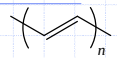
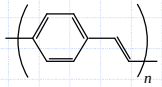
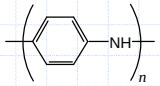
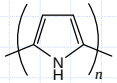
有機伝導体

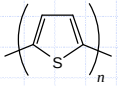
導伝性高分子：共役π系を持つ高分子

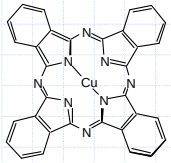

polyacetylene


poly(phenylenevinylene)
PPV


polyaniline

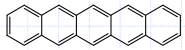

polypyrrole


polythiophene

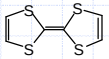

phthalocyanine CuPc

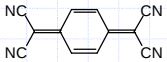
低分子

有機半導体

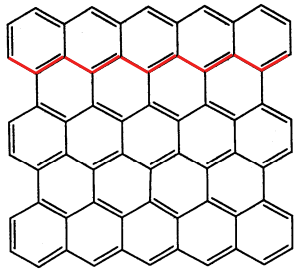

pentacene

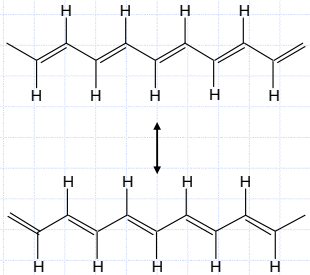
電荷移動錯体


tetrathiafulvalene
TTF


tetracyanoquionodimethane
TCNQ

グラファイトから1本鎖を切り出す(両側にHをつける)
→ ポリアセチレン



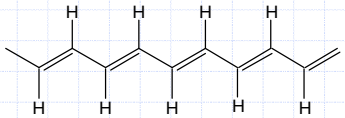


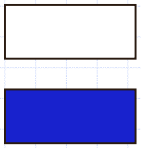
半導体

やはり二重結合の位置を動かせるので電気を流しやすい。

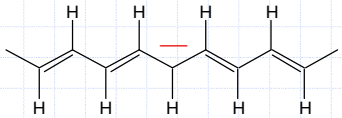
白川英樹　2000年ノーベル賞

ポリアセチレンにドープ

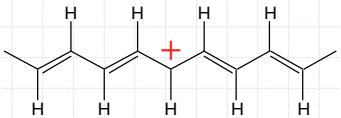


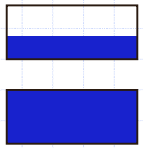


K^+



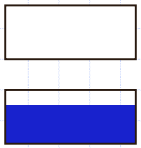
Br^-





Negative

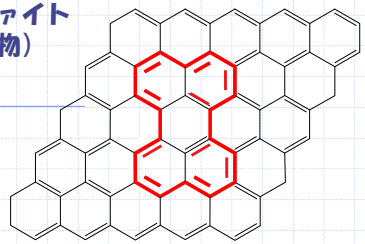
電子ドープ (N型)

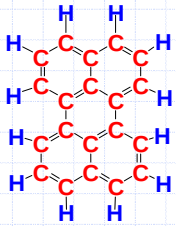


Positive

ホールドープ (P型)

グラファイト
(無機物)





Perylene

初めての電気を流す有機物

Br^-

e^-

電荷移動

電荷移動錯体

PerylenemにBrをドープしたものが
0.1 Scm^{-1}の高い伝導性を示す。
最初の高伝導の有機電荷移動錯体。
赤松，井口，松永, *Nature*, **173**, 168 (1954).

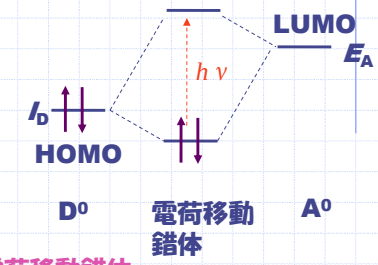
電荷移動錯体 charge-transfer complex

電子供与体 electron donor

酸化されて$D^0 \rightarrow D^+$になりやすい物質
HOMOのレベルが高い物質

電子受容体 electron acceptor

還元されて$A^0 \rightarrow A^-$になりやすい物質
LUMOのレベルが低い物質



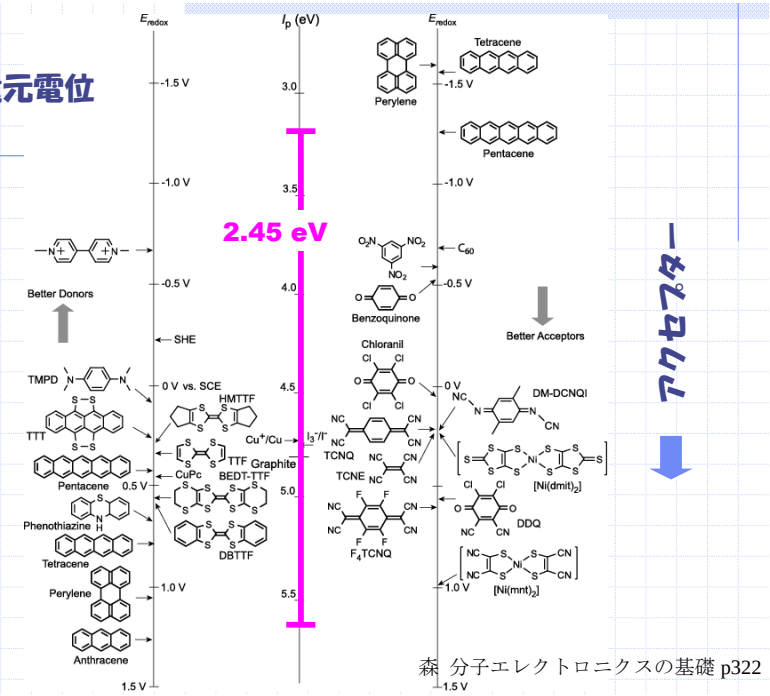
$D^0A^0 \rightarrow D^+A^-$となったのがイオン性電荷移動錯体

ほとんどD^0A^0のままなのが中性電荷移動錯体　しかしこの場合でも

$\varphi = \varphi(D^0A^0) + c\varphi(D^+A^-)$

のようにイオン性の寄与が若干混じり(右上図)、 $D^0A^0 \rightarrow D^+A^-$

酸化還元電位



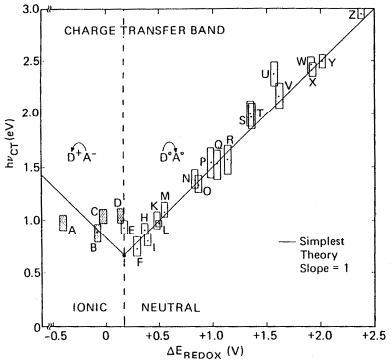
電荷移動吸収 (可視～近赤外)

(無色の中性ドナーとアクセプターの溶液を混ぜると橙色～黄色に着色する。)

$h\nu = I_D - E_A - E(D^+A^-)$

I_D ：ドナーのイオン化エネルギー
E_A ：アクセプターの電子親和力
$E(D^+A^-)$： D^+とA^-の静電エネルギー

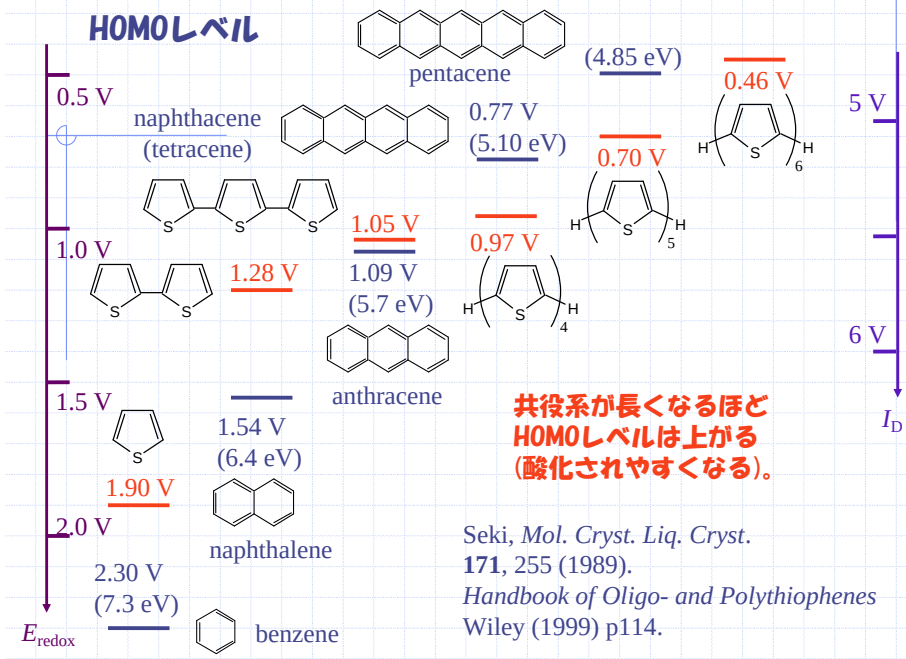
$h\nu = I_D - E_A - E(D^+A^-) \sim E_{redox}(HOMO) - E_{redox}(LUM$



>0.1 V　D^0A^0がD^+A^-より安定：中性

<0.1 V　D^+A^-がD^0A^0より安定：イオン性

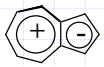
HOMOレベル



共役系が長くなるほどHOMOレベルは上がる(酸化されやすくなる)。

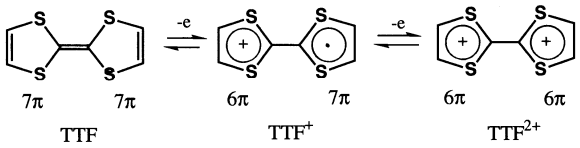
Seki, *Mol. Cryst. Liq. Cryst.* **171**, 255 (1989).
Handbook of Oligo- and Polythiophenes Wiley (1999) p114.

よいドナー、アクセプター



Azulene

よいドナー　Tetrathiafulvalene (TTF)

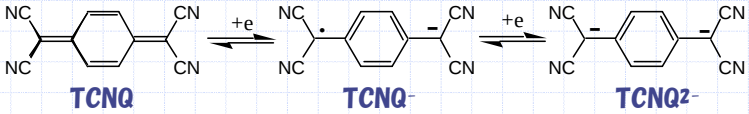


0.38 V

7π系なので、1個電子を放出してヒュッケル則を満たす6πになりやすい。(C→1π、S→2πと数える。)

$-NH_2$, $-OCH_3$など電子供与基はドナー性を強くする。

よいアクセプター　Tetracyanoquionodimethane (TCNQ)

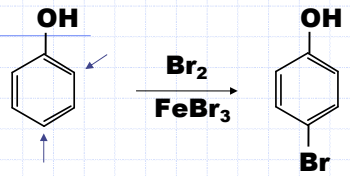


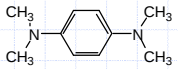
還元されるとキノイド構造が6πのベンゼン環に戻って安定化する。

−は2つの電子吸引基の根元に出る。

−CN、$-NO_2$など電子吸引基はアクセプター性を強くする。

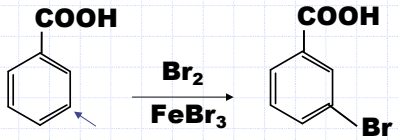
電子供与基：$-OH$、$-OCH_3$、$-NH_2$ → 電子供与体を安定化



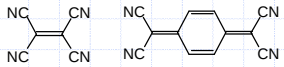


オルト、パラ配向

電子求引基：$-NO_2$、−CN、ハロゲン、−COOH、$-COOCH_3$、−CHO



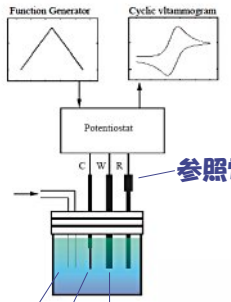
→ 電子受容体を安定化



メタ配向

Cyclic voltammetry

電気化学的酸化還元電位の測定

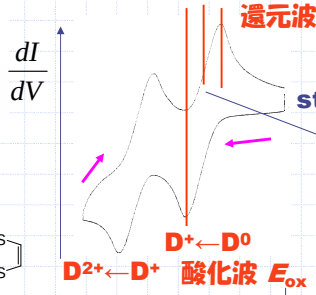


参照電極 Ag/AgNO3

作用電極

補助電極

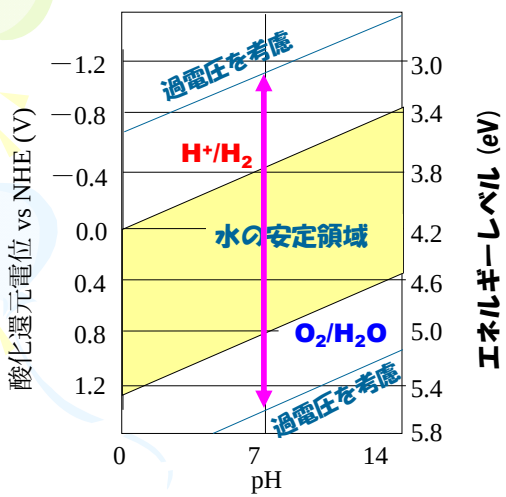
TTF + Bu_4NPF_6 in PhCN



$$E^{1/2} = \frac{E_{ox} + E_{red}}{2}$$

通常酸化波と還元波の平均を使う

水の安定領域



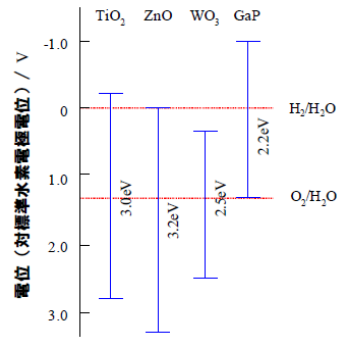
LUMO 3.15 eV

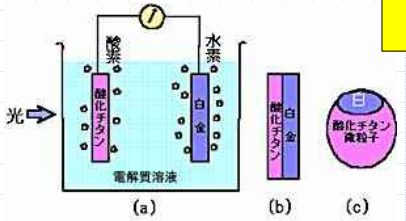
HOMO 5.6 eV

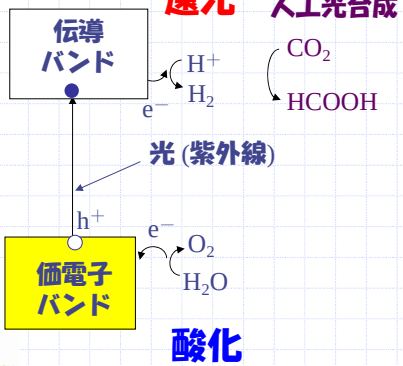
シュライバー・アトキンス　無機化学 p225

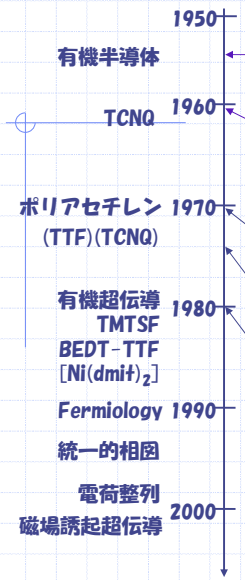
光触媒：TiO_2に光を当てると水をH_2とO_2に分解

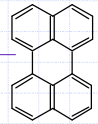
（本多・藤嶋効果）











PeryleneにBrをドープしたものが0.1 Scm^{-1}の高い伝導性を示す。
最初の高伝導の有機電荷移動錯体。
赤松，井口，松永,*Nature*, **173**, 168 (1954).

テフロンに関連してCN置換された有機物を研究していたde PontのグループがTCNQを開発。
Acker et al. *J. Am. Chem. Soc.* **82**, 6408 (1960).

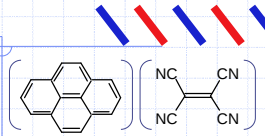
TTFが開発される。
Wudl et al. *J. C. S. Chem. Commun.* **1970**, 1453.

(TTF)(TCNQ)：Organic Metal

$(TMTSF)_2PF_6$：最初の有機超伝導
D. Jérome, K. Bechgaard, *J. Phys. Lett.* **41**, L95(1980).

混合カラム構造(mixed stack)

中性、イオン性の場合：低伝導

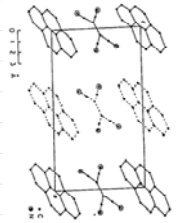


pyrene　tetracyanoethylene
TCNE

平面分子はスタックする

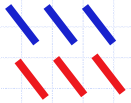
10^{-11} S/cm

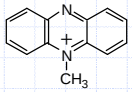
pyrene　TCNE　pyrene



分子積層型(segregate stack)

部分電荷移動の場合：高伝導，金属

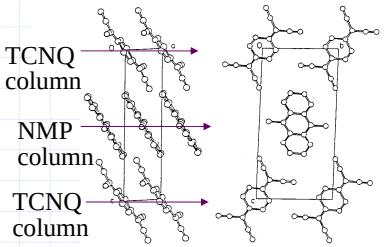




N-methylphenazinium
(NMP)

Segregated

170 S/cm

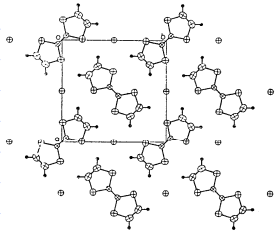


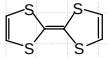
(NMP)(TCNQ)：最初の「Organic Metal」1966

$(TTF)X_x$：典型的な一次元金属

(X＝Cl, Br, I, SCN, x～0.71)

1D スタック⊥紙面

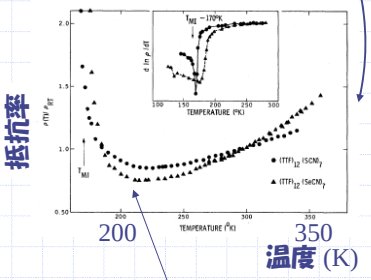




tetrathiafulvalene
TTF

500 S/cm

絶縁体　金属



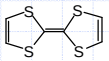
金属半導体転移：200 K

平面分子はスタックする

(TTF)(TCNQ)

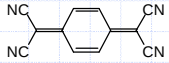
1973

$(TTF^{0.59+})(TCNQ^{0.59-})$



tetrathiafulvalene

TTF

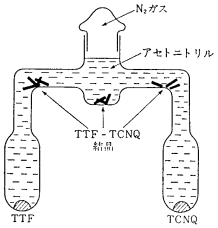


tetracyanoquionodimethane

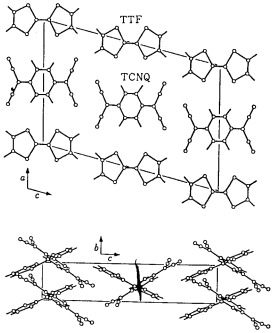
TCNQ

拡散法結晶成長　　分離積層型

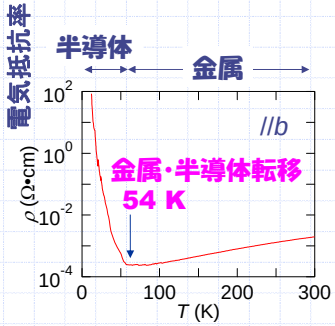
TTFとTCNQの
アセトニトリル
溶液から



TTF



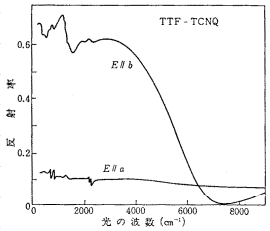
TCNQ　　TCNQ



温度

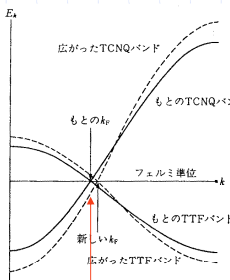
(TTF)(TCNQ)

反射率
一次元金属



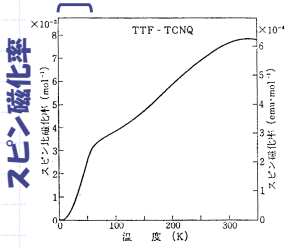
TTF－TCNQ の反射スペクトル

エネルギーバンド

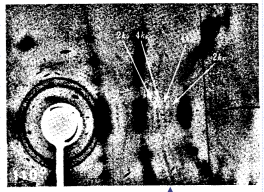


54 K以下で非磁性

スピン磁化率

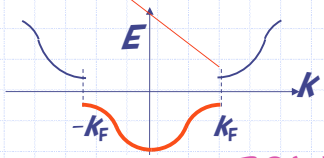


TTF－TCNQ のスピン磁化率



X線：$2k_F$に周期

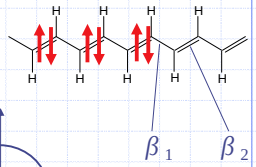
TTFのHOMOバンドとTCNQのLUMOバンドが
k_F＝0.1475b^*＝0.295p/b＝(0.59/2)(p/b)でクロス。



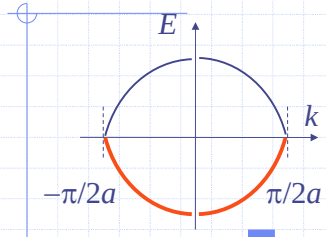
$2k_F$ → このとき格子の周期は$2k_F$

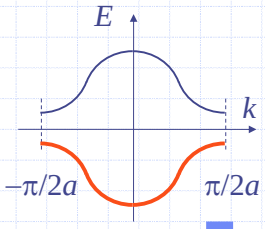
非磁性絶縁体に
(Peierls転移)

一重結合と二重結合のβは異なる。

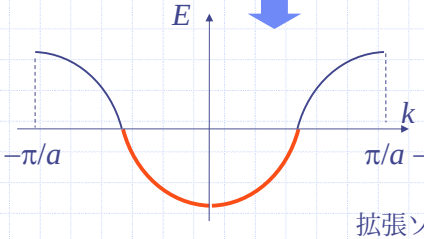


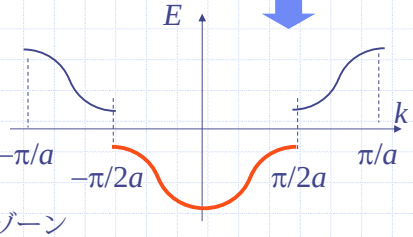
$\beta_1 = \beta_2$　　$\beta_1 \neq \beta_2$





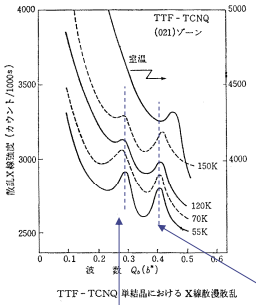
還元ゾーン





拡張ゾーン

(TTF)(TCNQ)



TTF－TCNQ 単結晶における X線散漫散乱

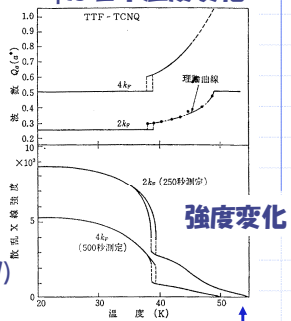
$2k_F$＝ 0.295b^*

$D^{1/2+}$　　1/2e/mol

1/2k_Fの波長で電子密度に
波ができている。
(電荷密度波)
Charge density wave (CDW)

$4k_F$＝ 0.59b^*

k_Fは若干温度変化

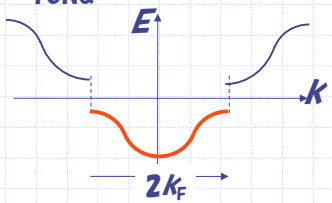


TTF－TCNQ の $2k_F$ と $4k_F$ の衛星反射の波数および強度の温度依存性

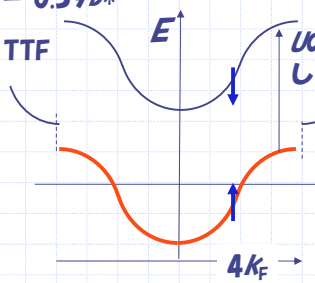
強度変化

54 K

TCNQ



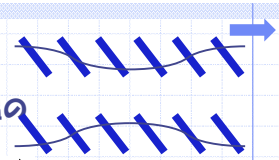
TTF



Uのため片方のスピン
しか入れない。

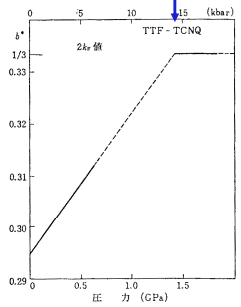
このとき格子
の周期は$4k_F$

(TTF)(TCNQ)

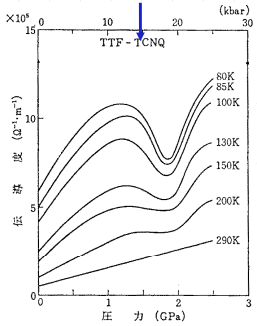


圧力をかけると$2k_F$が変化。
15 kbar以上で1/3に「lock in」

15 kbar以上で低温の伝導度が減少。



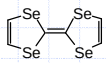
TTF - TCNQ の $2k_F$ 値の圧力依存性



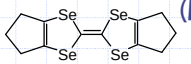
TTF - TCNQ の b 軸にそう直流電気伝導度の圧力依存性

電荷密度波が全体として動いて運んでいた電流。
(CDWの集団運動)
(Fröhlich mode)

パイエルス転移の温度を下げる試み：Seを入れて鎖間相互作用を増やす。

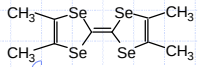


(TTF)(TCNQ) 54 K
(TSF)(TCNQ) 29 K

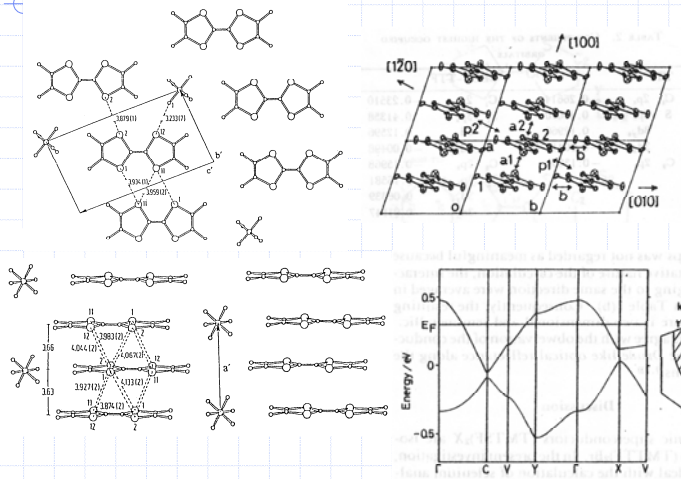


(HMTTF)(TCNQ) 50 K
(HMTSF)(TCNQ) 24 K
ほとんど上がらない。

$(TMTSF)_2PF_6$：最初の有機超伝導



擬一次元金属：フェルミ面は開いているが
鎖間に鎖方向の1/10程度の相互作用がある。



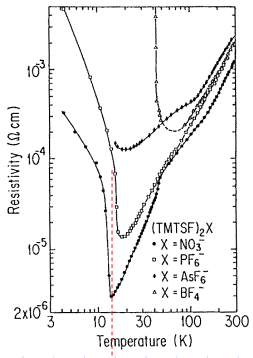
トランスファー積分(meV)

方向	HOMO
a1	200
a2	230
b	35
p1	20
p2	7

分子軌道計算からの計算値

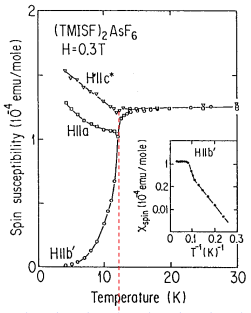
$(TMTSF)_2PF_6$：最初の有機超伝導

電気抵抗率



12 K付近で金属－半導体転移

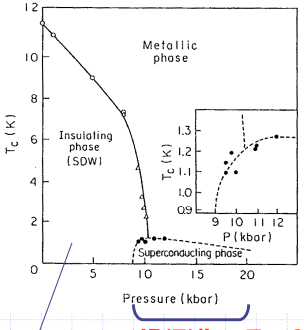
静磁化率



12 K以下で静磁化率に異方性

反強磁性
(スピン密度波)
Spin density wave
(SDW)

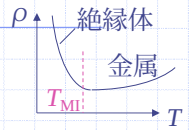
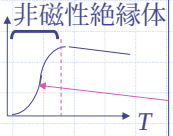
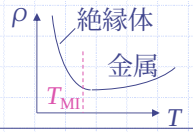
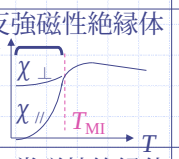
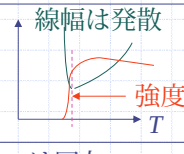
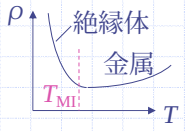
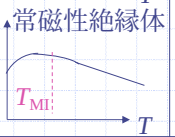
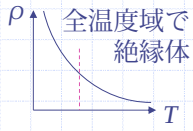
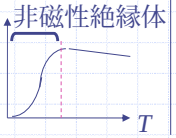
圧力下の相図



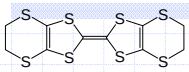
超伝導 T_c～1 K

反強磁性(SDW)絶縁相

金属-絶縁体転移の原因と実験的区別

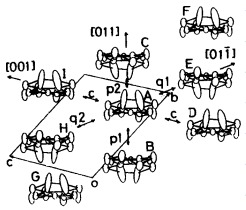
	電気抵抗率	静磁化率 (SQUID)	スピン磁化率 (ESR)	X線散乱
電荷密度波(CDW) (Peierls転移)			χ_sは同左 線幅はT_{MI}で連続 $\chi \propto \frac{1}{k_B T(3+e^{E_g/k_B T})}$	$2k_F$の長周期 $> T_{MI}$ 散漫散乱 $< T_{MI}$スポット
スピン密度波(SDW)				なし
モット絶縁体・電荷整列			χ_sは同左 線幅はT_{MI}で連続 通常さらに低温でSDWかspin-Peierlsのどちらかが起こる。	モット：なし 電荷整列：長周期
Spin-Peierls転移			χ_sは同左 線幅はT_{MI}で連続 CDW同様 singlet-triplet model	$2k_F$の長周期

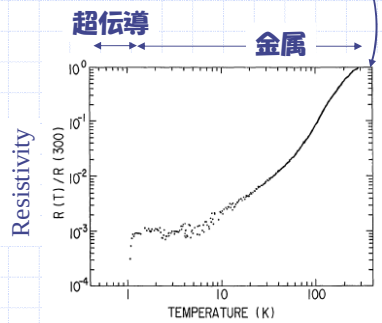
β-(BEDT-TTF)$_2$I$_3$



BEDT-TTF (T_c=1.5 K)での最初の常圧超伝導体

30 S/cm





Transfer integrals

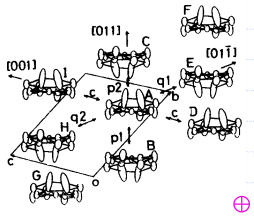
β (meV) 方向	HOMO
p1	245
p2	84
c	50
q1	127
q2	68

鎖間～p2

From MO calc.

➡ 2次元金属

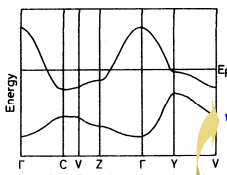
Shubnikov- de Haas Oscillation in β -(BEDT-TTF)$_2$I$_3$

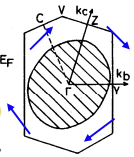


Oscillation of electrons rotating around the Fermi surface is observed at low T (< 1 K) and under strong magnetic field (> 10 T).

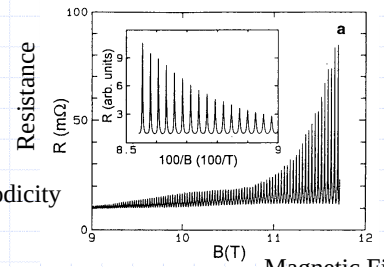
Shubnikov-de Haas oscillation

⊕ Magnetic Field





100 mK



Magnetic Field

Hatched Area

Periodicity

Fermi surface is 50% of the 1st Brillouin zone.

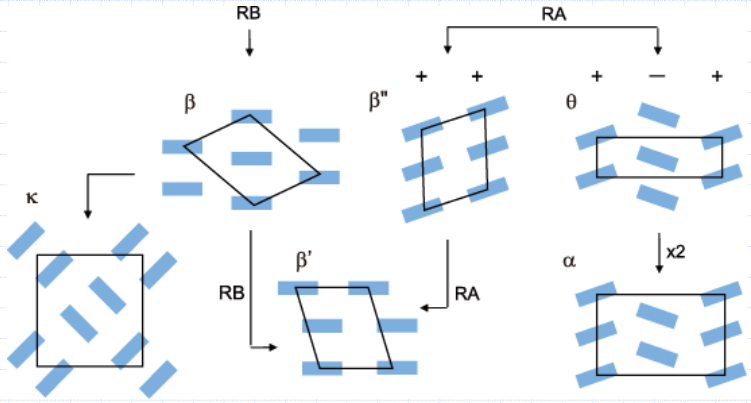
$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar S_k}$$

Kang, et al. *Phys. Rev. Lett.* **62**, 2559 (1989).

BEDT-TTF塩の構造分類

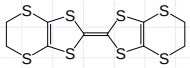
Mori, *Bull. Chem. Soc. Jpn*. **71**, 2509 (1998); **72**, 179 (1999); **72**, 2011 (1999).

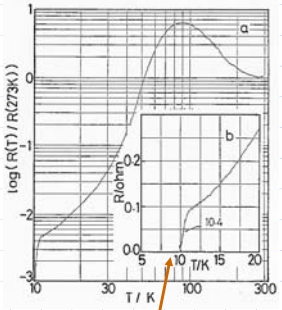
Ring over bond 長軸方向にずれる "Ring over atom" 短軸方向にずれる。



κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

1/2+ + −





Electrochemical Crystal Growth

Superconductivity at 10.4 K (1987)

BEDT-TTF → BEDT-TTF$^+$

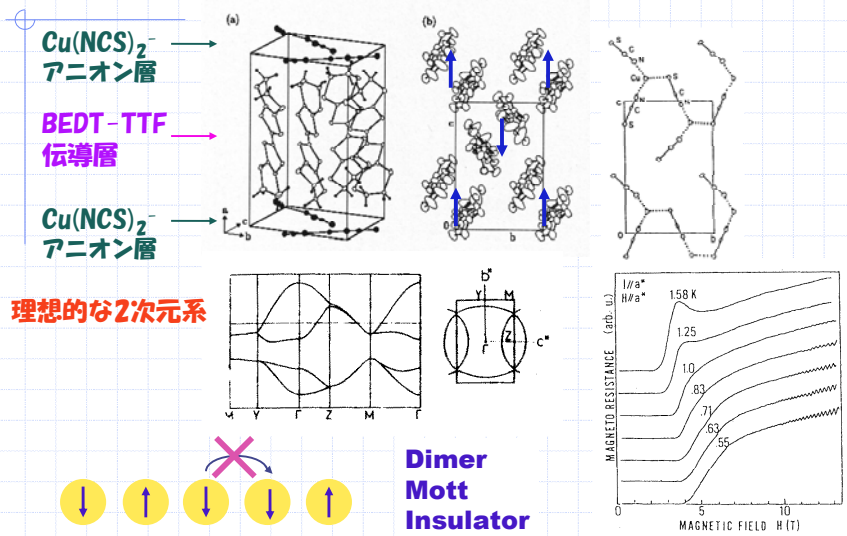
$[Cu(NCS)_2]^-$

→ (BEDT-TTF)$_2$Cu(NCS)$_2$

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

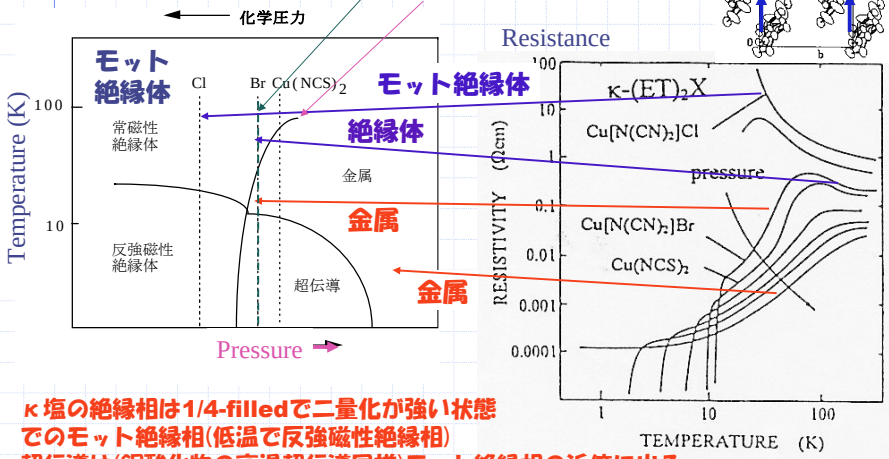
T_c= 10 Kを超える最初の有機超伝導体(T_c=10.4 K)

Urayama et al. *Chem. Lett.* **1988**, 55; **1988**, 463.



Metal-insulator transition

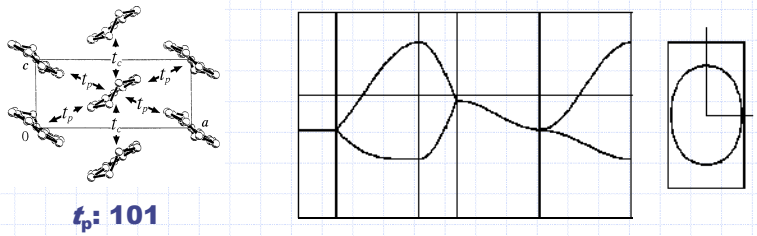
κ -(BEDT-TTF)$_2$Cu[C(CN)$_2$]Cl
κ -(BEDT-TTF)$_2$Cu[C(CN)$_2$]Br
κ -(BEDT-TTF)$_2$Cu(NCS)$_2$



κ塩の絶縁相は1/4-filledで二量化が強い状態でのモット絶縁相(低温で反強磁性絶縁相)超伝導は(銅酸化物の高温超伝導同様)モット絶縁相の近傍に出る。

θ相 ～ Herringbone

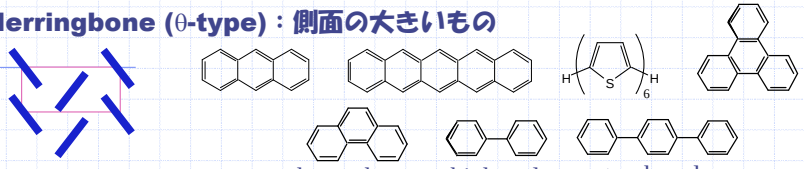
θ -(BEDT-TTF)$_2$MM'(SCN)$_4$



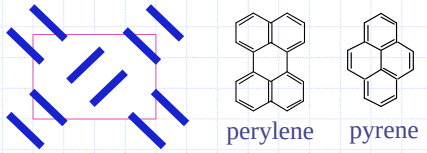
t_p: 101
t_c: 25 meV

有機半導体の中性結晶の構造 *Acta Crystallogr.* B **45**, 473 (1989).

Herringbone (θ-type)：側面の大きいもの

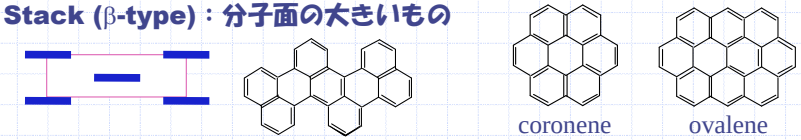


Dimer (κ-type)：中間



γ−構造(θ-type)：分子面の大きいもの

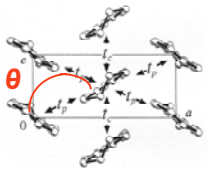
Stack (β-type)：分子面の大きいもの



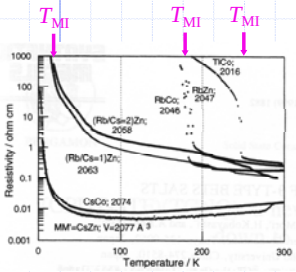
分子面が大きくなるにしたがって傾きが小さくなる。

θ 相の統一的相図

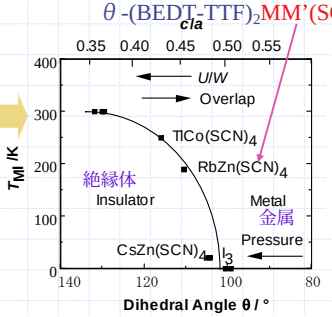
H. Mori et al. *Phys. Rev.* B **57**, 12023 (1998).

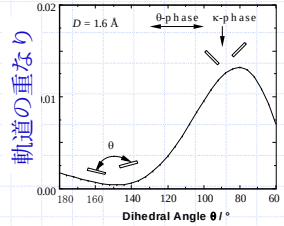


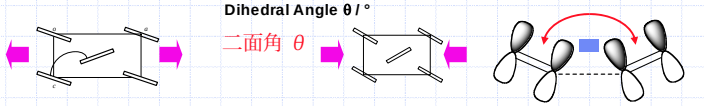
θ -(BEDT-TTF)$_2$MM'(SCN)$_4$



θ -(BEDT-TTF)$_2$MM'(SCN)$_4$



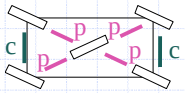




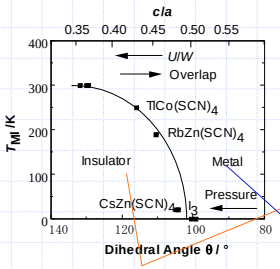
軌道の重なり　大↑

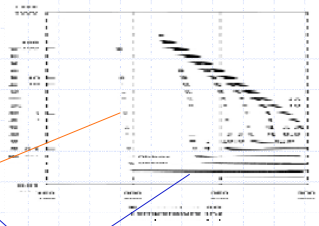
θ 相の電荷整列

θ 相：ユニフォームな2次元格子
絶縁化するには電荷整列するしかない。

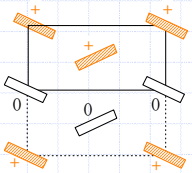


θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$

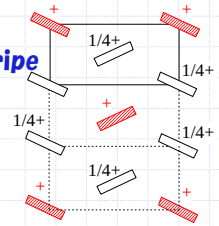




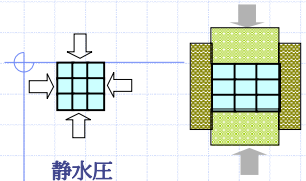
低温の絶縁相：電荷整列
Horizontal stripe



「金属」相でも3倍、あるいはそれ以上の周期のnon-stripeの電荷整列が起こっている。
平坦な電気抵抗
NMR, ラマン, X線
T_{MI}が1次転移



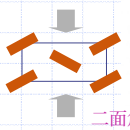
一軸圧縮法による統一的相図の検証

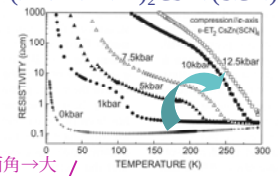


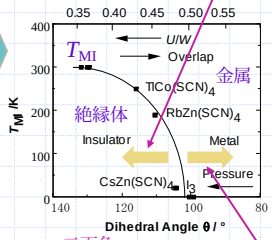
静水圧ではできない微妙な構造制御
柔らかい有機物は圧縮に特に敏感

一軸下で初めて超伝導を示す
α -(BEDT-TTF)$_2$KHg(SCN)$_4$
α -(BEDT-TTF)$_2$I$_3$
θ -(DIETS)$_2$Au(CN)$_4$

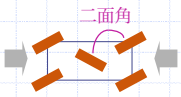
θ -(BEDT-TTF)$_2$CsZn(SCN)$_4$



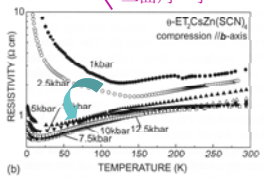




θ 相の統一的相図
θ -(BEDT-TTF)$_2$A



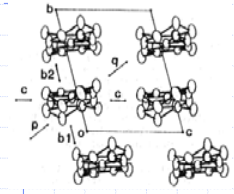
二面角
二面角→小

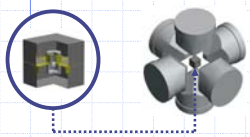


超高圧下のβ'- (BEDT-TTF)$_2$ICl$_2$の超伝導

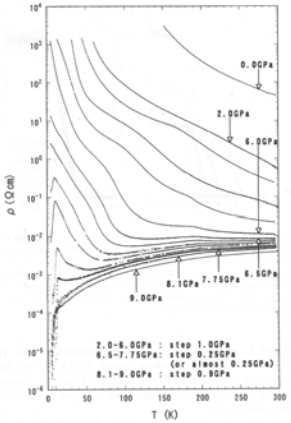
T_c= 14.2 K (82 kbar)

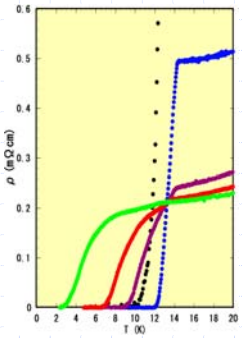
Taniguchi, et al. *J. Phys. Soc. Jpn*, **72**, 468 (2003).





六方アンビル

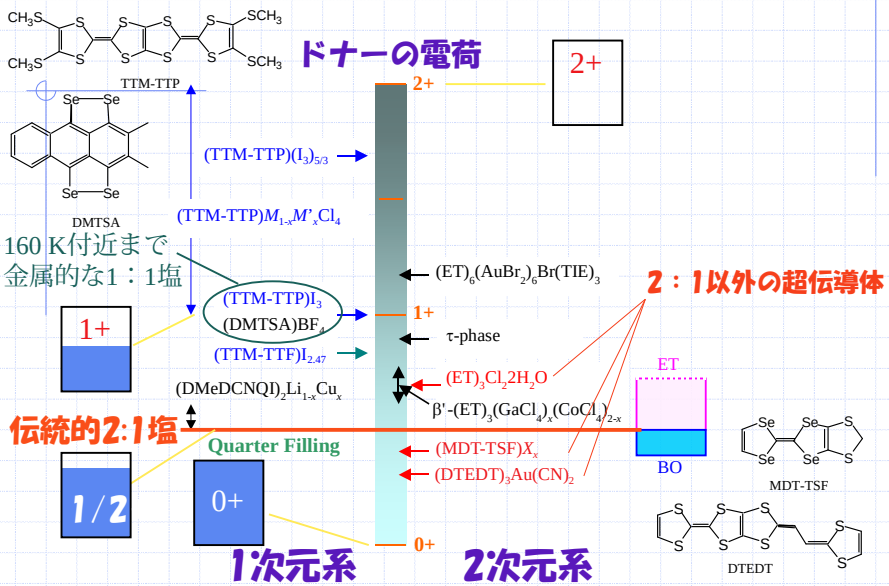




室温で半導体のモット絶縁体に超高圧をかけて T_cの記録を更新。

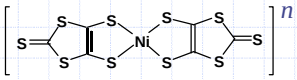
2：1組成以外の有機伝導体

T. Mori, *Chem. Rev.* 104, 4947 (2004).



[M(dmit)$_2$]：唯一のアニオン性超伝導体

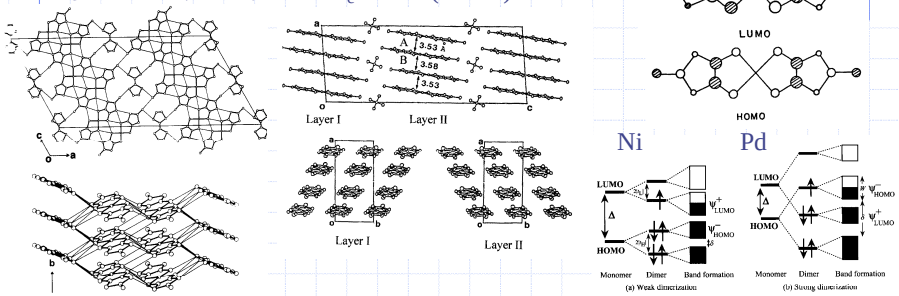
R. Kato, *Chem. Rev.* **104**, 5319 (2004).



n=0～2－　M=Ni, Pd

(TTF)[Ni(dmit)$_2$]$_2^{1/2-}$
T_c＝1.62 K (7 kbar)

((CH$_3$)$_4$N)[Ni(dmit)$_2$]$_2^{1/2-}$
T_c＝ 5 K (7 kbar)

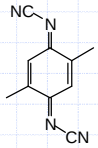


(EDT-TTF)[Ni(dmit)$_2$](1.3 K)以外は高圧下での超伝導体。
バンド構造は一次元的。HOMOとLUMOが左右の配位子の位相を逆にしたようなものであるため、エネルギーレベルが近く、二量化の大きいPd錯体ではフェルミ面がHOMOバンドに来る。

Cu(DMDCNQI)$_2$　金属に直接配位した有機伝導体

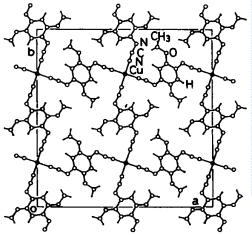
森, 固体物理, **24**, 113 (1989).
R. Kato, *Bull. Chem. Soc. Jpn.* **73**, 515 (2000).
S. Hünig, *Chem. Rev.* **104**, 5535 (2004).

一次元スタック
CNのNがCuに配位

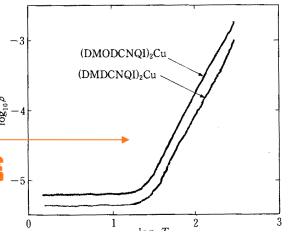


DMDCNQI

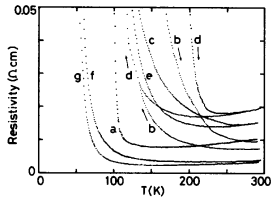
N,N'-dicyano-quinonediimine

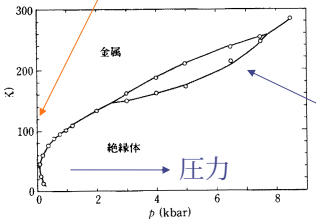


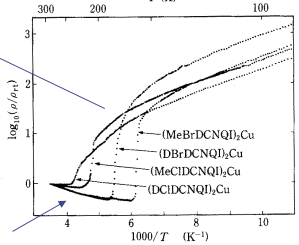
Cu$^{1.3+}$が鎖間相互作用を媒介するため低温まで金属



Cu→Li, Na, Agなどの錯体はPeierls転移



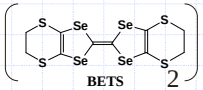




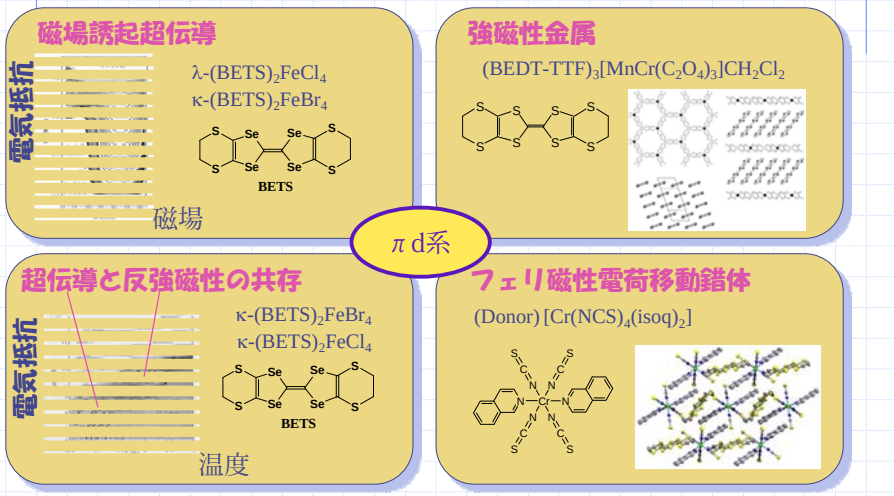
ハロゲン置換DCNQIは金属－半導体転移

磁性アニオンを含む有機伝導体(πd系)のさまざまな物性

磁性アニオン



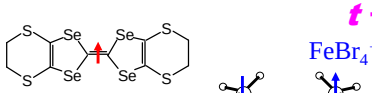
BETS 2　$FeCl_4$



バンド理論を越えて (1) πd系の理論

T. Mori, *J. Phys. Soc. Jpn.* **71**, 826 (2002).

t → *J* の見積もり



$FeBr_4^-$ 磁性アニオン

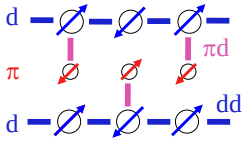
S = 5/2

$$J_{\pi d} = -\frac{2\sum^{5} t_{\pi d}^2}{5\Delta}$$

$$J_d = -\frac{2\sum^{25} t_d^2}{25U}$$

磁気構造

κ-$(BETS)_2FeBr_4$

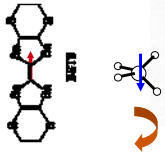


$$k_B T_N = \frac{35}{6}\left[J_d + \frac{\chi_q}{2k_B C_\pi} J_{\pi d}^2\right] = (dd) + (\pi d)$$

～2.5 K

反強磁性転移温度

λ-$(BETS)_2FeCl_4$

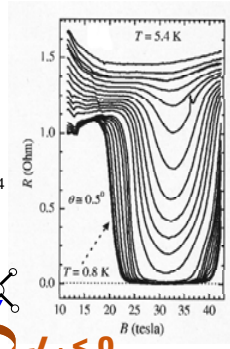


$J_{\pi d} < 0$

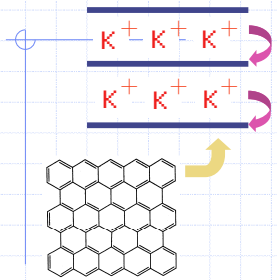
↓ + ↑ =0

外部磁場　内部磁場

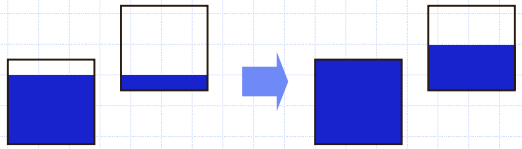
磁場誘起超伝導中心磁場



グラファイト層間化合物



さらに電気がよく流れるようになる。



ドープ

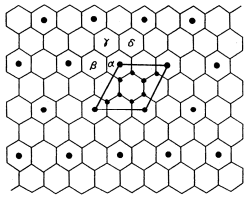


図6　グラファイト・カリウム C_8K 中のカリウム原子(●印)の配置

C_8K

非常に低温で超伝導になる。

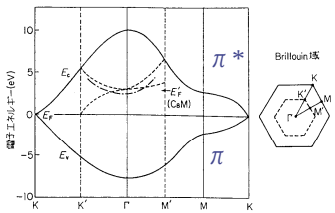
C_8K　T_c = 0.39-0.55 K

C_8Rb　T_c = 0.03-0.15 K

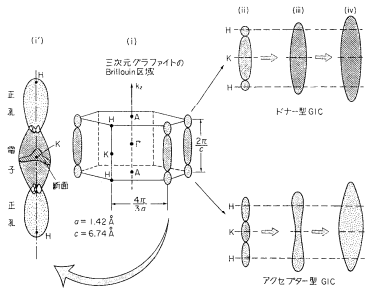
C_8Cs　T_c = 0.02-0.14 K

グラファイトのエネルギーバンド

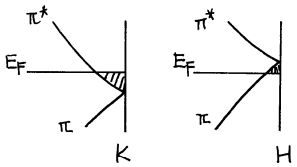
2次元半金属



二次元グラファイトの電子エネルギー帯
〔破線，一点鎖線は CaM (M はアルカリ金属)の場合〕

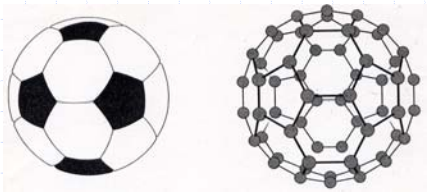


グラファイトの Fermi 面と GIC への拡張

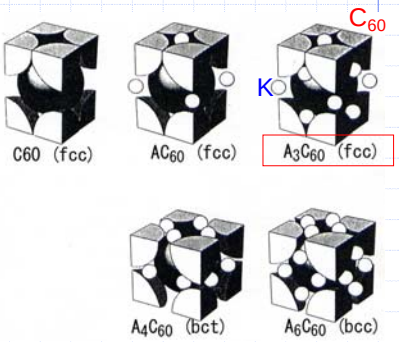


3次元的分子性超伝導体：K_3C_{60}

Fullerene

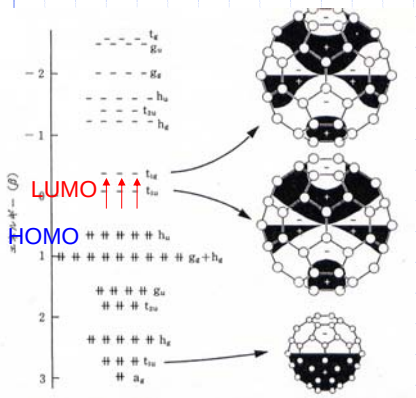


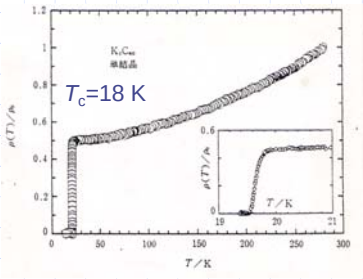
C_{60}



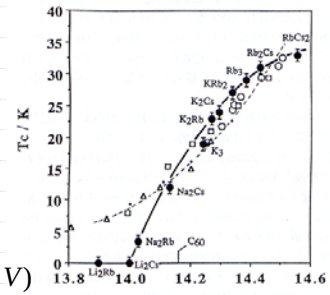
Buckminster Fuller制作ドーム

K_3C_{60}の分子軌道と超伝導

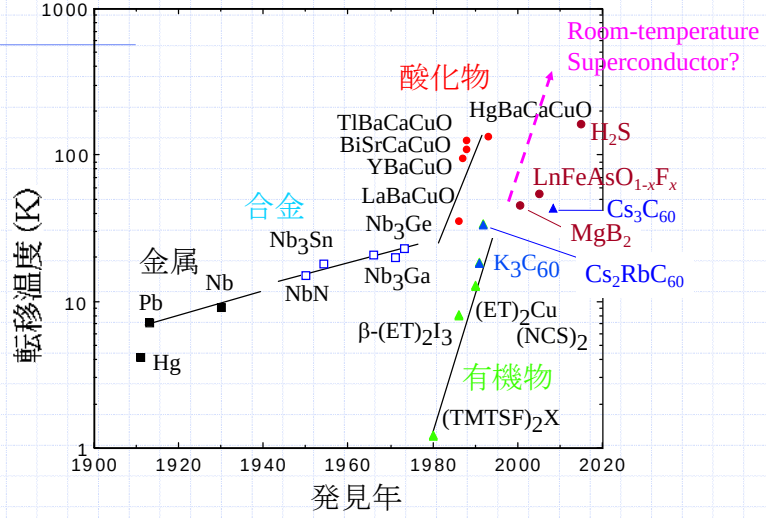




cf. Tc=33K (Cs_2RbC_{60})



弱結合BCS

$$k_B T_c = 1.13 h\omega_D \exp(-1/D(E_F)V)$$

超伝導物質の転移温度と発見年