2007.11.23 Yukawa Institute

YKIS2007

Strongly Correlated Electrons in Molecular Solids

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Acknowledgement

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K. Kanoda, R. Kato

Hayao and Akiko Kobayashi

S. Shin, Y. Harada

K. Miyake, Matsuura

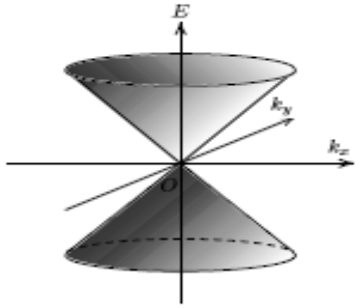
T. Tohyama

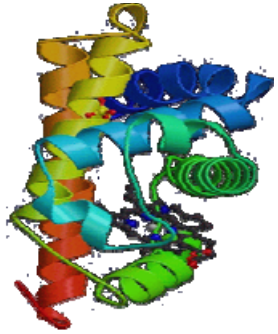
S. Tsuneyuki

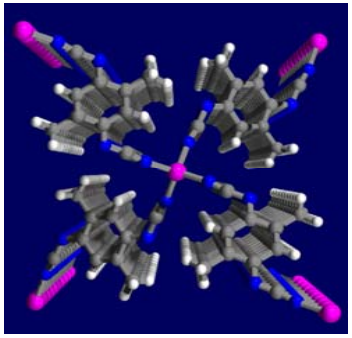
HF, J. Phys. Soc. Jpn 75 (2006) 051001.

Outline

1) Brief history of conducting molecular solids
2) Charge transfer salts of the type A_2B:
   "quarter-filling"
3) Two paradigm: dimer Mott and charge ordering
4) Systematic understanding of various expt. facts
   based on extended Hubbard model
5) π - d systems:
   * localized d-spins
   * valence fluctuations
   * M-Bz
   * FeS
   * Myoglobin
6) Toward Bio-materials science







Strongly correlated electrons

* π electrons: Mott insulators, Charge ordering

* **p-d coupled systems**

d: Transition metal ions

A. localized spins

(1) λ -BETS $(FeCl_4)_2$

(2) $TTP[Fe(CN)_2]_2$

B. fluctuating valences

(1) $DCNQI_2Cu$

(2) Single component metals, $[M(tmdt)_2]$

M = Ni, Au

➔ metalloproteins, e.g. myoglobin, FeS cluster,--

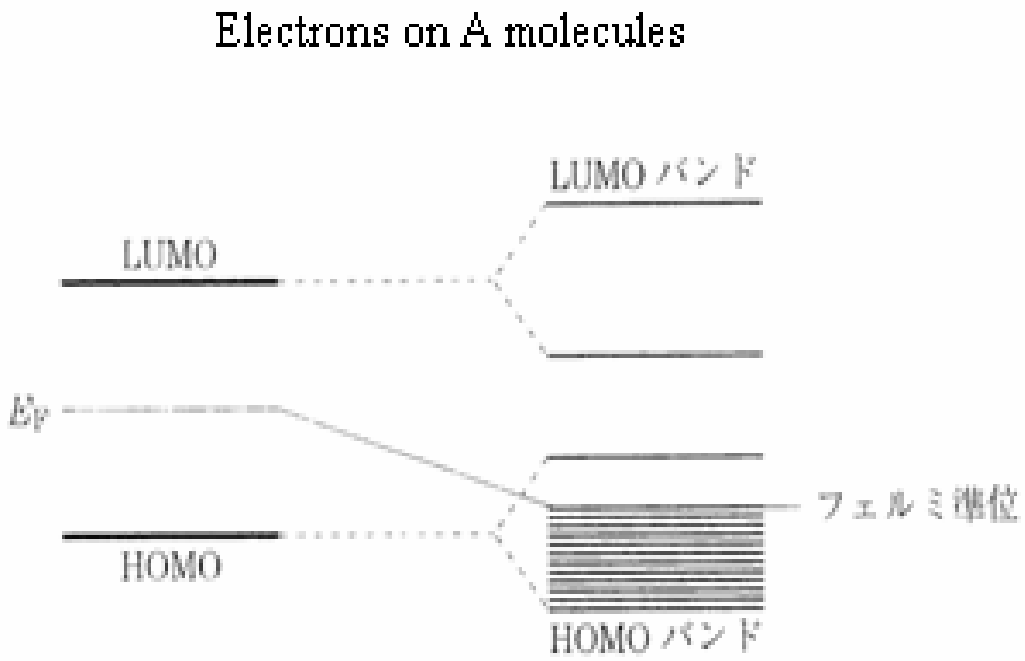
Molecular Solids for Metallic States by Charge Transfer between Molecules

NMP-TCNQ	CT Mott insulator	1d AF(TCNQ)
TTF-TCNQ	CT 1d semimetal p-dep. n	Peierls transition, CDW, gigantic conductivity peak, sliding conduction
(CH)x	Peierls insulator (Dimer)	doping , carriers as ingap states (solitons)
$TMTCF_2X$	CT metal	SDW, SC, AF, Spin-Peierls, CO, ferroelectricity
$DCNQI_2X$	CT metal	CO(Ag), CO-Mott with Peierls (Cu)
$BEDTTTF_2X$ (ET_2X)	CT metal	Mott Insulator, Charge Ordering, SC
$BETS_2X$	CT metal	SC ($GaCl_4$), Mott insulator & Field-Induced SC($FeCl_4$)
$(DT\text{-}TTF)_2[Au(mnt)]$	1/4 -filled Spin Ladder	Charge Ordering ?
$(TTM\text{-}TTP)I_3$	1 : 1 Half-filled CT metal	Mott Transition I_3 --> $FeBr_{1.8}Cl_{2.2}$: Fe^{+3} S= 5 / 2
$Ni(tmdt)_2$ $Au(tmdt)_2$	Single Component Metal	HOMO-LUMO overlap->semimetal, magnetic phase transition

Typical Molecular Conductors caused by charge transfer

A_2B^- $\quad B^- =$ closed shell

$\Rightarrow A^{+0.5}$



How is this Bloch band described?

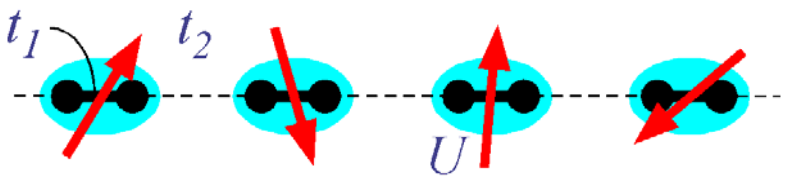
A_2B materials

$(A^{0.5+})_2B^-$ or $(A^{0.5-})_2B^+$ → A : ¼-filled (if all A equivalent)

two limiting cases of insulating states in **1/4-filling**

• case 1 : strong dimerization $t_1 >> t_2$

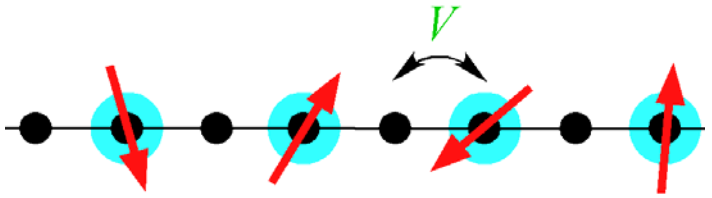
+ on-site Coulomb interaction U



S=1/2 per dimer

dimer Mott insulator

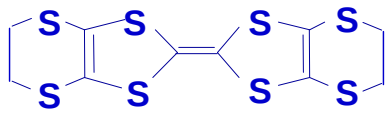
• case 2 : intersite Coulomb interaction V



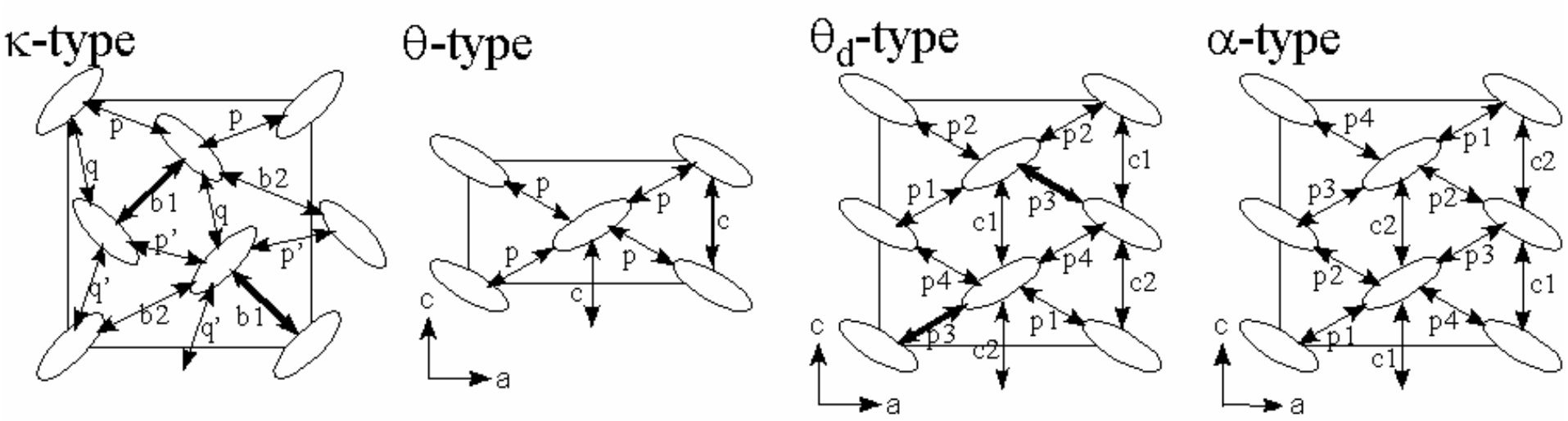
S=1/2 on every other site

Charge Ordering

Typical Examples: ET_2X “ 2d ”

ET=BEDT-TTF : 

variety in **in-plane** (2d) lattice structures : polytypes α, β, θ, κ, λ, …



mean-field calculations on Hubbard models

→ systematic understanding of ground states

Kino-Fukuyama JPSJ ’95,’96

Systematic Studies on
Electronic Properties of Molecular Solids

Hayao, Akiko Kobayashi

Effects of mutual interactions

Based on extended Hubbard model

$$H = \sum t_{i,i+1} (c_{is}\dagger c_{i+1s} + h.c.) + \sum U n_{i\downarrow} n_{i\uparrow} + \sum V_{i,i+1} n_i n_{i+1}$$

$t_{i,i+1}$

- takes full account of molecular orbitals, esp. anisotropy

H.Seo, C.Hotta, HF, Chemical Reviews 104, 5005(2004)

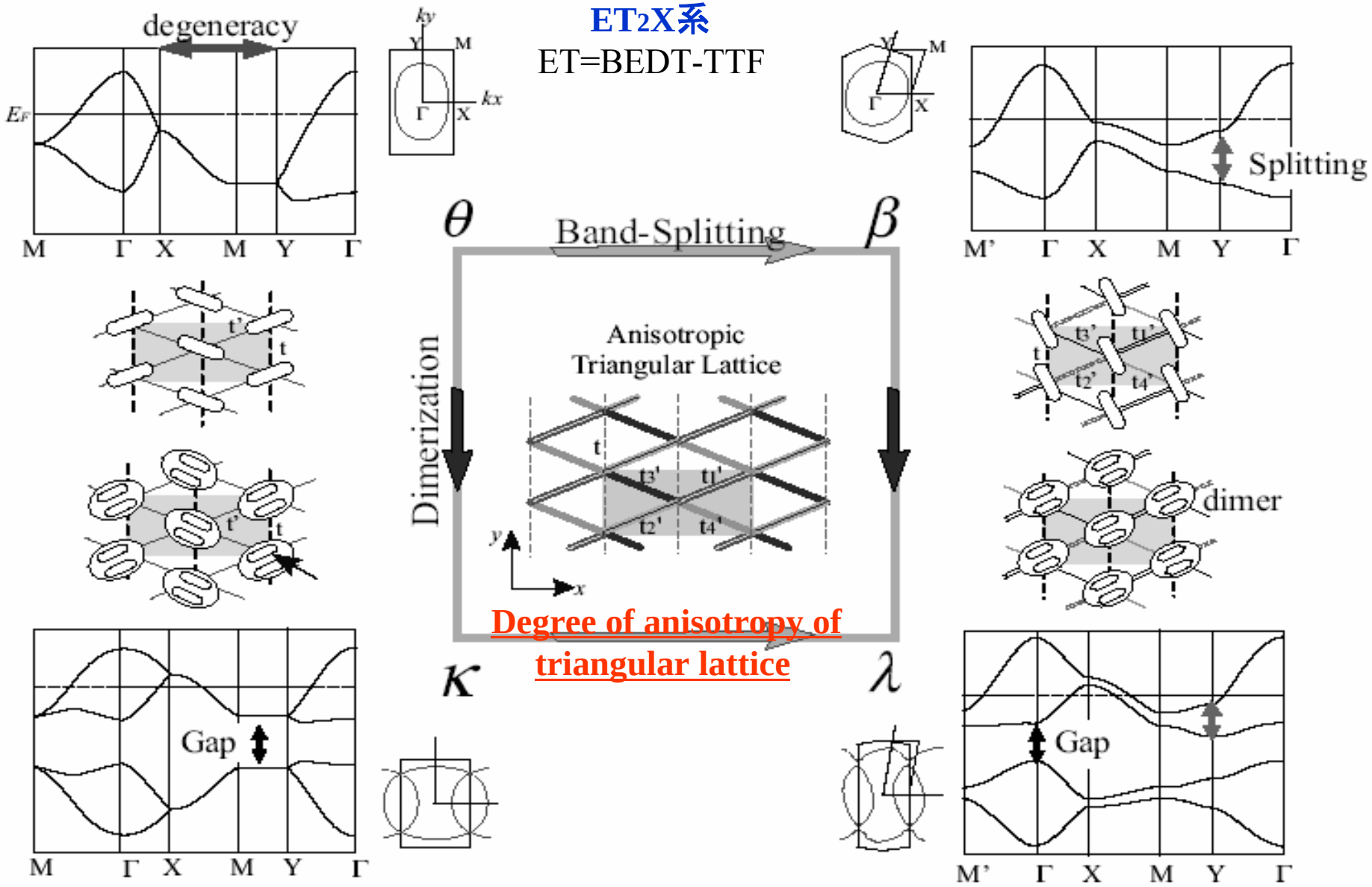


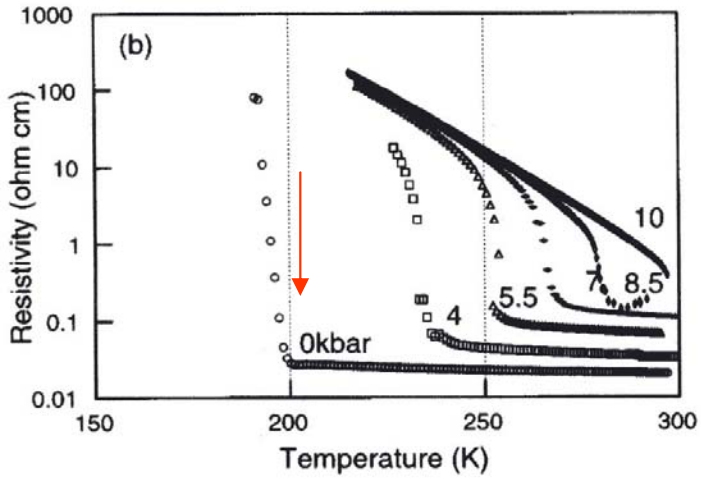
Figure 23: Relationship between different polytypes in 2D molecular solids based on the anisotropic triangular lattice shown in the center.

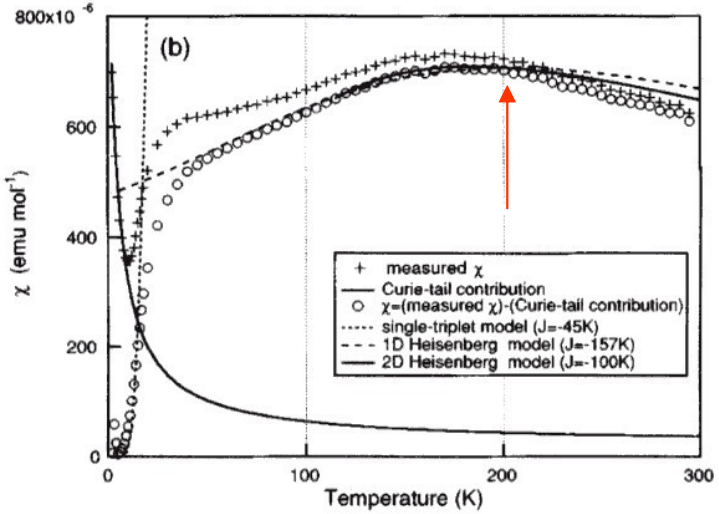
C.Hotta, JPSJ 72, 840(2003)

ET_2X with no/weak dimerization

θ-type

θ-$ET_2RbZn(SCN)_4$

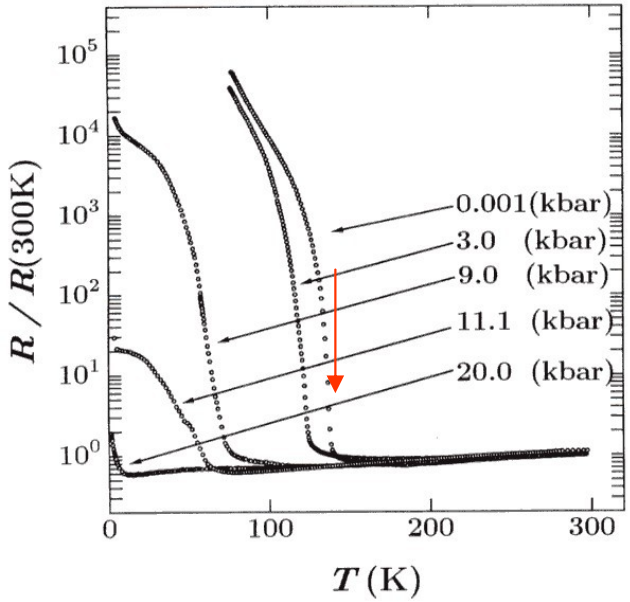




H.Mori, S.Tanaka, T.Mori ‘98

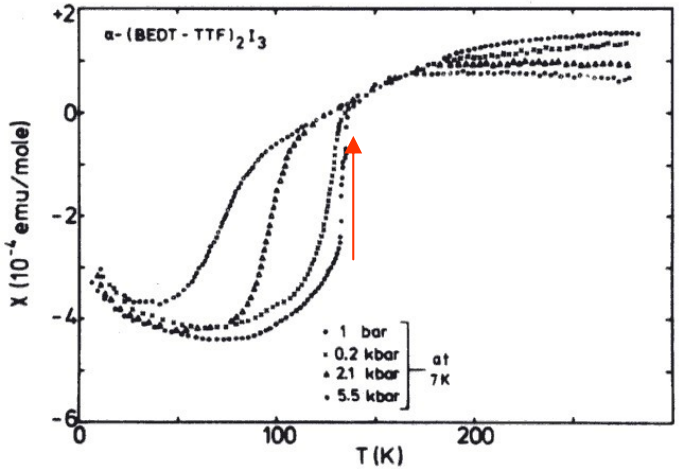
α-type

α-ET_2I_3



Bender et al. ’84
N.Tajima et al. ‘00

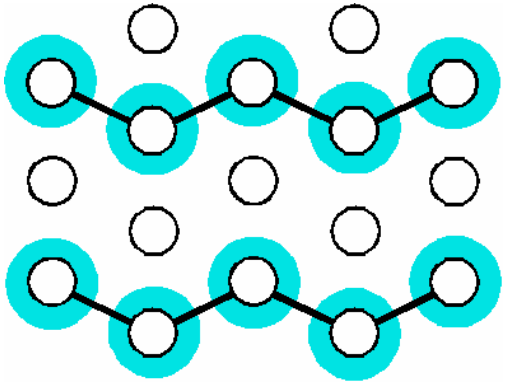
Rothaemel et al. ’86

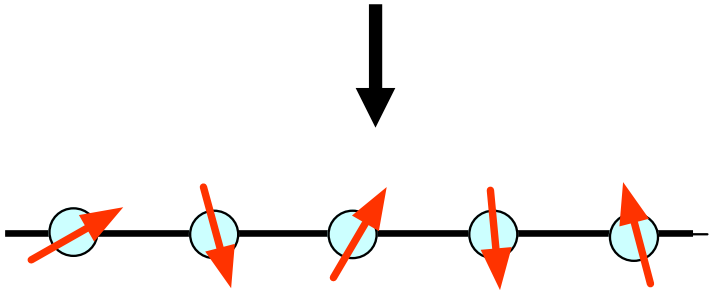


ET_2X with no/weak dimerization -charge order-

Seo (2000): Identification of origin of insulating states in θ-ET

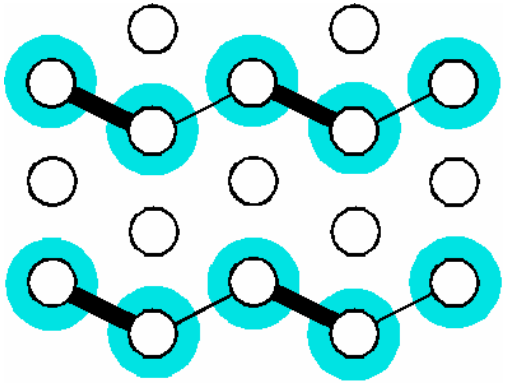
θ-$ET_2RbZn(SCN)_4$

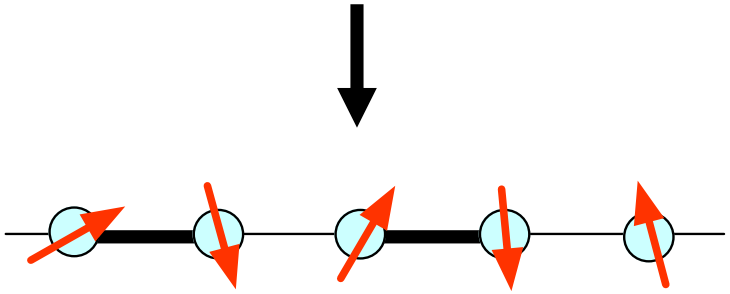




1D Heisenberg chain,
uniform J ~ 450K
(experiments : J ~ 160K)

α-ET_2I_3





1D alternating Heisenberg chain
J_1 ~ 1000K, J_2 ~ 200K
(experiments : J_1 ~ 500K, J_2 ~ 100K)

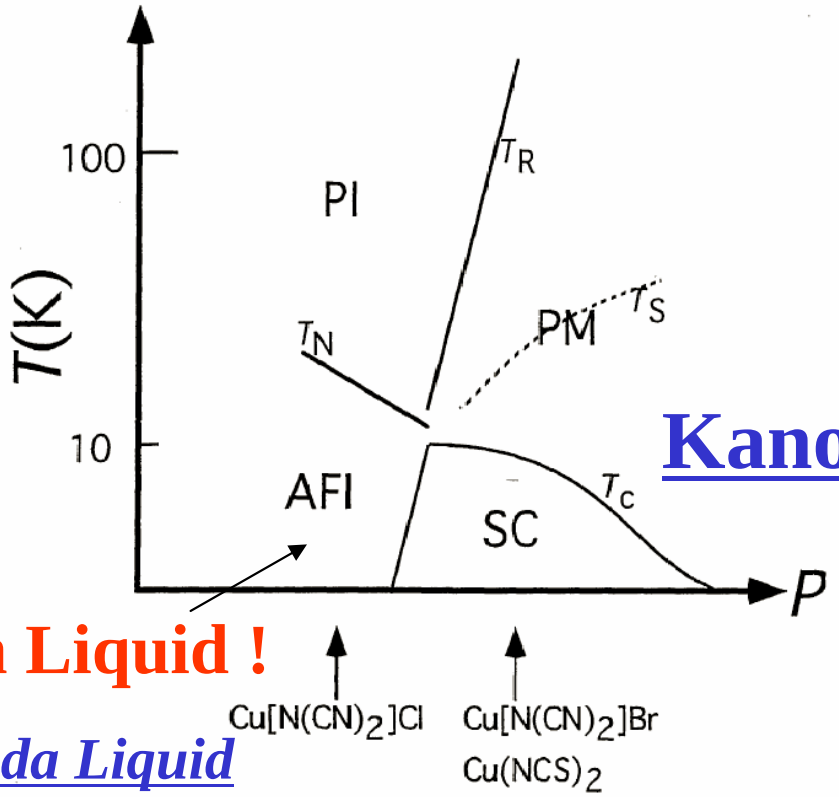
=> Singlet ground state

Cf. $TMTCF_2X$: Seo, Monceau , Brown,

ET_2X: κ and λ Types

Strongly Dimerized

=> Dimer Mott Systems

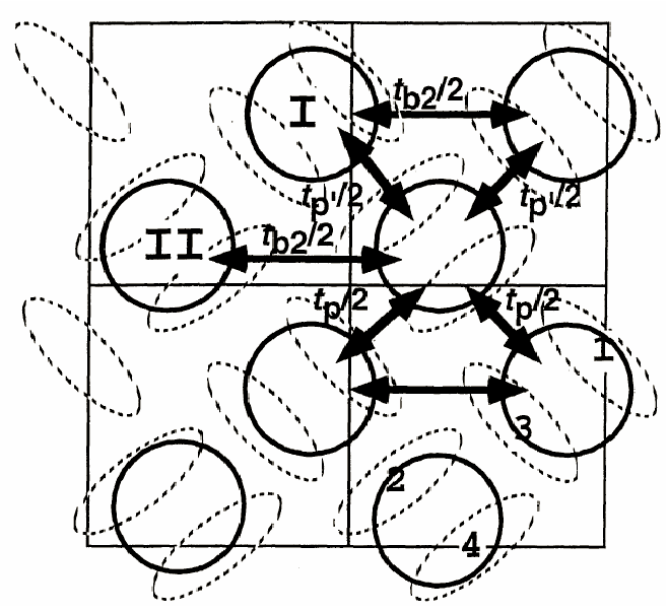


Kanoda

Spin Liquid !

Kanoda Liquid

Fig. 2. Experimental phase diagram of κ-$(ET)_2X$ on the plane of pressure (P) and temperature (T).



Anisotropic Triangular Lattice

Kino-HF: J.Phys.Soc.Jpn 65(1996)2158

Strongly correlated electrons

- So far, π electrons: Mott insulators, Charge ordering

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A. localized spins

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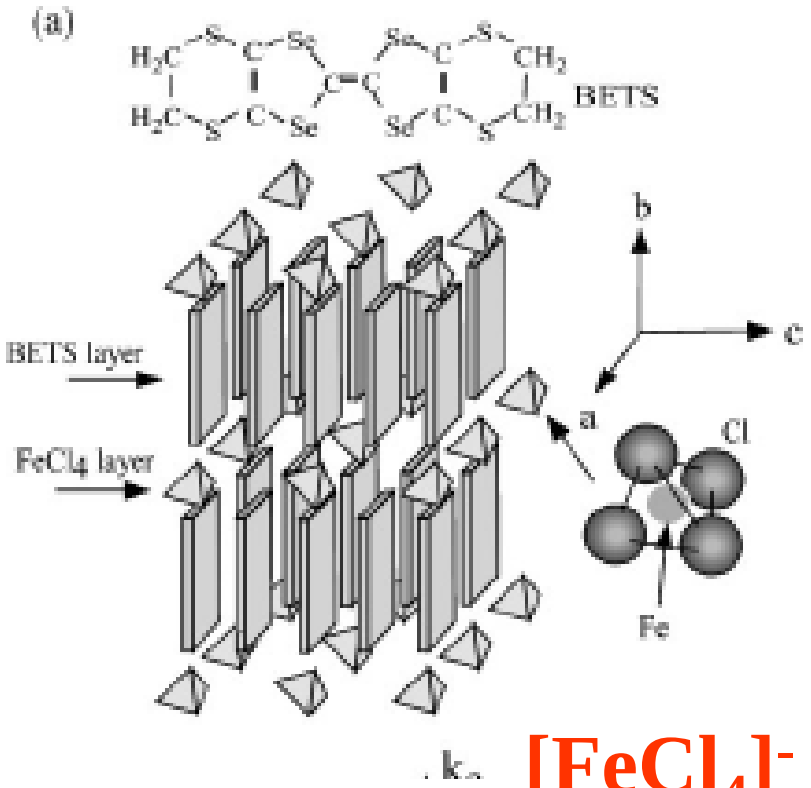
λ - $BETS_2X$ strongly dimerized

BETS: Kato, Kobayashi **2

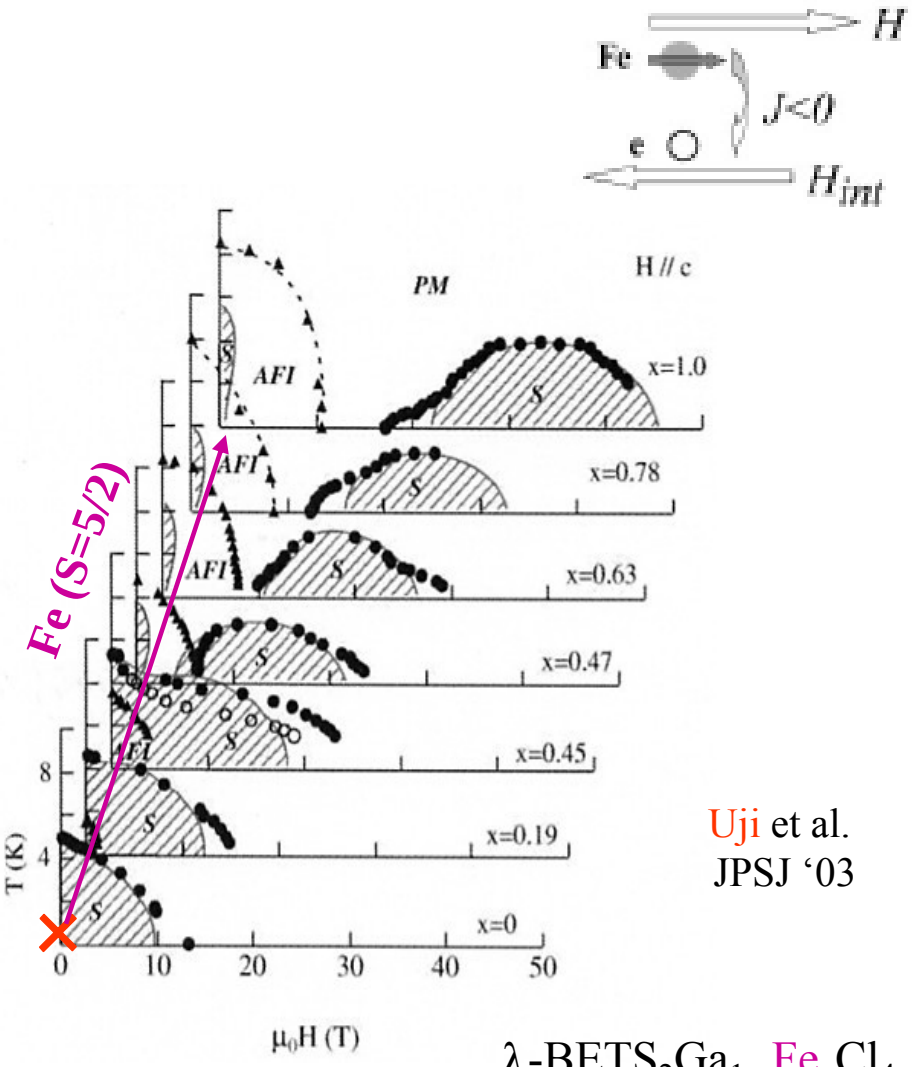
λ-type



'95

$[FeCl_4]^-$

Fe^{+3} S=5/2



Uji et al.
JPSJ '03

λ-$BETS_2Ga_{1-x}Fe_xCl_4$

Magnetic field induced superconductivity

Transition metal ions in molecular solids

Localized spins

* λ - $BETS_2X$: $X^{-}=Fe^{+3}Cl^{-}_{4}$ S=5/2

* Phthalocyanine

$TTP^{+}\,[M^{+3}\,(Pc)^{-3/2}\,(CN)^{-}_{2}]_2$

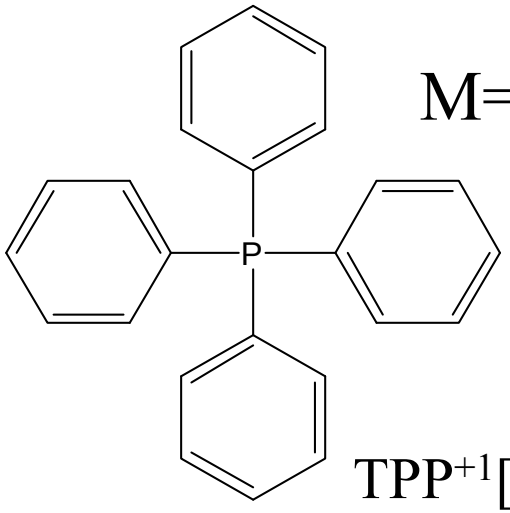
M=Co (S=0), Fe (S=1/2)

Phthalocyanine

$TPP[M(Pc)(CN)_2]_2$

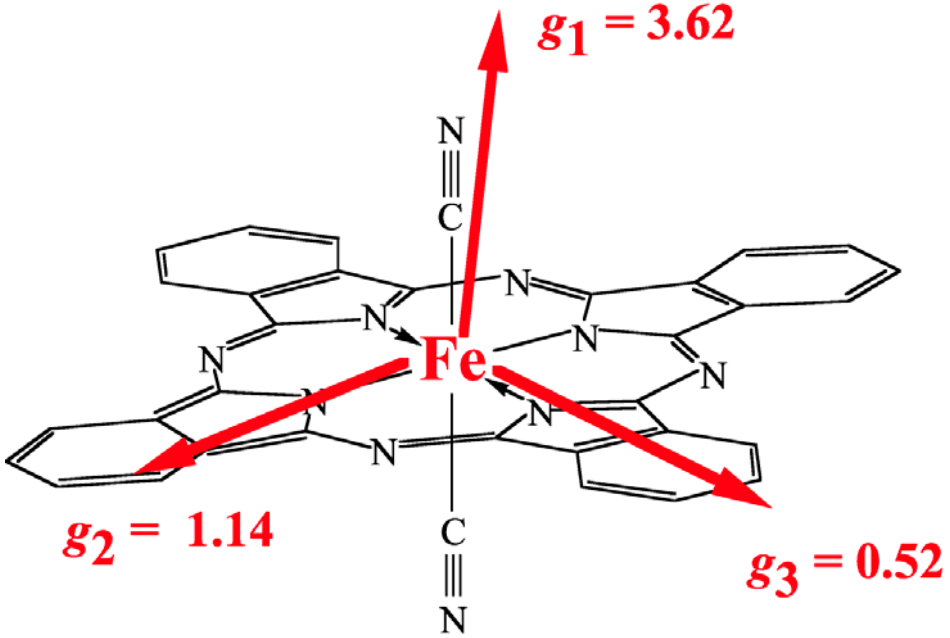
M=Co (S=0), Fe (S=1/2)

Same structure

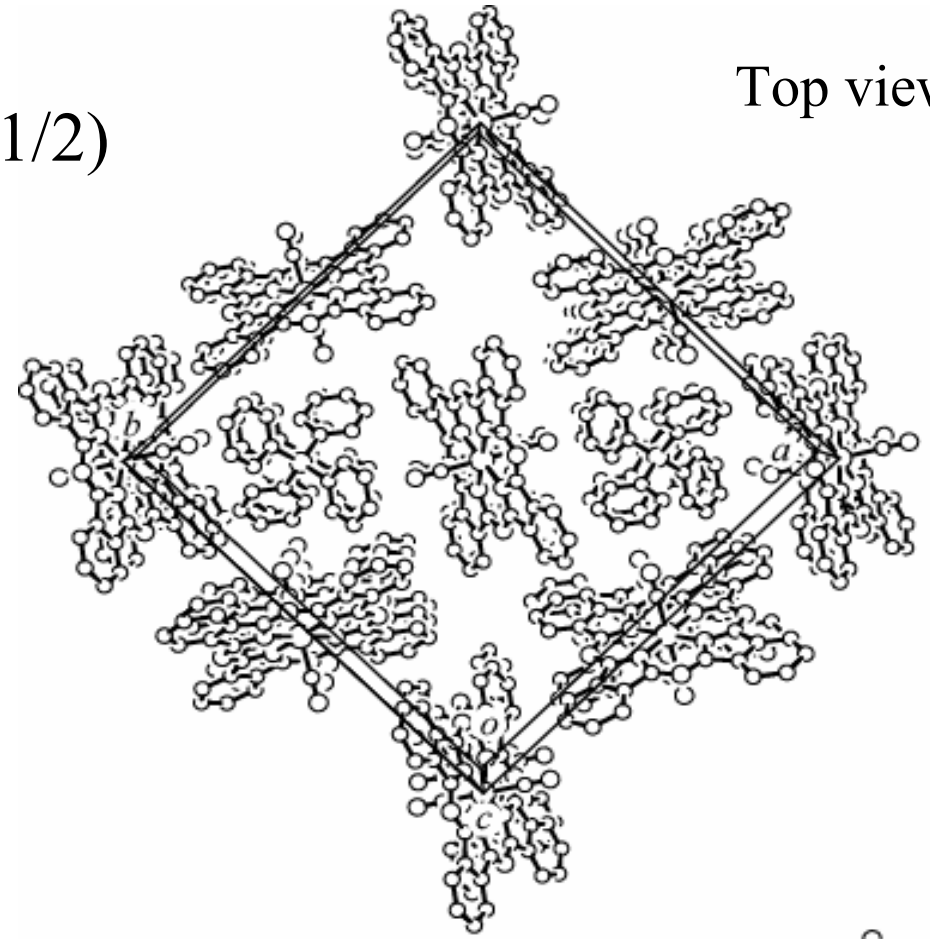


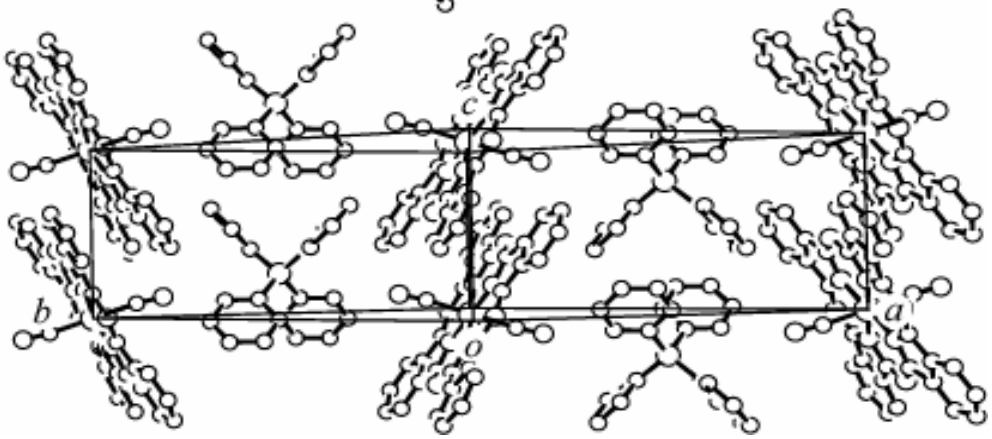
$TPP^{+1}[M^{+3}\ Pc^{-3/2}(CN)^{-}_2]_2$

TPP



1d stacking

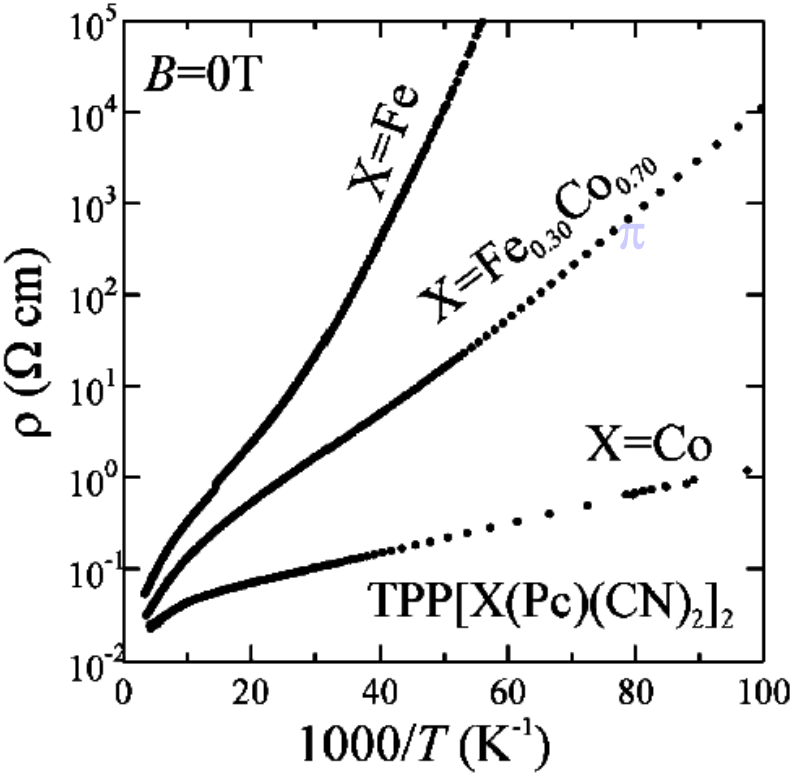


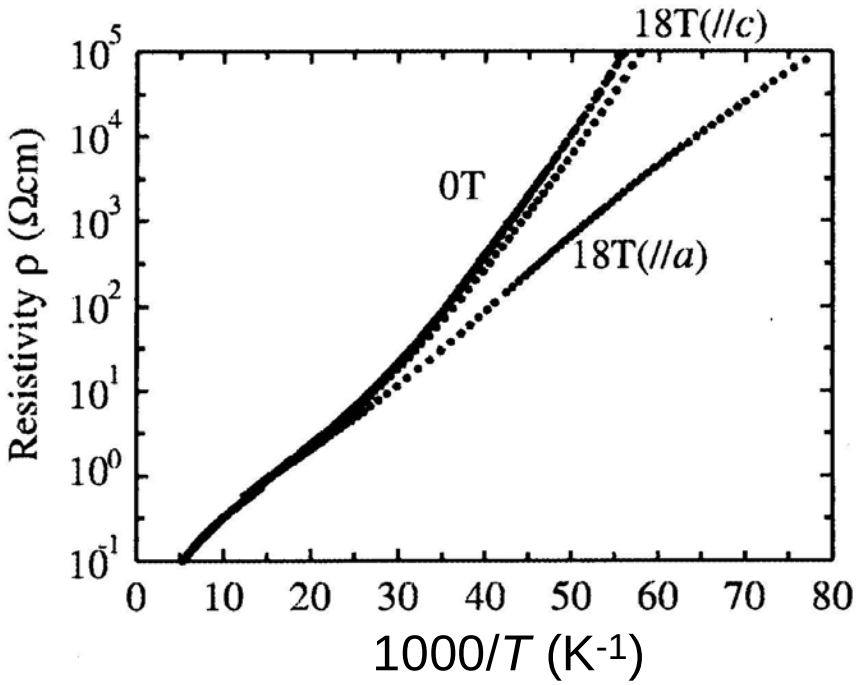


H. Tajima

Experiments

π d





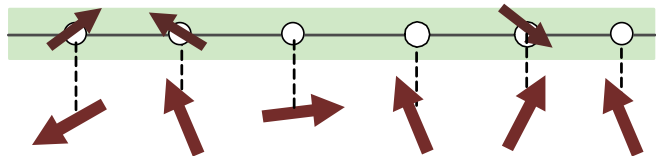
X= Fe

Hanasaki, et.al

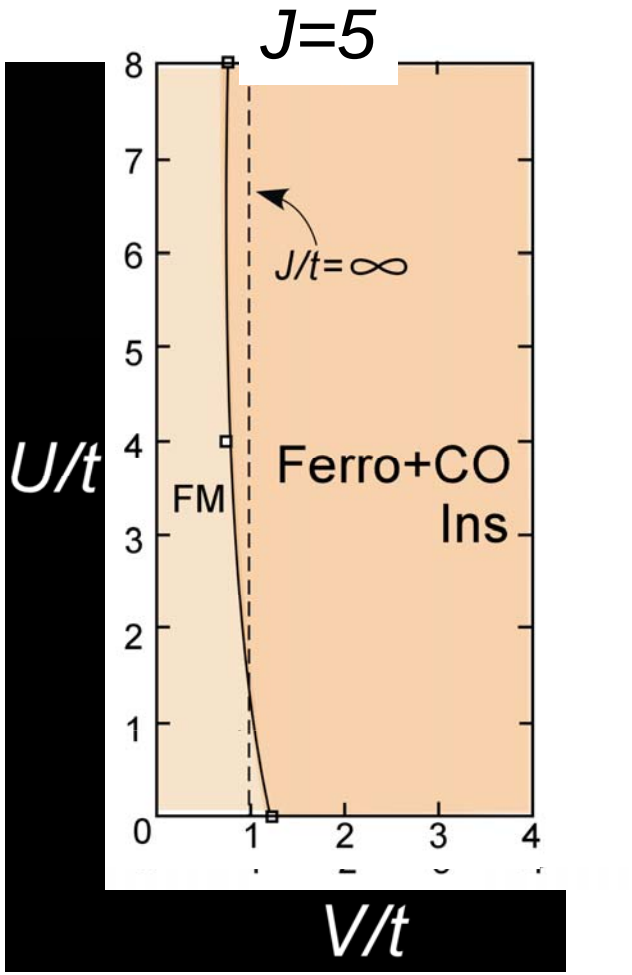
Role of ***J***

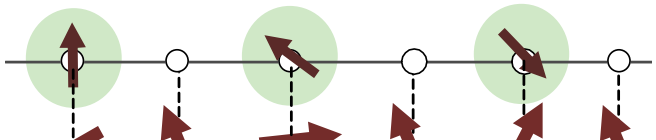
"Bandwidth control (reduction)"

effective enhancement of *UV*

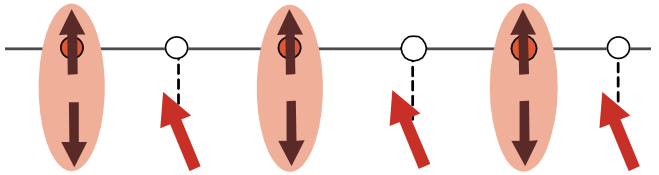


ParaMetal





Para CO



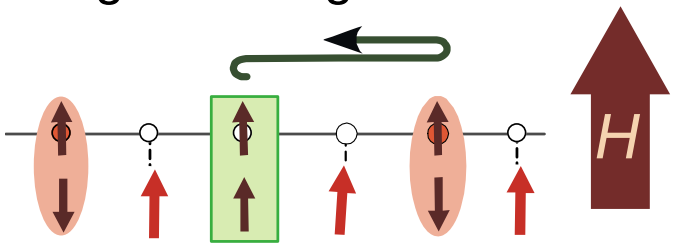
Ferro CO

singlet

t → t/2

Negative magnetoresistance

singlet → triplet



triplet

C. Hotta, M. Ogata, HF, PRL(2005)

Strongly correlated electrons

- So far, π electrons: Mott insulators, Charge ordering

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A. localized spins

(1) λ -BETS $(FeCl_4)_2$

(2) TTP$[Fe(CN)_2]_2$

(3) M-Benzene M= V, Ti -> Miyake-Matsuura

B. Fluctuating valences

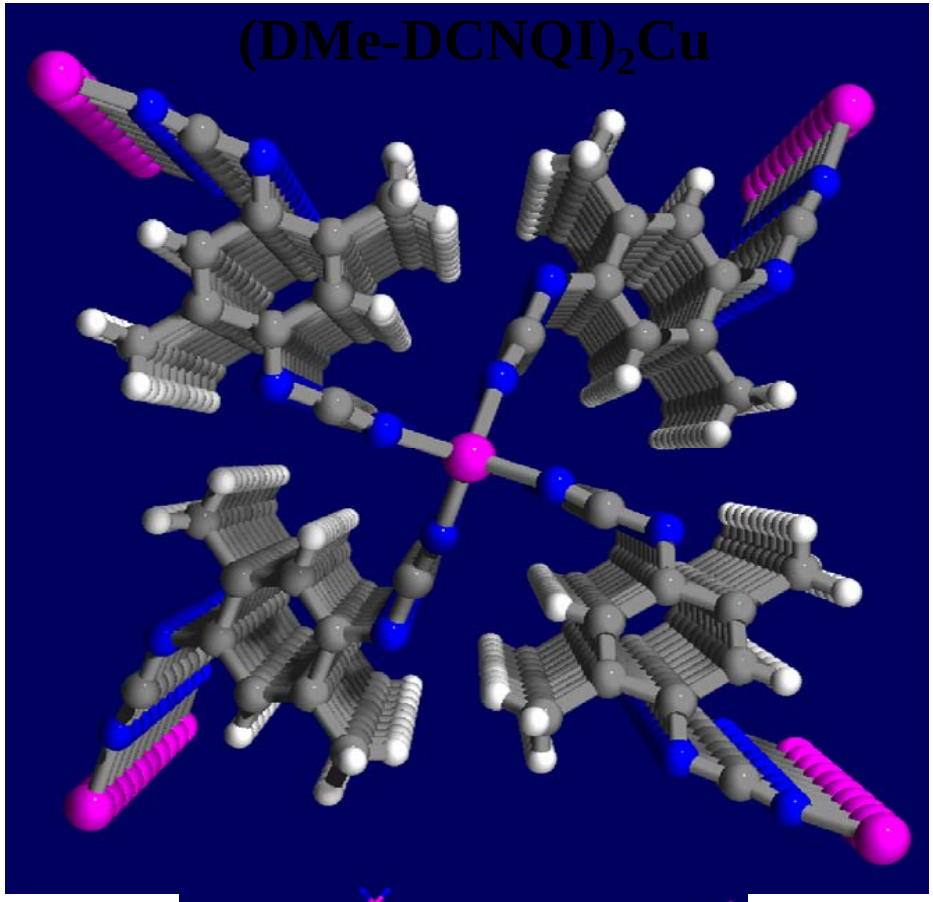
(1) $DCNQI_2Cu$

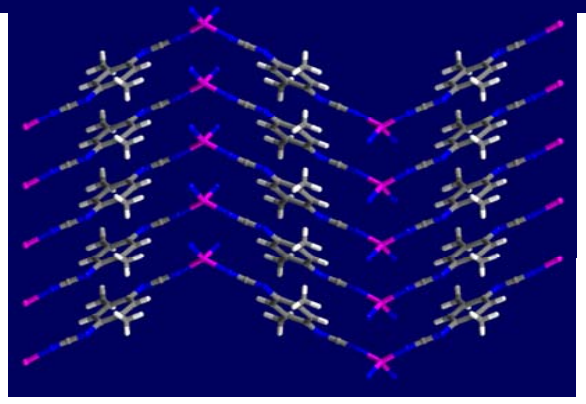
(2) Single component metals, $[M(tmdt)_2]$

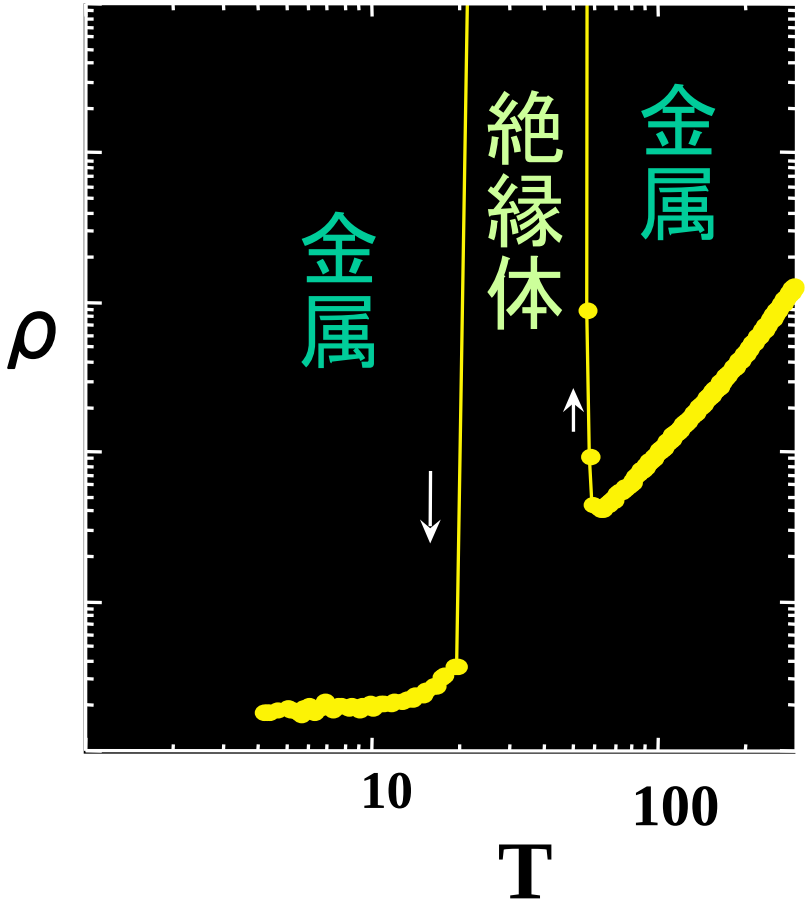
M = Ni, Au

➔ metalloproteins, e.g. myoglobin, FeS cluster,--

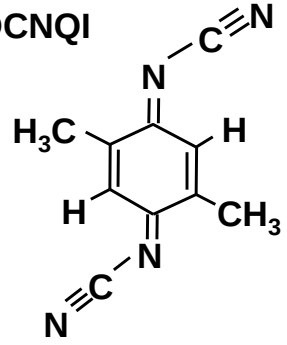
$DCNQI_2Cu$ Hunig, Kobayashi



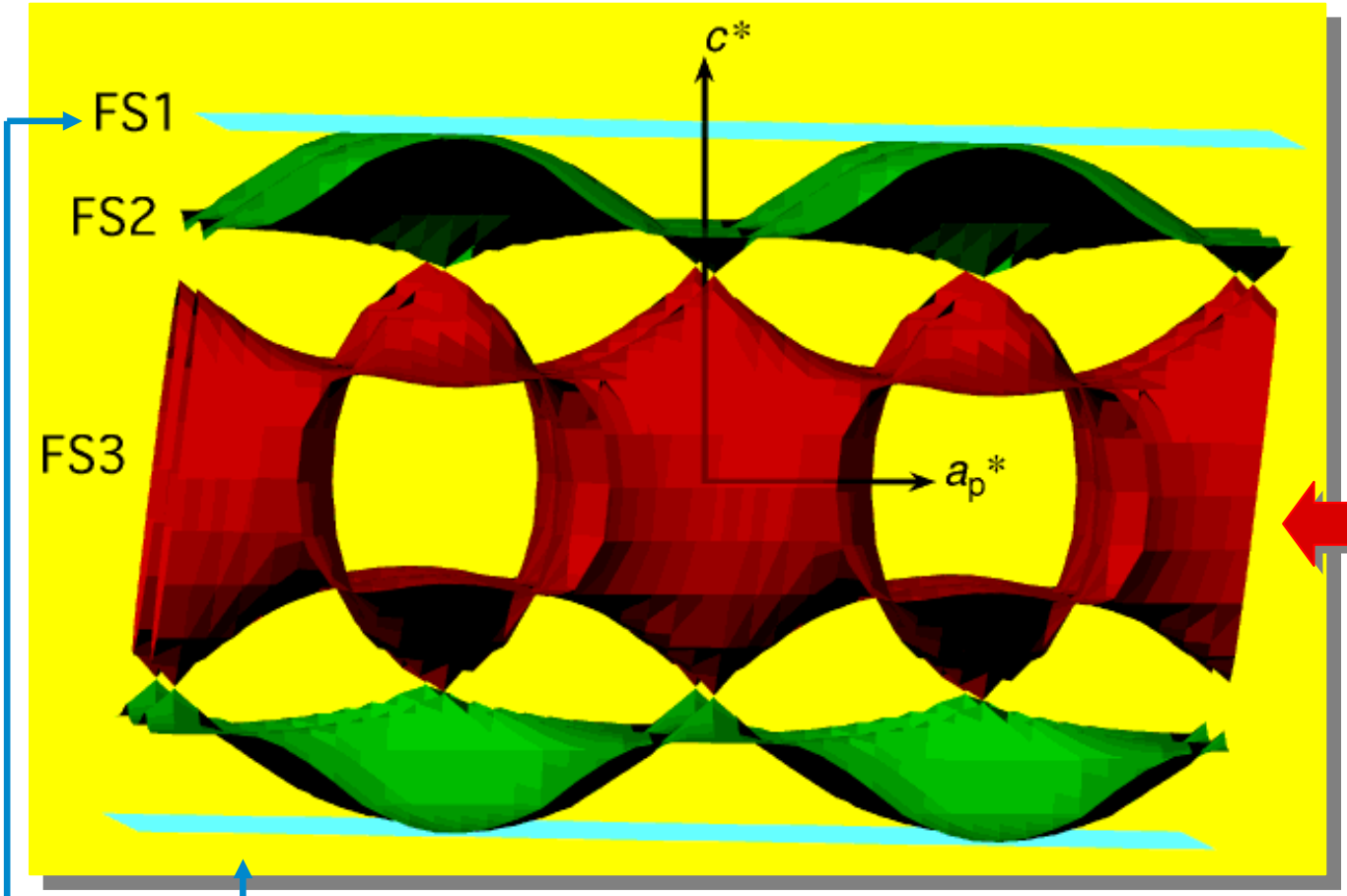


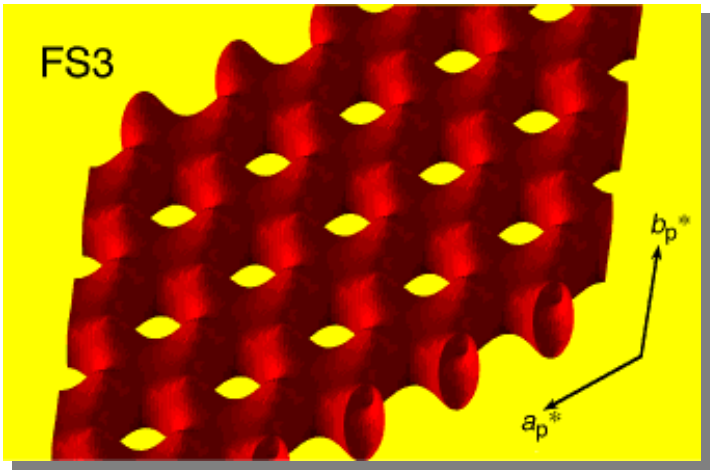


DMe-DCNQI



Calculated Fermi Surface of $(DMe\text{-}DCNQI)_2Cu$





Three-dimensional Fermi surface associated with (mainly) metal d ban

One-dimensional Fermi surface associated with organic π band

R.Kato

LDA: Miyazaki,Terakura

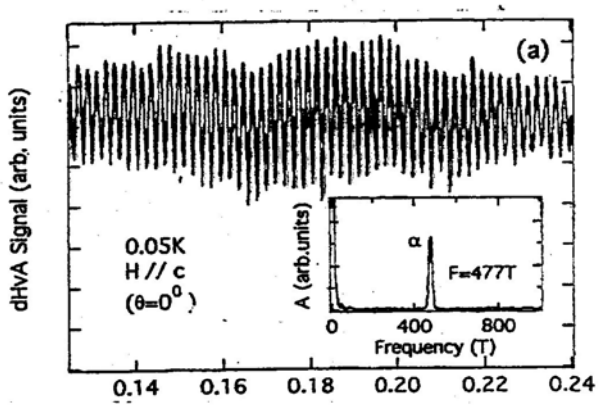
PHYSICAL REVIEW B VOLUME 50, NUMBER 21 1 DECEMBER 1994-I

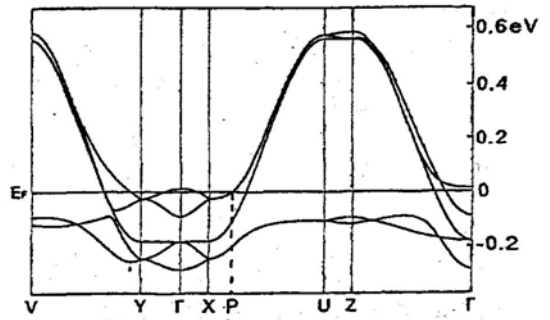
Coexistence of one- and three-dimensional Fermi surfaces and heavy cyclotron mass in the molecular conductor $(DMe\text{-}DCNQI)_2Cu$

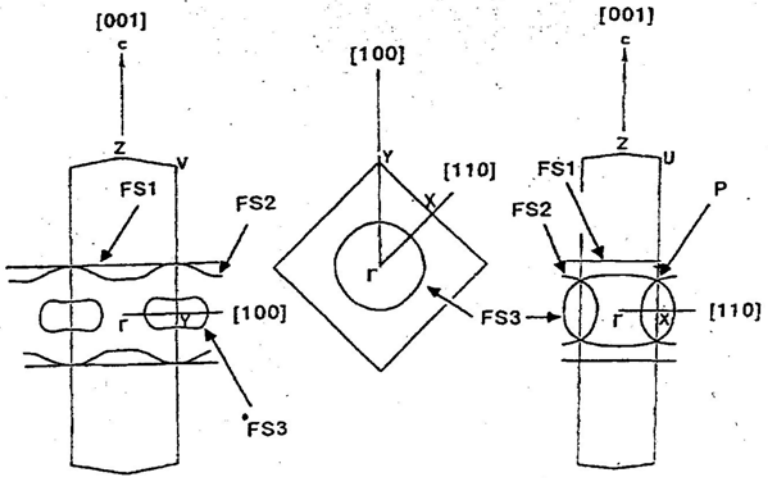
S. Uji, T. Terashima, and H. Aoki
National Research Institute for Metals, Tsukuba, Ibaraki 305, Japan

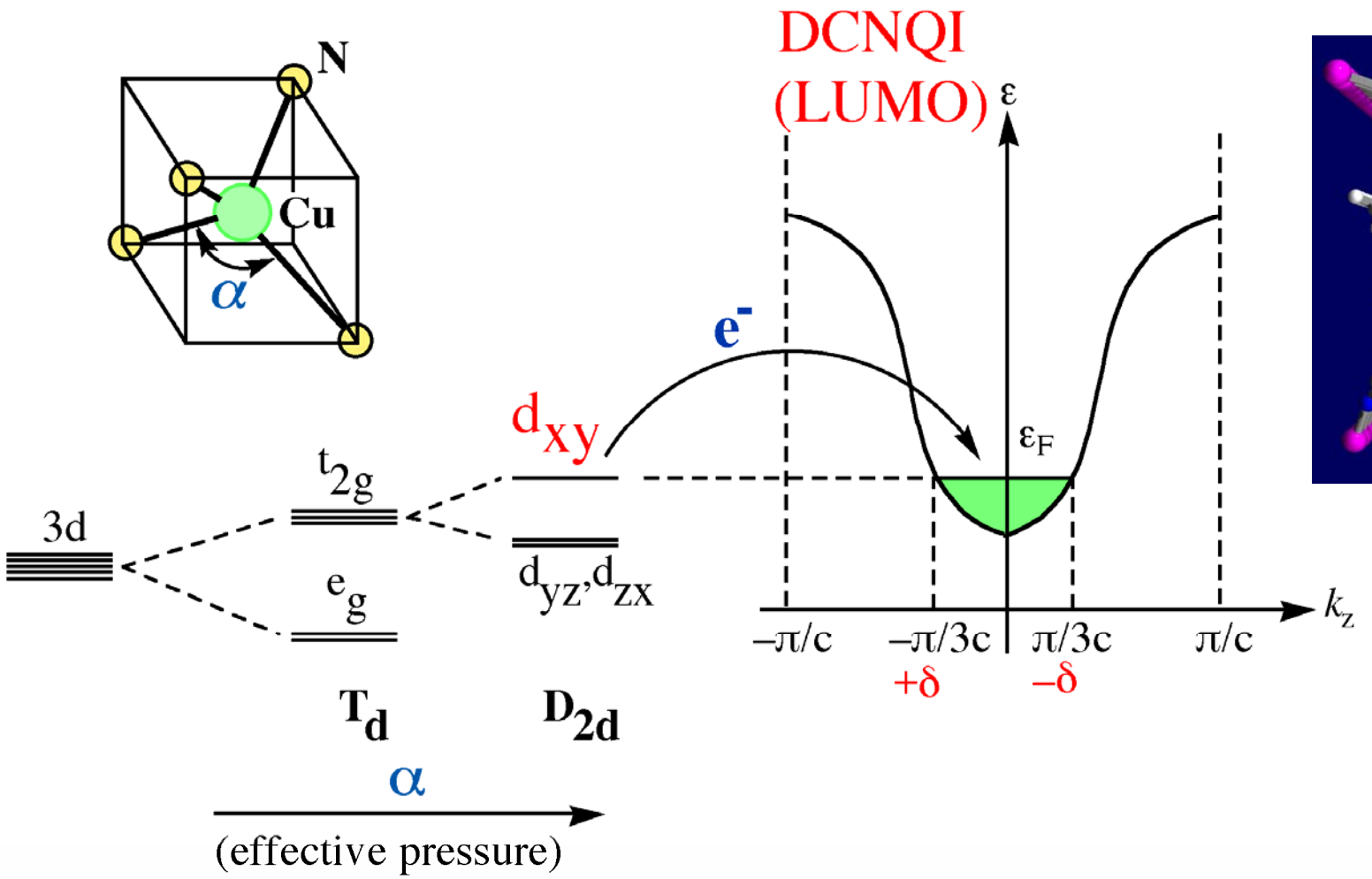
J. S. Brooks
Physics Department, Boston University, Boston, Massachusetts 02215

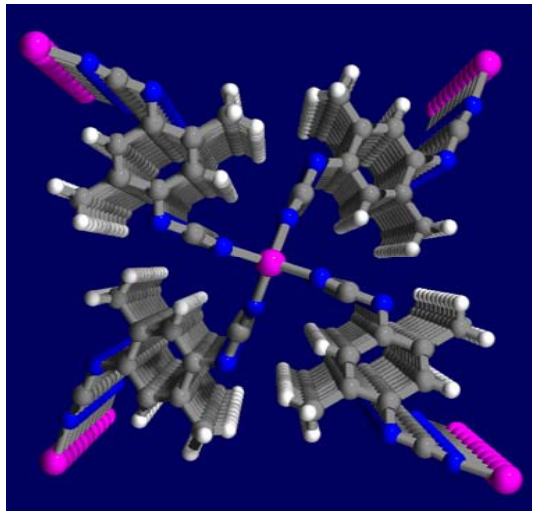
R. Kato, H. Sawa, S. Aonuma, M. Tamura, and M. Kinoshita









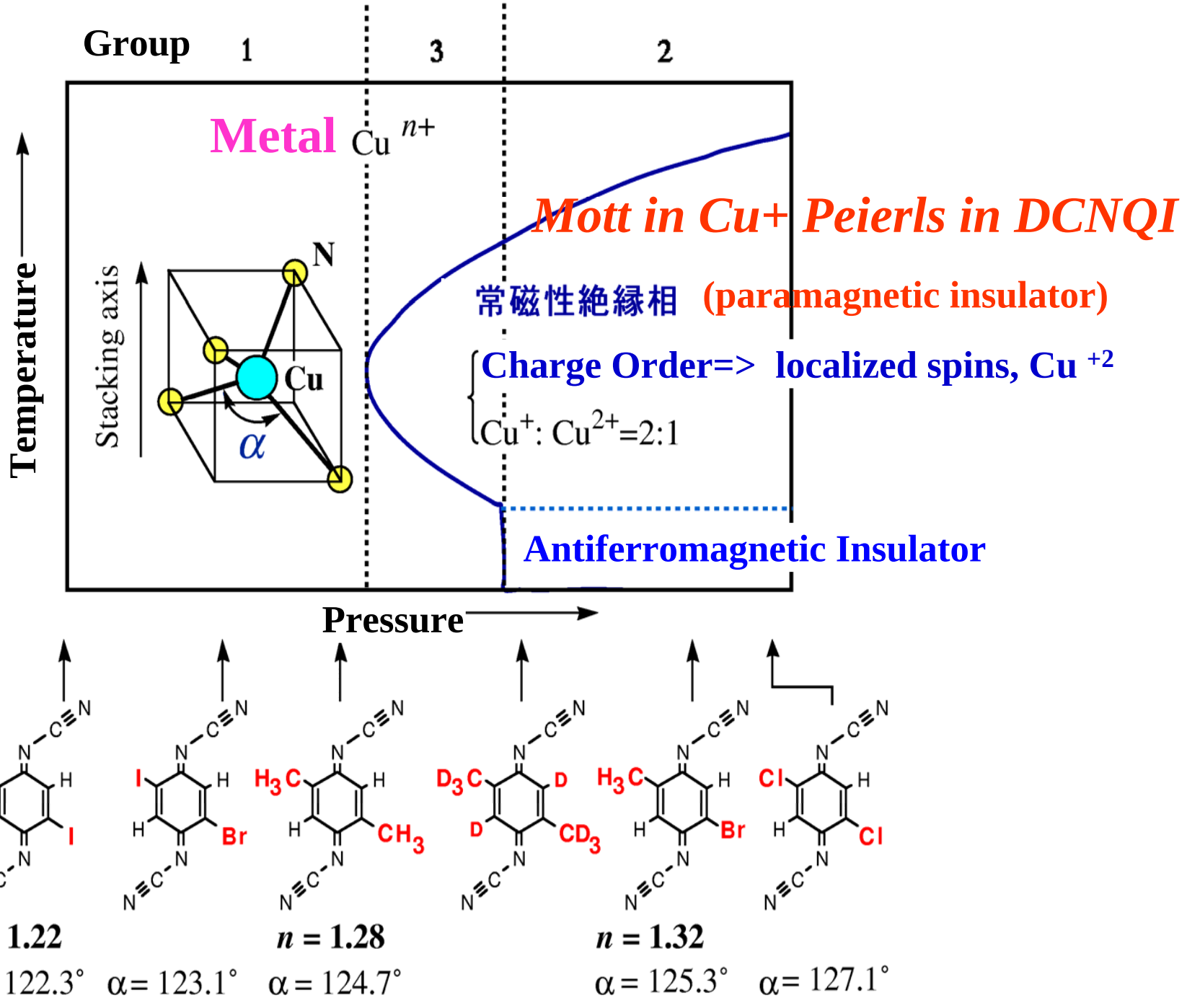


The distortion of the coordination tetrahedron associated with the pressure or size effect raises the d_{xy} level, and induces small extra electron transfer from Cu to DCNQI .

H. Sawa, et al., *J. Phys. Soc. Jpn.*, **63**, 4302 (1994)

Courtesy: R. Kato

$(R_1,R_2\text{-DCNQI})_2Cu$



Courtesy: R. Kato

Strongly correlated electrons

- So far, π electrons: Mott insulators, Charge ordering

* **p-d coupled systems**

d: Transition metal ions

A. localized spins

(1) λ -BETS $(FeCl_4)_2$

(2) $TTP[Fe(CN)_2]_2$

(3) M-Benzene M= V, Ti

B. Fluctuating valences

(1) $DCNQI_2Cu$

(2) Single component metals, $[M(tmdt)_2]$

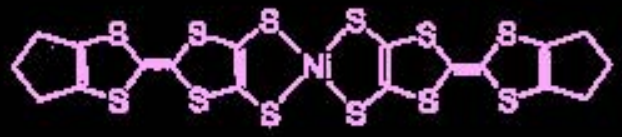
M = Ni, Au

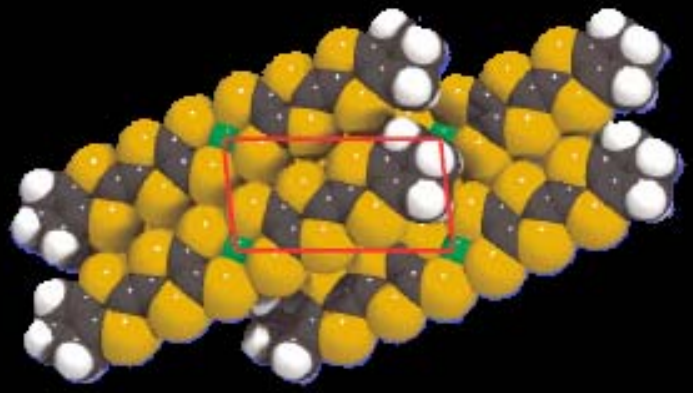
➔ metalloproteins, e.g. myoglobin, FeS cluster,--

Single Component Molecular Metals

A.Kobayashi-Tanaka-H.Kobayashi(2001)

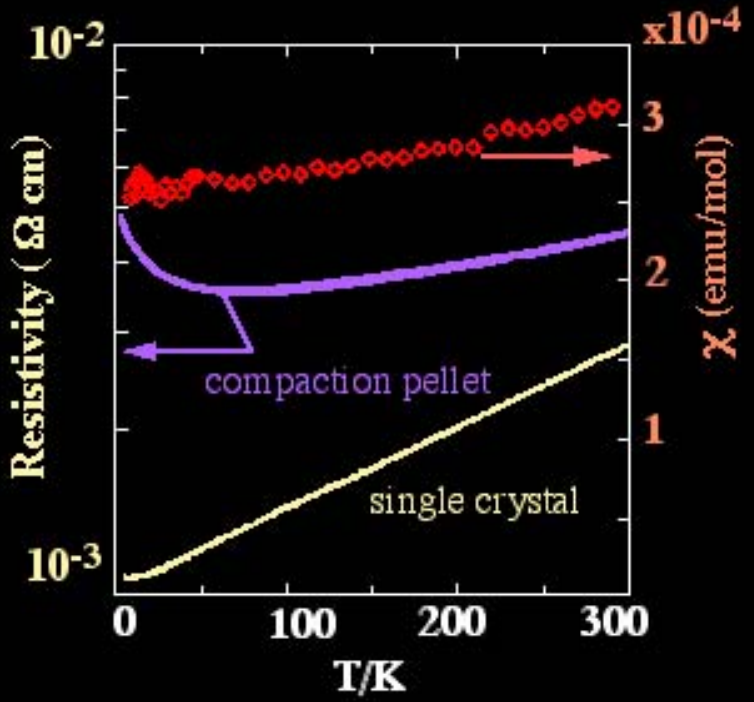
Single-component molecular metal

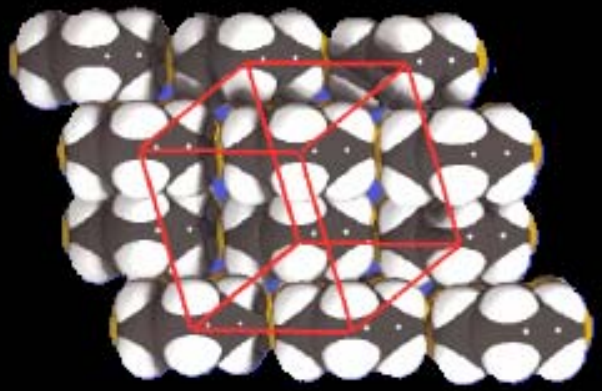




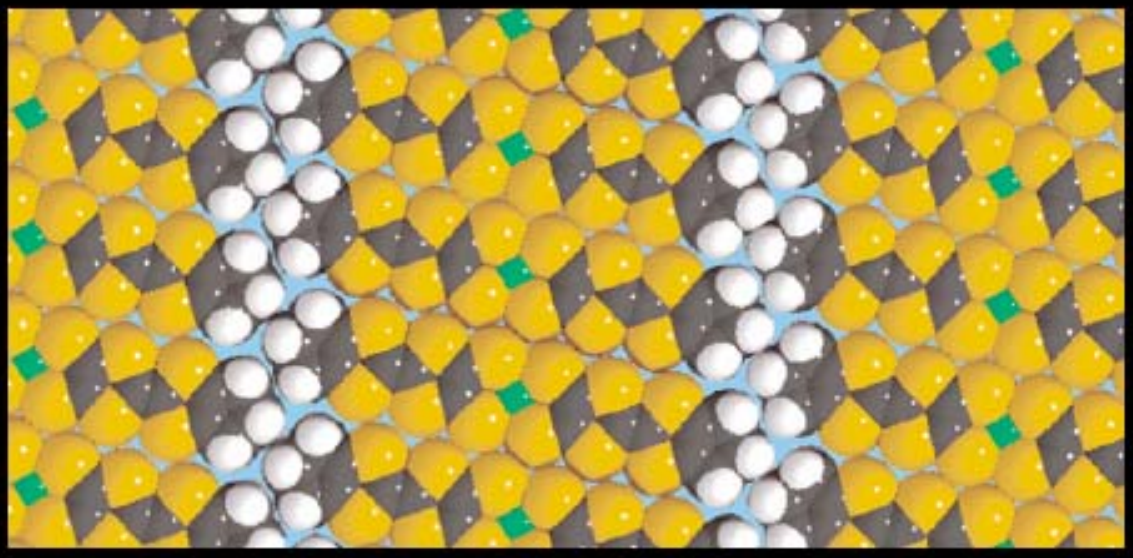
$Ni(tmdt)_2$

The unit cell contains only one molecule



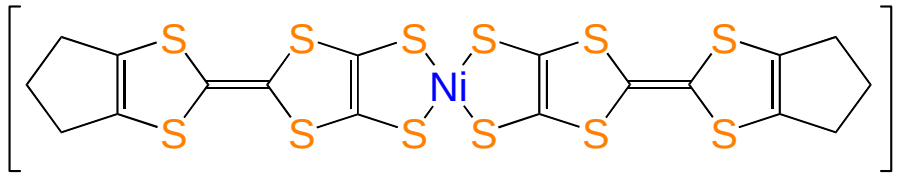


$Ni(tmdt)_2$ molecule are closely packed to form crystal plane (021)

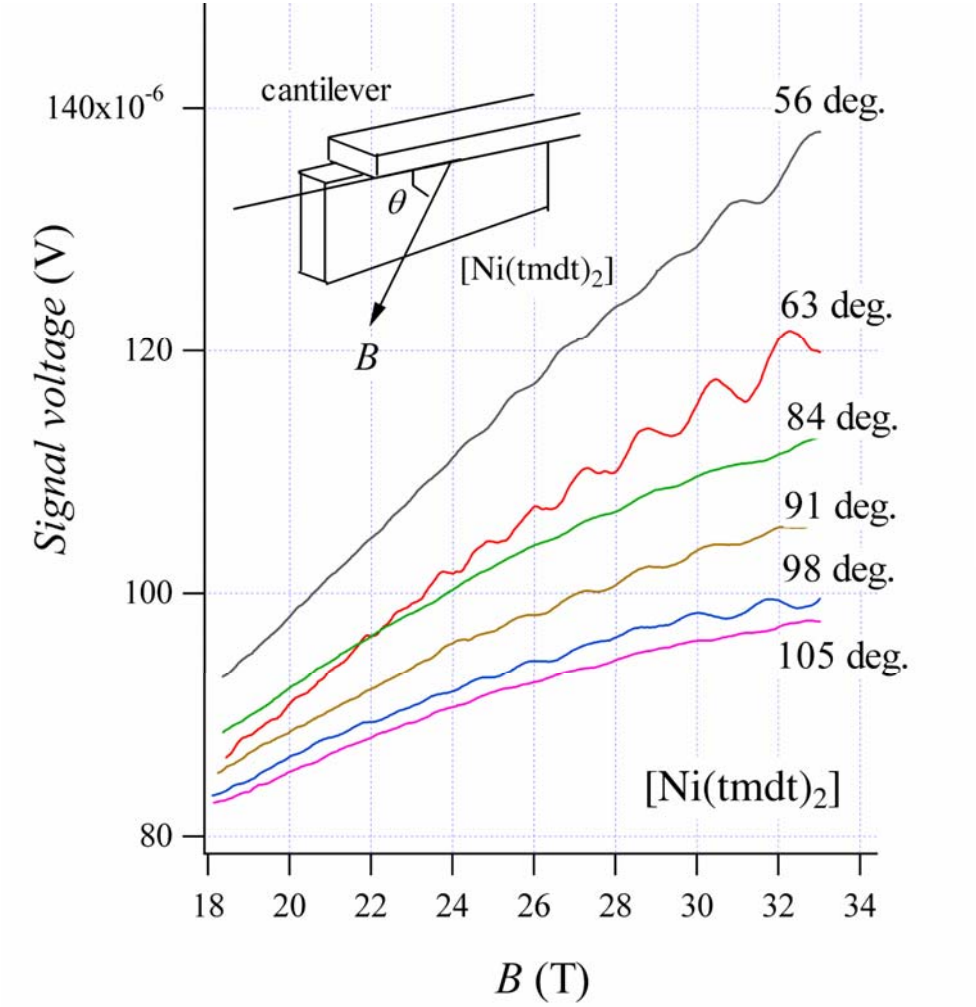


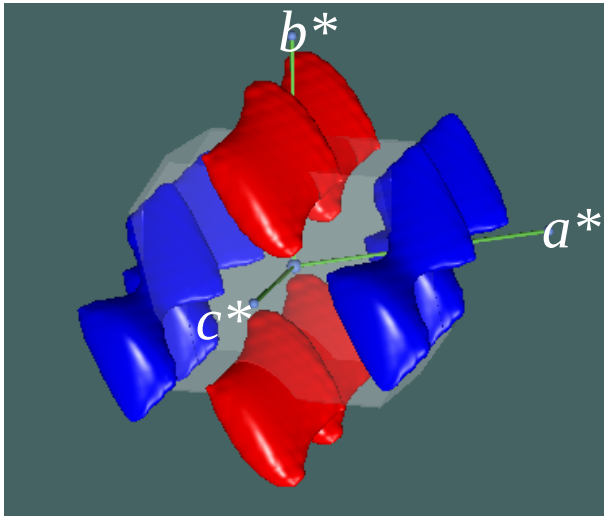
Ni-> Au, magnetic phase transition at around 100K

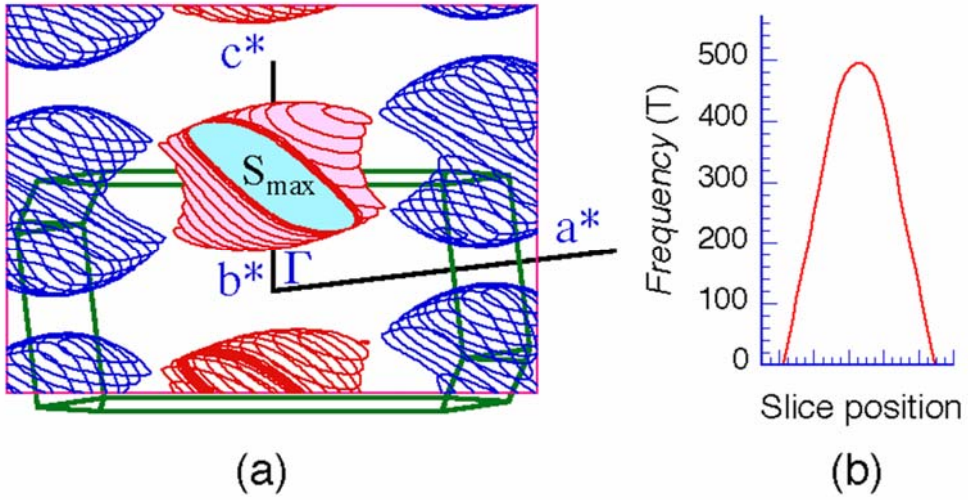
$[Ni(tmdt)_2]$



S. Ishibashi







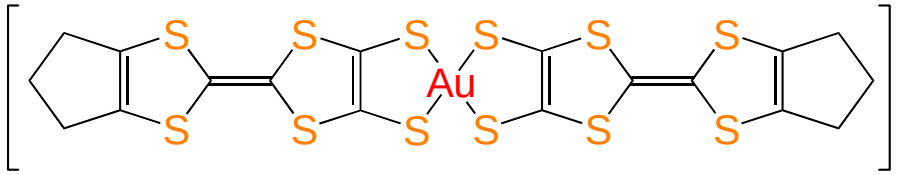
・The observation of dHvA oscillation
(510 Tesla ~ 10% of the 1st Brillouin zone)

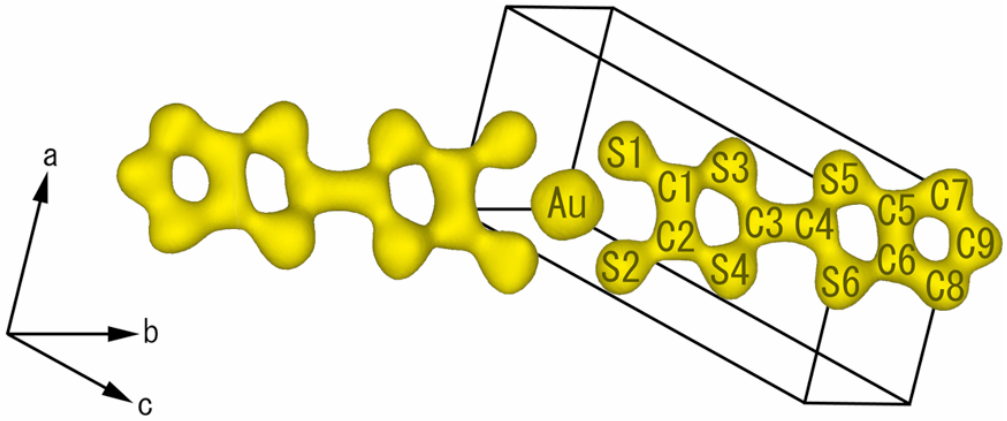
H. Tanaka, M. Tokumoto (AIST),----- J. Brooks(NHMFL/FSU)

1st principles density functional calculation
.....E. Canadell et al.

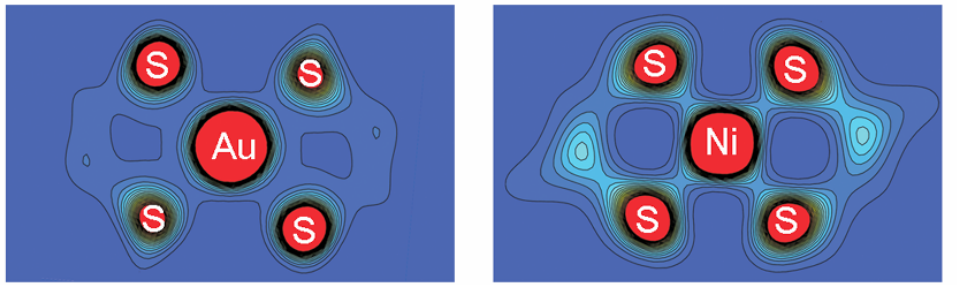
Structure of $[Au(tmdt)_2]$

W. Suzuki, E. Fujiwara, A. Kobayashi, Y.Fujishiro, E. Nishibori, M. Takata, M. Sakata, H. Fujiwara, H. Kobayashi, *J. Amer. Chem. Soc.*, 125 (2003), 1486-1487,





(a)

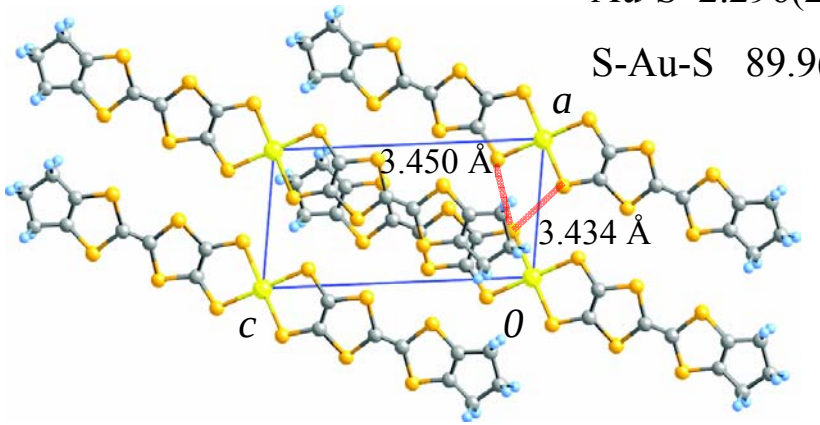


(b)

Comparison of electron densities of $[Au(tmdt)_2]$ and $[Ni(tmdt)_2]$

Au-S 2.296(2) Å

S-Au-S 89.9(1) °



Crystal structure of $[Au(tmdt)_2]$

Crystal data for $[Au(tmdt)_2]$

Empirical Formula $C_{18}H_{12}S_{12}Au$

Formula Weight 810.05

Color black

crystal system triclinic

space group $P\bar{1}$

a / Å 6.4129(1)

b / Å 7.5514(2)

c / Å 12.1543(3)

α / ° 90.473(3)

β / ° 96.698(2)

γ / ° 103.008(3)

Z value 1

V / Å^3 569.21(2)

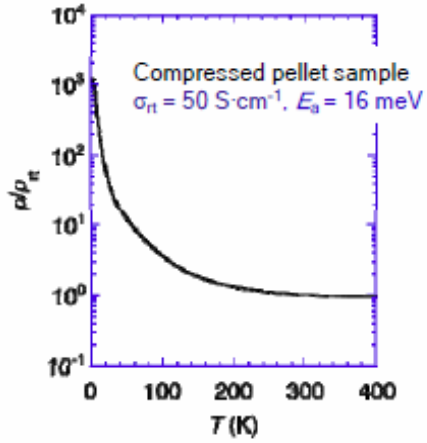
R_{wp} 0.028

R_I 0.073

SCMC w/ magnetic phase transition: $Au(tmdt)_2$

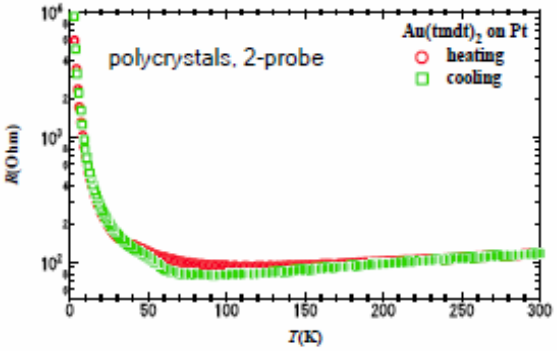
W. Suzuki et al, JACS 125 (2003) 1486

resistivity



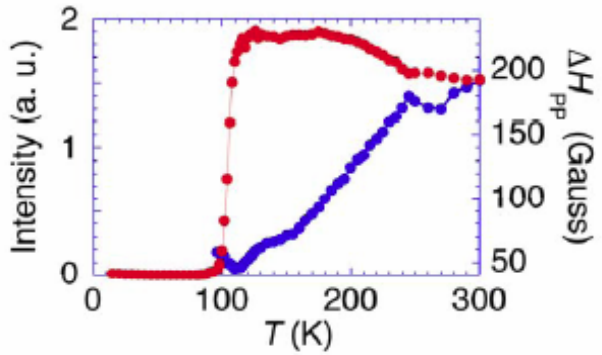
small crystals on fine patterned electrodes

H. Tanaka et al



ESR

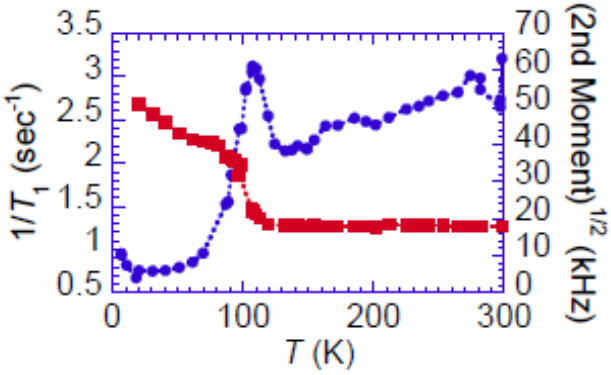
E. Fujiwara, B. Zhou, M. Shimamura



Kanoda

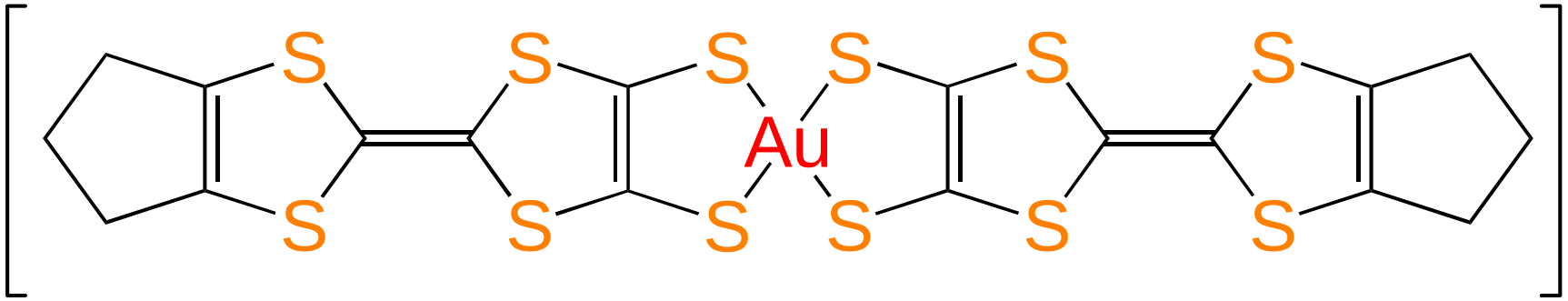
^{1}H-NMR

K. Miyagawa, K. Kanoda



antiferromagnetic phase transition at 100 K !

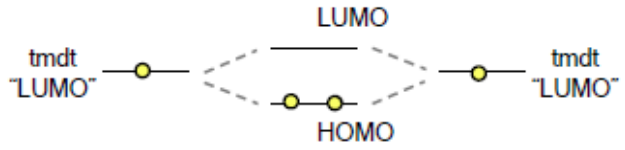
[M(tmdt)2]
M= Ni, Au



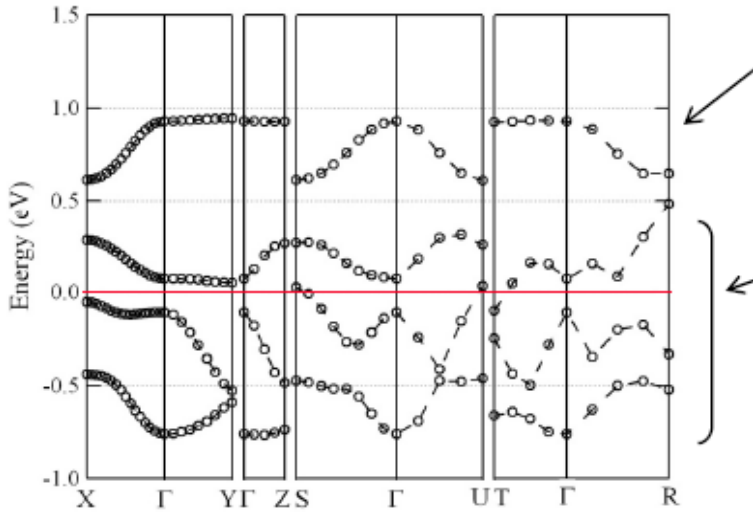
Metallic ions are coupled with π conduction electrons !!

electronic structure; $Ni(tmdt)_2$

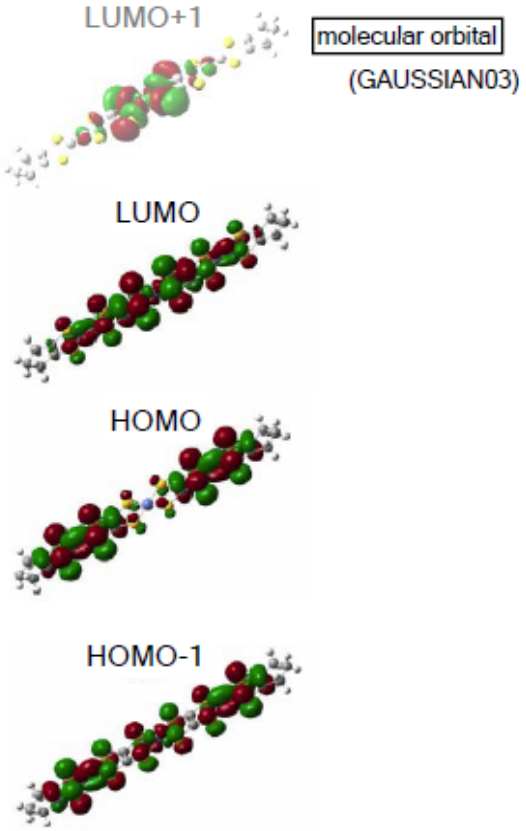
nominal charge : $Ni^{2+}[(tmdt)^{-}]_2$ ~ Ni: $(3d)^8$, tmdt: ("LUMO")^1



first principle band calculation



Rovira et al. PRB 65 (2002) 081104
Ishibashi et al. private communications



complete mixing of LUMO & HOMO & HOMO-1

LDA:Terakura-Ishibashi

Tight-binding fitting to LDA

Transition metal ions in molecular solids

Localized spins

* λ - $BETS_2X$: $X^-=Fe^{+3}Cl^-_4$ S=5/2

* Phthalocyanine

$TTP^+ [M^{+3} (Pc)^{-3/2} (CN)^-_2]_2$

M=Co (S=0), Fe (S=1/2)

Valence fluctuations

* $DCNQI_2Cu$

* Single component molecular metals

M(tmdt)2 M=Ni, Au

=> Myoglobin

Phthalocyanine, MPc

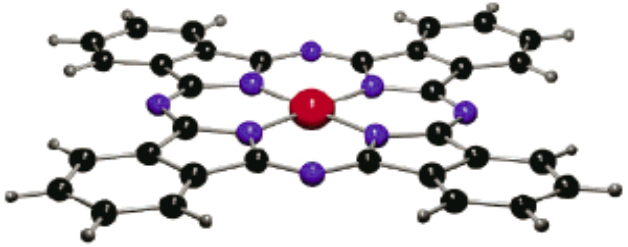
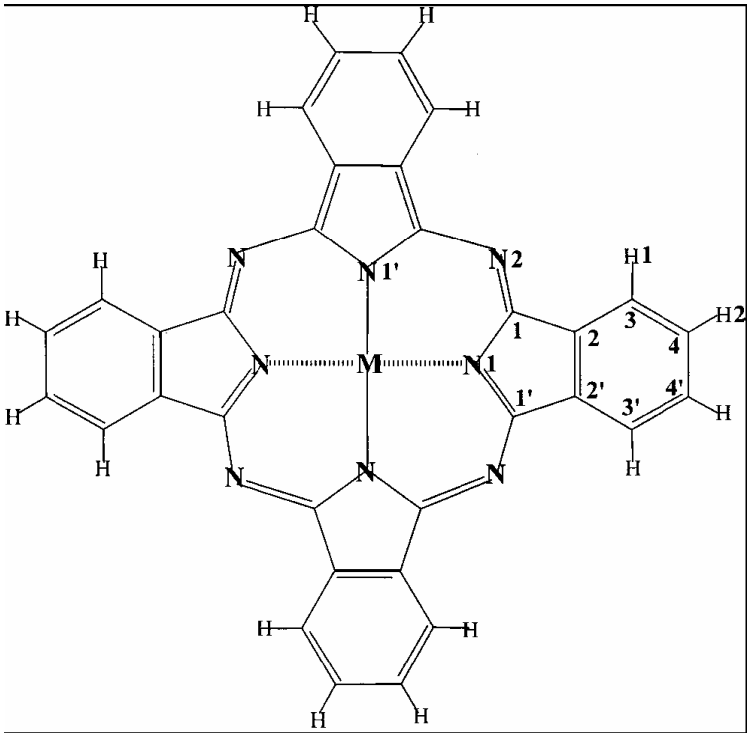


Figure 1. Molecular structure of metal−phthalocyanines; they consist of a ring of carbon, nitrogen, and hydrogen atoms, surrounding a metallic ion.

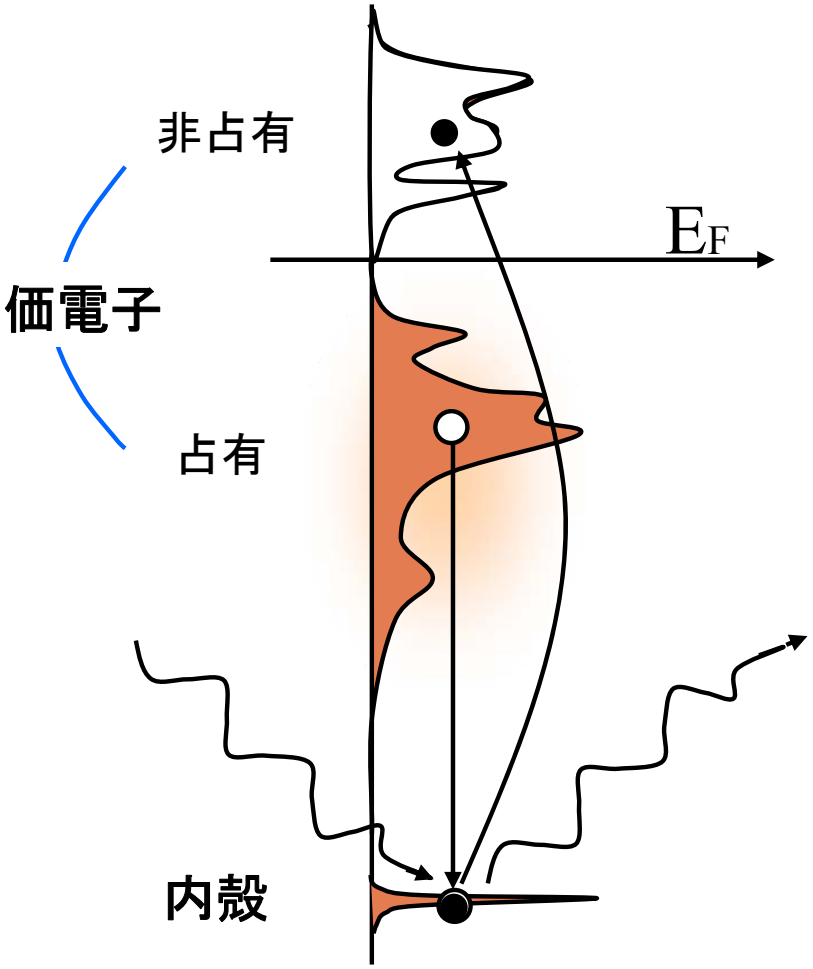


Craciun et al.(2005)

M= Fe, Co, Ni, Cu, Zn, Mg

Cf. Cu(F_8Pc),Cu(F_{16}Pc): N. Sato

S. Shin (ISSP)
Soft X-ray Emission Spectroscopy (SXES)

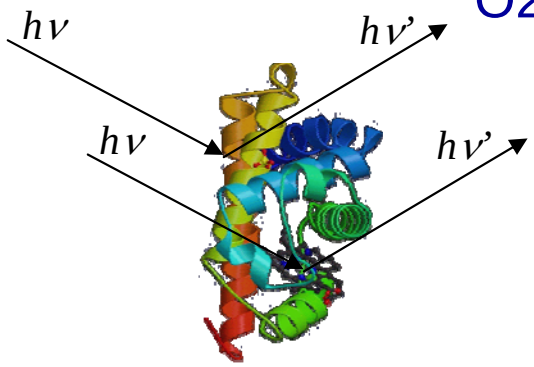


Shin : SP8 BL17

価電子の状態密度

軟X線領域の主な許容遷移

- **■遷移金属元素　・・・　2*p*,3*p* → 3*d***
- **■希土類金属元素　・・・　3*d*,4*d* → 4*f***
- **■軽元素　・・・　1*s* → 2*p***



O2*p*, N2*p*, C2*p* DOS

Fe 3*d* DOS
Fe *dd*励起

Strongly correlated electrons

- So far, π electrons: Mott insulators, Charge ordering

* **p-d coupled systems**

d: Transition metal ions

A. localized spins

(1) λ -BETS $(FeCl_4)_2$

(2) $TTP[Fe(CN)_2]_2$

B. fluctuating valences

(1) $DCNQI_2Cu$

(2) Single component metals, $[M(tmdt)_2]$

M = Ni, Au

➔ metalloproteins, e.g. myoglobin, FeS cluster,--

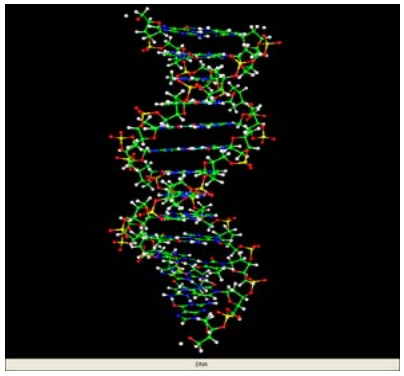
Studies are now possible on electronic states of metallic ions in proteins in a way similar to those of conventional condensed matter physics.

Targets in Bio-condensed matter science

HF : JPSJ 75(2006) May

1. Metallic ions in proteins: e.g. heme Fe
2. Metallic clusters in proteins : e.g. Fe_4S_4
3. Functional molecules in proteins:

   e.g. retinal-rhodopsin
4. DNA
5. H_2O



"another condensed matter"
similar to molecular solids

Key factors:

**Local structure*

**Associated electronic states (spectroscopy)*

Bio-materials are most efficient systems for electronics, though hard to understand at present.

Studies are now possible on electronic states of metallic ions in proteins in a way similar to those of conventional condensed matter physics.

Bio-material science !!

Structure and Electronic Properties of Molecular Assemblies
--- Toward Bio-Material Science

Date: 2007. 4. 4 13:00 - 4. 6 17:00
Place: RIKEN
Sponsors:
+ Forum “Electronic Properties of Molecular Assemblies” (CREST”Nanostructured Materials”)*
+ Molecular Ensemble Research Group, RIKEN
+ CREST“Creation of Innovative Technology by Integration of Nanotechnology with Information, Biological and Environmental Technologies”

Scope:
There has been great progress in the microscopic and systematic understanding of electronic properties of molecular solids for the past decade in spite of the apparent complexity in their crystal structures.
In view of the success of these studies on periodic systems, it is natural to extend research activities to bio-related materials, such as proteins and DNA, by viewing them as just another form of condensed matter consisting of molecules but of course with much more complexity in structure without periodicity. This will be toward “Bio-Materials Science”.
In this Workshop, deeper mutual understanding is pursued among scientists working in different disciplines, condensed matter physics, chemistry and biology, through reporting and exchanging modern understanding in each subject, by keeping in mind the basic factors in the studies of materials properties, local structure and associated electronic states.

More concretely, subjects to be discussed include;
1. Molecular solids, especially π-d systems.
2. Photosynthesis.
3. DNA
4. Active centers of proteins
   4-1. Functional molecules
   4-2. Metal ions and ligands ; heme, non-heme
   4-3. Metal clusters
5. Theories of electronic states of large molecules

http://www.riken.jp/lab-www/molecule/index.html

Outline

1) Brief history of conducting molecular solids
2) Charge transfer salts of the type A_2B:
   "quarter-filling"
3) Two paradigm: dimer Mott and charge ordering
4) Systematic understanding
   based on extended Hubbard model
5) π-d systems:
   * localized d-spins
   * valence fluctuations
   * M-Bz
   * FeS
   * Myoglobin
6) Toward Bio-materials science

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* π electrons: Mott insulators, Charge ordering

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