Role of Precise Structure Analysis for Molecular Crystal System

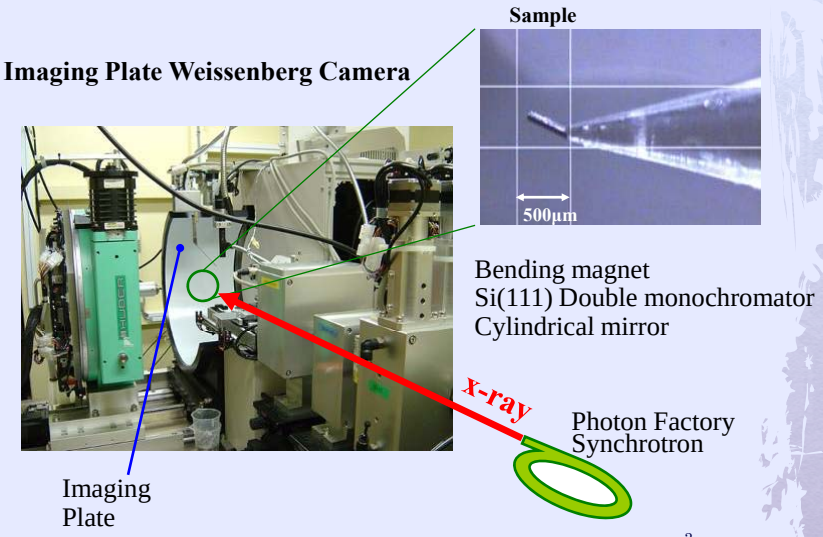
Hiroshi Sawa
Nagoya University

Structural study of Molecular Crystals

- Novel and exotic electronic state in molecular conductor
  - Salts of BEDT-TTF and their analogues
  - MMX 1D systems
  - New molecular superconductors
- Wigner Crystallization
- Precise structural analysis for Fullerene

Synchrotron Radiation X-ray diffraction

@KEK PF BL-1A,1B



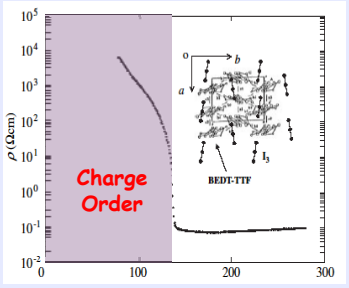
3

Charge Ordering of α-(BEDT-TTF)$_2$I$_3$

Metal-Insulator Transition

K. Bender, et. al., *Mol. Cryst. Liq. Cryst.* **108**, (1984) 359

Resistivity measurement T_{MI} = 135K



^{13}C-NMR

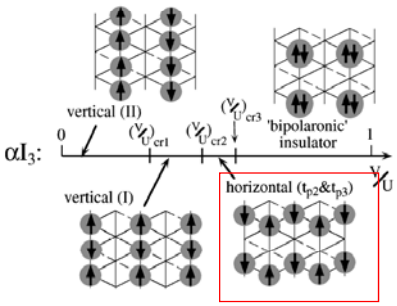
Y. Takano *et.al* *Synth. Met.* **120** (2001) 1081

Y. Takano *et.al* *J. Phys. Chem. Solids* **62** (2001) 393

Raman

R.Wojcechowski *et.al* PRB **67** (2003) 224105

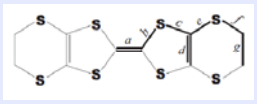
Theoretical predictions

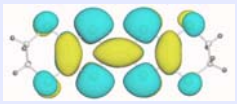


H. Kino and H. Fukuyama, *JPSJ* **64** (1995) 1877
(Hubbard model)

H.Seo, *JPSJ* **69** (2000) 805
(Extended Hubbard model)

Estimated Charge Distribution using Structure Analysis



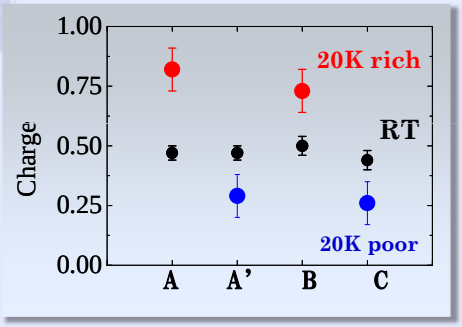


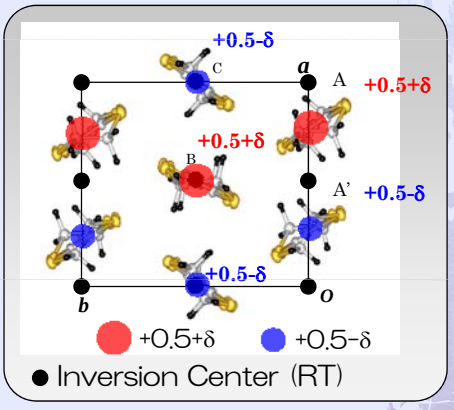
Empirical Estimation of BEDT-TTF

Charge: $Q = 6.347 - 7.463p,$

$p = (b + c) - (a + b)$

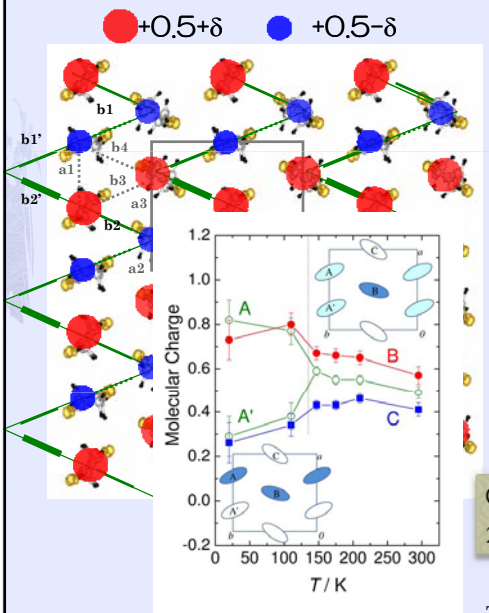
Guionneau, *et.al.*

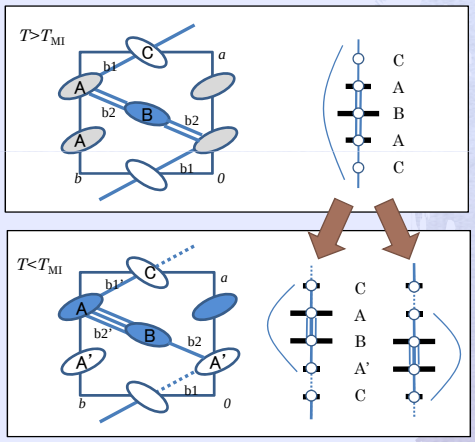




Horizontal Stripe type Charge Ordering

Charge Ordering Pattern and Transfer Integral





Charge disproportionation above T_{MI}

$2k_F$ Charge Gap & Spin Gap

T.Kakiuchi *et al.*, *JPSJ.*, *76 (2007) 113702-1-4*

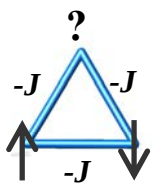
Structural study of Molecular Crystals

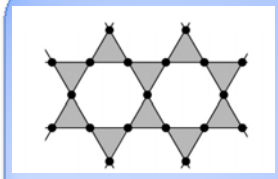
- Novel and exotic electronic state in molecular conductor
  - ✓ Salts of BEDT-TTF and their analogues
  - ✓ MMX 1D systems
  - ✓ New molecular superconductors
- Wigner Crystallization
- Precise structural analysis for Fullerene

GEOMETRICAL FRUSTRATION

Well-known Frustration pattern;
the equilateral triangle is a motif

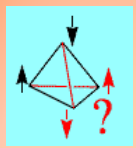
Frustration in
Antiferro type
Ising spin system

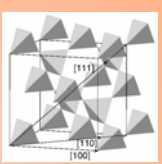


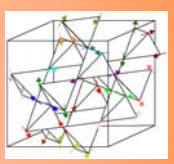


Frustration in Kagome lattice

Frustration in tetrahedral lattice



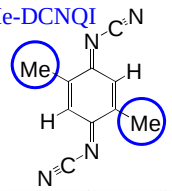




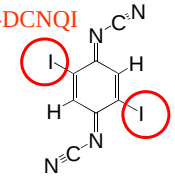
Pyrochlore lattice

Physical Properties in $(R_1R_2\text{-DCNQI})_2Ag$

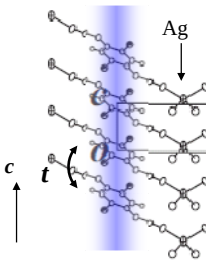
DMe-DCNQI

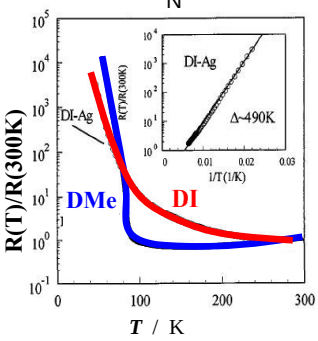


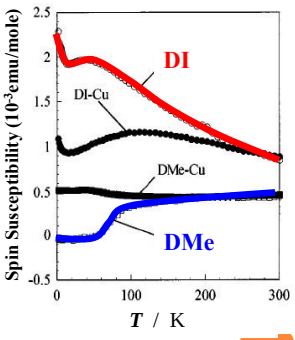
DI-DCNQI



Stacking structure of DCNQI molecules



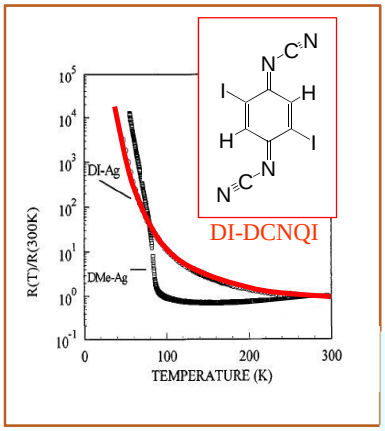




K.Hiraki and K.Kanoda *Phys.Rev.***B**54, 17276(1996) 12

Different Substitutions give Different Ground States

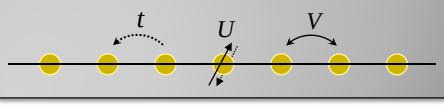
Electron Correlation Realizes Charge Ordering Ground State



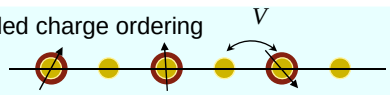
Extended Hubbard model

$$\mathcal{H} = -\sum_{<i,j>\sigma} t_{ij}(c_{i\sigma}c_{j\sigma} + h.c.) + \sum_i U n_{i\uparrow}n_{i\downarrow} + \sum_{<i,j>} V_{ij} n_i n_j$$

t_{ij} : transfer integral
U : on site Coulomb
V : inter site Coulomb



¼ filled charge ordering

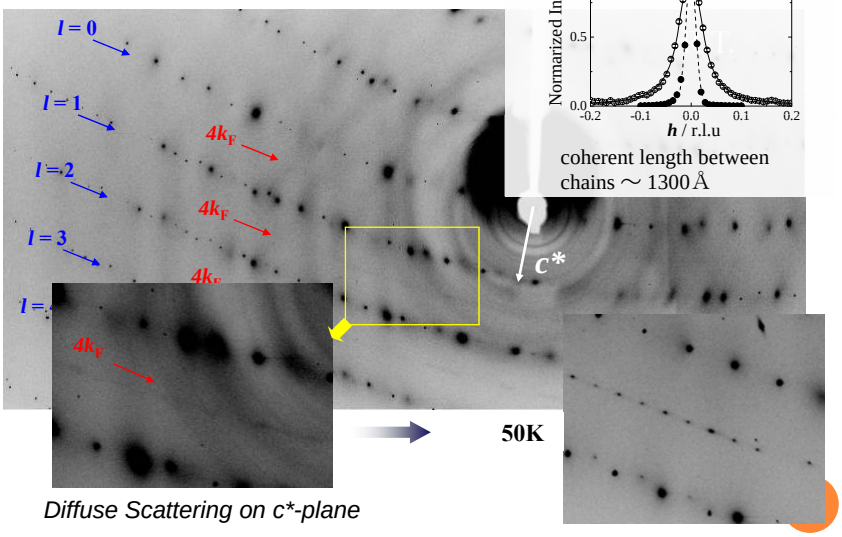


Theoretical predictions : H. Seo, et.al., *JPSJ* **66** (1997) 1249

13

Oscillation Photograph @BL1A

10min / 1frame



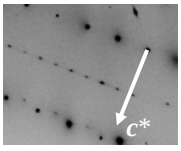
coherent length between chains ~ 1300 Å

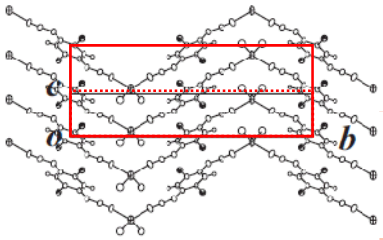
Diffuse Scattering on c-plane*

3D-order

Structure Analysis at Low Temperature

- two-fold *c*-axis





- Space Group

P2/a (Monoclinic)

Data Collection

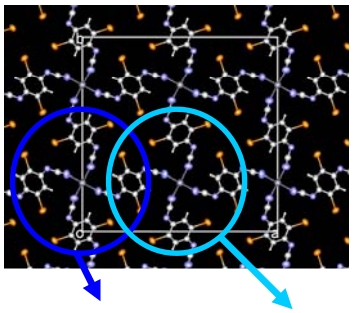
SPD @BL1A
Oscillation photograph
exposure time: 10min
Wave length: 0.687
Sample size: 0.35×0.05×0.05mm3
Temperature : 50K

Result of Analysis at 50K

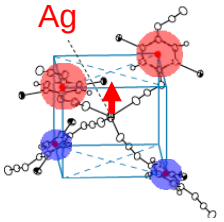
Space Group : *P2/a* Twined Crystal
Obs. : 28177
Resolution : 0.45
***R*(all) : 0.058** ***R*($I > 4\sigma$) : 0.044**
domain ratio : 0.52 : 0.48

15

Determination of Spatial Charge Ordering using Displacement Pattern of Ag cations



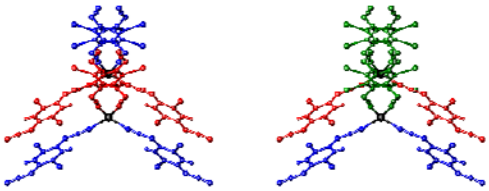
- **Ag mono-cation has a closed shell.**
- **Shift of Ag cation is proportional to the electronic field modulated by the charge ordering on DCNQI molecules.**

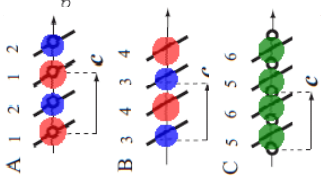


Ag → + ion

attractive

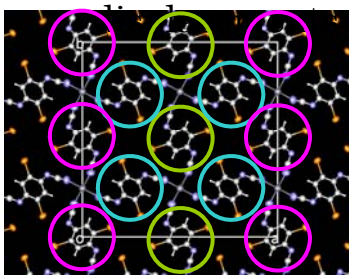
DCNQI → – charged





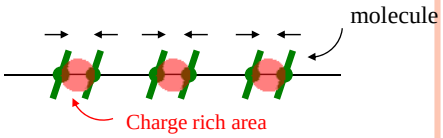
Success of qualitative determination for charge ordering in DCNQI columns.

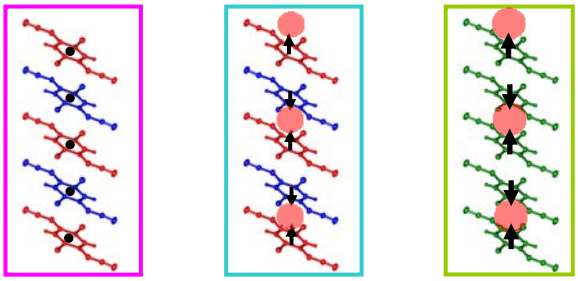
Another instance of Charge modulation from DCNQI



Displacements of DCNQI cause Modulation of Charge Density

One-dimensional Chain

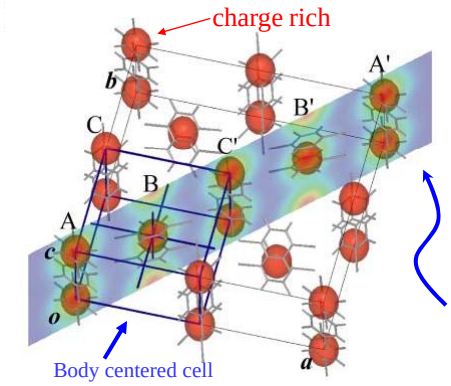




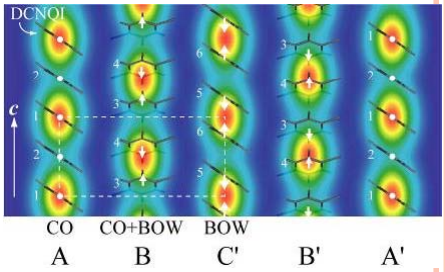
No shift | Small shifts | Large shifts

17

WIGNER CRYSTALLIZATION



Charge(electron)-rich areas form Body Centered Tetragonal
↓
Wigner Crystallization



Coexistence of site- and bond-CDW
↓
We can describe the crystal structure as "Charge Density Wave"

T.Kakiuchi *et al.*, *PRL* **98**, 066402(2007)

Conclusion

- Standard structure analysis is suitable technique for determination of the ground state in molecular crystal systems.
- A more complex structure analysis becomes possible by combining with Resonant X-ray Scattering, too.