分子性導体の外場応答
強電場効果

（物性研究所・新物質科学研究部門）
森　初果

強相関電子系の特徴

非ダイマー型　1/4-filled系

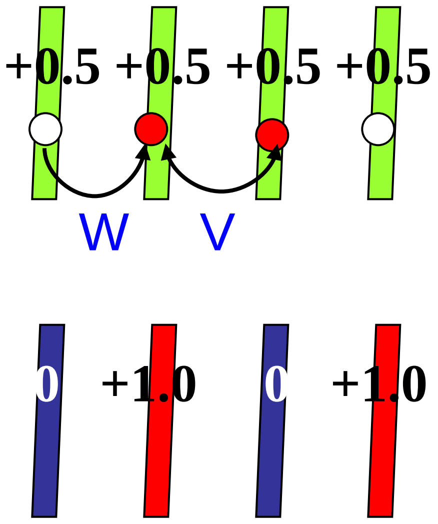
（W ~ 0.8 eV, V ~ 0.5eV）

W (分子軌道間相互作用＝運動エネルギー)
→**金属**

vs.

V(分子間クーロン斥力)
→ vs. **電荷秩序絶縁相**

H.Seo, H.Fukuyama, J.Phys.Soc.Jpn., 66, 1249(1997).



外場応答

１　圧力　電荷秩序絶縁相 →超伝導→金属相

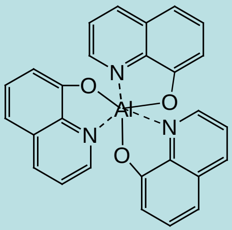
２　電場　巨大非線形伝導、電場誘起準安定状態、有機サイリスタ

３　磁場　巨大磁気抵抗

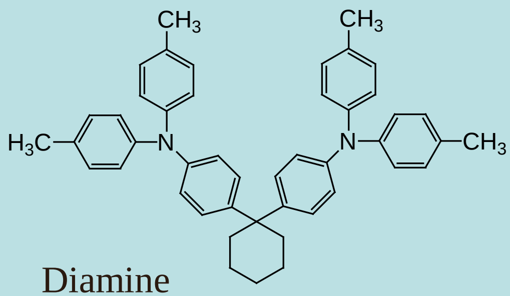
４　光　光誘起金属状態

Organic electronics

Organic EL (Electroluminescence)

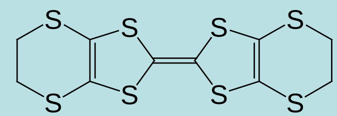


Alq_3



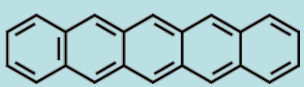
Diamine

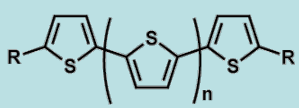
Organic Supercon.

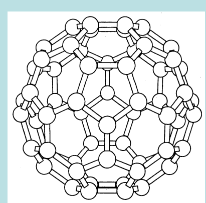


BEDT-TTF

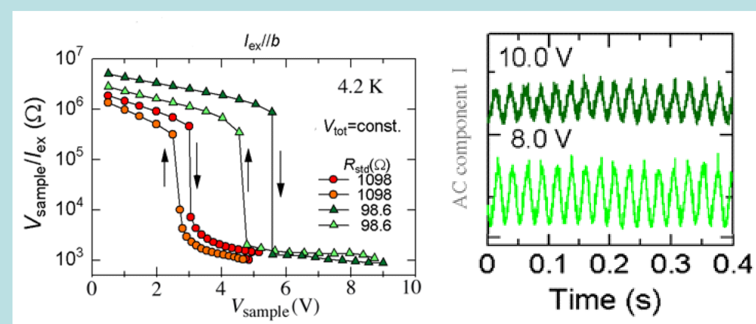
Organic FET (Field-Effect Transistor)







Organic nonlinear device (Organic thyristor)



Responses by Electric Field

（1）直流ー交流変換⇒振動、リズム
Organic thyristor (4K); θ-$ET_2CsCo(SCN)_4$
F. Sawano *et al.*, Nature 437 (2005) 522.

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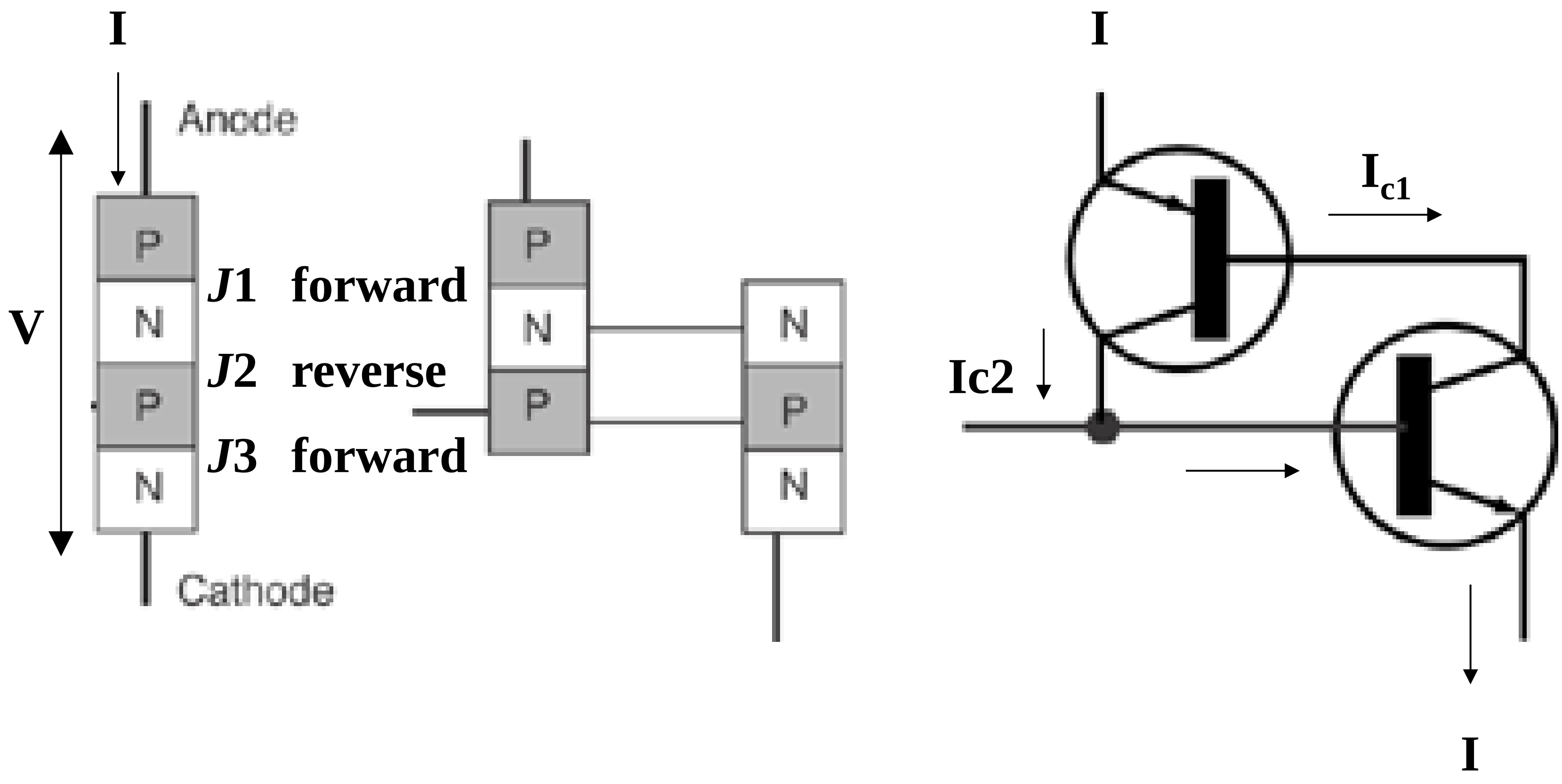
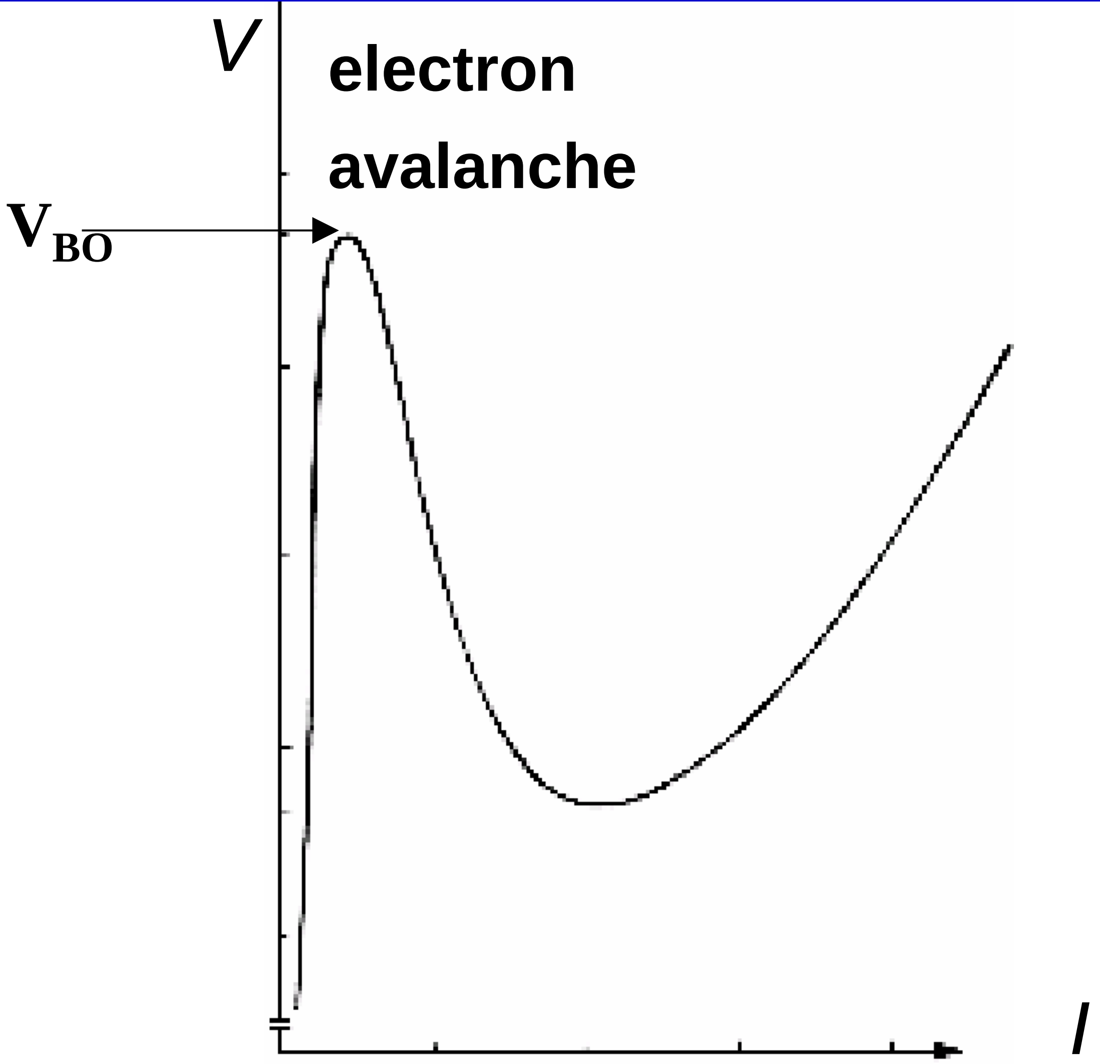
Voltage oscillation (88 K); α-ET_2I_3
K. Tamura *et al.*, J. Appl. Phys. **107**, 103716(1-5) (2010).

⇒非平衡科学（舞台：有機伝導体）

Thyristor


I
Anode
V
P
N
P
N
J1 forward
J2 reverse
J3 forward
Cathode
P
N
P
N
P
N
I
I_{c1}
Ic2
I

I-*V* Characteristics of Thyristor

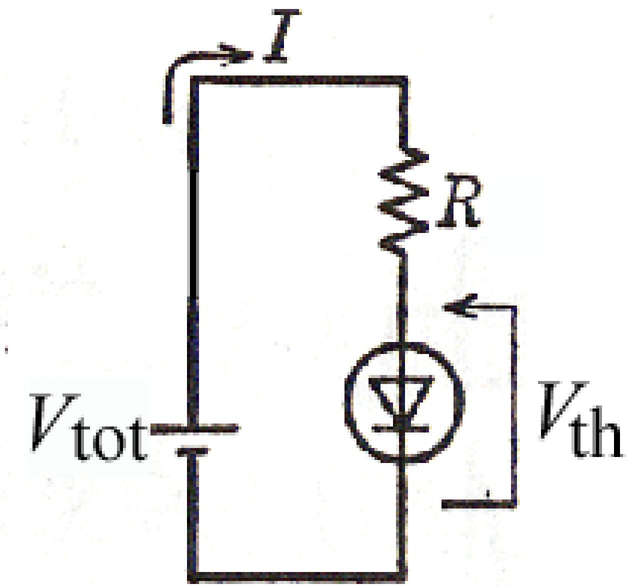


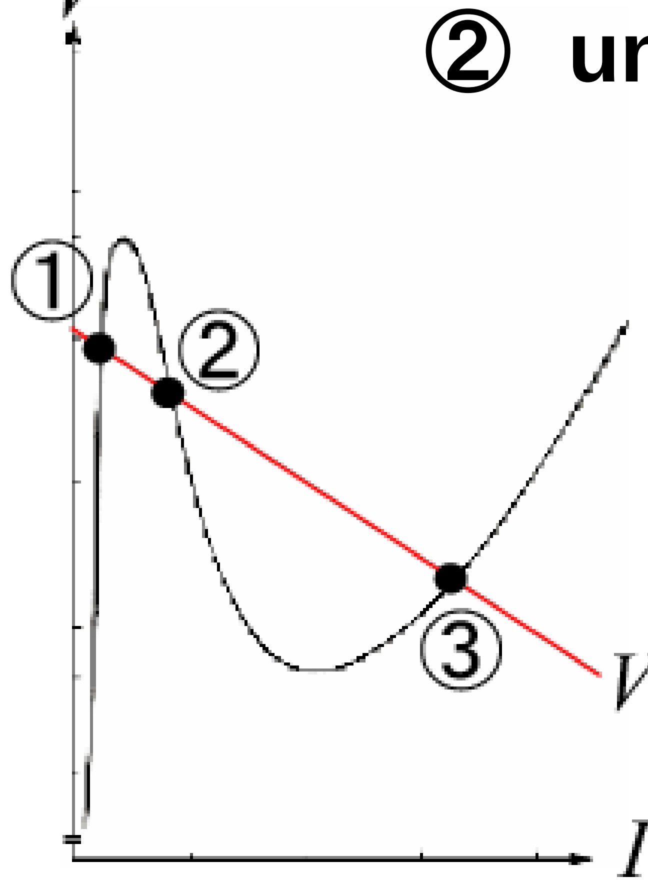
I-*V* Characteristics of Thyristor

①、③ stable point

② unstable point

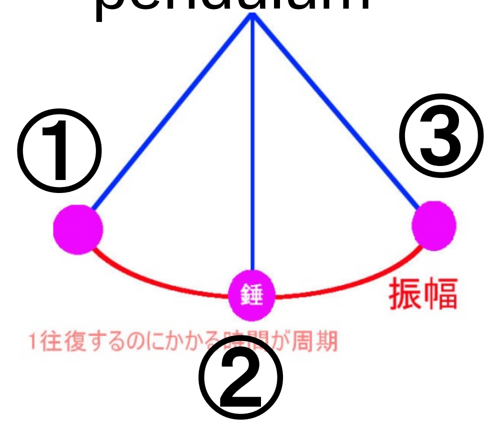
thyristor



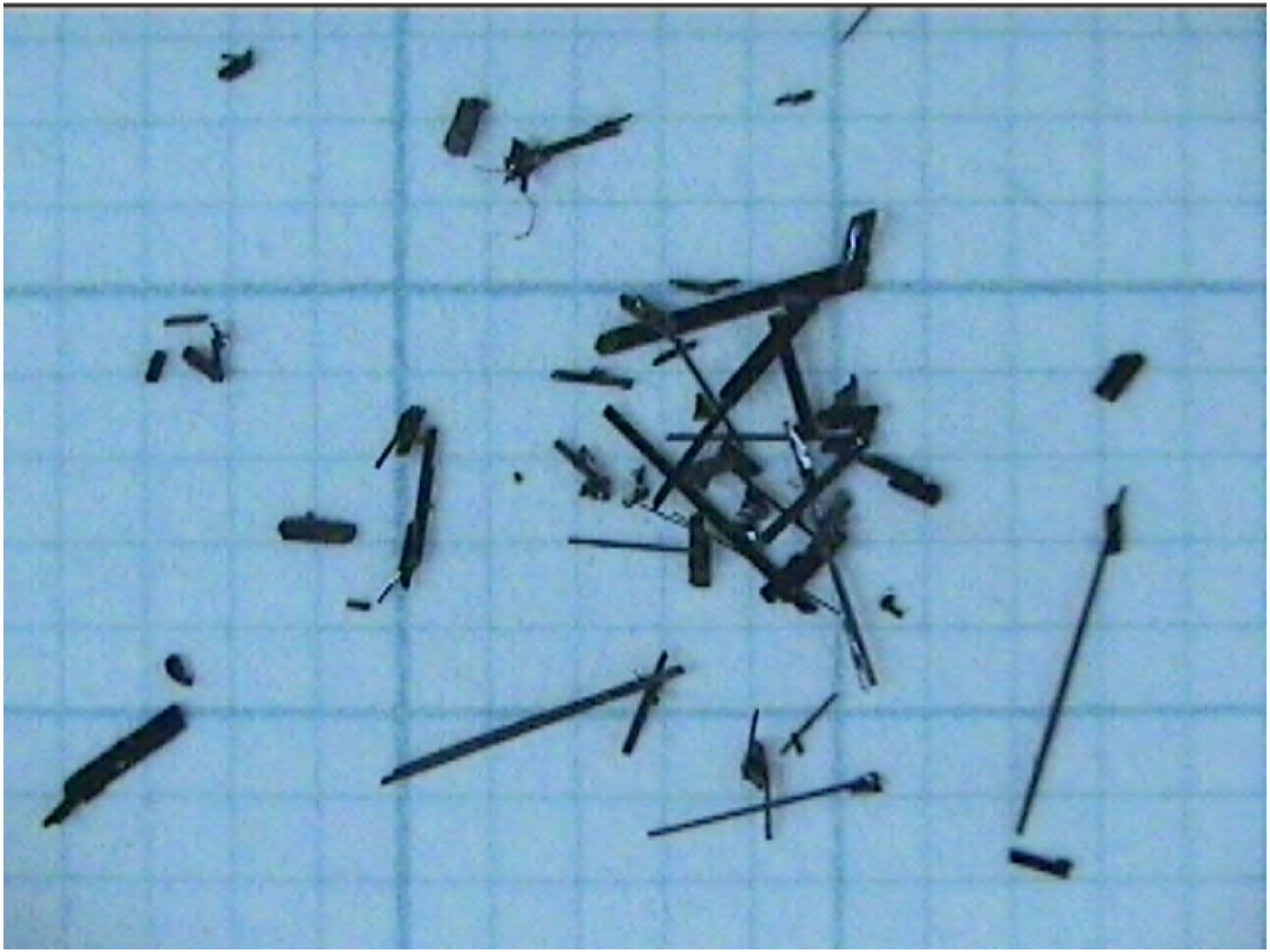


$V_{th} = V_{tot} - RI$

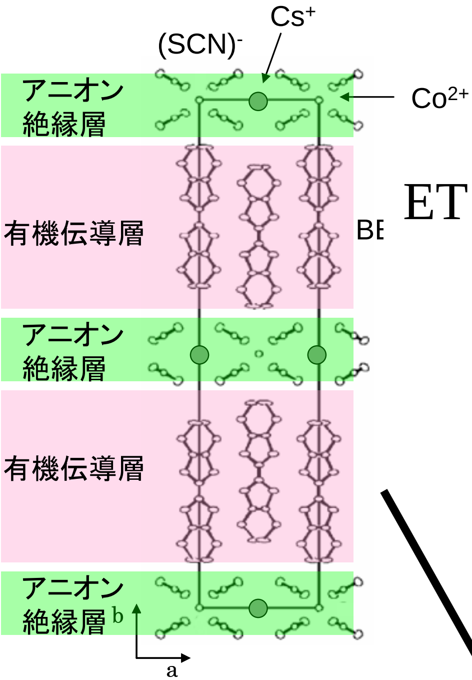
pendulum

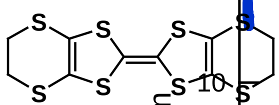


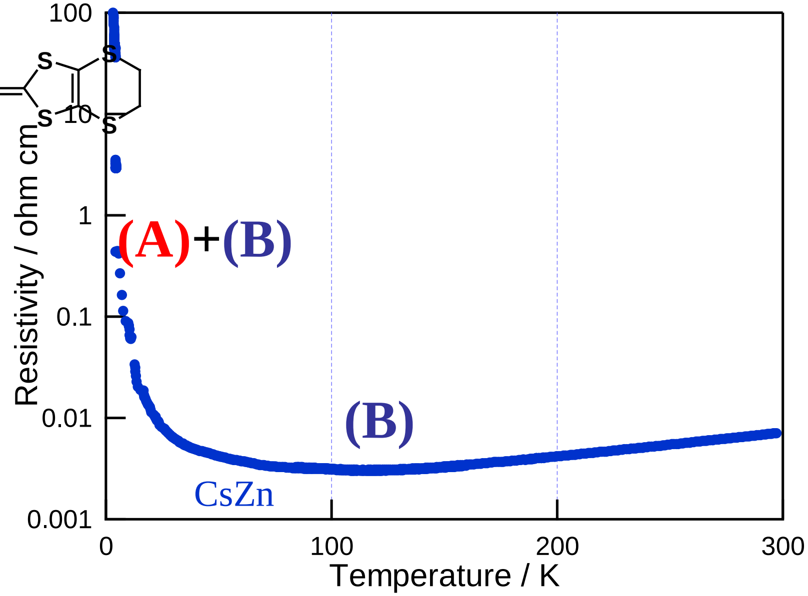
Single Crystals of theta-$ET_2CsCo(SCN)_4$

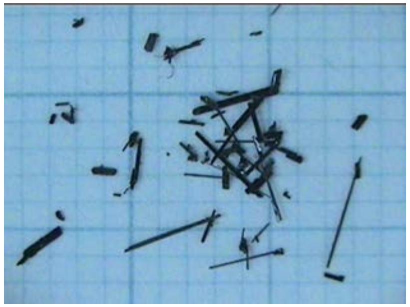


Competition and Co-existence of two kinds of CO
Organic thyristor θ-$[ET_2]^+[CsCo(SCN)_4]^-$

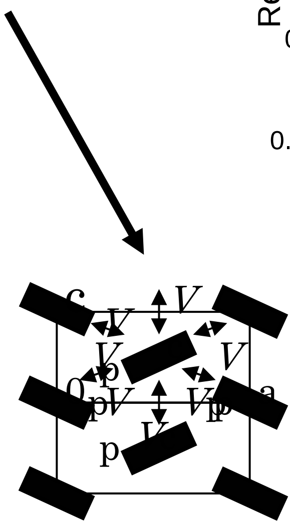


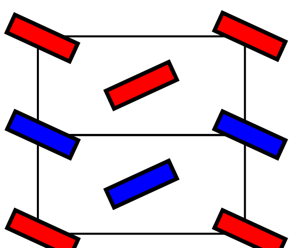
ET 

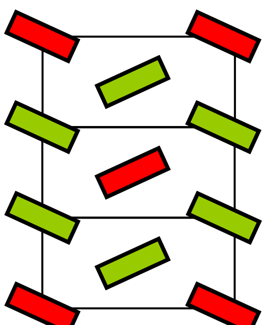




H.Mori et al., PRB 57, 12023 (1998).





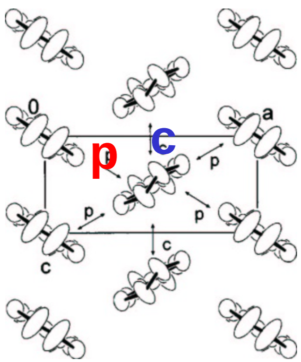


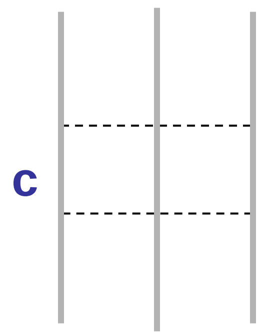
(A)Stripe 2-fold
Insulating state

(B) 3-fold Itinerant state

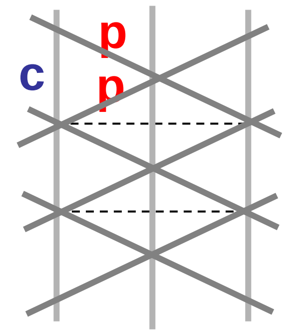
M.Watanabe et. al: JPSJ 68 (1999) 2654.

θ-type ET Salts

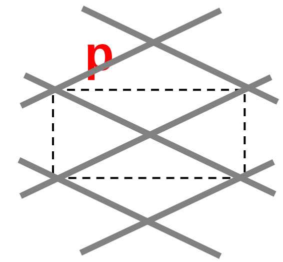




$p = 0$
1D lattice



$p = c$
triangular lattice

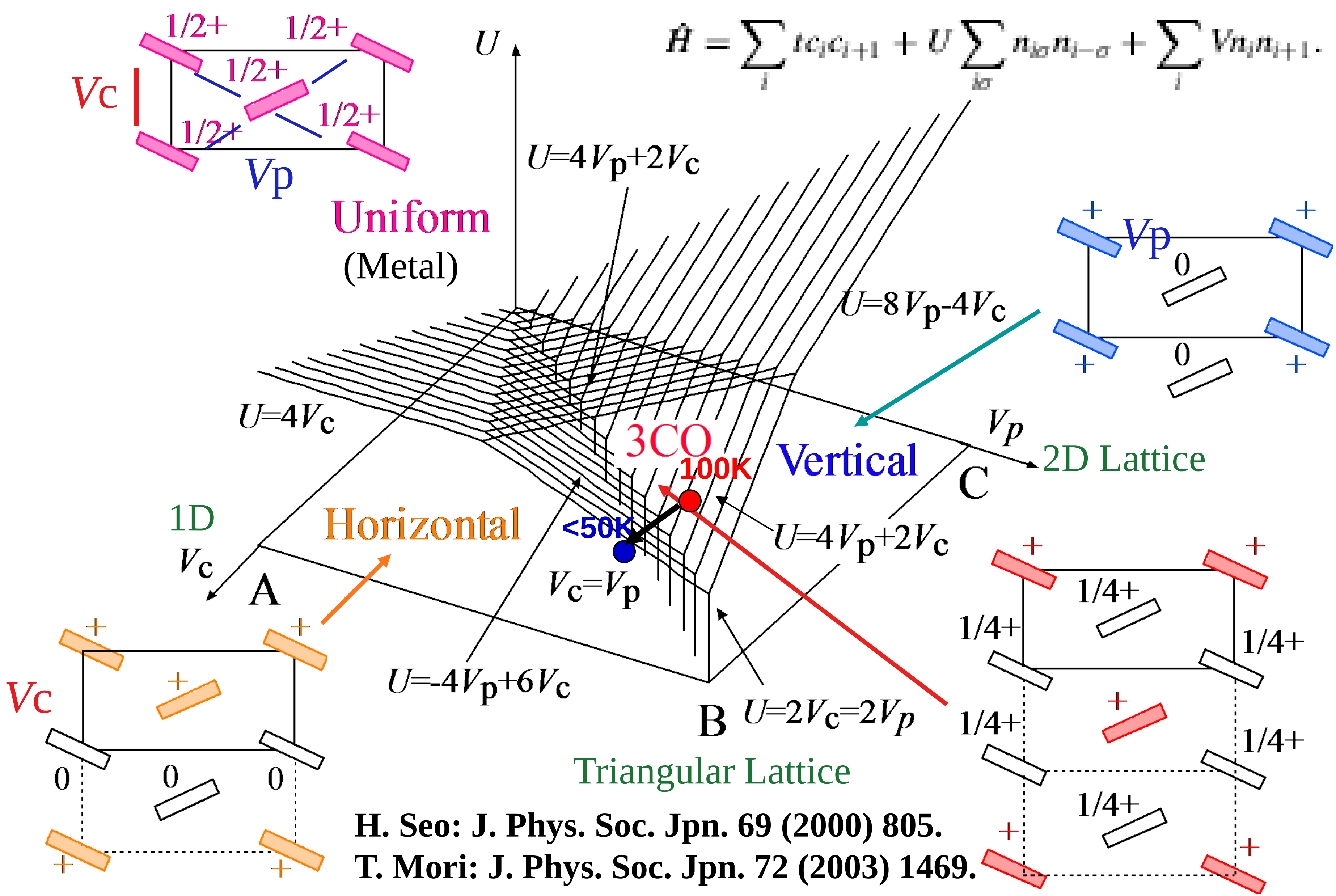


$c = 0$
2D lattice

V

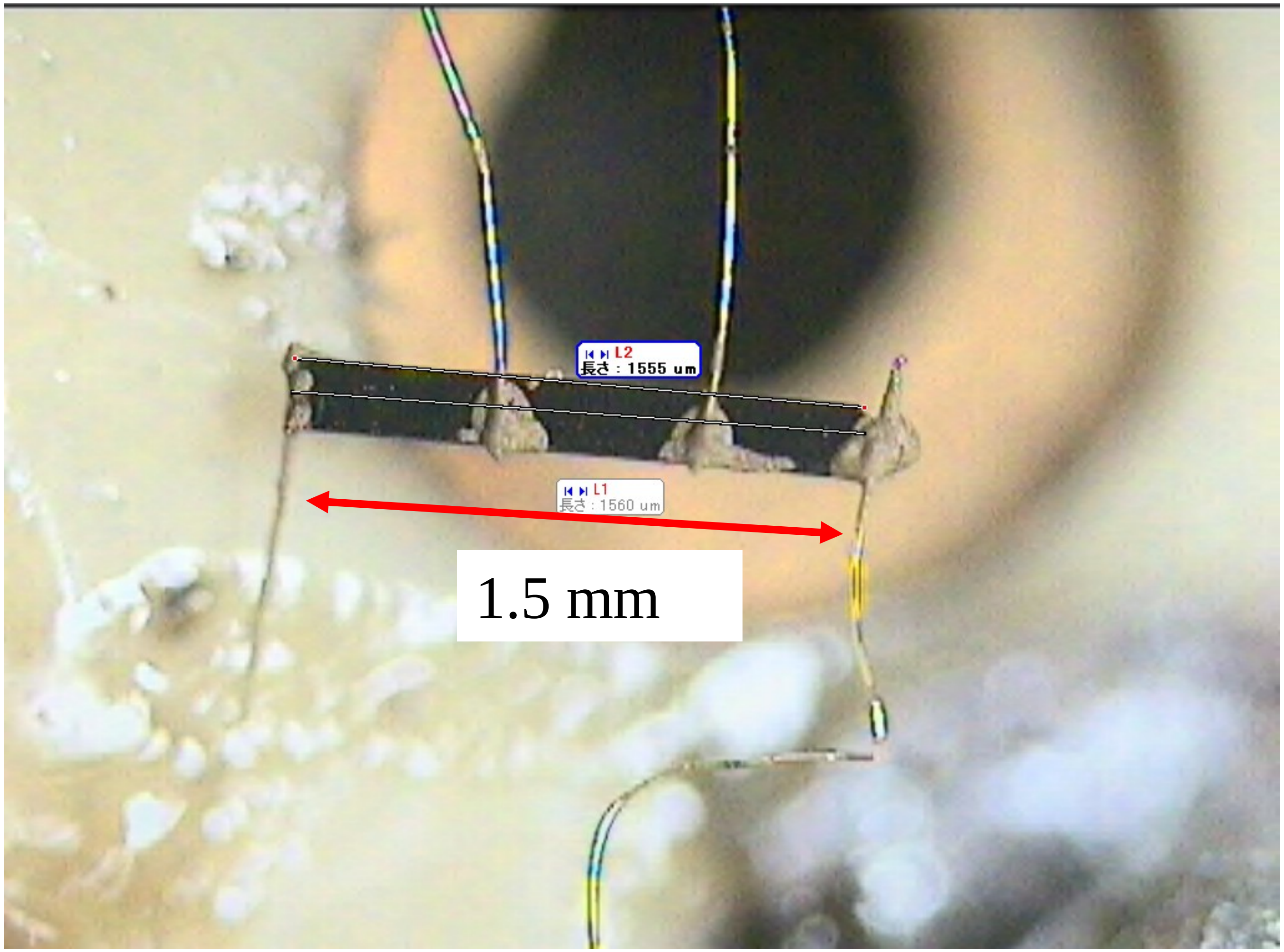
t

θ-type Charge Ordered Pattern

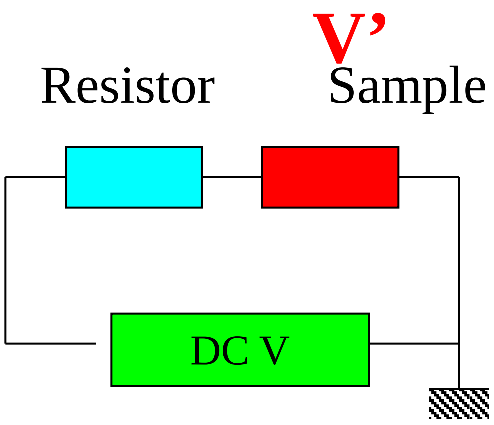


H. Seo: J. Phys. Soc. Jpn. 69 (2000) 805.
T. Mori: J. Phys. Soc. Jpn. 72 (2003) 1469.

Single Crystals of theta-$ET_2CsCo(SCN)_4$

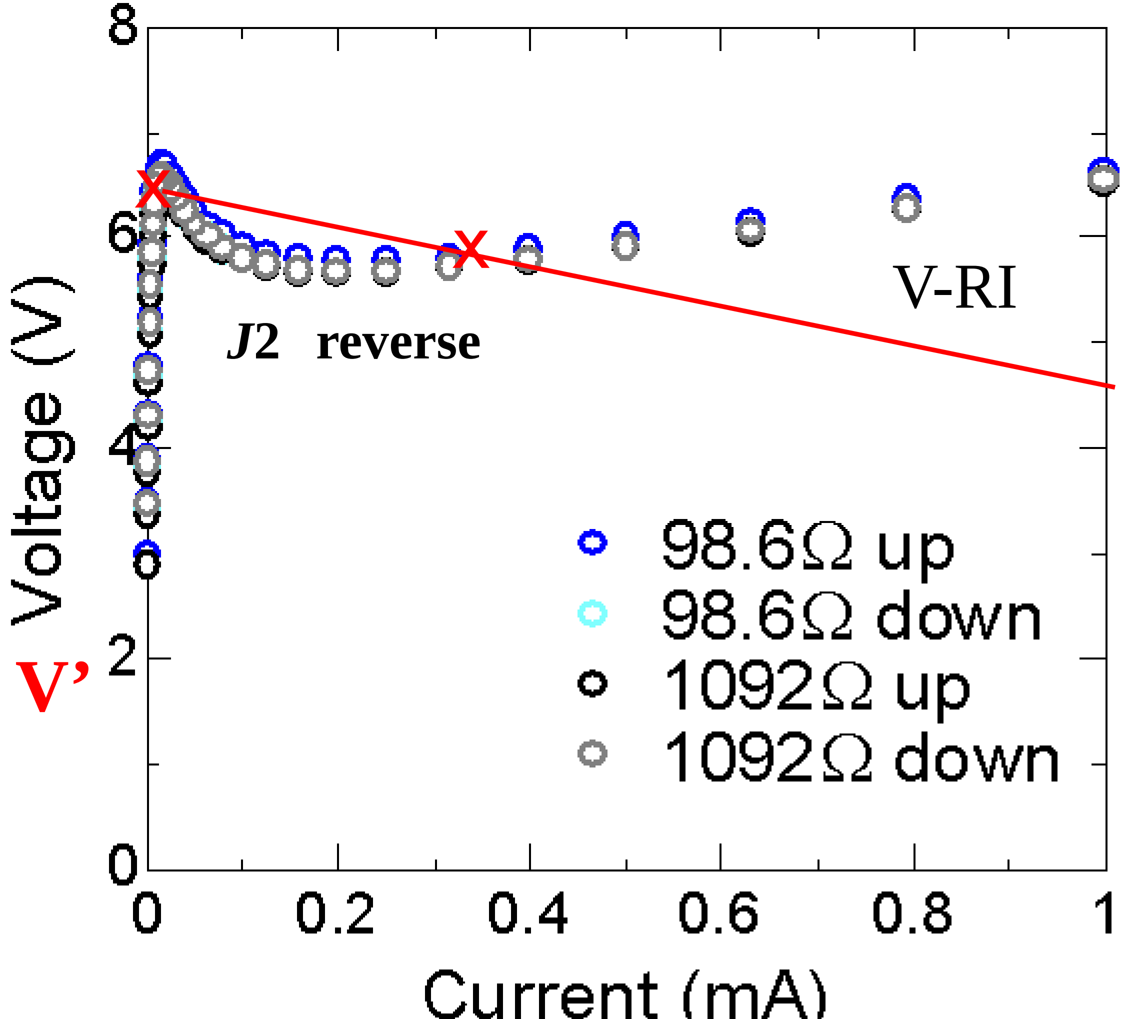


I-V Characteristics

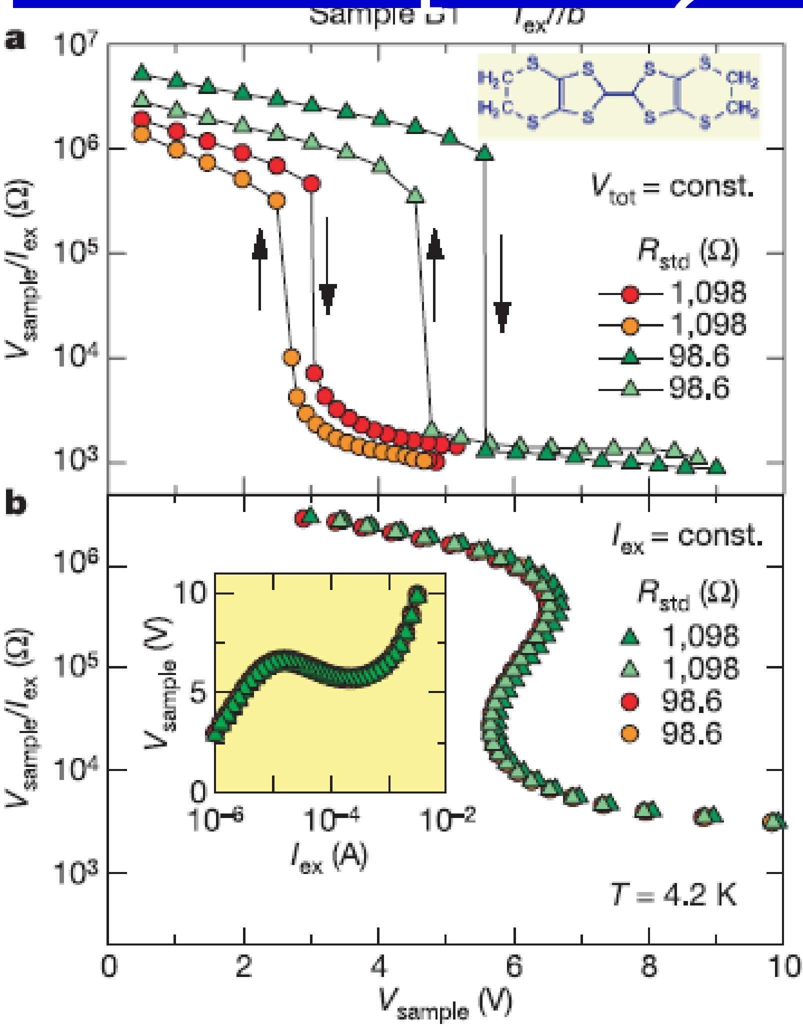


Two stable points

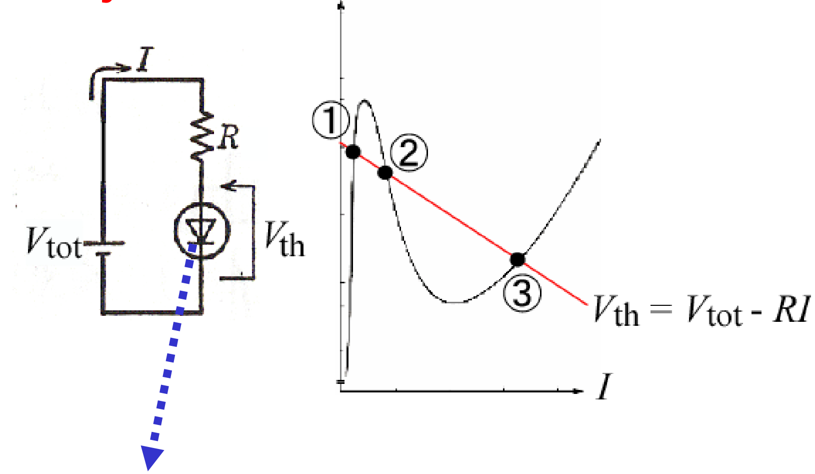
→Oscillation of Current



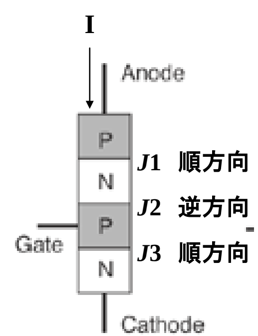
Bias dependence [θ-ET$_2$CsZn(SCN)$_4$]

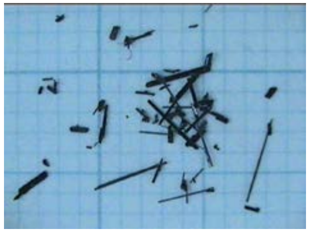


Thyristor

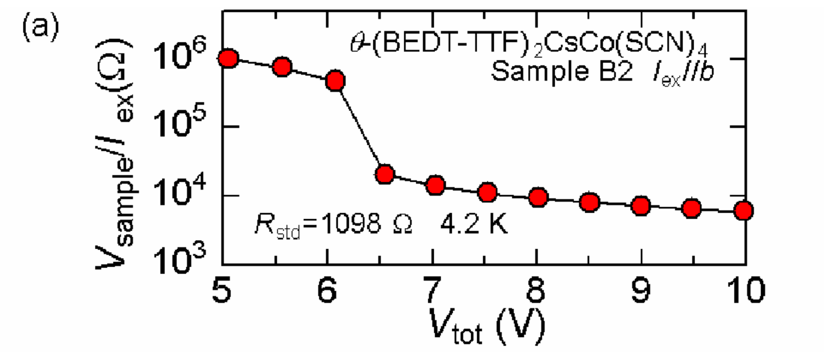


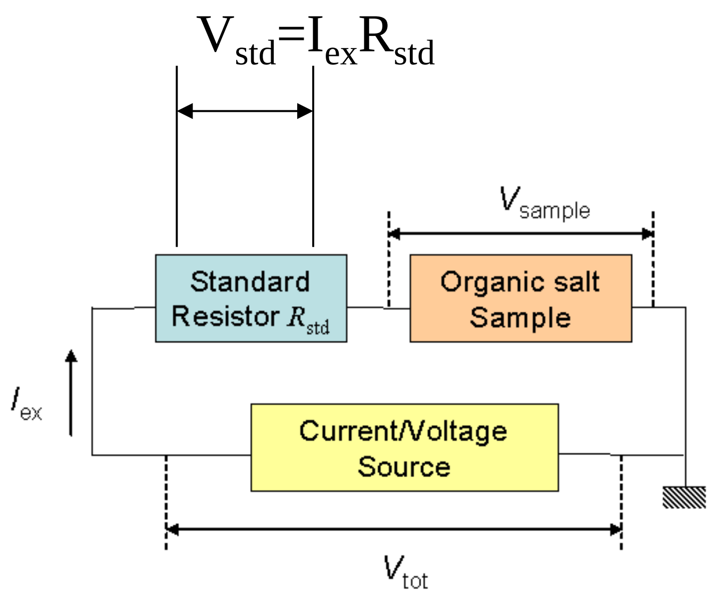
Silicon pnpn junction -> Organic Crystal

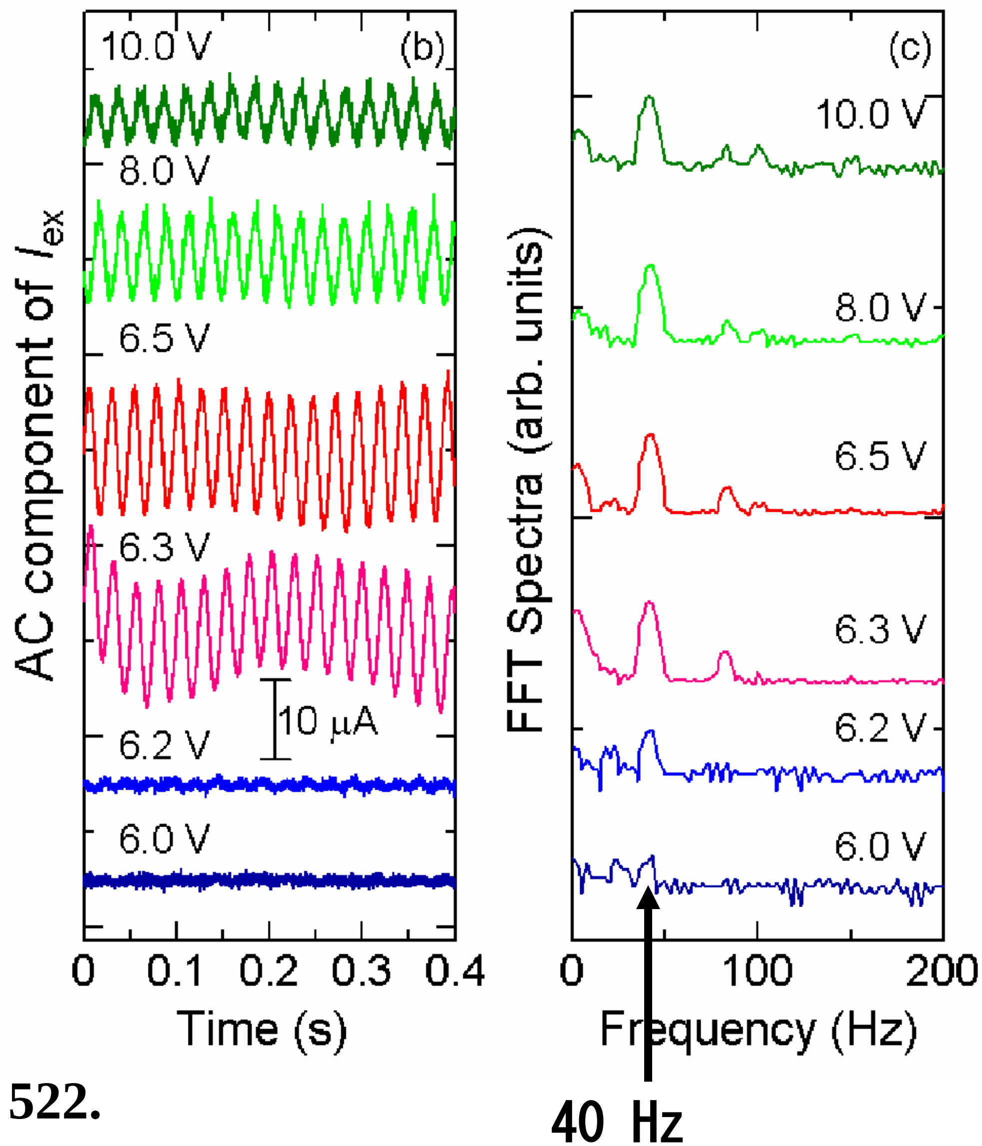




Inverter DCV-ACI Conversion







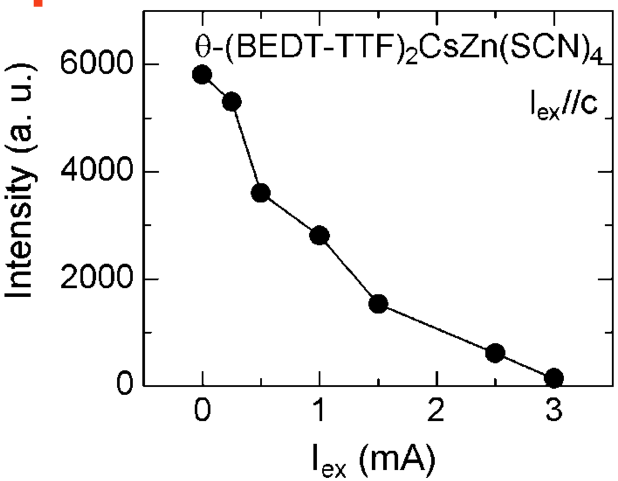
F. Sawano et al.: Nature 437 (2005) 522.

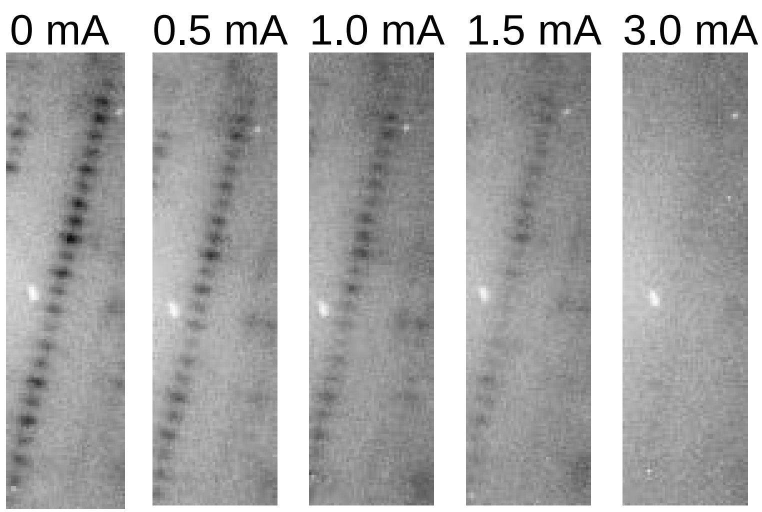
θ-$ET_2CsCo(SCN)_4$

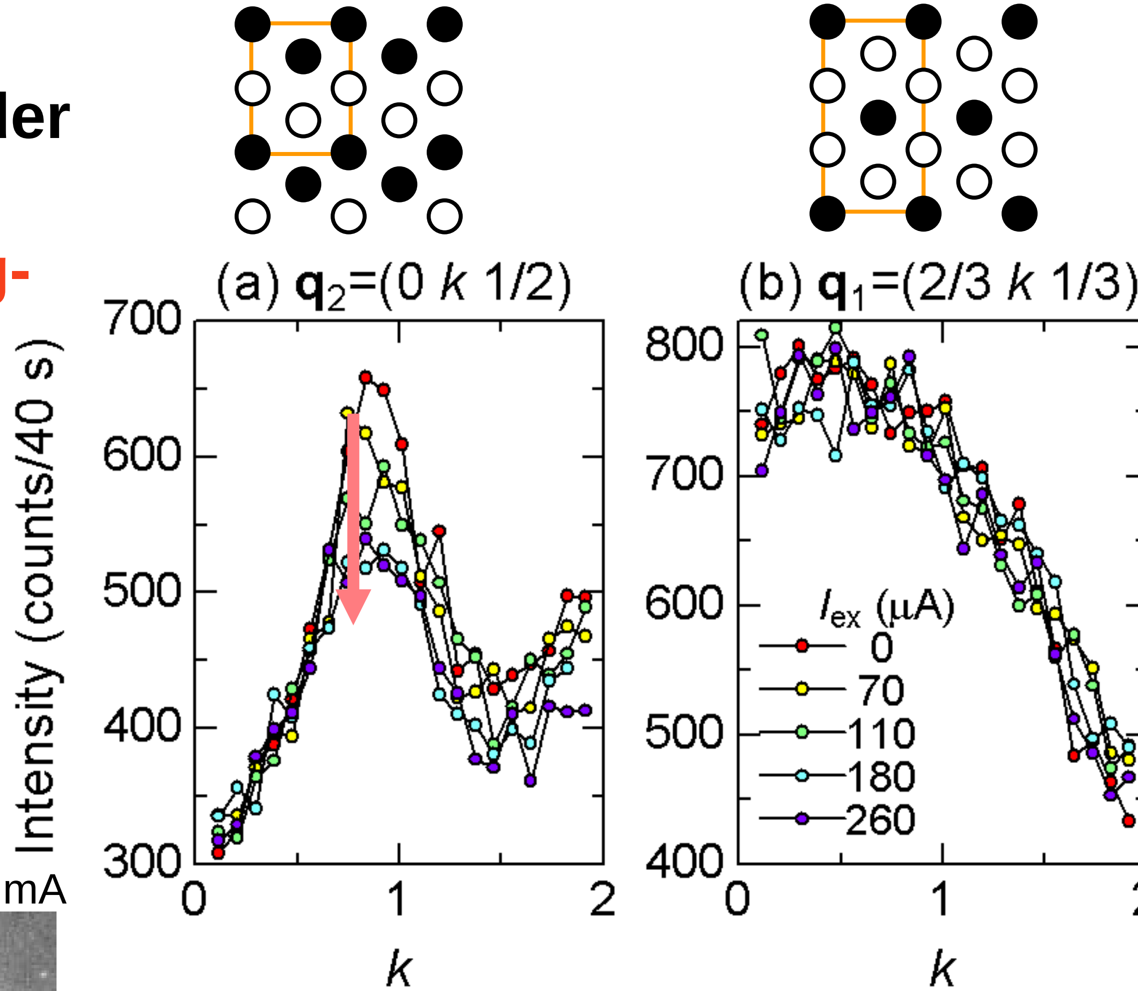
X-ray measurement under current

⬇

Disappearance of Blagg-spots





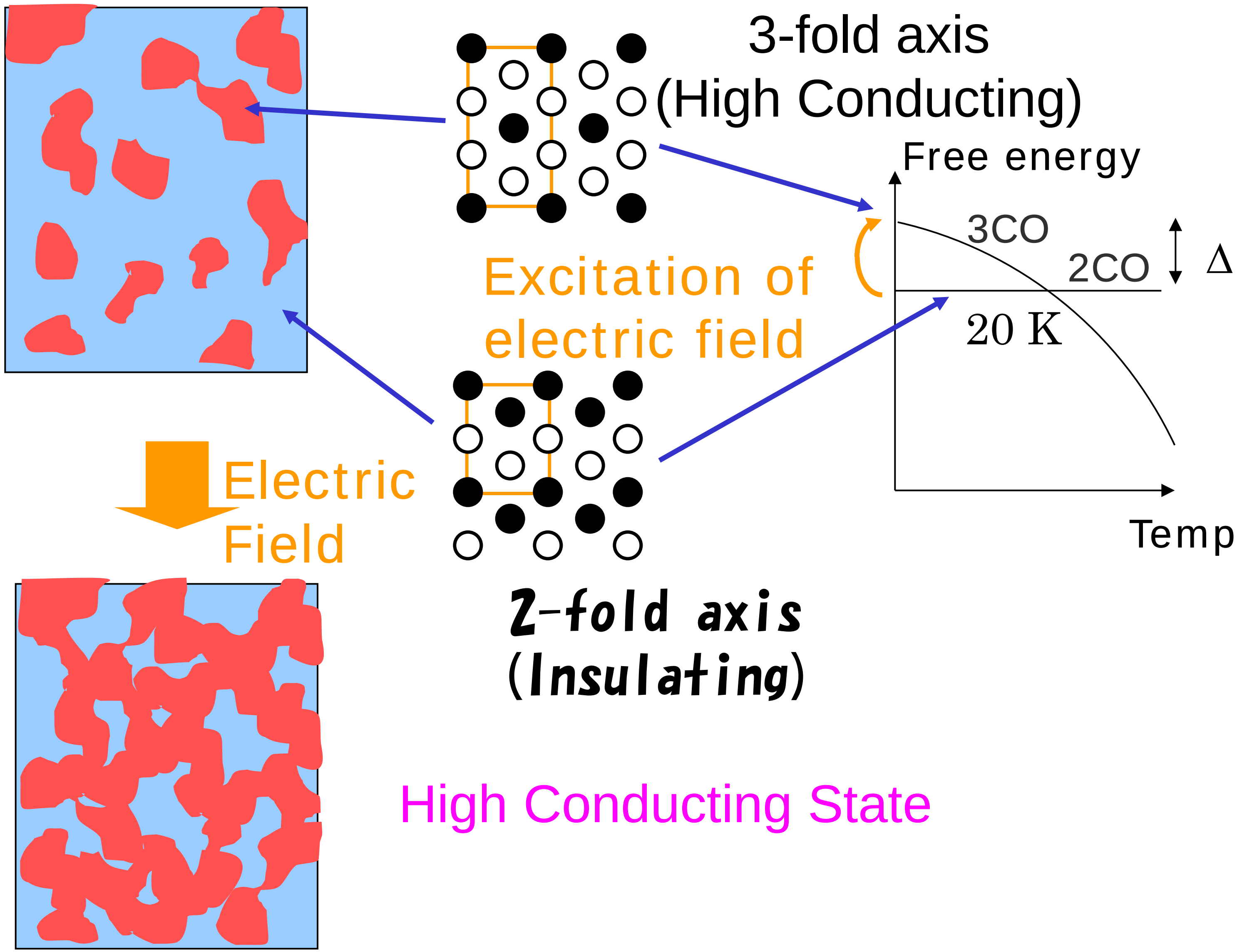


2-fold (Insulating State) ⬇ Disappear

3-fold (Conducting) ⬇ No change

θ-$ET_2CsCo(SCN)_4$
: Inhomogenous 2 and 3-folds

→ Melting by Electric Field



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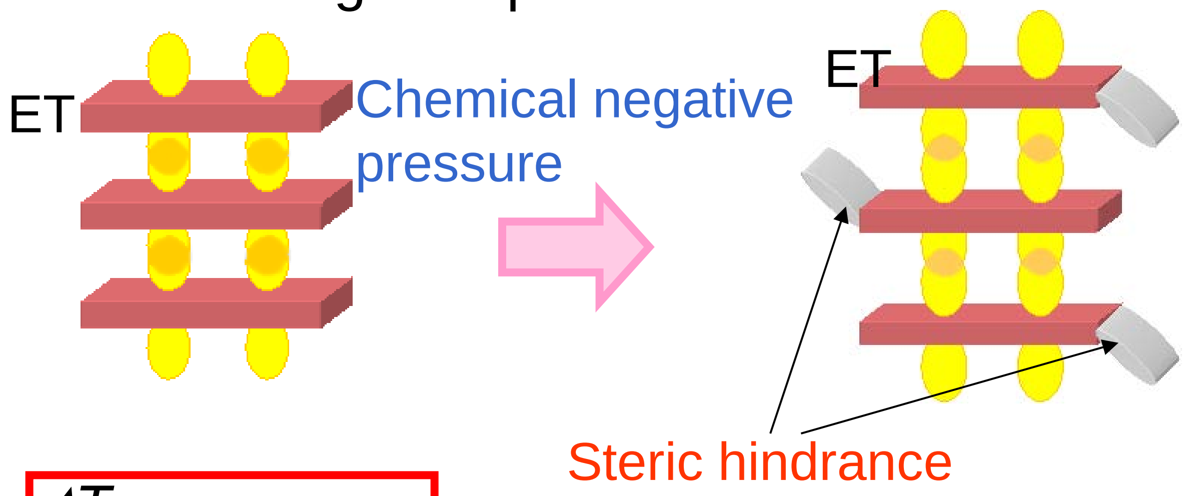
⇒非平衡科学（舞台：有機伝導体）

Recent research

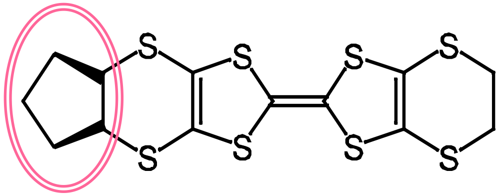
Introduction of steric hindrance

→ Chemical negative pressure

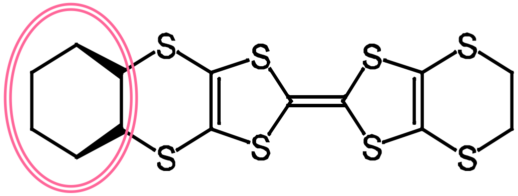


→ $\frac{\Delta T_c}{\Delta P} \approx -1\text{K/kbar}$

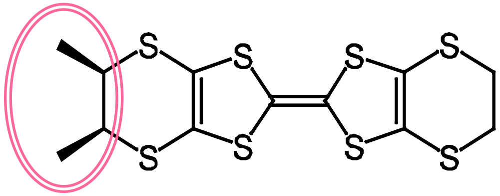
ET derivatives



C5ET



C6ET



***meso*-DMBEDT-TTF**

強相関パラメータの制御

化学修飾

↓

分子構造の自由度

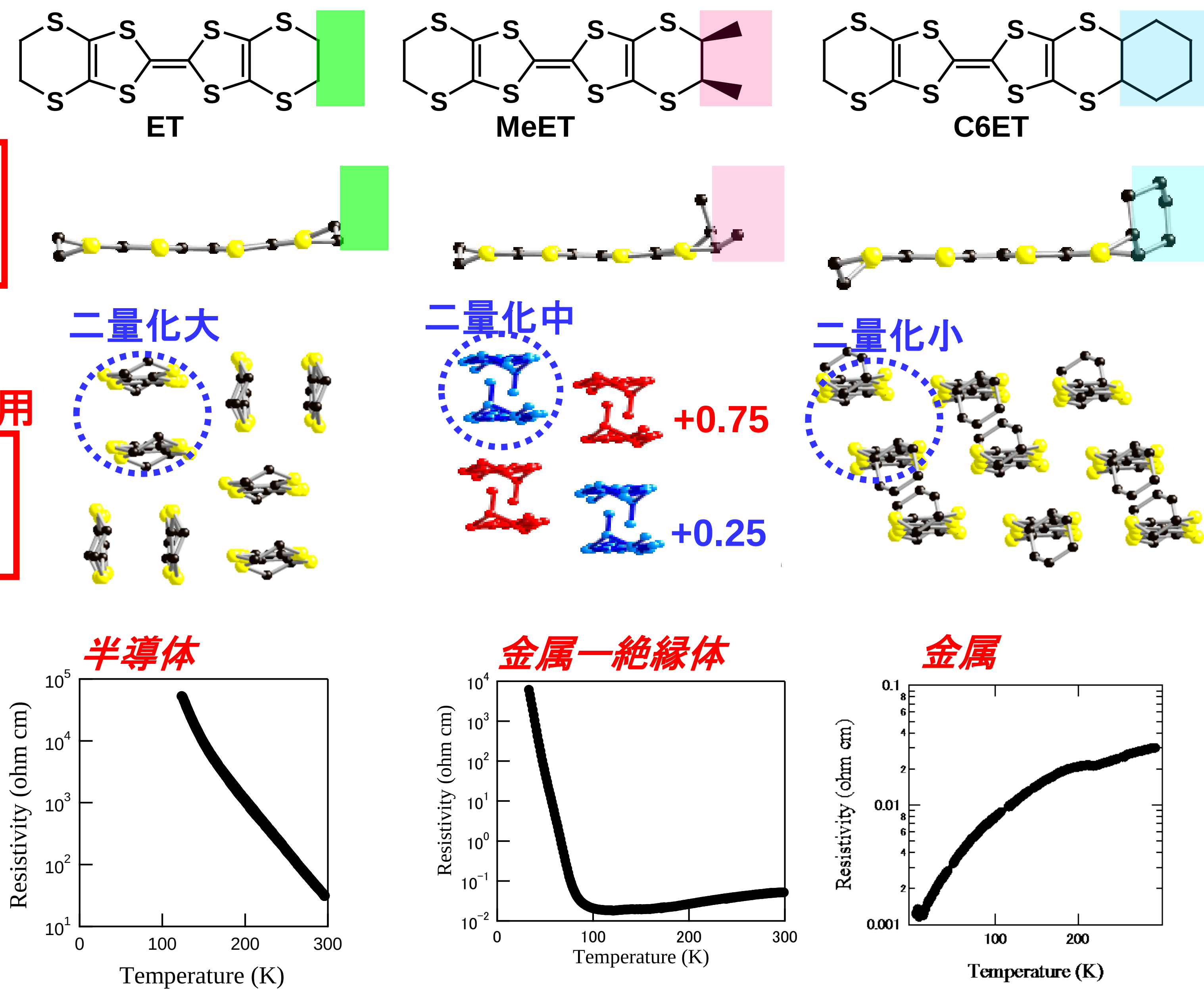
↓

分子間相互作用

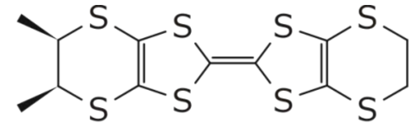
分子配列の自由度

↓

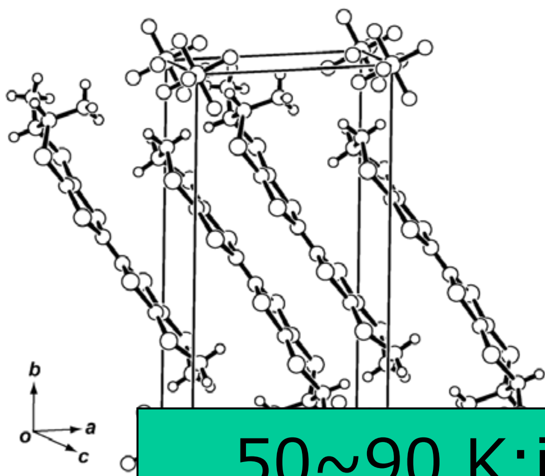
多彩な電子機能

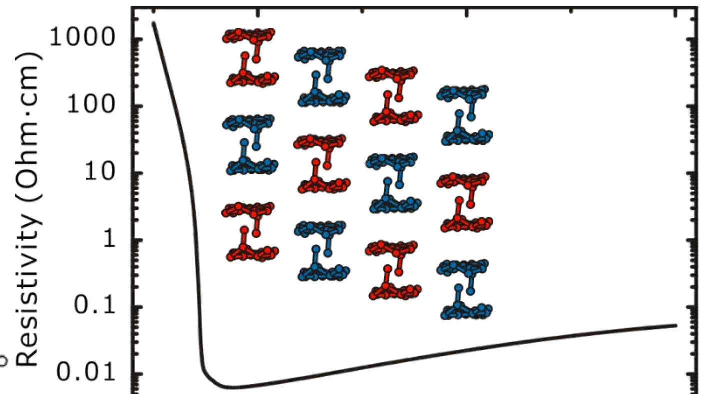


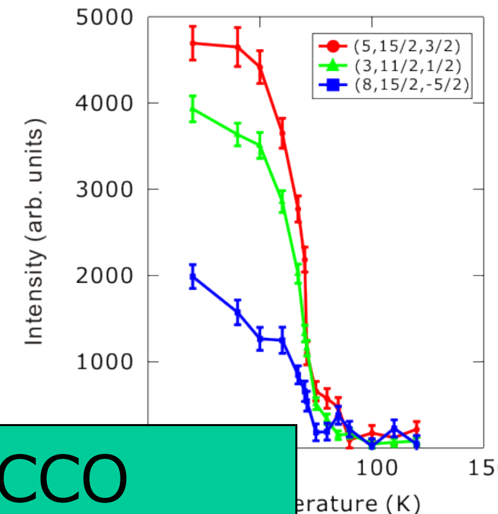
β-(*meso*-DMBEDT-TTF)$_2$PF$_6$



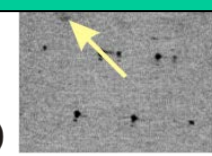
meso-DMBEDT-TTF



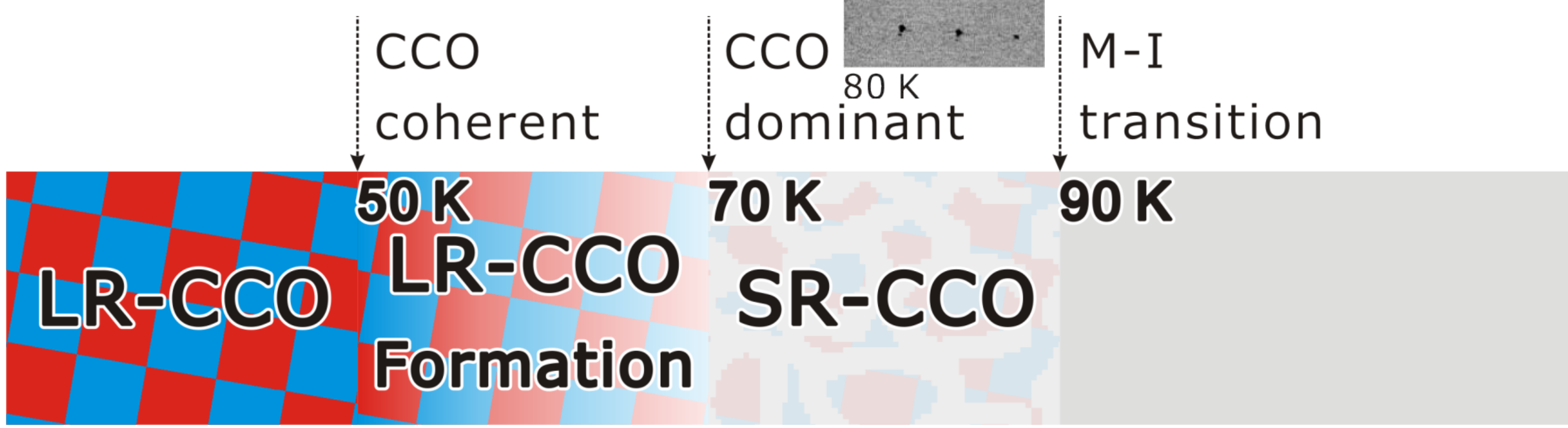




50~90 K:imperfect formation of CCO
→Melting of CCO & nonlinear conduction

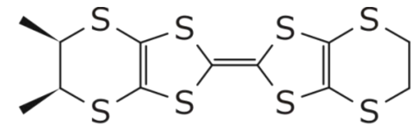


80 K



S. Kimura *et al.*: *Chem. Commun.* (2004).
S. Kimura *et al.*: *JACS* (2006).

Experiment: Nonlinear Conduction



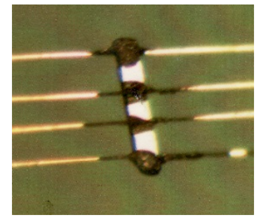
meso-DMBEDT-TTF

Nonlinear conduction

Cryogenic

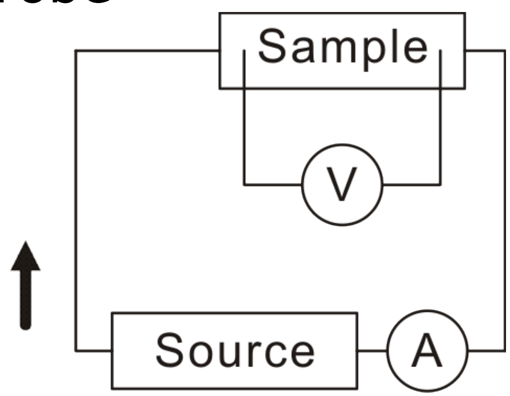
Liquid He cryostat

Electrical transport

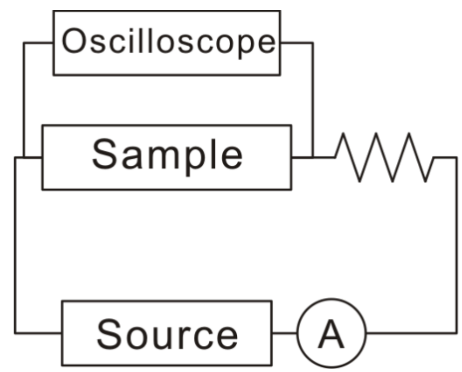


Source-Meter Keithley model 2611

I-driven *V* measurement:
4-probe



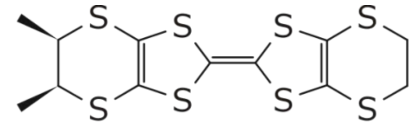
V-driven *I* measurement:
2-probe



Pulsed source: 2 ms~20 ms

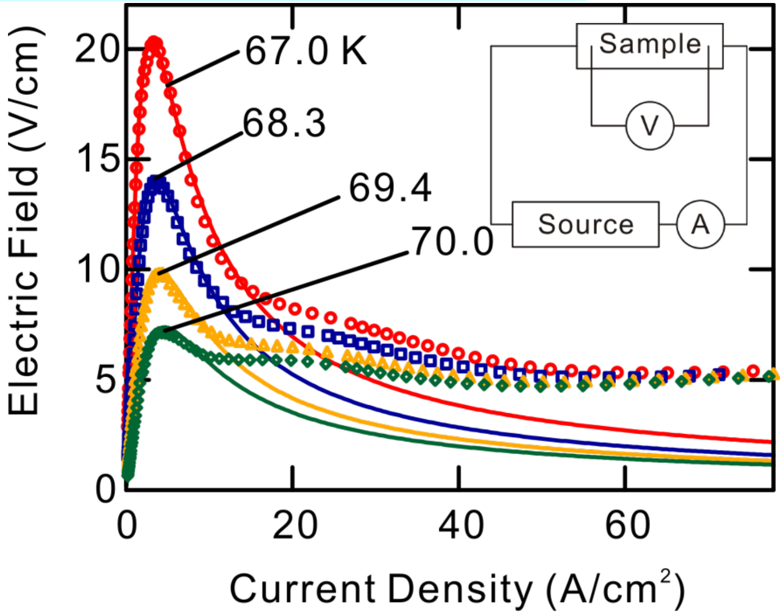
Oscilloscope···to observe the temporal change of V_{sample}

Result: Nonlinear Conduction

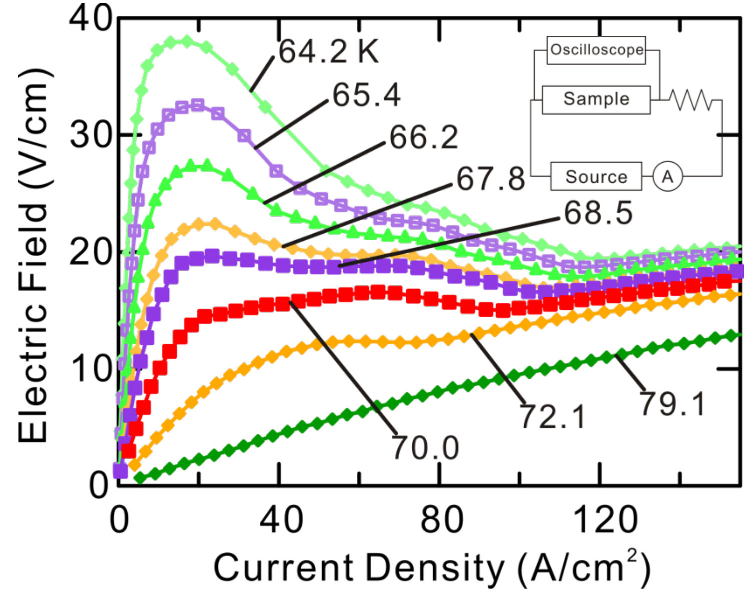


meso-DMBEDT-TTF

I-driven 4-probe (2ms)



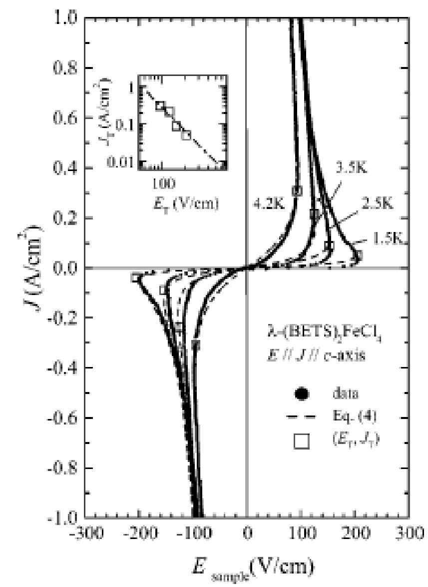
V-driven 2-probe (2ms)



Fitting Function

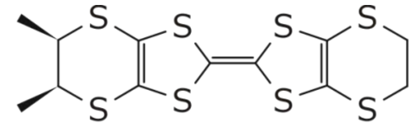
$$\sigma(J,T)=\sigma_1\exp(-\Delta/T)+\sigma_2 J^n$$

$$\sigma(J,T)=\sigma_1\exp\left(-\frac{\Delta}{T}\right)\left[1-\frac{1}{n-1}\left(\frac{J}{J_T}\right)^n\right]$$



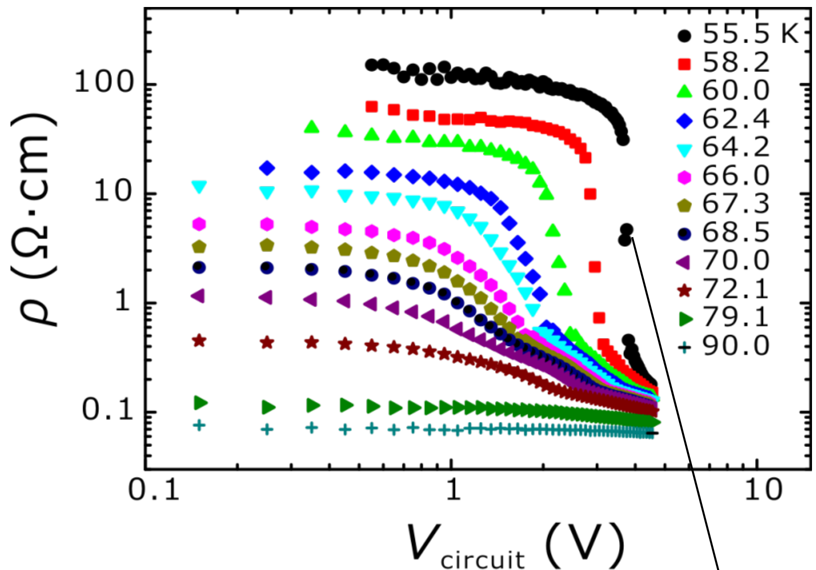
N. Toyota *et al.*: *Phys. Rev.* B **66** (2002) 033201.

Results: Nonlinear Conductivity

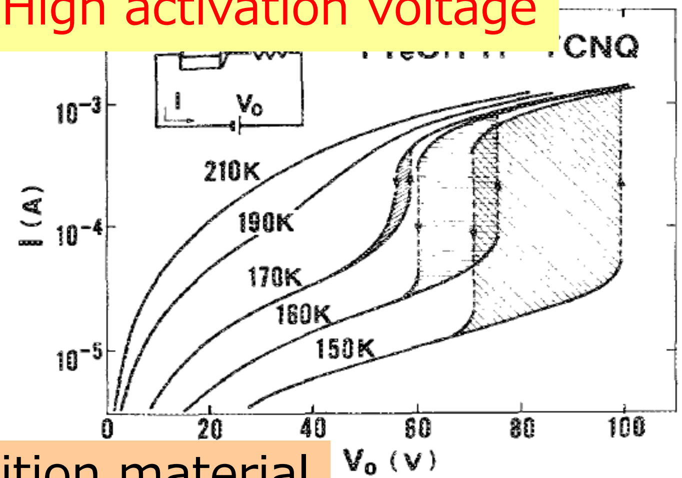


meso-DMBEDT-TTF

$\rho_{\text{samples}} = (R_{\text{circuit}} - R_{\text{L}})\, S/l$



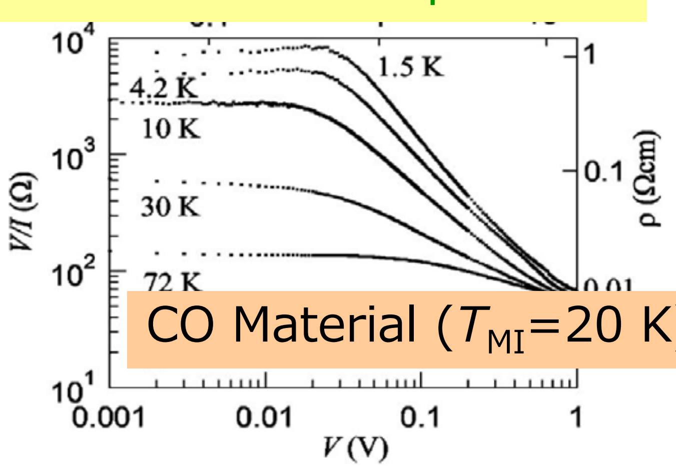
High activation voltage



NI transition material (T_{C}=240 K)

Y. Iwasa *et al.*: Appl. Phys. Lett. **55** (1989) 2111.

Low activation temperature



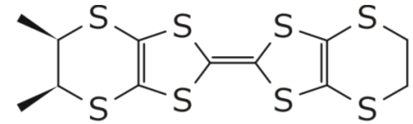
CO Material (T_{MI}=20 K)

ρ change of 3 orders @55.5 K, V_{c}=4 V

Giant Nonlinear Conduction at high temperature and low voltage

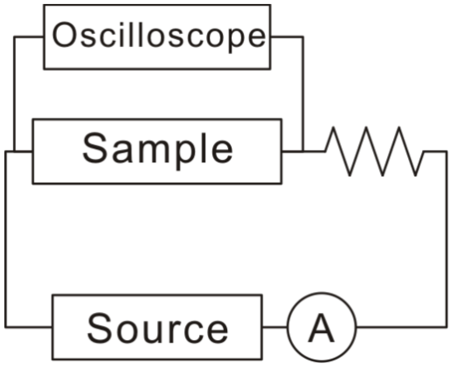
T. Mori *et al.*: Phys. Rev. B **75** (2007) 235103.

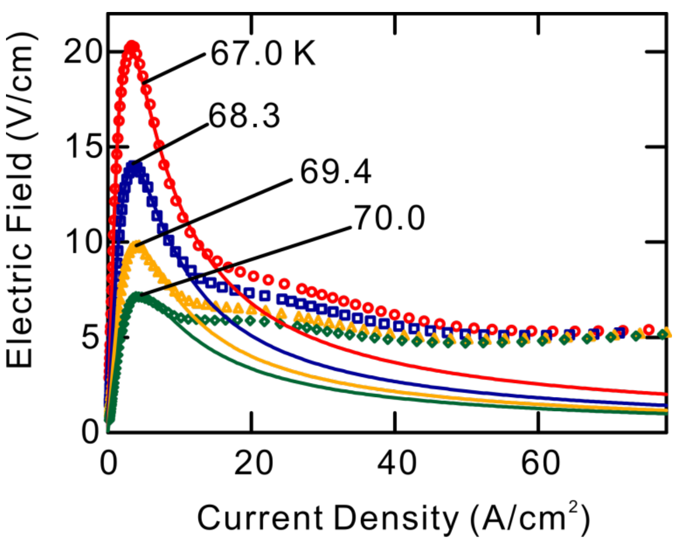
Results: Time-dependent V_{sample}



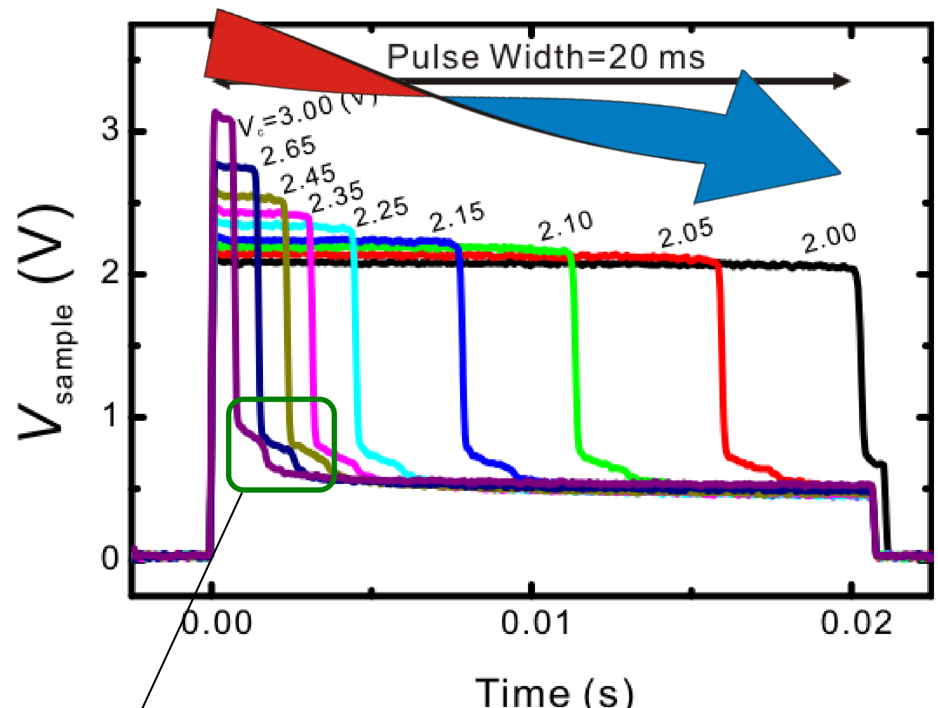
Oscilloscope images

60.8 K





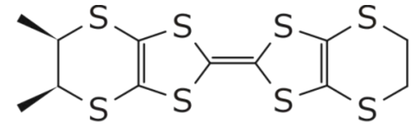
Flipping of the relation of magnitude
⇨NDR



60.8 K, V_c sweep, R_L=470 Ω

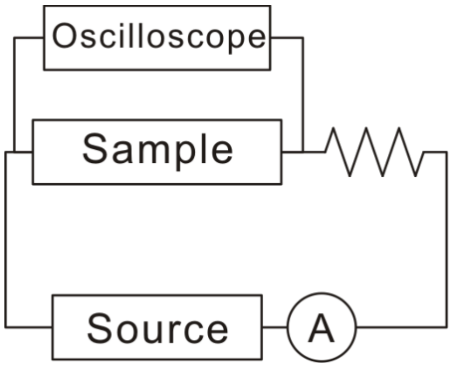
2-stepped change
Field-induced metastable state?

Simulation of Heating Effects



meso-DMBEDT-TTF

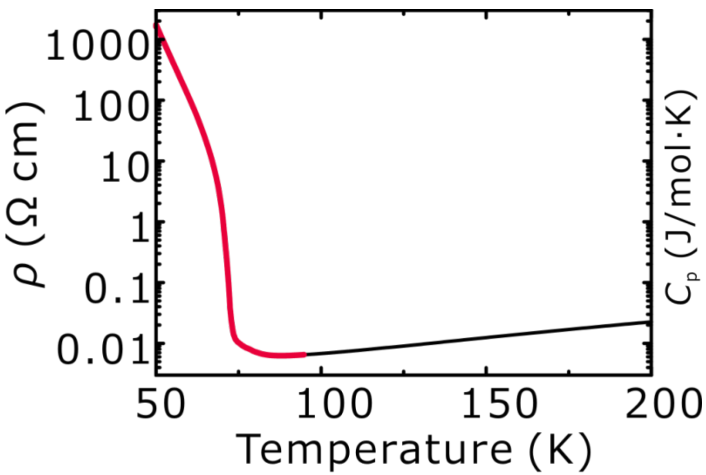
Pseudo nonlinear conduction
caused by self-heating?

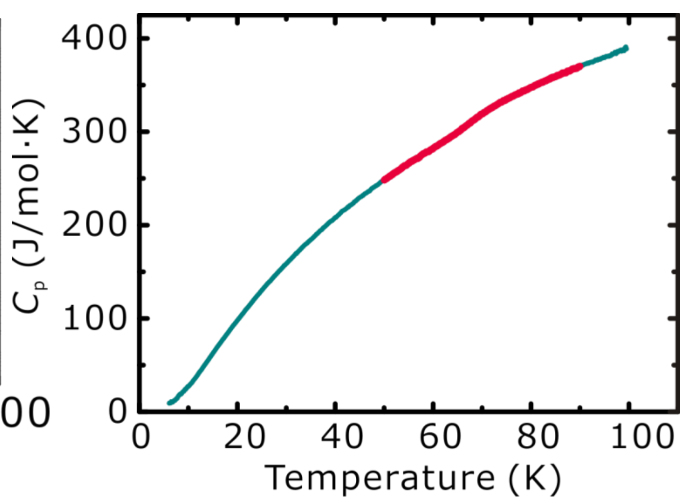


$$\frac{dT}{dt} = \frac{P}{C}$$

$$= \frac{N_A V_{unit} R_{sample} V_{circuit}^2}{lwhC_{p,m}(R_{sample} + R_L)^2}$$

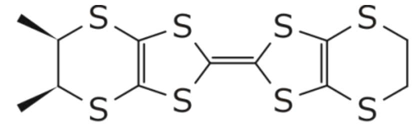
Heat outflow neglected
Q_{Joule} completely converted into ΔT





$C_p(T)$ for
β-(*meso*-DMBEDT-TTF)$_2$PF$_6$
(Prof. Nishio, Toho University)

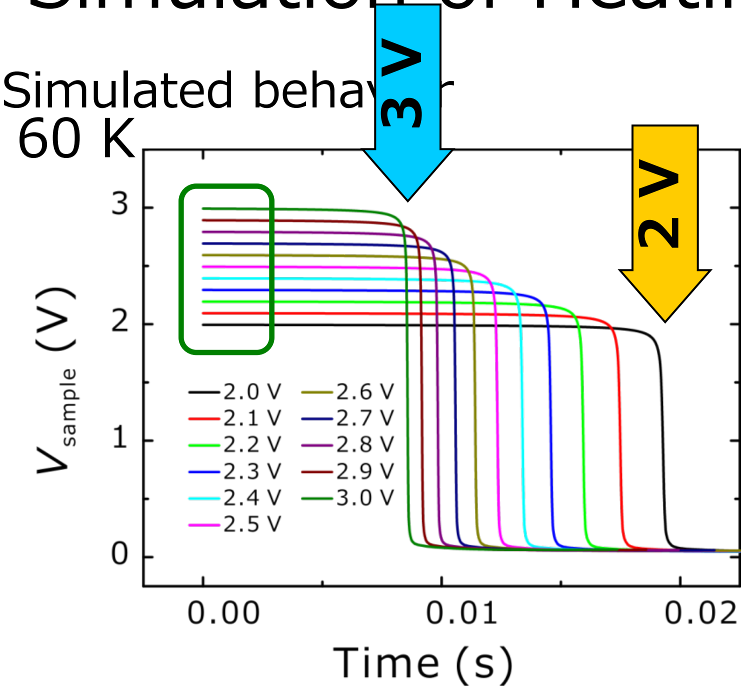
Simulation of Heating Effects



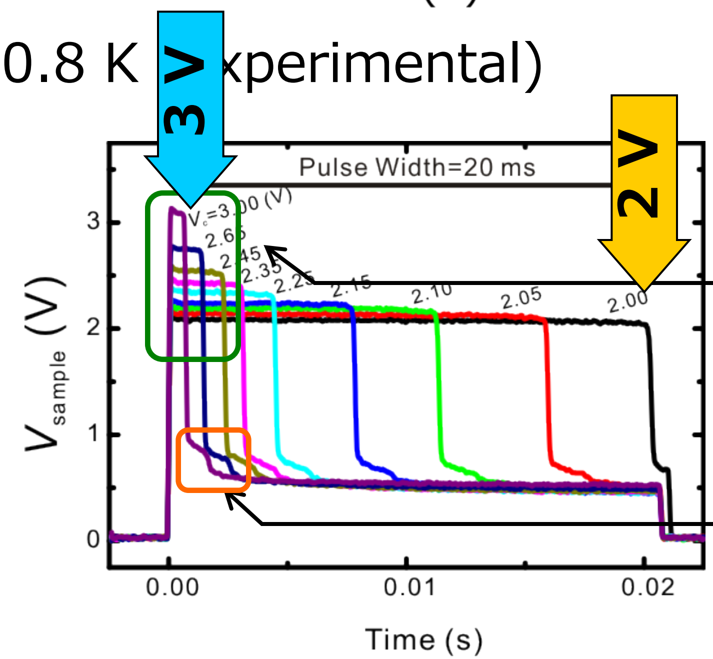
meso-DMBEDT-TTF

Simulated behavior

60 K



60.8 K (experimental)

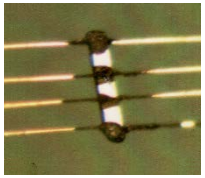


$$\frac{dT}{dt} = \frac{P}{C}$$

$$= \frac{N_A V_{unit} R_{sample} V_{circuit}^2}{lwhC_{p,m}(R_{sample} + R_L)^2}$$

Heat outflow neglected

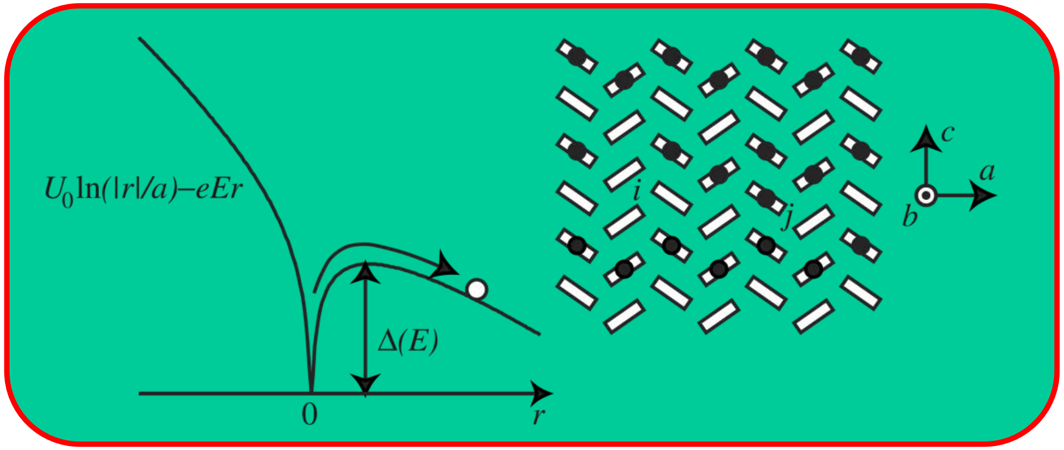
Q_{Joule} completely converted into ΔT



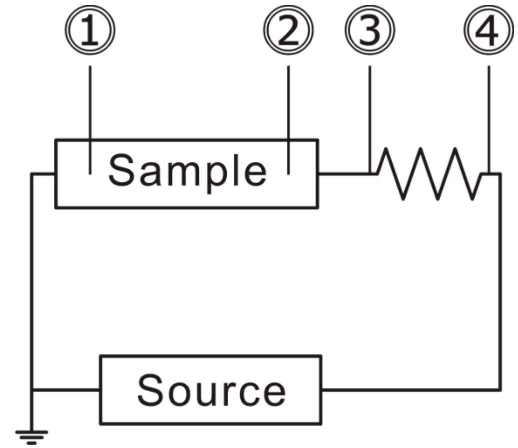
Fast experimental response
Inexplicable by self-heating

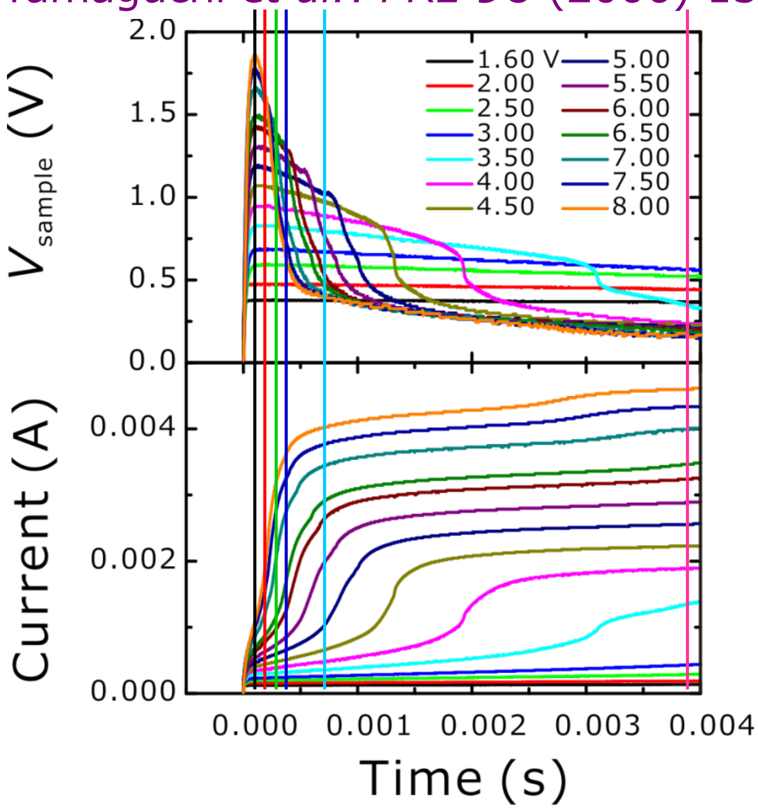
Bump in the experiment
⇨Field-induced metastable state

Microscopic picture of nonlinear conduction

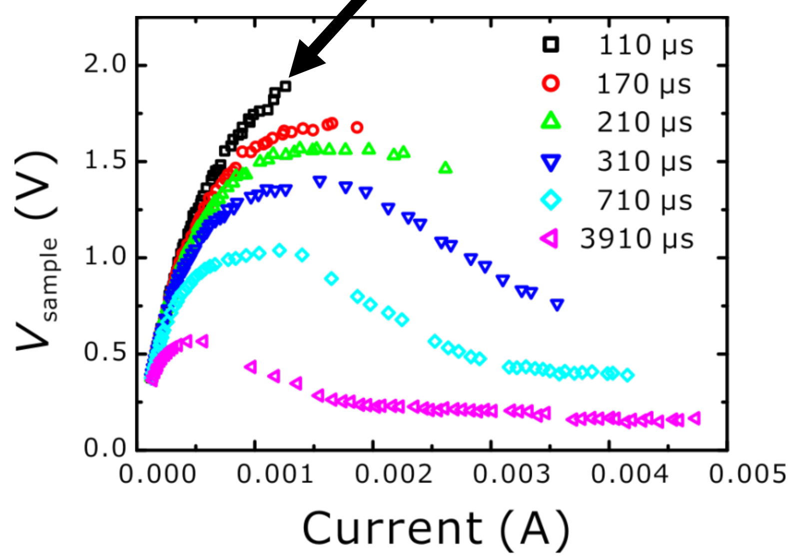


T. Yamaguchi *et al.*: *PRL* **96** (2006) 136602.

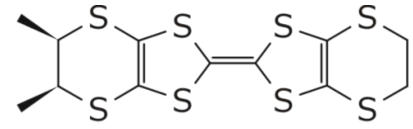




Nonlinear conduction at 110 μs



Experiment: Raman Scattering



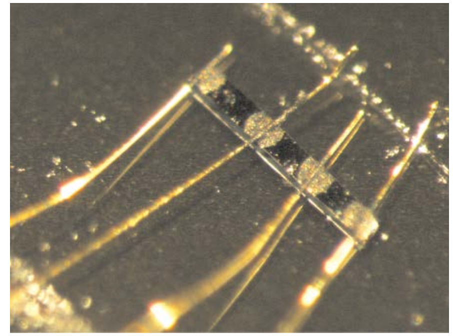
meso-DMBEDT-TTF

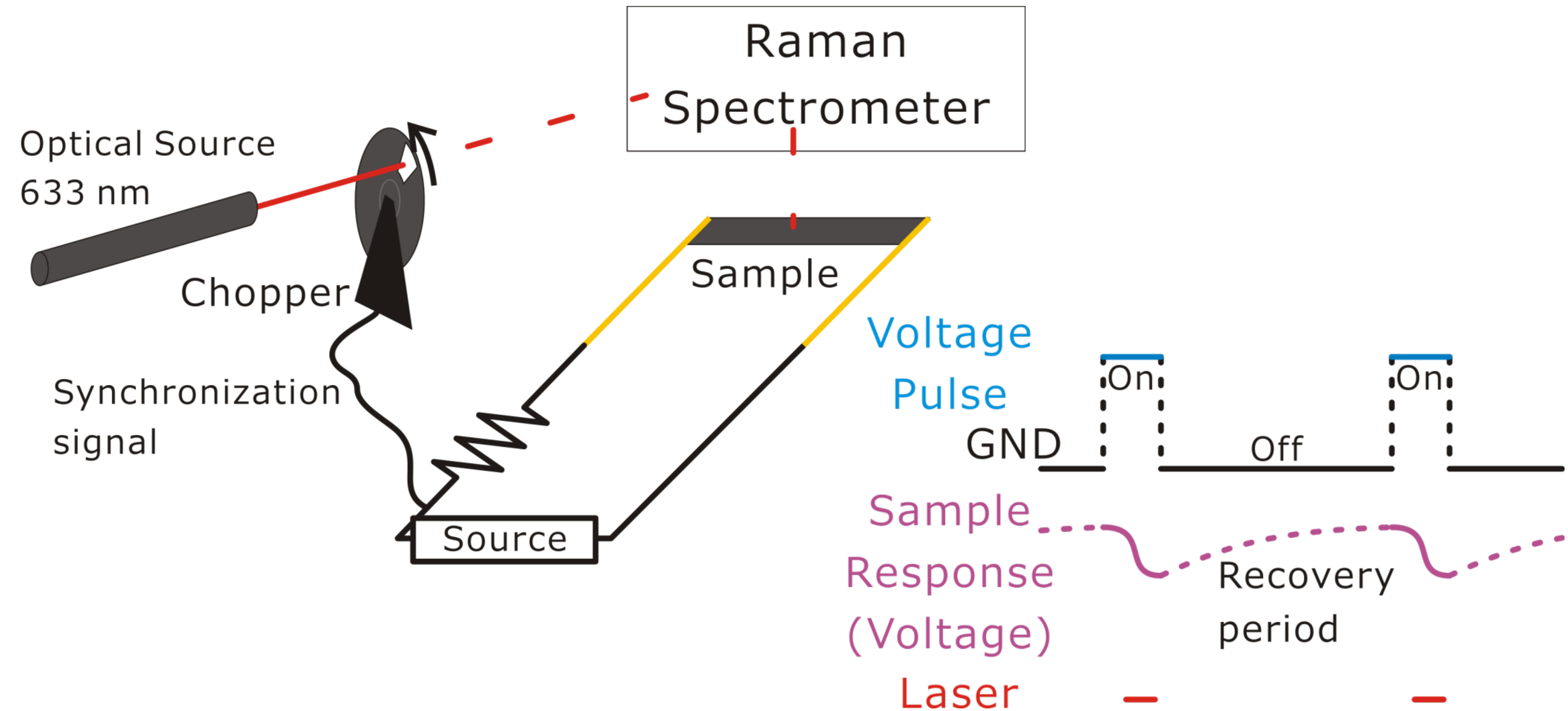
Cryogenic

Thermal conduction

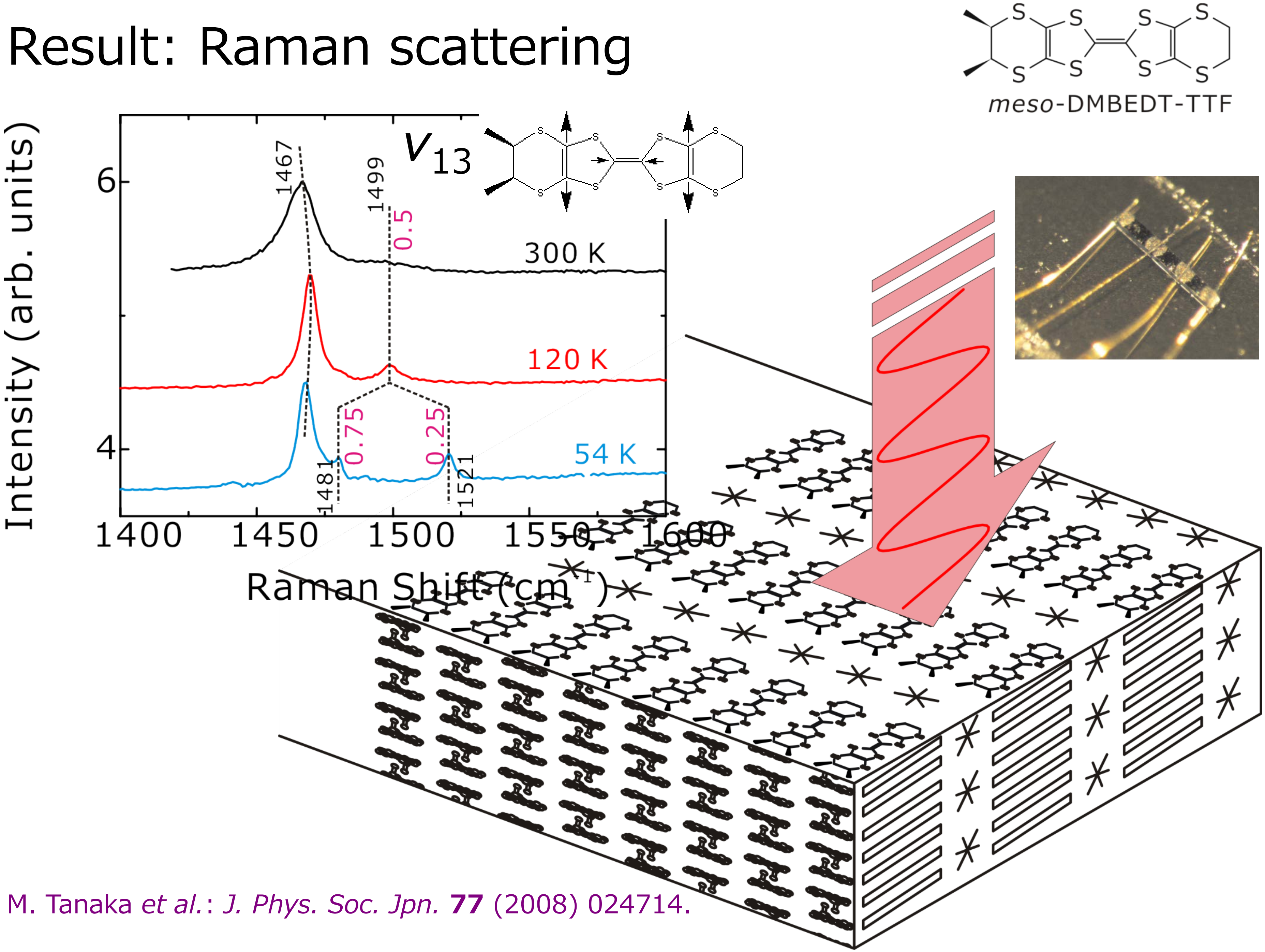
Raman scattering

Okamoto Lab.



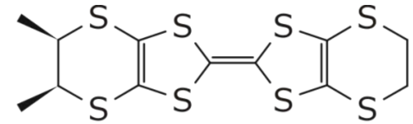


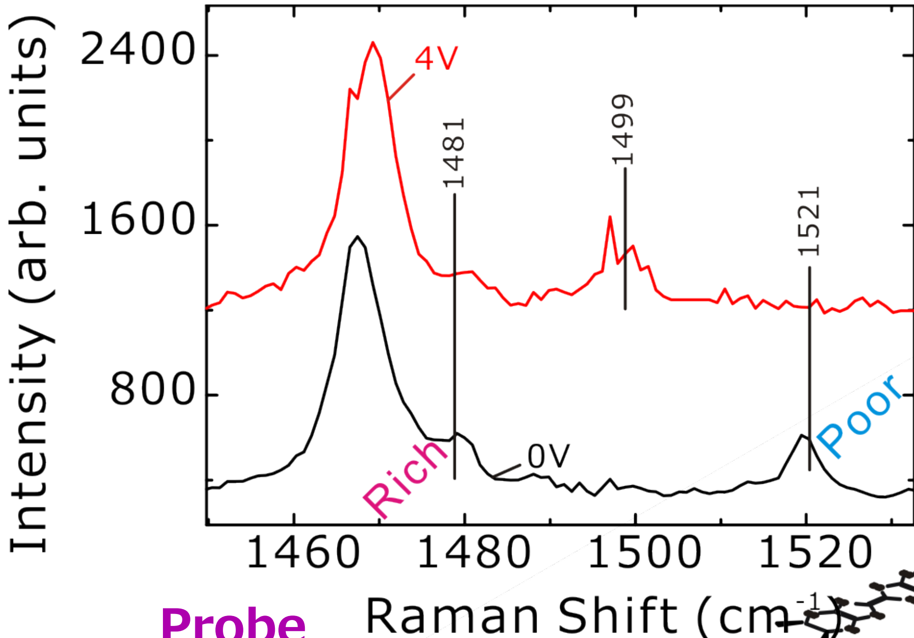
Result: Raman scattering

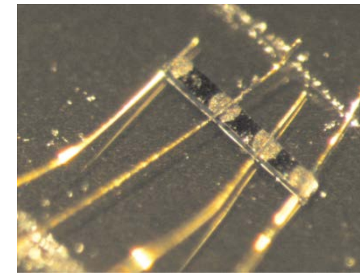


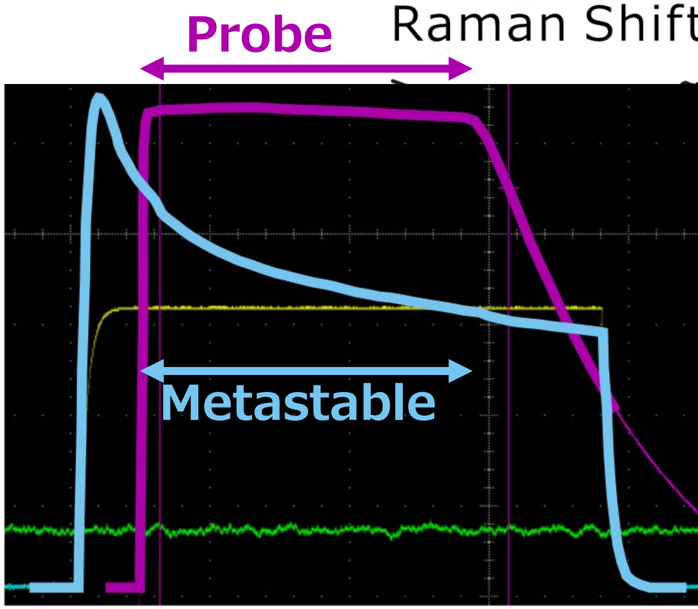
M. Tanaka *et al.*: *J. Phys. Soc. Jpn.* **77** (2008) 024714.

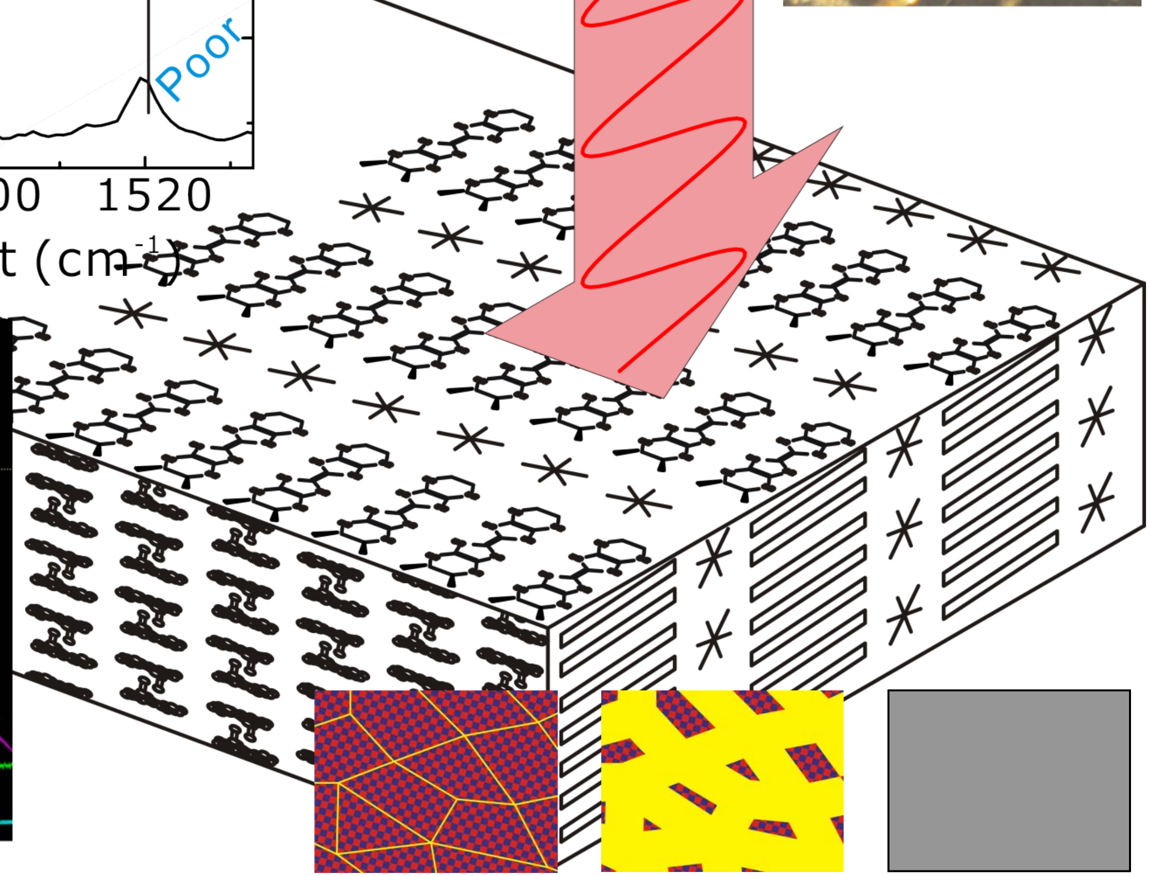
Results: Raman scattering


meso-DMBEDT-TTF







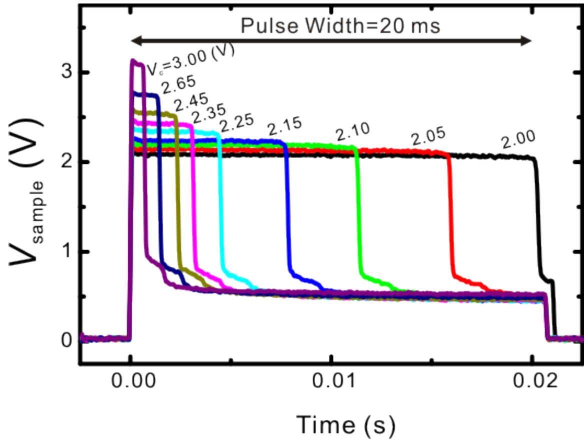


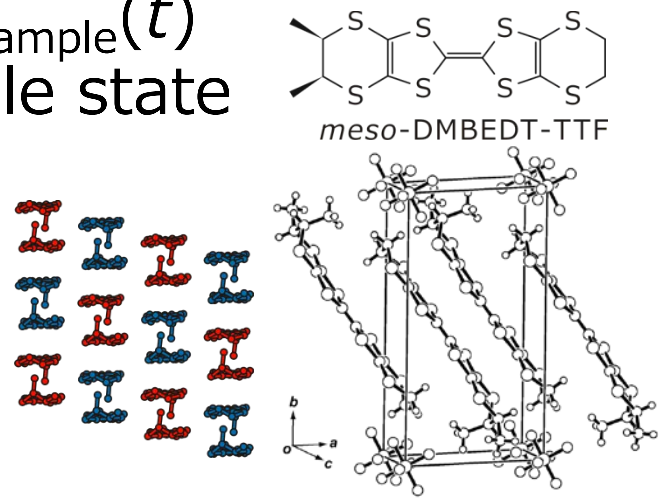
Summary

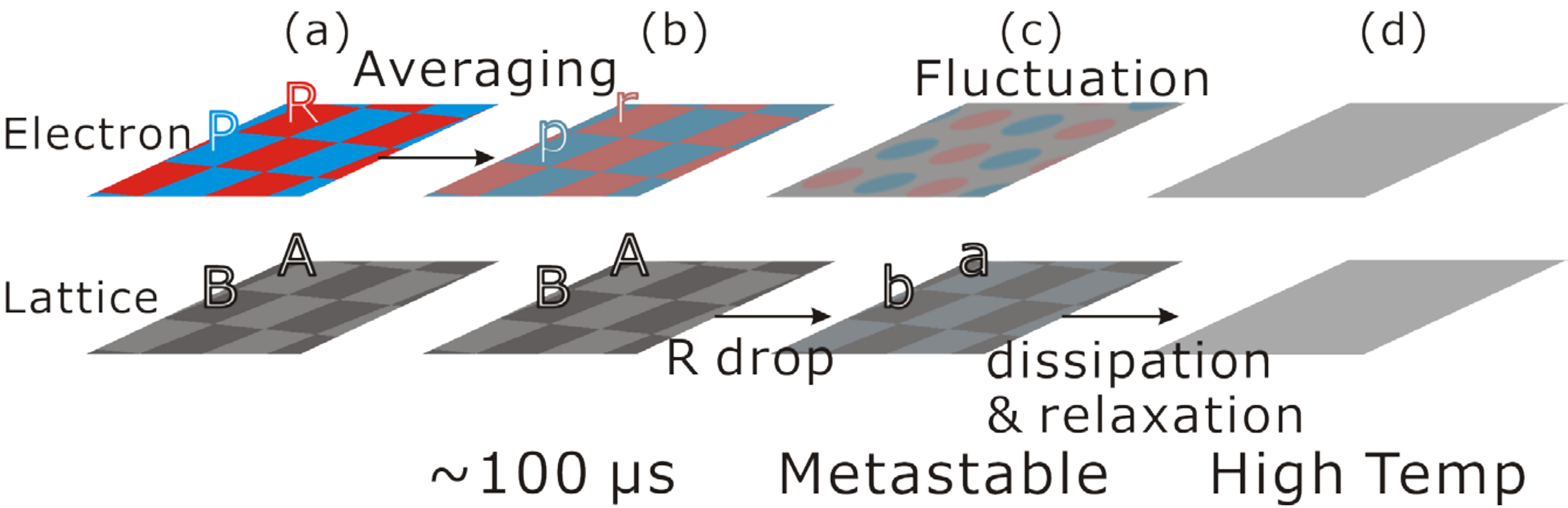
Temperature independent nonlinear conduction

- 2-type NDRs below 70 K
- 2-stepped drop of $V_{sample}(t)$

Field-induced Metastable state







Responses by Electric Field

（1）直流一交流変換⇒振動、リズム

Organic thyristor (4K); θ-$ET_2CsCo(SCN)_4$

F. Sawano *et al.*, Nature 437 (2005) 522.

（2）電場誘起準安定状態

Electric field induced metastable state

(<70K); *β*-(*meso*-DMeET)$_2$$PF_6$

S. Niizeki *et al.*, J. Phys.Soc.Jpn. **77**, 073710(1-4) (2008).

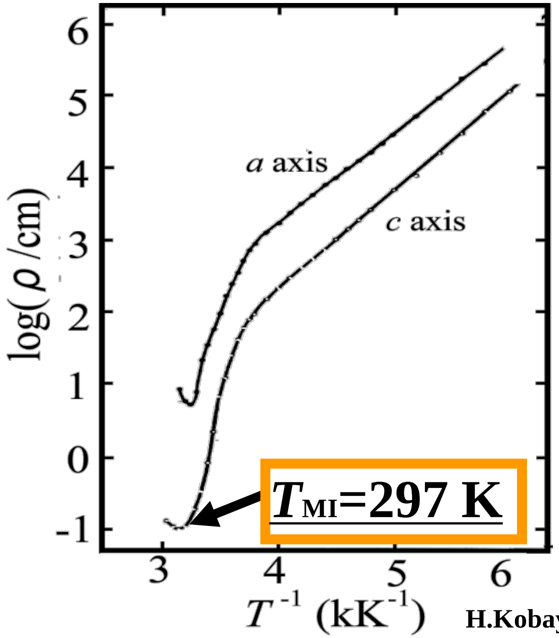
（3）電荷秩序の集団励起

Voltage oscillation (88 K); α-ET_2I_3

K. Tamura *et al.*, J. Appl. Phys. **107**, 103716(1-5) (2010).

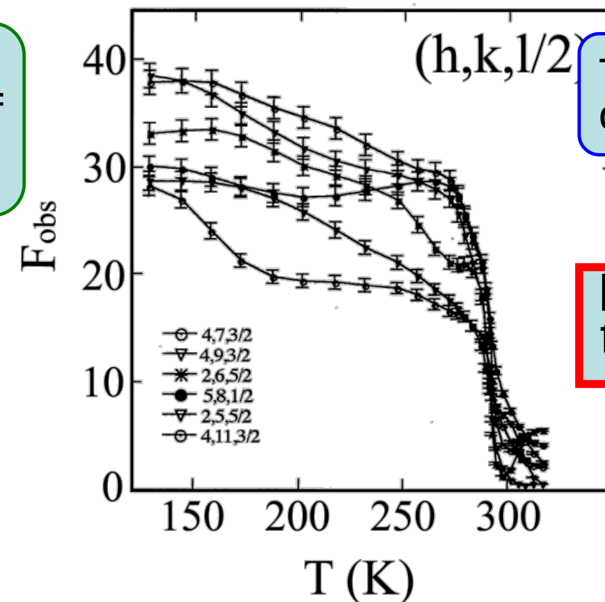
⇒室温での動作

Properties of β-ET_2PF_6 : T_{CO} = 297 K



H.Kobayashi *et al. Chem. Lett.* **581** (1983).

Temperature dependence of resistivity

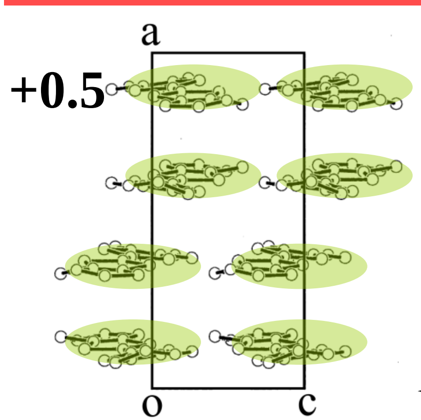


The formation of superlattice

First-order transition

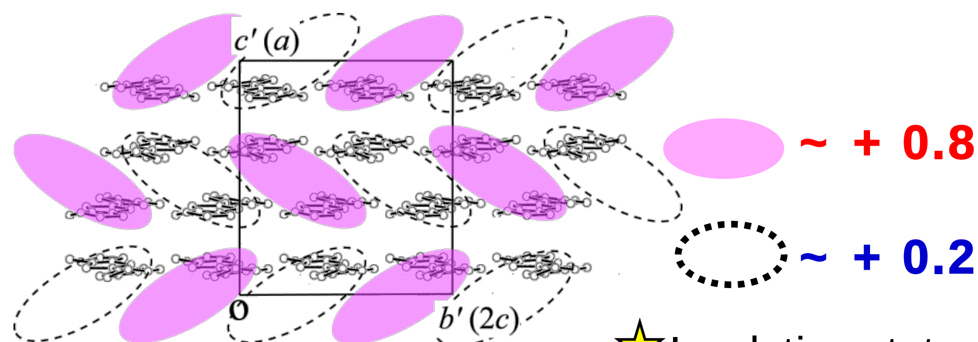
G.K.Rohan Senadeera *et al. J.Phys Soc. Jpn*,67,4193 (1998)

High temperature (T > 297 K)



Metallic state

Low temperature (T < 297 K)

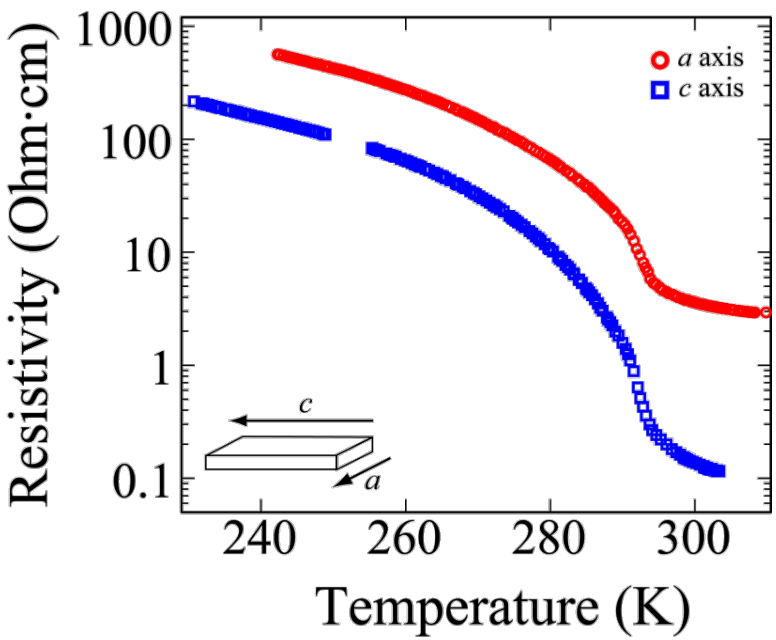


Insulating state

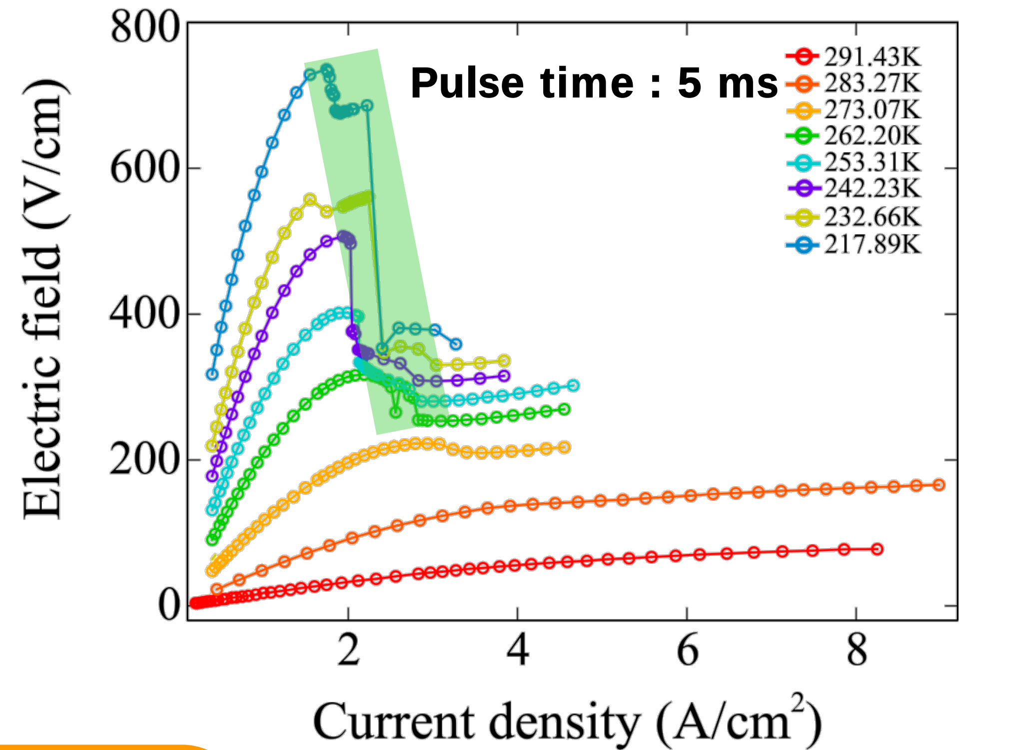
Y. Nogami *et al. J.Phys. France* 12 Pr9-233 (2002)

The long range charge ordered (LRCO) state below T_{co} = 297 K

Electric field responses : *I*-driven mode



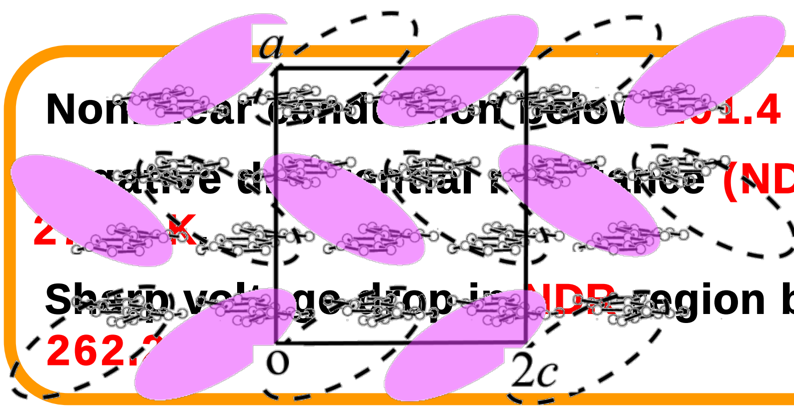
I-*V* characteristics along *a* axis

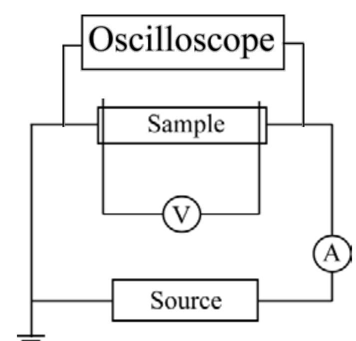


Nonlinear conduction below [illegible]1.4 K.

Negative differential resistance (NDR) below [illegible] K

Sharp voltage drop in NDR region below 262.[illegible]



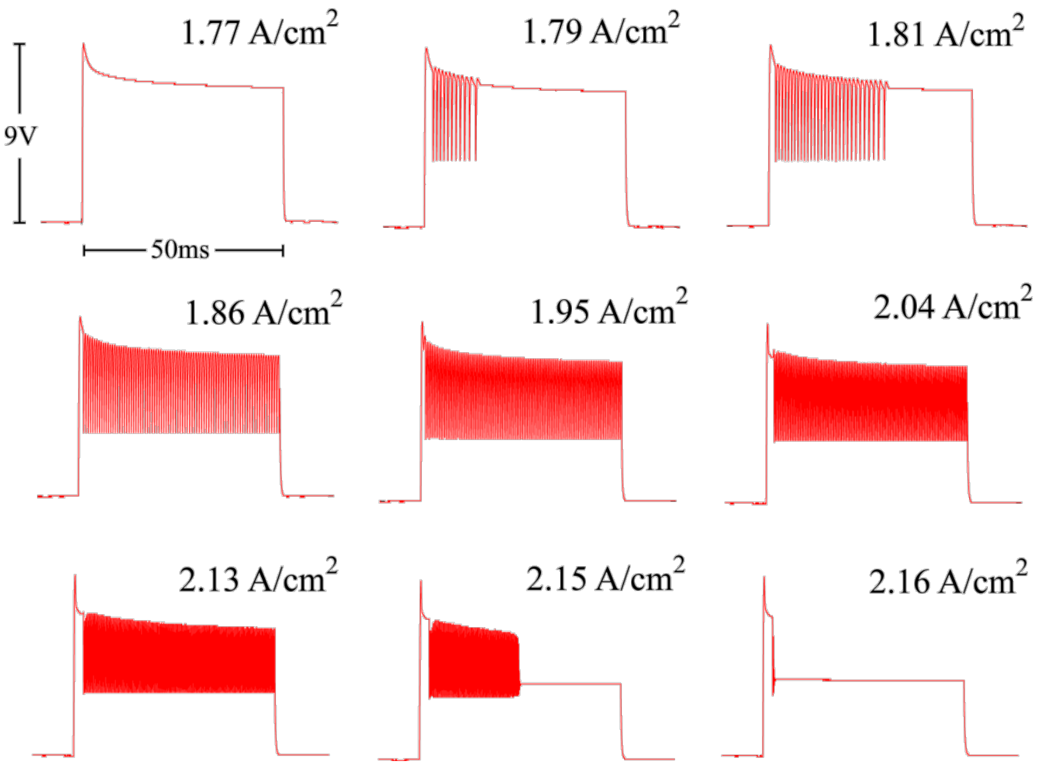


Time dependence of V_{sample}

Electric field responses : *I*-driven mode

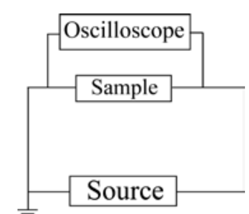
Pulse time : 50 ms

230 K



- **Voltage oscillation begins at 1.79 A/cm².**
- **Long voltage oscillation at 1.86 A/cm².**
- **Applying current , oscillation oscillation becomes faster .**
- **Suddenly oscillation vanishes in high current region.**

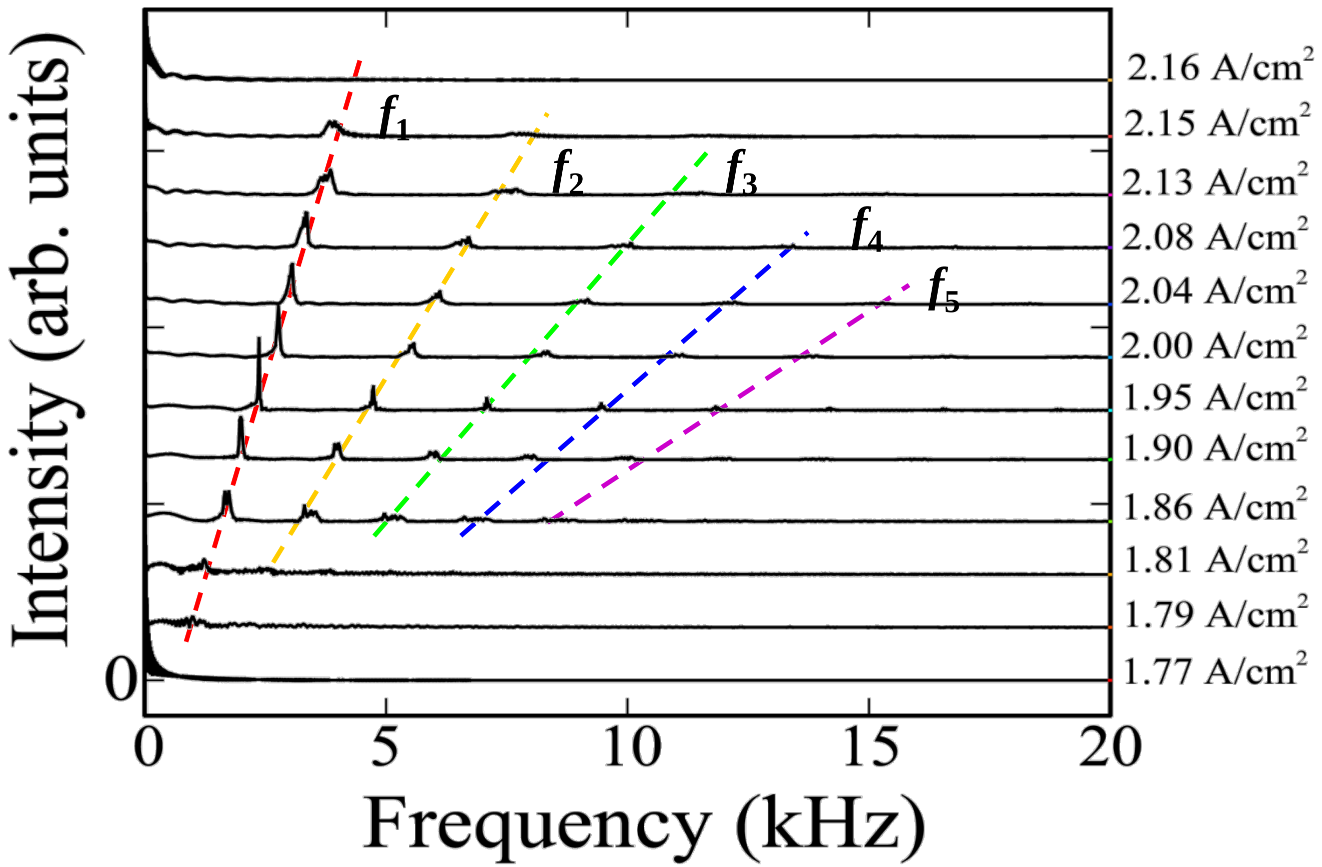
Voltage oscillation in sharp voltage drop region below 260 K.



Fourier- transform spectra from oscillation

Electric field responses : *I*-driven mode

Pulse time : 50 ms

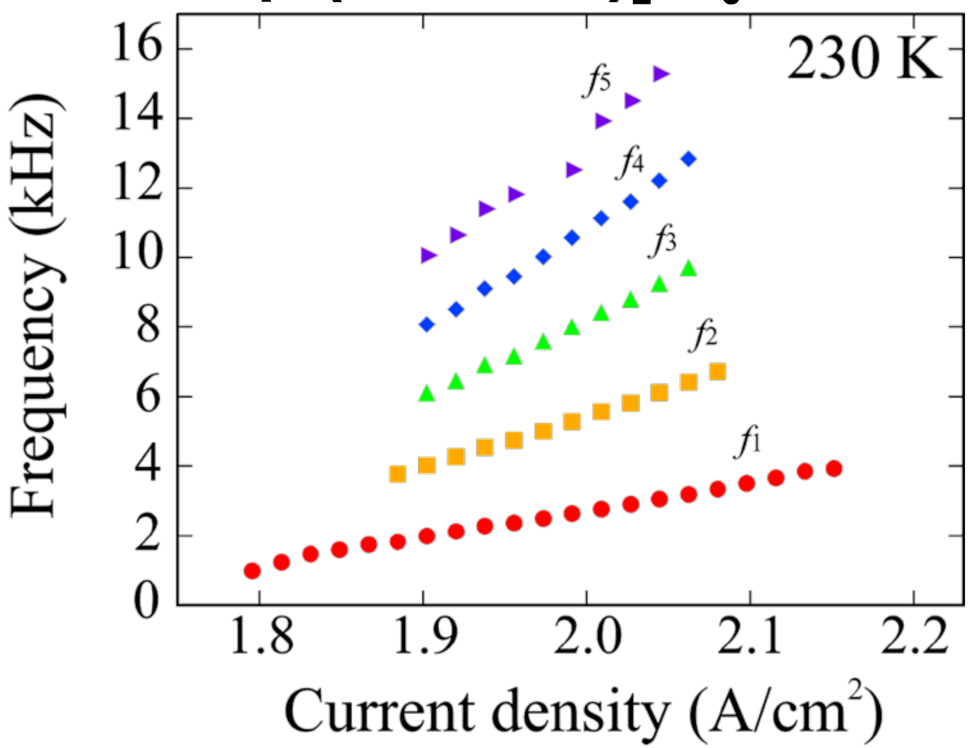


- **Fundamental frequency f_1 : 1 — 3 kHz**
- **Harmonic frequencies : f_2 ~ f_5**
- **Frequencies increase linearly to current density.**

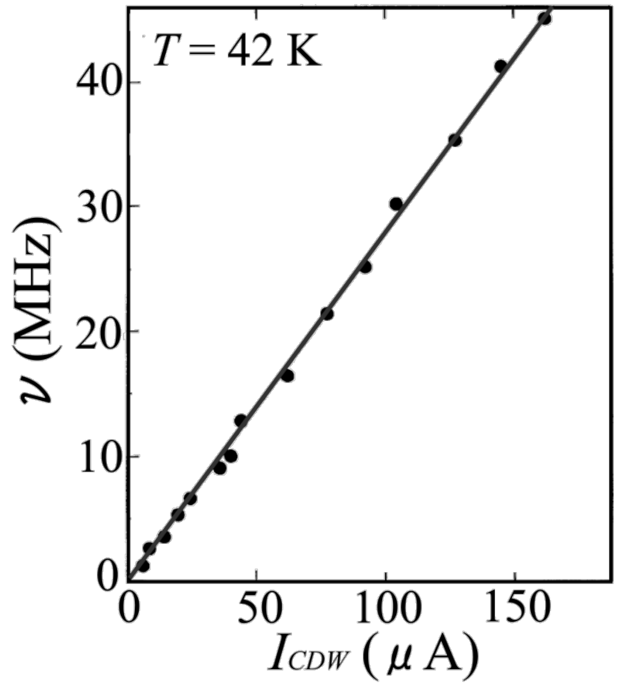
Collective excitations

Electric field responses : *I*-driven mode

β-(BEDT-TTF)$_2$PF$_6$



1D Conductor : NbSe$_3$



H. Fukuyama, J. Phys. Soc. Jpn., 41, 513(1976).
J. Bardeen *et al*., *Phys. Rev. Lett*. **49** (1982) 493.

Collective excitations of LRCO

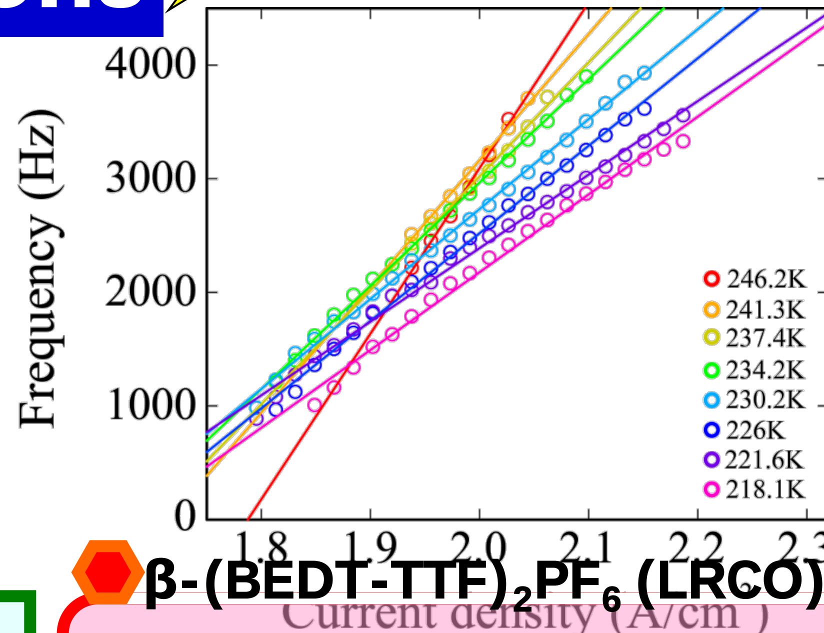
$\nu \propto I_{CDW}$

Collective excitations
CDW sliding

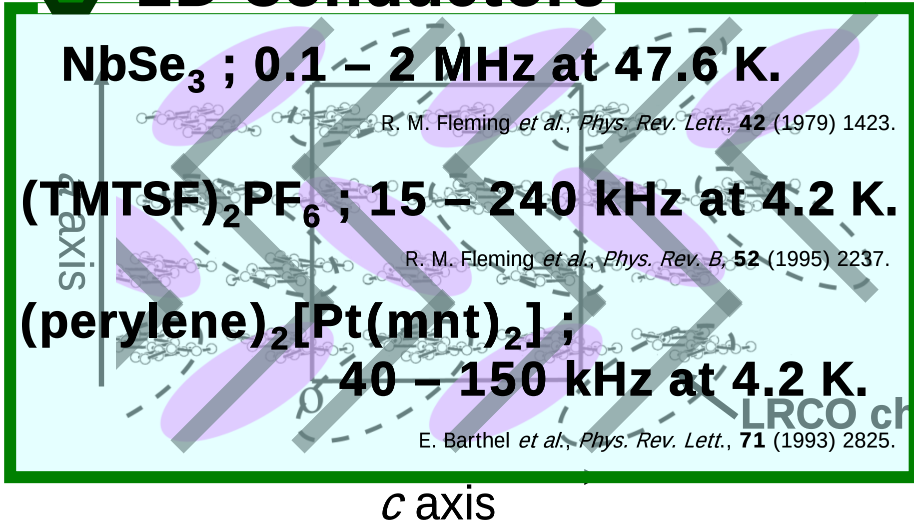
Collective excitations

$$\frac{J}{f_1} = Nne\lambda_0$$

J : current transported by aggregate
f_1 : fundamental frequency
n : carrier density from composition
Nn : carrier density from experiments
e : charge of electron, λ_0 : lattice length



1D Conductors



$NbSe_3$; 0.1 – 2 MHz at 47.6 K.

R. M. Fleming *et al.*, *Phys. Rev. Lett.*, **42** (1979) 1423.

$(TMTSF)_2PF_6$; 15 – 240 kHz at 4.2 K.

R. M. Fleming *et al.*, *Phys. Rev. B*, **52** (1995) 2237.

$(perylene)_2[Pt(mnt)_2]$; 40 – 150 kHz at 4.2 K.

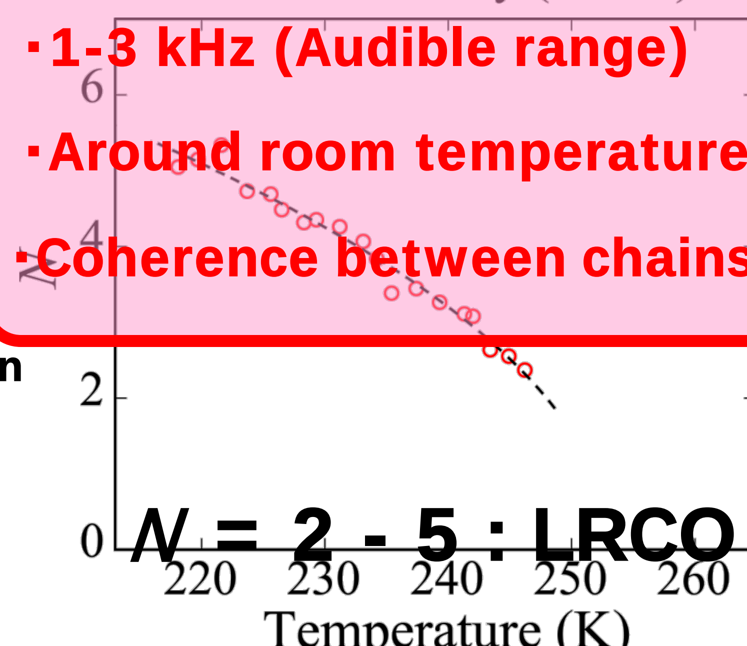
E. Barthel *et al.*, *Phys. Rev. Lett.*, **71** (1993) 2825.

a axis: LRCO chain
c axis: Coherence of chains

N = 1 : 1D Conductors

β-$(BEDT\text{-}TTF)_2PF_6$ (LRCO)

- **1-3 kHz (Audible range)**
- **Around room temperature**
- **Coherence between chains**

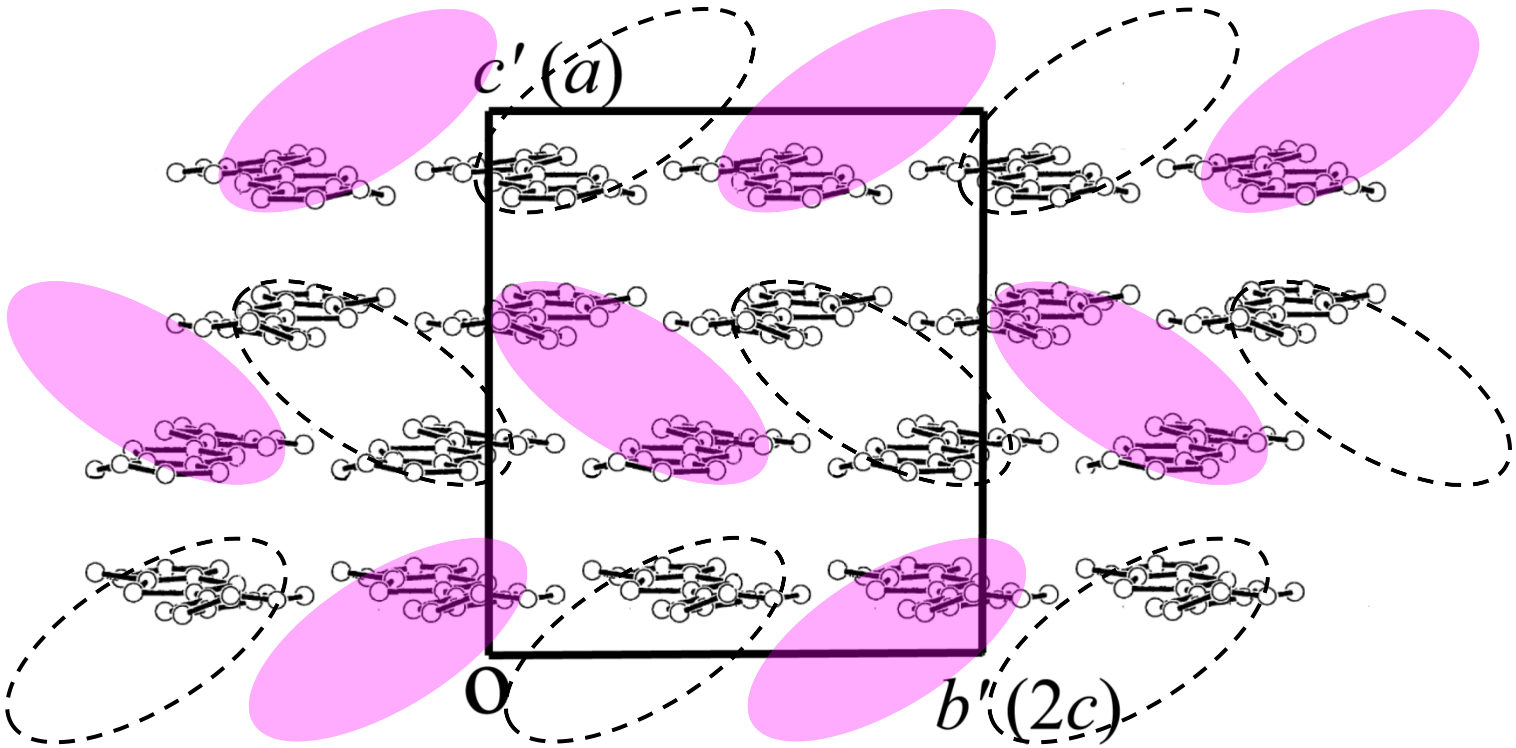


N = 2 - 5 : LRCO

Collective excitations in β-(BEDT-TTF)$_2$PF$_6$

Electric field responses : **/-driven mode**

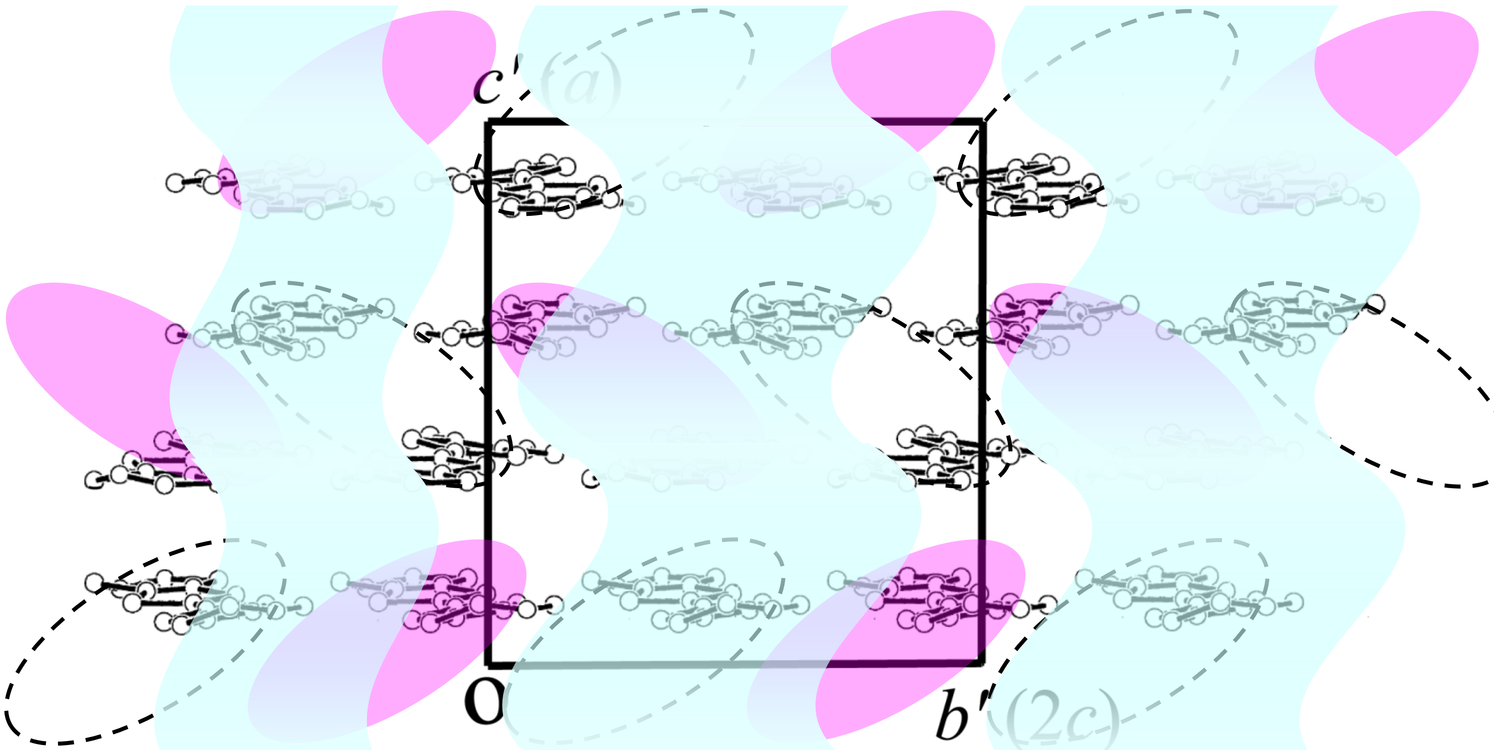
$N = 0$



Collective excitations in β-(BEDT-TTF)$_2$PF$_6$

Electric field responses : /-driven mode

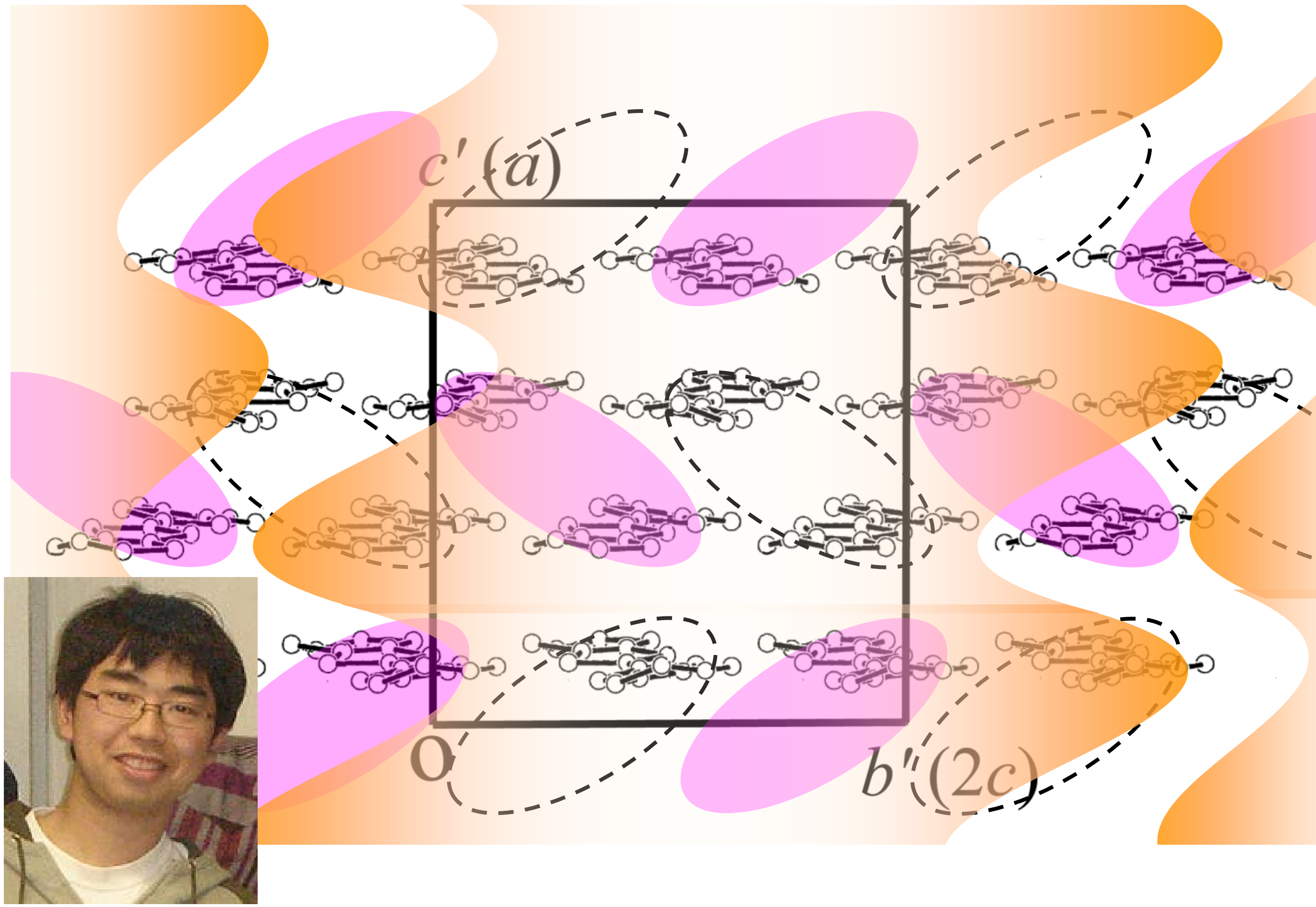
$N = 2$



Collective excitations in β-(BEDT-TTF)$_2$PF$_6$

Electric field responses : /-driven mode

$N = 5$



Singing Organic Conductor

by Mr. T. Asano

非線形伝導　⊂　非線形科学

＊準安定状態

＊サイリスタ(交流発振)

⇒有機伝導体が舞台

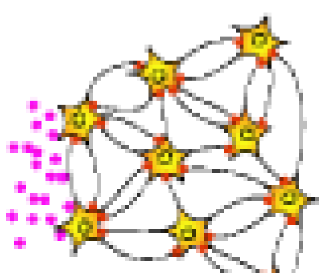
＊準安定状態

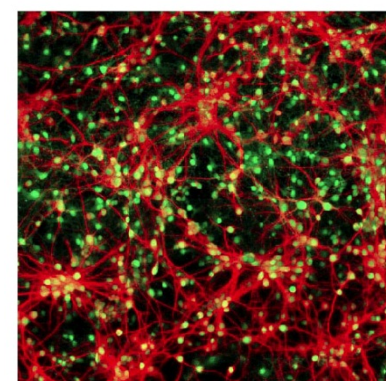
＊同期→正と負の フィードバック

ジャボティンスキー反応

幾万の蛍の同期発光（アフリカ）

脳波
アルファ波 8~13 Hz
ガンマ波 20~80 Hz





脳内ニューロン（神経細胞）の同期発火

レポート（有機物性論）

講義では、分子性物質の結晶構造、バンド構造、フェルミオロジー、（超）伝導性、磁性、外場応答について言及した. 講義に登場したキーワードに関係する最近の論文1編を選び, レポート用紙２～３枚程度で解説し、最後に興味深いと感じた点について簡単に述べよ.

〆切　6月17日(金)

hmori@issp.u-tokyo.ac.jp
タイトル　有機物性論レポート