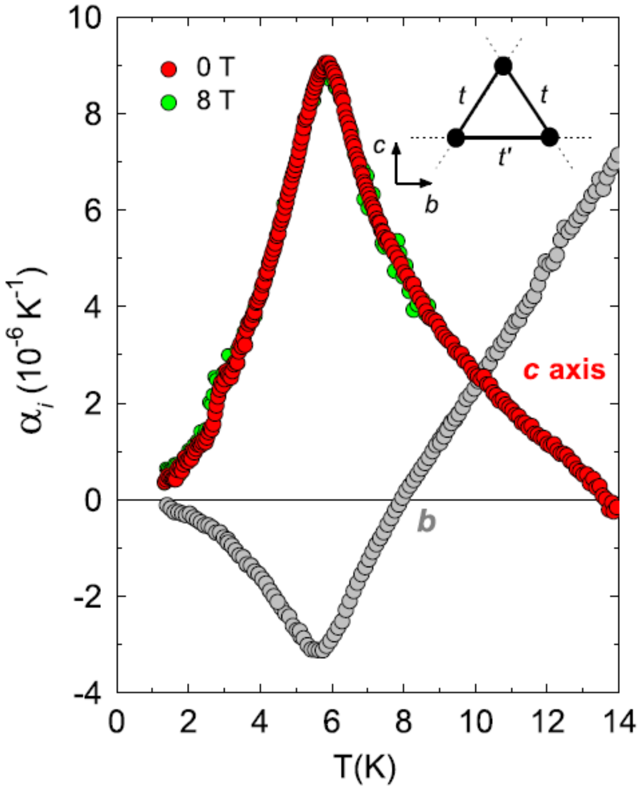


M. Yamashita et al.,
Nature Physics **5**, 44 (2009)

Suggestive of a phase transition!?

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

Thermal expansion



R. S. Manna *et al.*,
PRL **104**, 016403 (2010)

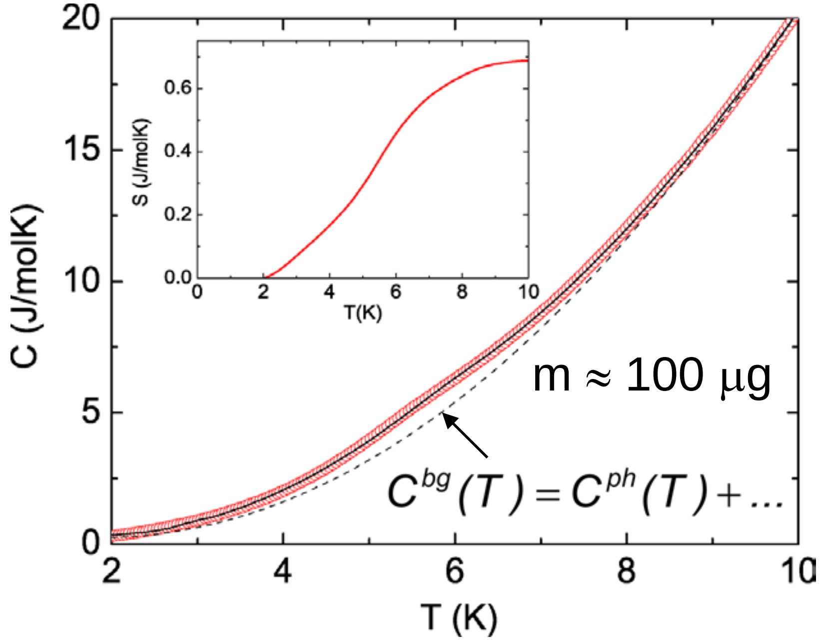
- strong lattice effects & pronounced in-plane distortions
- no hysteresis
- no field effect for $B \leq 8$ T

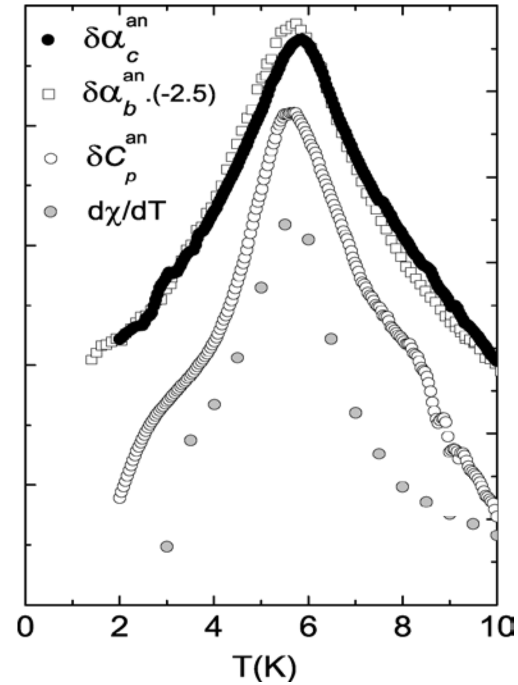
⇒ 2nd order phase transition with strong coupling to the lattice

Cf. ultrasonics M. Poirier *et al.*, PRB 89, 0145138 (2014)

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

R. S. Manna *et al.*,
PRL **104**, 016403 (2010)





- $\delta C \sim \delta\alpha \sim d\chi/dT \Rightarrow$ 2nd order phase transition
- $d\chi/dT$: spin degrees of freedom are involved

$\delta S^{6K} \approx 7\cdots8\%\ R\ln 2$ (for 1 mole S = ½ spins)

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

$\delta S^{6K} \approx 7 \cdots 8\%\ R\ln 2$ (for 1 mole S = ½ spins)

Cf. spin entropy for 2D triangular-lattice ($t' = t$) S = ½ system
for $T \leq 0.04\ J$ (= 10 K):

- Heisenberg afm (J = 250K): $S^{spin}|_{T \leq 10K} \sim 2.3\%\ R\ln 2$

Bernu, Misguich PRB **63**, 134409 (2001)

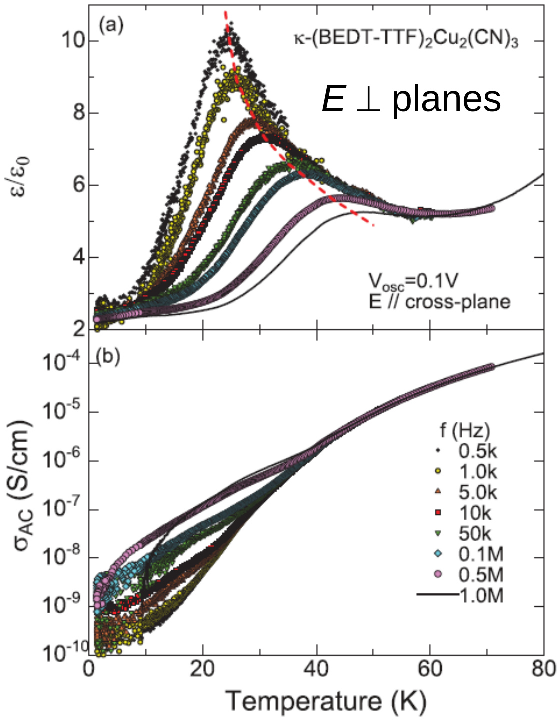
- Heisenberg afm
+ ring exchange processes: $S^{spin}|_{T \leq 10K} \sim 5.2\ \%\ R\ln 2$

Motrunich, PRB **72**, 045105 (2005)

⇒ “*spin degrees of freedom alone cannot acount for the phase transition anomaly in C(T)*“

R. S. Manna *et al.*, PRL **104**, 016403 (2010)

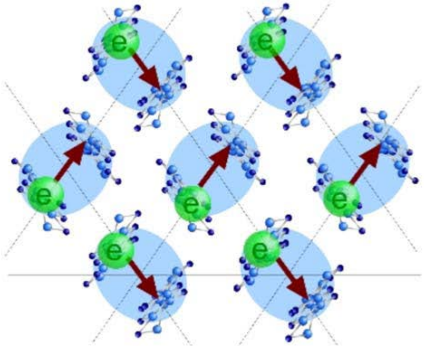
Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$



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

- Dielectric anomaly (relaxor-type)
- Curie-Weiss behavior $\epsilon' \sim \frac{1}{T-T_C}$ $\quad T_C \sim 6\ K$

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)

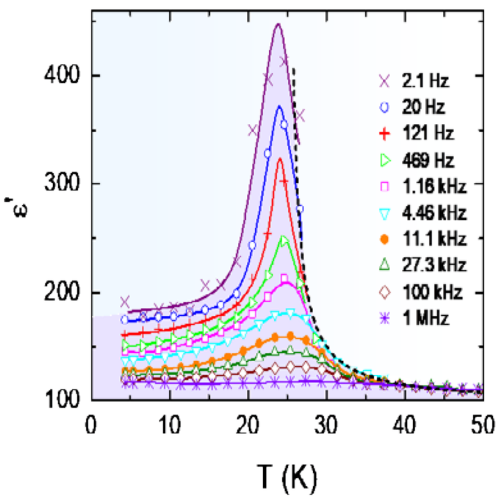
H. Gomi *et al*., Phys. Rev. B **87**, 195126 (2013)

IR-spectroscopic: charge disproportionation δ < 0.005 *e*!

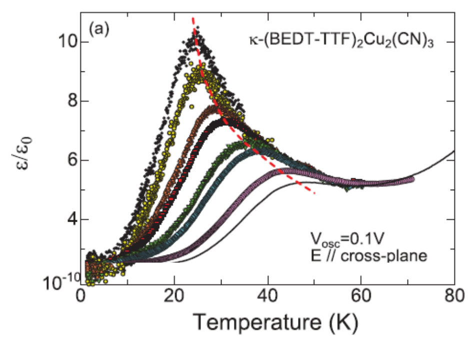
K. Sedlmeier *et al*., PRB **86**, 245103 (2012)

Dielectric anomalies in frustrated κ-$(ET)_2X$

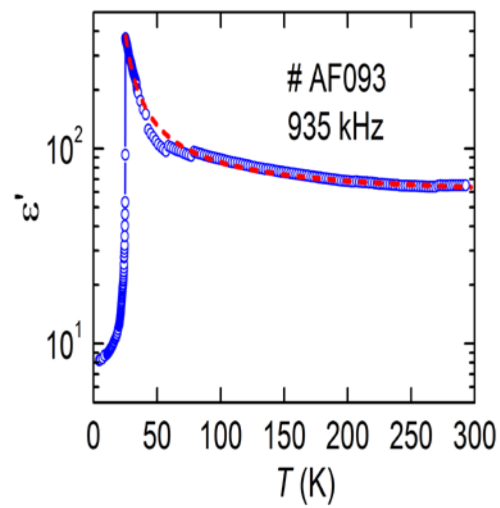
X =	$Cu[N(CN)_2]Cl$	$Cu_2(CN)_3$	$Hg(SCN)_2Cl$
$t_d/t' =$	5	4.2	3
$t'/t =$	0.44	0.86	0.79



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



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



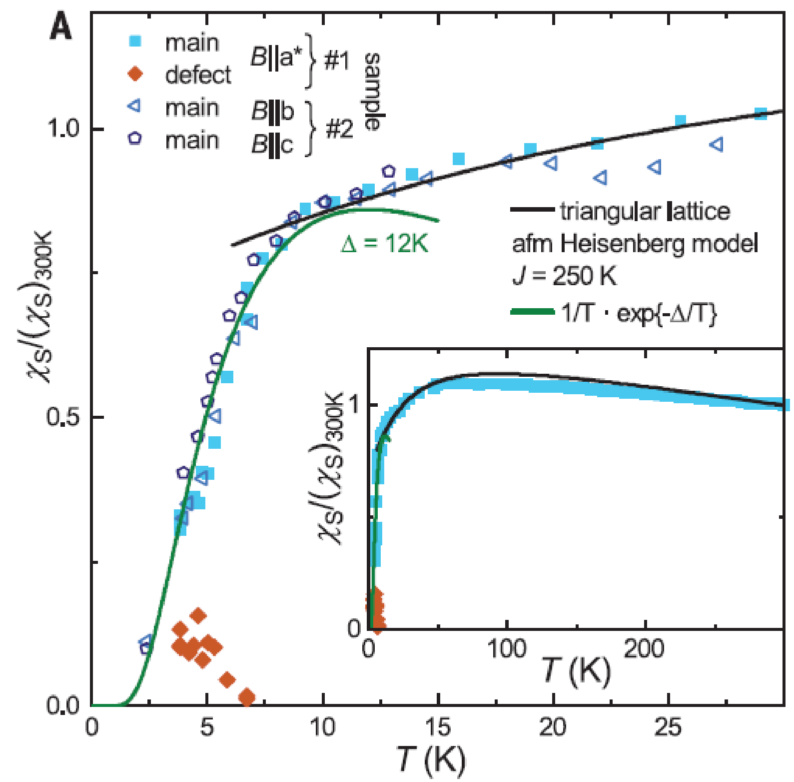
E. Gati *et al.*,
PRL **120**, 247601 (2018)

⇒ importance of intra-dimer charge degrees of freedom!

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

ESR-derived
spin susceptibility:

$\chi = \chi_s + \chi_{imp}$



B. Miksch *et al.*,
Science **372**, 276 (2021)

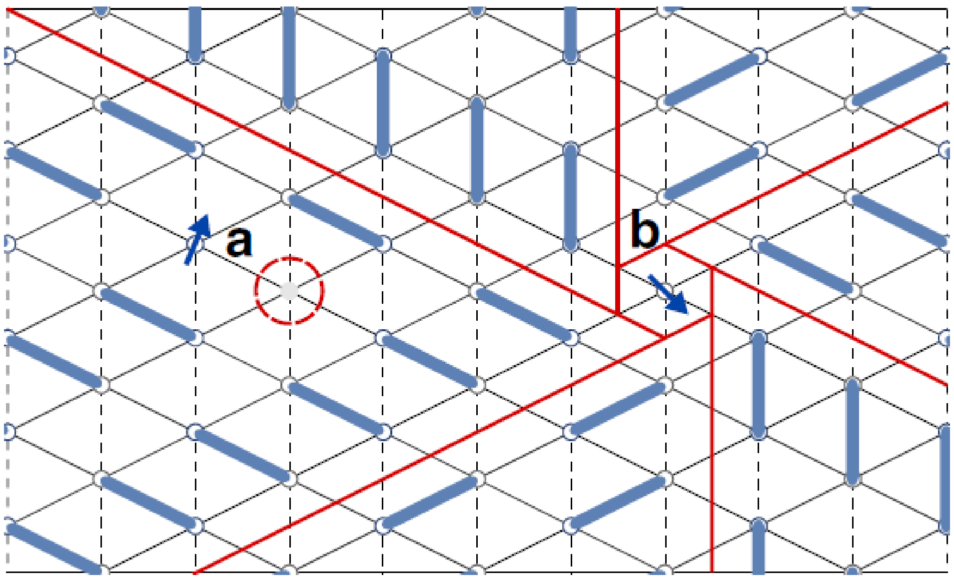
⇒ *Opening of spin gap & drop of χ_s below ~ 6 K*

⇒ *Identification of an impurity contribution that dominates at low T*

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

Analysis of torque data (T. Isono *et al.,* Nat. Commun. **7**, 13494 (2016)):

Close to valence bond solid ⇒ disorder-induced defect spins!



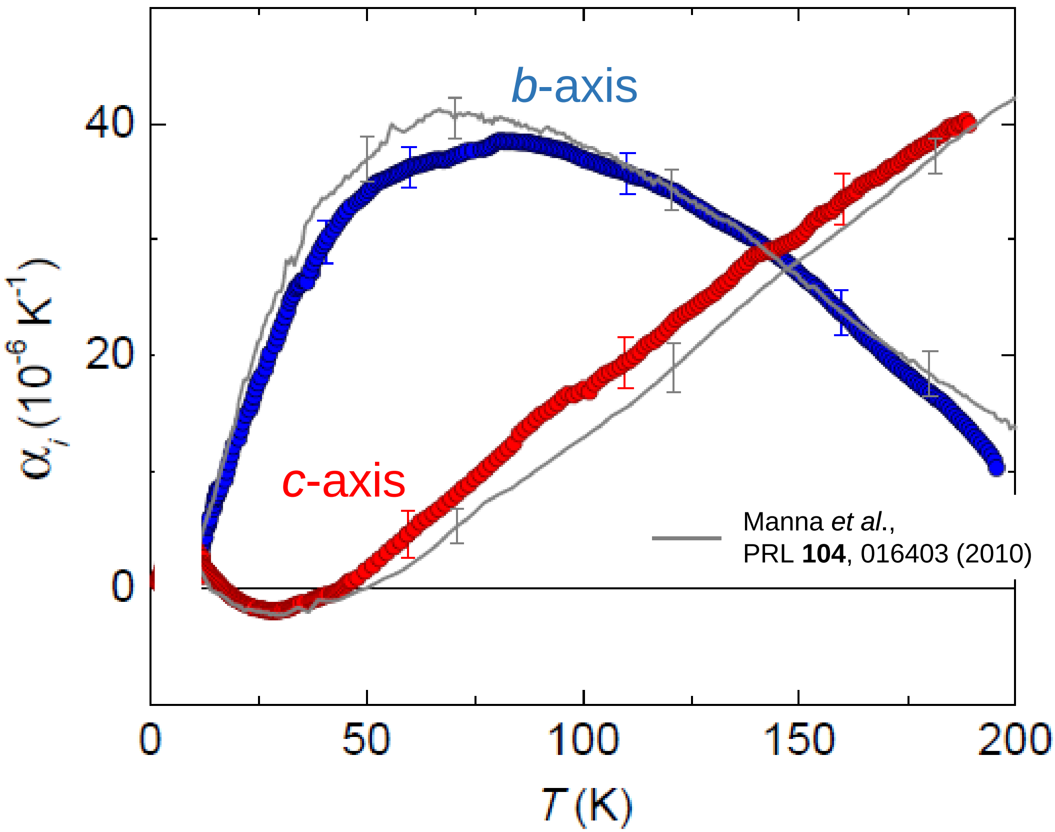
- Random modulation of magnetic interactions
- Defects in the anion layer ⇒ unpaired spin due to nonmagnetic vacancy

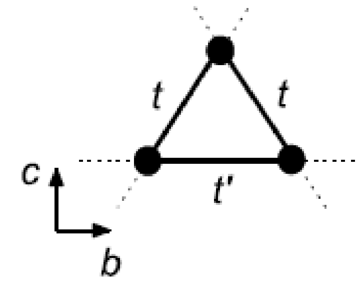
K. Riedl *et al*., Nat. Commun. **10**, 2561 (2019)

⇒ *suggesting a valence-bond-glass ground state*

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$

Sample-to-sample variations (study of 9 crystals from var. sources)

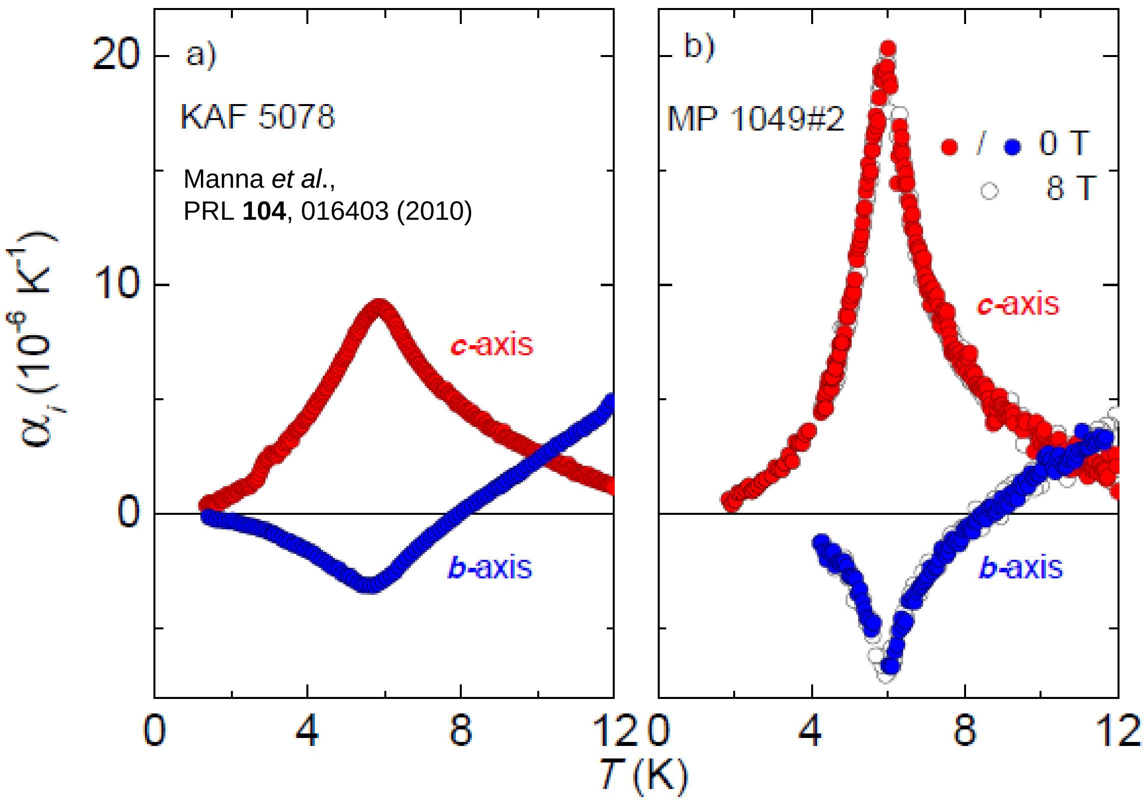




R. S. Manna *et al.*, Crystals **8**, 87 (2018)

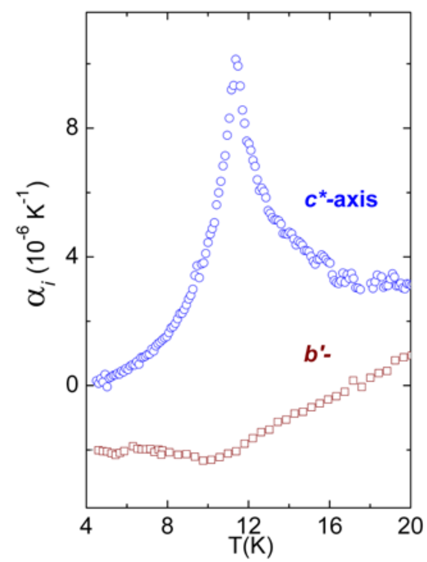
T > 6 K: anomalous behavior; similar for samples studied

Mysterious “6 K anomaly“ in X = $Cu_2(CN)_3$



R. S. Manna *et al.*, Crystals **8**, 87 (2018)

$(TMTTF)_2AsF_6$



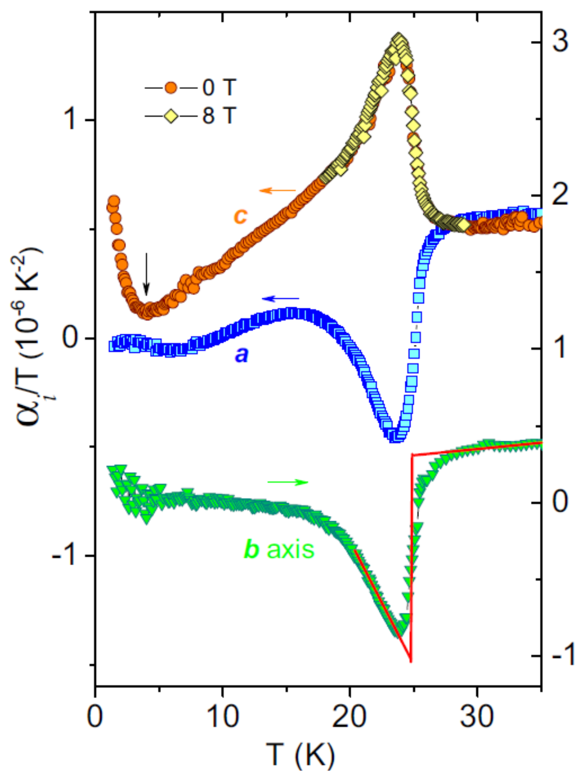
Spin-Peierls transition

M. de *Souza et al.*, Physica B **404**, 494 (2009)

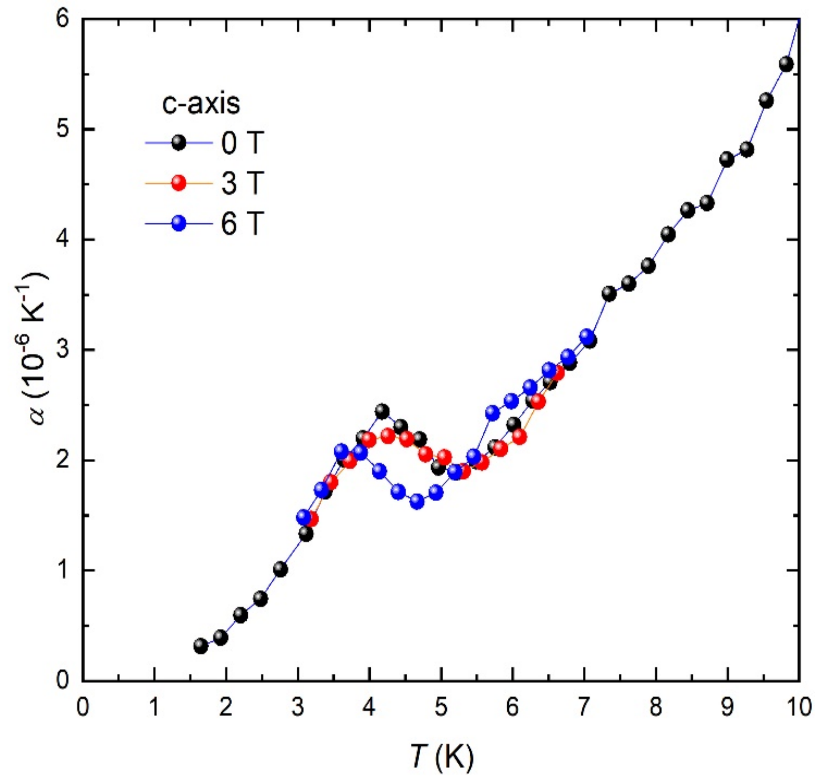
- 2^{nd} order phase transition at ~ 6 K!
- Same in-plane anisotropy $\alpha_c \sim 3|\alpha_b|$; No field dependence for *B* ≤ 8 T
- Significant sample-to-sample variations in size of anomaly

Cf. α(T) anomalies at VBS phase transition

$EtMe_3P[Pd(dmit)_2]_2$

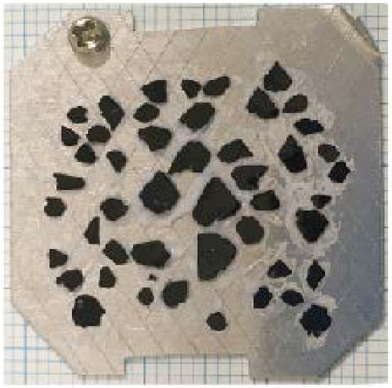


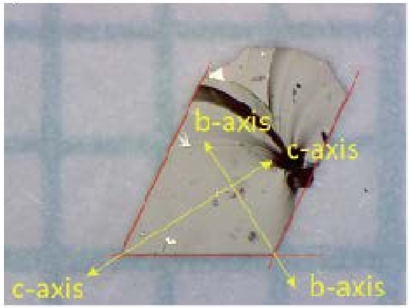
κ-$(ET)_2B(CN)_4$



No clear conclusion to be drawn from the shape of the phase transition anomaly!

Inelastic neutron scattering on κ-(d8-ET)$_2$Cu$_2$(CN)$_3$



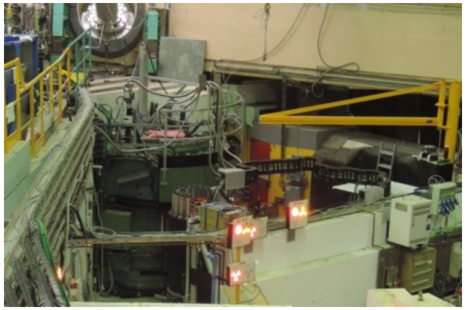


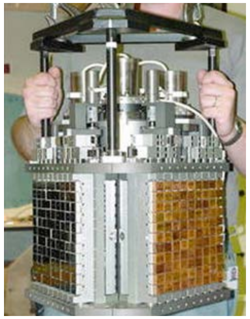
T. Sasaki

47 single crystals (m_{tot} ~ 26 mg)

Triple-axis spectrometer

M. Matsuura





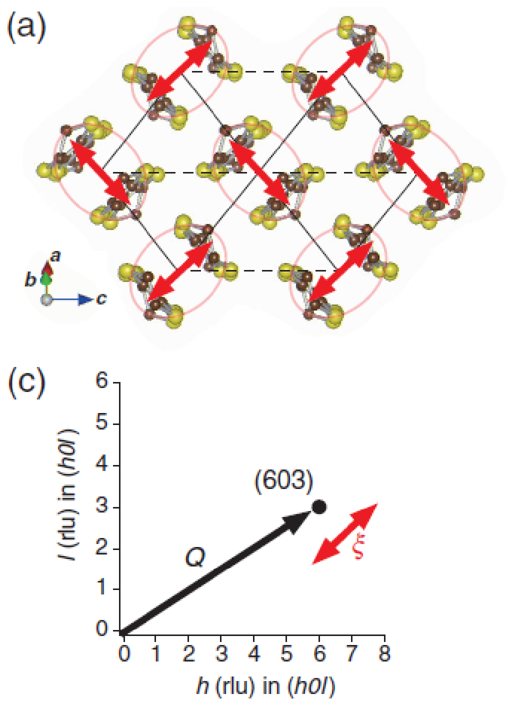
O. Stockert

IN8@ILL France, 2×10^8/cm^{-2}s^{-1}

Phonon anomalies in κ-(d8-ET)$_2$Cu[N(CN)$_2$]Cl

Strong renormalization effects of intra-dimer mode ⇔ spin- & charge d.o.f

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



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

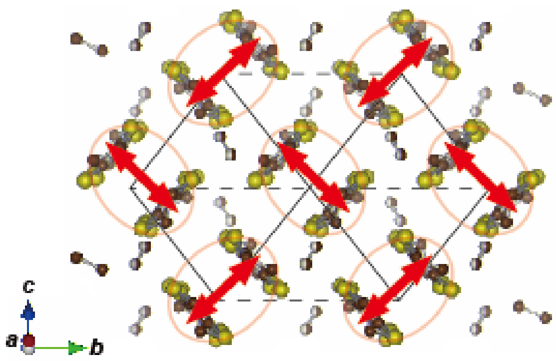
momentum transfer

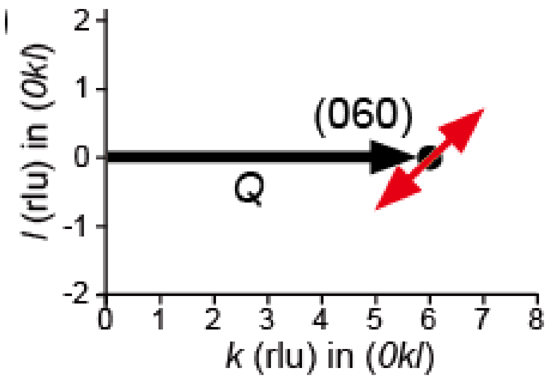
polarization vector of phonon mode

⇒ Q = (603) selected

Inelastic neutron scattering on κ-$(d8\text{-}ET)_2Cu_2(CN)_3$

monoclinic symmetry

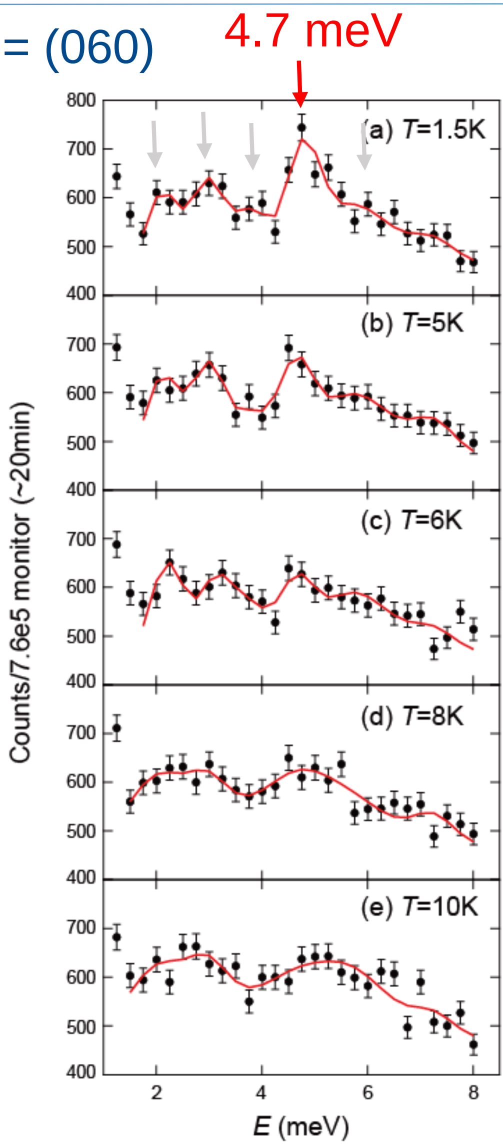




⇒ Q = (060) selected

Inelastic neutron scattering on κ-$(d8\text{-}ET)_2Cu_2(CN)_3$

Q = (060)



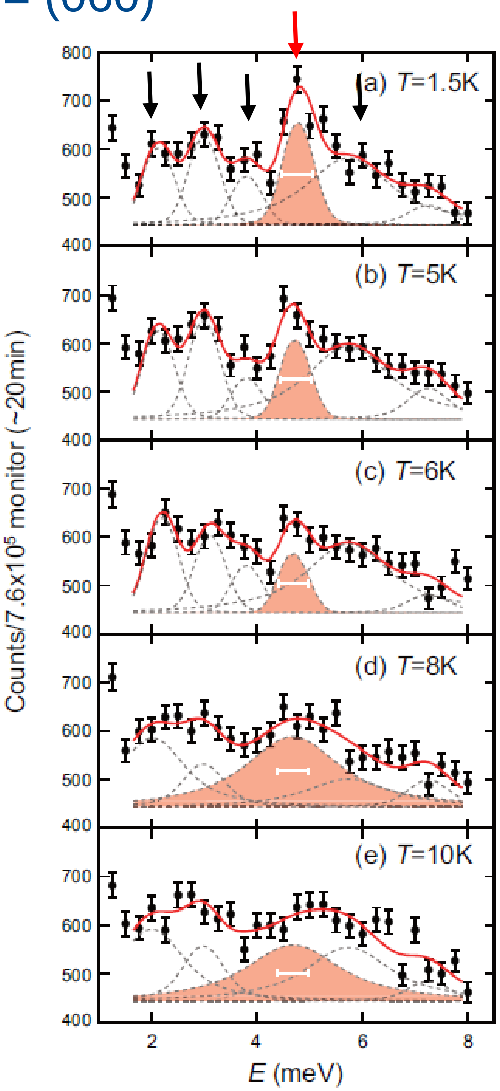
- Phonon peaks at E = 2, 2.9, 3.7, 4.7 & 5.7 meV

  (DFT calculations; SI of Dressel *et al.*, PRB **93**, 081201 (2016))

- Strongly T dependent intensity and width

Inelastic neutron scattering on κ-(d8-ET)$_2$Cu$_2$(CN)$_3$

Q = (060)



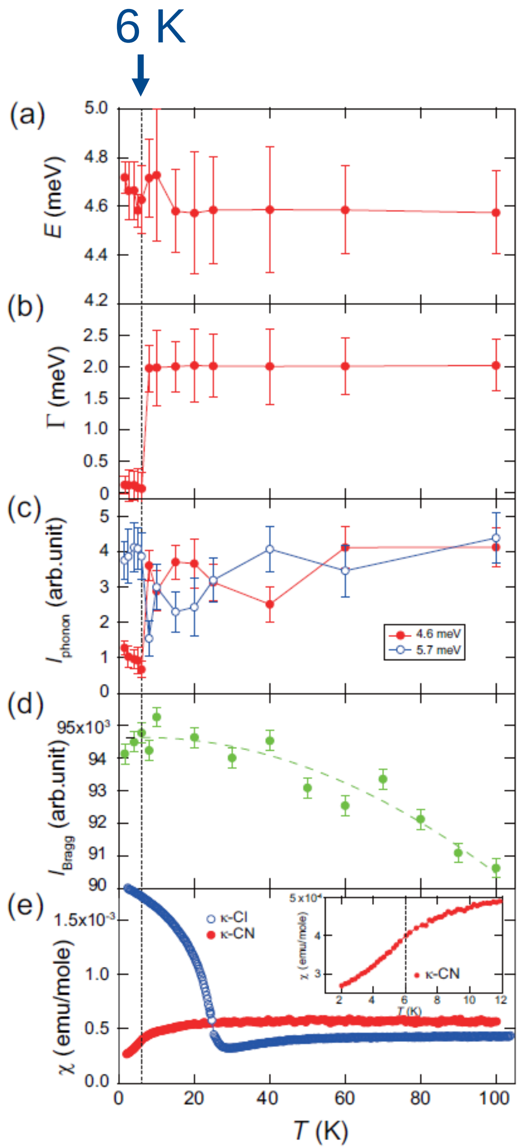
Fits by using damped harmonic oscillator functions

- Strong renormalization of peak at E = 4.7 meV

  (Breathing mode of ET dimers)

⇒ Drastic change in width around 6 K

Inelastic neutron scattering on κ-$(d8\text{-}ET)_2Cu_2(CN)_3$



Fit parameters for breathing mode @ E = 4.7 meV

- Drastic change in damping Γ_q (lifetime $\tau_q \sim \Gamma_q^{-1}$)

  ⇒ strong damping at $T \geq 8$ K

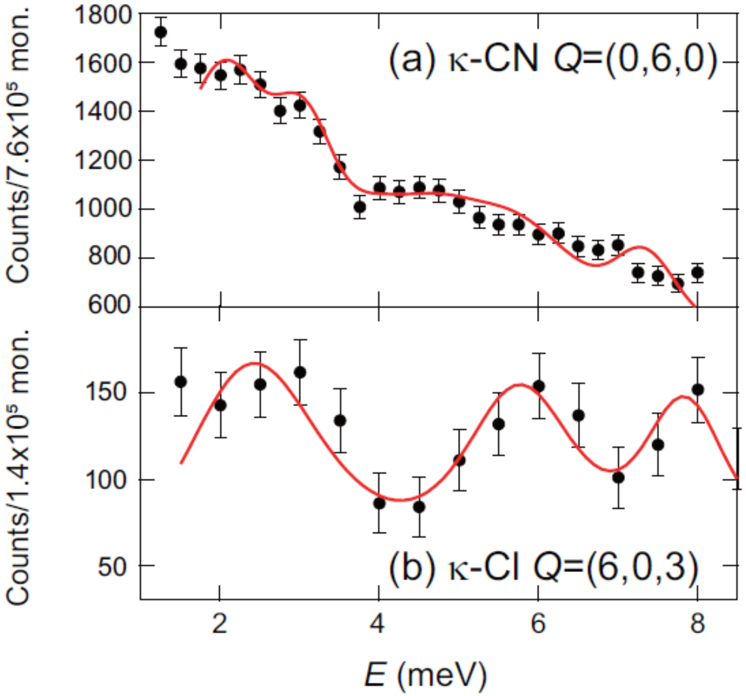
  ⇒ resol.-limited long lifetime below 6 K!

  ⇒ Freezing of phonon-? scattering processes below 6 K

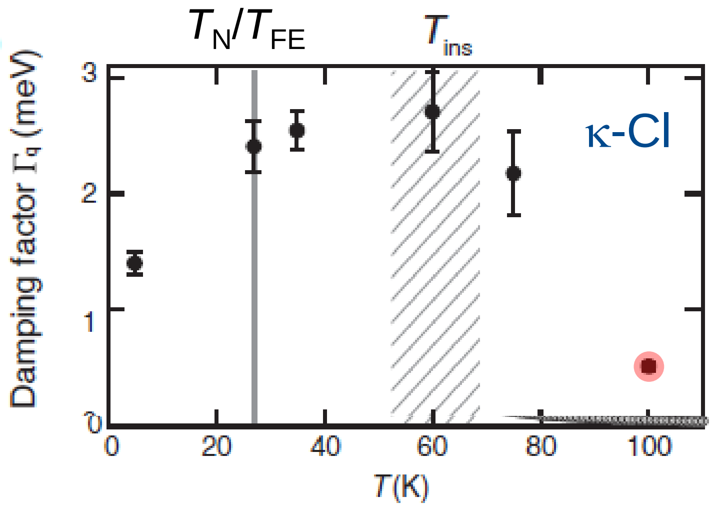
What is the nature of these scatterers?

Inelastic neutron scattering on κ-(d8-ET)$_2$Cu$_2$(CN)$_3$

Phonon modes at 100 K



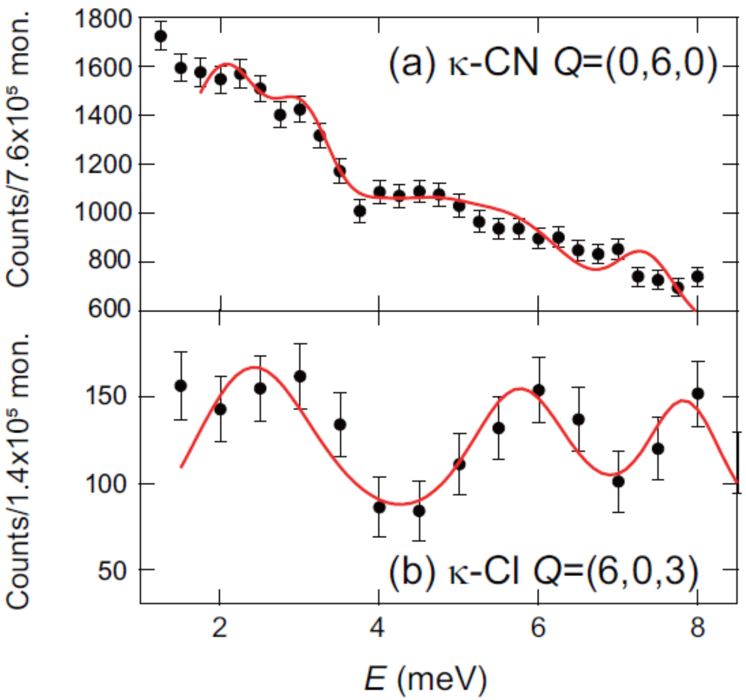
Opening of charge gap



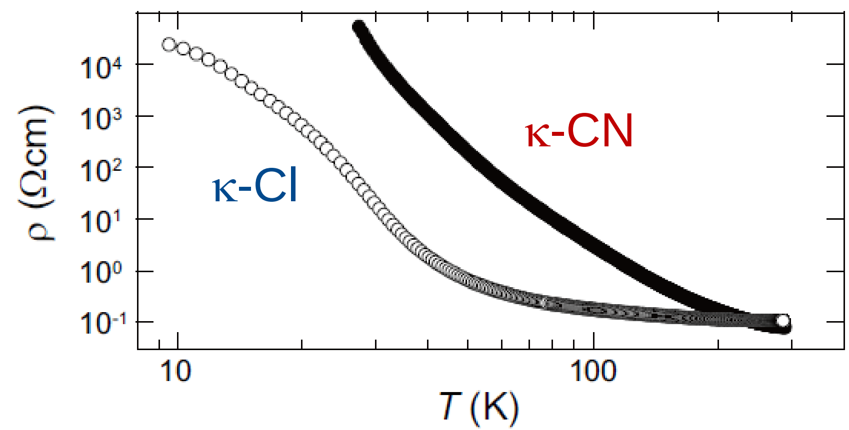
M. Matsuura *et al.*, PRL **123**, 027601 (2019)

Inelastic neutron scattering on κ-$(d8\text{-}ET)_2Cu_2(CN)_3$

Phonon modes at 100 K



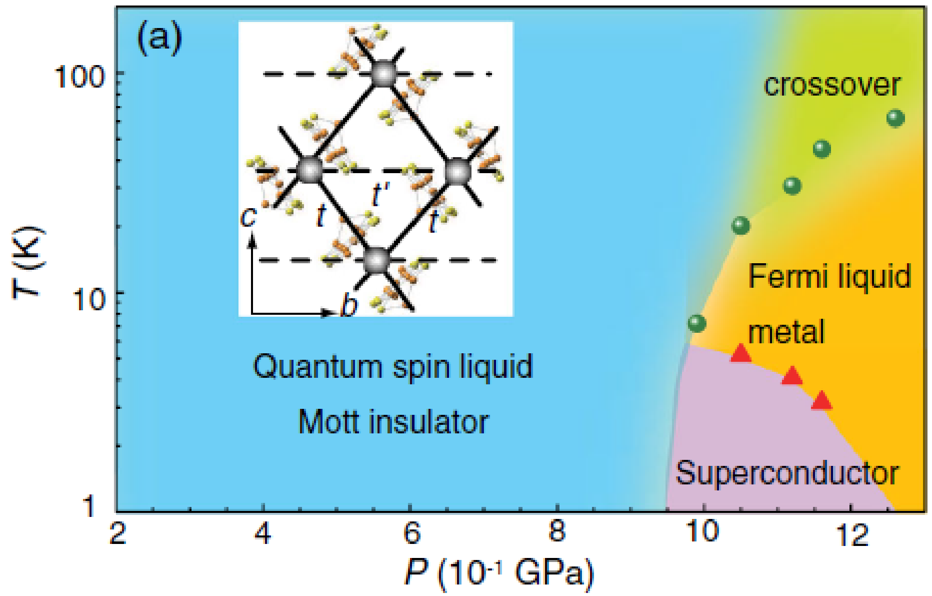
Γ ⇔ charge localization on dimer



Suggesting for κ-CN:

- Phonon damping ⇔ charge- (and spin-) fluctuations on dimer
- Scattering off these fluctuations is frozen below 6 K

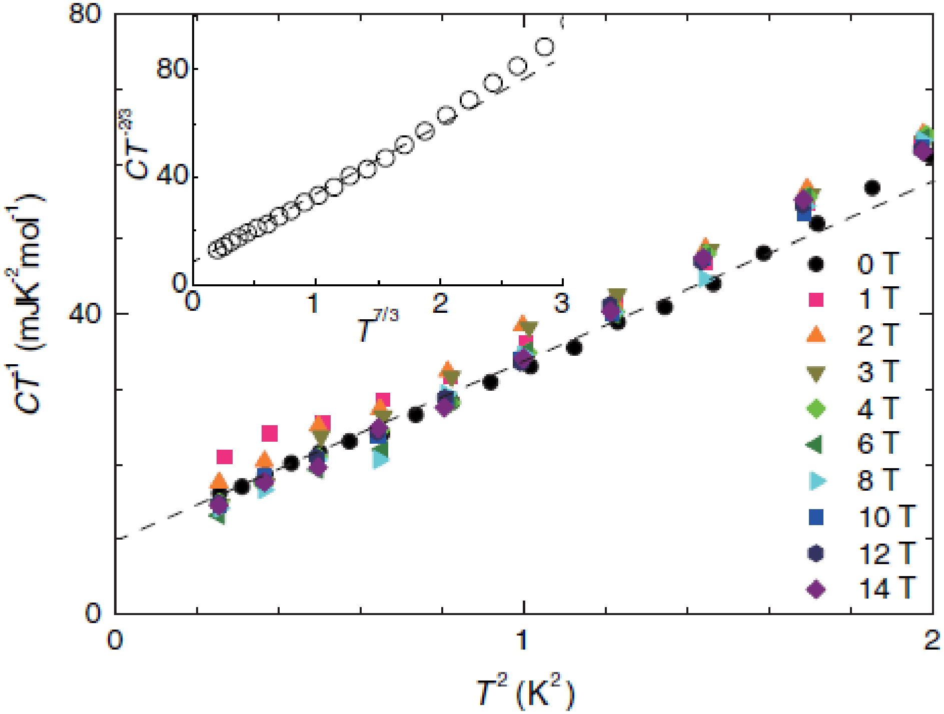
2) κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$



Y. Shimizu *et al.*, Phys. Rev. Lett. **117**, 107203 (2016)

- Phase diagram: similar to X = Cu$_2$(CN)$_3$, except offset ΔP = 0.6 GPa
- Fit to $\chi(T)$: S = ½ triangular−lattice Heisenberg afm with $J \sim$ 175 K
- No long-range order down to 110 mK

κ-$(BEDT\text{-}TTF)_2Ag_2(CN)_3$

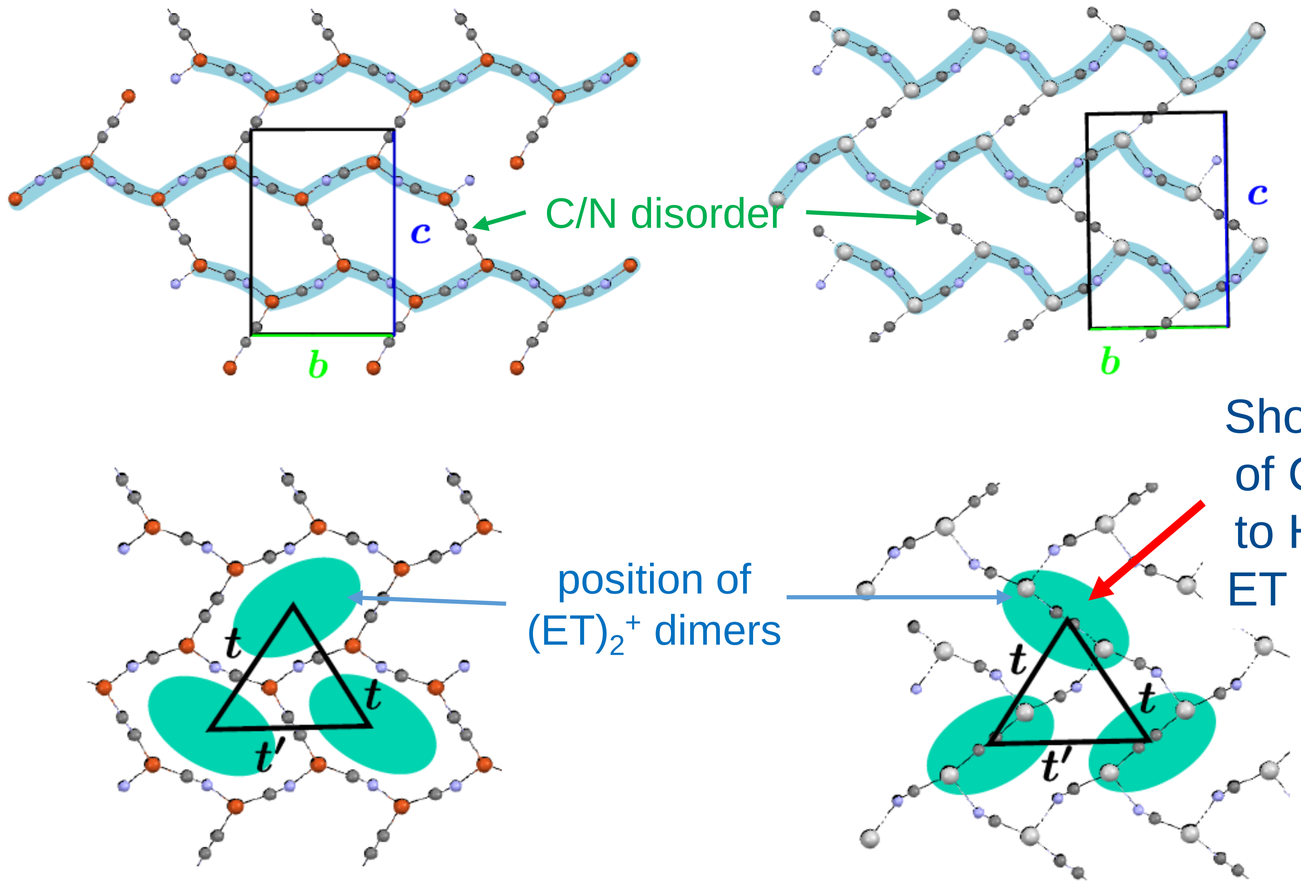


Y. Shimizu *et al.*, Phys. Rev. Lett. **117**, 107203 (2016)

$$\left(C/_T\right)_{T\to 0} = \gamma \sim 10 \text{ mJ mol}^{-1}\text{K}^{-2}$$

Role of anion – template for triangular lattice

$X = Cu_2(CN)_3$ $X = Ag_2(CN)_3$



T. Hiramatsu *et al.*, Bull. Chem. Soc. Jpn. **90**, 1073 (2017)

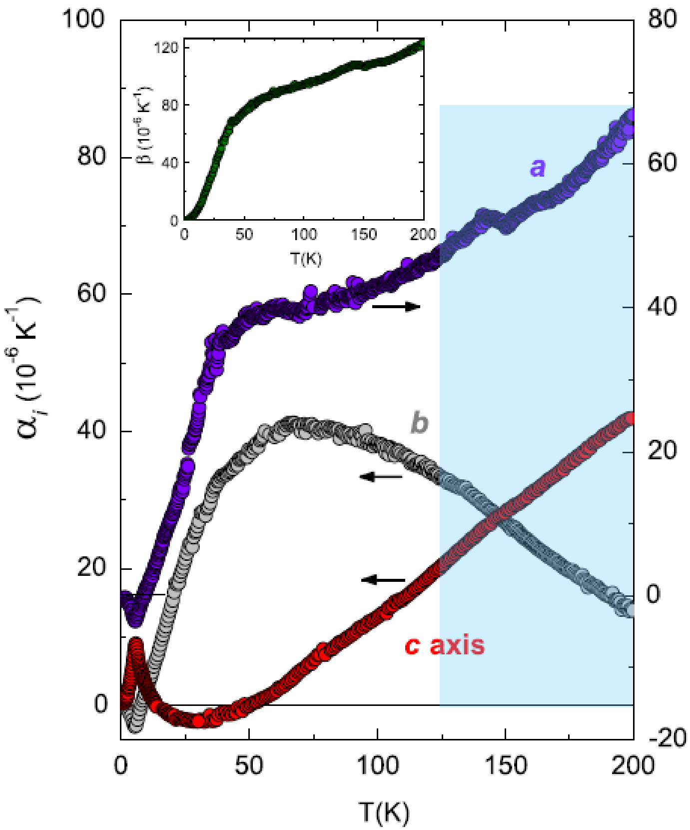
Role of anion – ethylen group conformation

Conformation of ethylen (C_2H_4) endgroups (links between ET ⇔ anion):

	X = $Cu_2(CN)_3$	X = $Ag_2(CN)_3$
300 K	disordered (fluctuating)	ordered (!)
150 K	ordered	ordered

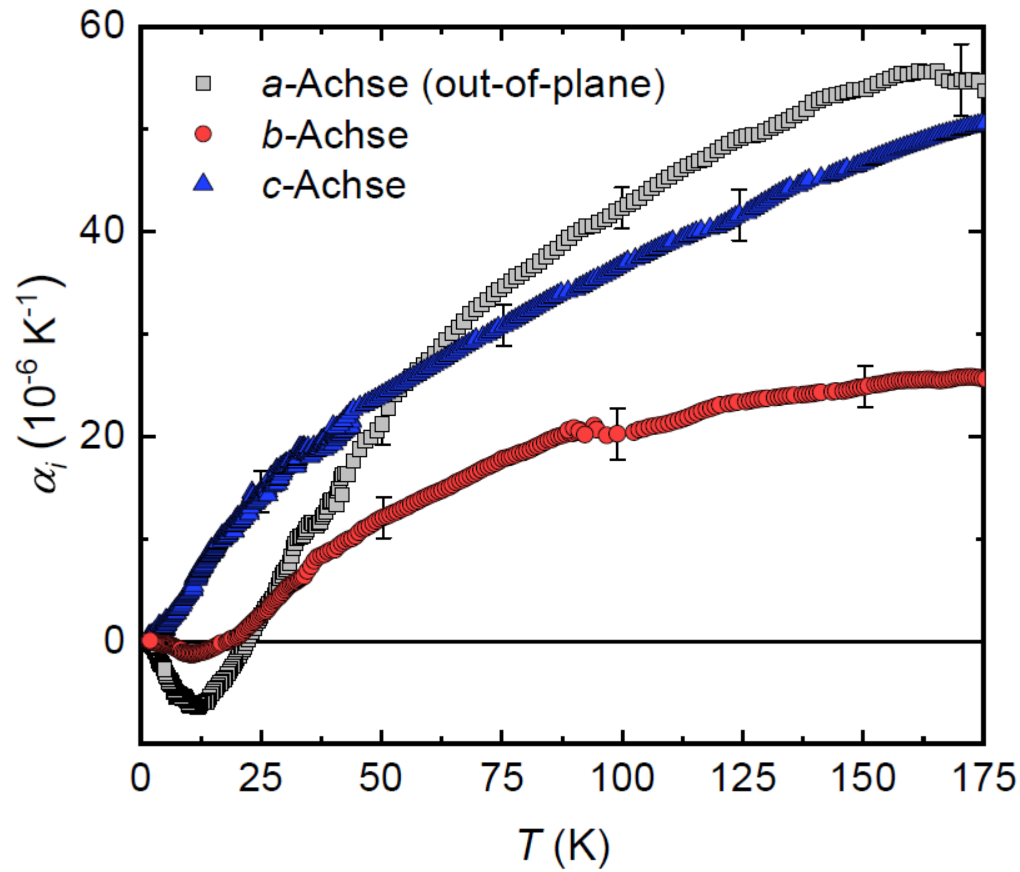
κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$

X = $Cu_2(CN)_3$



- Strong distortions due to motions of ethylene endgroups !

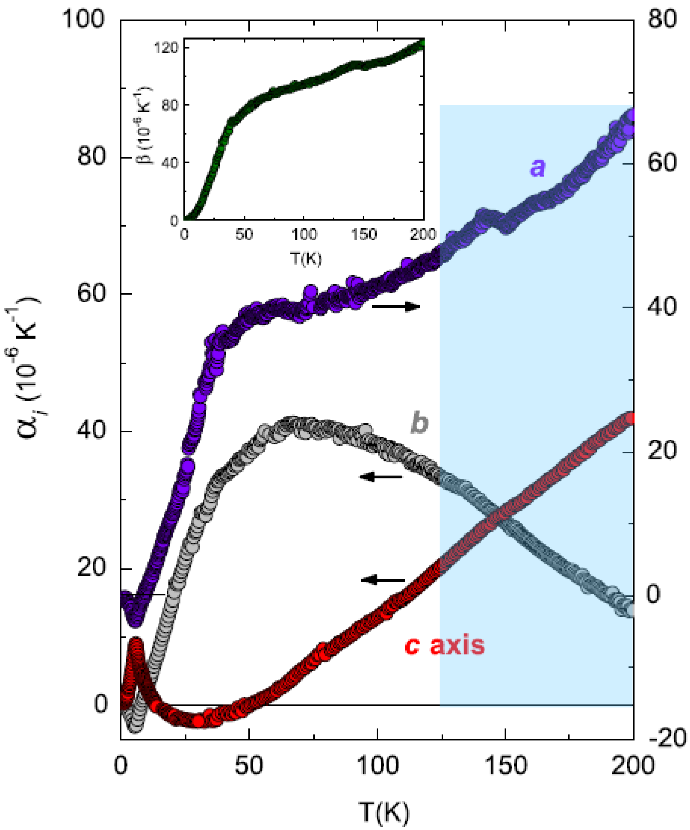
X = $Ag_2(CN)_3$



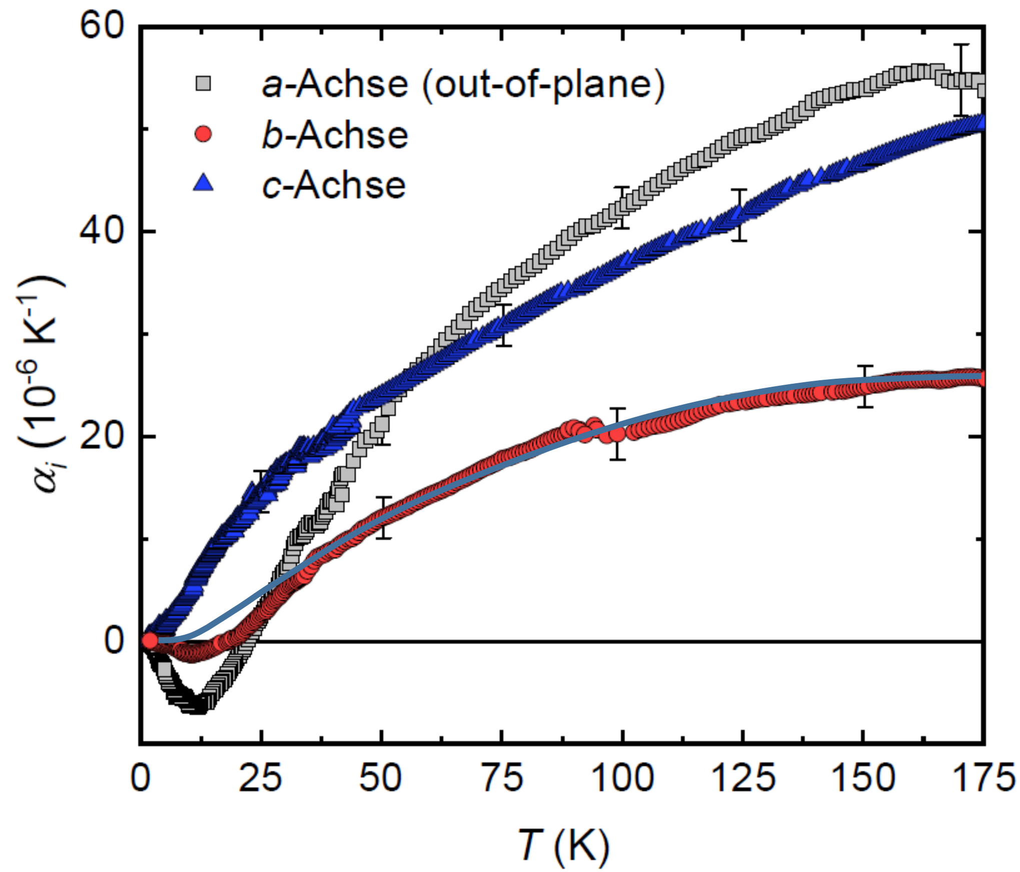
- Free of anomalies related to ordering of ethylene endgroups !

κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$

X = Cu$_2$(CN)$_3$



X = Ag$_2$(CN)$_3$

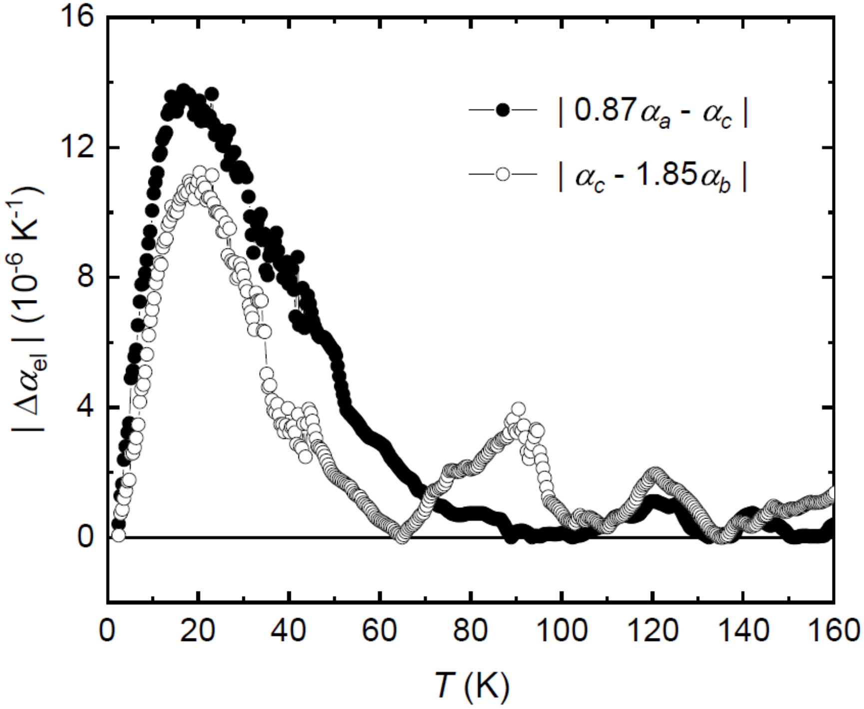


- Strong distortions due to motions of ethylene endgroups !

- Enable to access the anomalous contribution at low T

Extraction of anomalous “electronic contribution“

Ass.: $|\alpha_a^{el}| \propto |\alpha_b^{el}| \propto |\alpha_c^{el}|$ and $|\alpha_a^{latt}| \propto |\alpha_b^{latt}| \propto |\alpha_c^{latt}|$



S. Hartmann *et al.*, Phys. Stat. Sold. B **256**, 1800640 (2019)

$\alpha_i^{el} \Leftrightarrow$ thermodynamics of the strongly frustrated S = ½ triangular lattice

Hubbard model on an anisotropic triangular lattice

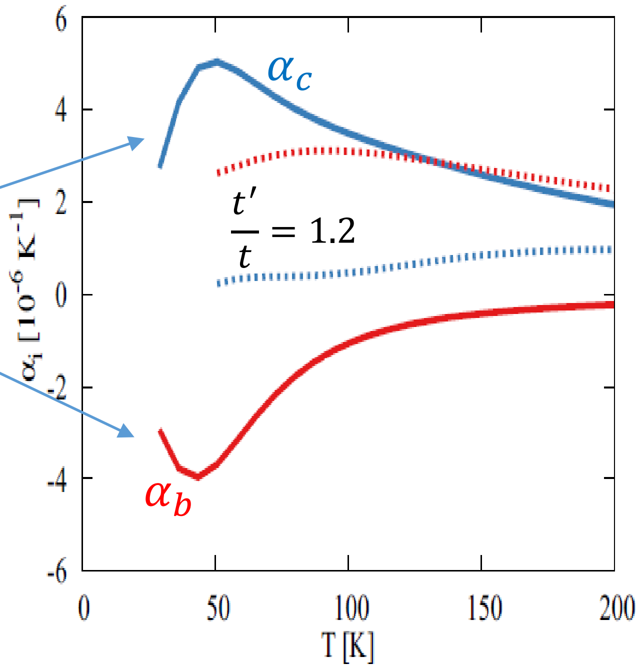
$$\alpha_i(T) \sim \frac{\partial t}{\partial l_i} \cdot \left(\frac{\partial S}{\partial t}\right)$$

using parameters
for X = $Cu_2(CN)_3$

$U = 8t$

(Mott insulator)

$\frac{t'}{t} = 0.8$



J. Kokajj and R. McKenzie,
PRB **91**, 205121 (2015)

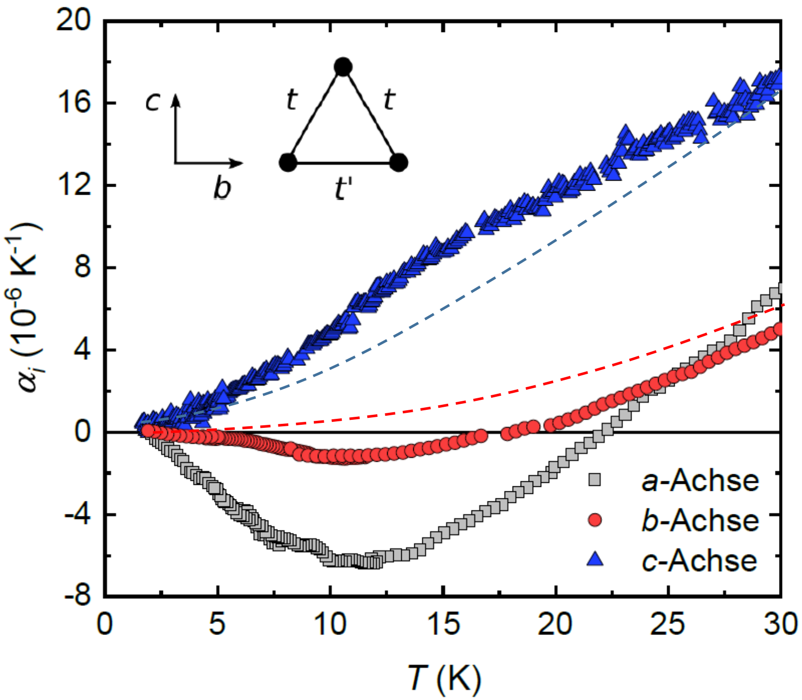
- Pronounced low-*T* anomaly in α_i^{el} (similar to exp. observation)
- Position and anisotropy depend sensitively on $\frac{U}{t}$ and $\frac{t'}{t}$

$\Rightarrow \alpha_i(T)$: Sensitive tool to extract Hubbard parameters

Implications

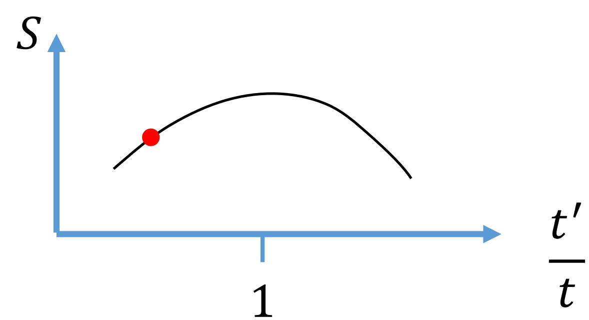
X = $Ag_2(CN)_3$

$$\alpha_i = -\frac{1}{L}\cdot\frac{\partial S}{\partial p_i}$$



$\alpha_c^{el} > 0$: increasing $p_c, t \Rightarrow$ decrease of S

$\alpha_b^{el} < 0$: increasing $p_b, t' \Rightarrow$ increase of S



X = $Ag_2(CN)_3$ $\Rightarrow$ $\frac{t'}{t} < 1$

X = $Cu_2(CN)_3$ $\Rightarrow$ $\frac{t'}{t} > 1$!

G. Saito *et al*., Bull. Chem. Soc. Jpn. **80**, 1 (2007)
S. M. Winter *et al*., PRB **95**, 060404 (2017)

H. O. Jeschke *et al*., PRB **85**, 035125 (2012)
S. M. Winter *et al*., PRB **95**, 060404 (2017)

Summary

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- 2^{nd} order phase transition at 6 K
  pronounced in-plane lattice distortion,
  no *B* dependence for $B \leq 8$ T
  significant sample-to-sampe variations in the size of the anomaly

- Pronounced phonon renormalization (intra-dimer mode) around 6 K
  strong damping for $T \geq 8$ K $\Leftrightarrow$ charge- (and spin-) fluctuations on dimer
  scattering off these fluctuations is frozen below 6 K

- Anomalous (& strong) lattice effects at high $T \leftrightarrow$ motions of ethylen endgroups

Summary

κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$

- Ordered ethylene endgroups for $T \leq 300$ K! $\Leftrightarrow$ ordinary lattice contraction

- Enabling to access the "electronic contribution" around 20 K
  $\Rightarrow$ thermodynamics of the triangular-lattice S = ½ system $\Leftrightarrow$ consistent with theoretical predictions

- No indication for a phase transition anomaly for $T > 1.5$ K !

- Still candidate for QSL ground state

Thank you for your attention