Magnetic TTF-Based Charge Transfer Complexes

Toshiaki Enoki
Tokyo Institute of Technology

1st France-Japan Advanced School on Chemistry and Physics of Molecular Materials

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Contents

1. Charge transfer complexes
   1.1. molecular stacking manners and electronic structures

2. Low dimensional conductors
   2.1. low-D electronic structures
   2.2. electronic instability

3. Magnetic charge transfer complexes
   3.1. magnetic charge transfer complexes

4. Typical examples of TTF-based magnets
Organic charge transfer complexes

\[ D + A \rightarrow D^{+\delta} A^{-\delta} \quad 0 < \delta < 1 \text{ fractional} \]

D: donor, A: acceptor having \( \pi \)-electrons

cf. \( \text{Na}^+\text{Cl}^- \)

mixed stack

\[
D^+ \quad A^- \quad D^+ \quad A^- \quad D^+ \quad A^- \quad \ldots
\]

segregate stack

\[
D^+ \quad D^+ \quad D^+ \quad D^+ \quad D^+ \quad \ldots
\]

\[
A^- \quad A^- \quad A^- \quad A^- \quad A^- \quad \ldots
\]

low-dimensional structure \( \rightarrow \) 1D, 2D
low-dimensional electronic structure

a variety of electronic phases

metal, semiconductor, superconductor, ferromagnet, antiferromagnet

structural, electronic and magnetic transitions
important factors in low-D electronic systems

radical anion pair \( A^- \quad A^- \)

transfer integral \( t = \int \psi^1(x)^*H\psi^2(x)dx \)

on-site Coulomb int. \( U = \frac{e^2}{\varepsilon r} \)

e- e-

two limiting cases

\[
\begin{cases}
\cdot \text{Heitler-London limit} & (U \gg 2t) \\
\cdot \text{molecular orbital limit} & (U \ll 2t)
\end{cases}
\]
organic solids

H.L.limit

M.O.limit

antibonding bonding

A\textsuperscript{0} A\textsuperscript{2-}

A\textsuperscript{-} A

2t

2t

 localized strongly correlated

U

delocalized free electrons

 localized spins

insulator (Mott insulator)

metal

Mott-Hubbard boundary
Mott metal-insulator transition

1D system

$4t > U \quad \text{metallic}$

$4t < U \quad \text{insulating with localized spins}$

Fractional charged state

Always metallic

$A^* - \cdot \leftrightarrow A \cdot A^*$
Donor molecules in the TTF family

- TTF
- BEDT-TTF
- C₁ TET-TTF
- VT
- DMET
- EDTDM
- EDO-TTFX₂ X=Cl, Br
- TTM-TTP
- BDH-TTP
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2.1. low-D electronic structures

Fermi energy $\varepsilon_F$ (3D)

$$\varepsilon_F = \frac{\hbar^2}{2m_e} \left(3\pi n_e\right)^{2/3}$$

$n_e$: electron density
$L$: size of the system
2.2. low-D electronic instability

perturbation potential with a periodicity of \( Q \) \( V(x) = V_Q \exp(iQx) \)

perturbed wave function \( \psi_k = \phi_k + a_{k+Q} \phi_{k+Q} \)

\[ a_{k+Q} = \frac{V_Q}{\varepsilon_k - \varepsilon_{k+Q}} \]

spatial distribution of electron density subjected to the perturbation potential

\[
\rho(x) = \frac{1}{N_e} \sum_k |\psi_k|^2 \quad \rightarrow \quad \rho(x) = \frac{1}{N_e L} \sum_k (1 + a_{k+Q} \exp(iQx) + a_{k+Q}^* \exp(-iQx))
\]

\[
\rho(x) = \frac{1}{N_e L} \sum_k \left[ \frac{V_Q \exp(iQx)}{\varepsilon_k - \varepsilon_{k+Q}} + \text{c.c.} \right]
\]

\[
\rho(x) = -\frac{1}{N_e L} V(x) \sum_k \frac{1}{\varepsilon_k - \varepsilon_{k+Q}}
\]

for real potential \( V(x) = V_Q \exp(iQx) + V_Q^* \exp(-iQx) \)

Fourier transform \( \rho(x) = \frac{1}{L} \sum_Q \rho_Q \exp(iQx) \)
charge density

$$\rho(x) = \frac{1}{-N_e L} V(x) \sum_k \frac{1}{\varepsilon_k - \varepsilon_{k+Q}}$$

$$\rho(x) = \frac{1}{L} \sum_Q \rho_Q \exp(iQx)$$

$$\rho_Q = -V_Q \chi(Q)$$

susceptibility

$$\chi(Q) = \frac{1}{N_e} \sum_k \frac{1}{\varepsilon_k - \varepsilon_{k+Q}}$$

1D electronic system

$$\chi(Q) = \frac{2m_e L}{\pi N_e \hbar Q} \ln \left| \frac{Q + 2k_F}{Q - 2k_F} \right|$$

1D electronic system

$$\chi(2k_F) \to \infty$$

$$\rho_Q = \text{finite, even if } V_Q = 0$$

charge density forms a periodic spatial distribution with $Q = 2k_F$

$\chi(Q) \to \infty$ at $Q = 2k_F$
charge density wave (CDW)

electron-phonon interaction
CDW induces a lattice distortion

perturbation potential
induces a gap at $Q$ for $T < T_c$

metallic state
$T > T_c$

CDW insulating state
$T < T_c$

Peierls transition
metal to insulator
π-electrons

t, U → important role

transfer integral

U on-site Coulomb int.

on-site Coulomb int. → magnet

localized magnetic moments

spin density wave (SDW)
spin density wave (SDW)

periodic spin density distribution with $Q=2k_F$

SDW insulating state stabilized below $T_c$
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4. Typical examples of TTF-based magnets
Four regimes in the development of molecular magnets

(1) $U \gg 4t$  Mott insulator regime

localized magnetic moments generated

low-dimensional magnet

1D system

exchange interaction

$J = -t^2/U$

2D system
types of interaction

- paramagnetic
- ferromagnetic
- antiferromagnetic

exchange interaction

development of spin

spin density wave

spin ordering and dimensionality

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<thead>
<tr>
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<th>Ising</th>
<th>Heisenberg</th>
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<tbody>
<tr>
<td>1D</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>2D</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td>3D</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

low D magnet - anomalous features
quantum spin system
low D AF magnet

long range ordering short range ordering

Bonner-Fisher type $J' = 0$

singlet ground state

$\Delta E = 4J$
Four regimes in the development of molecular magnets

(1) $U \gg 4t$
localized magnetic moments generated

(2) $U \approx 4t$
the coexistence of electron transport and magnetism (highly correlated electron systems)
(3) $U \ll 4$

$t$ electrical conduction $\rightarrow \pi$-electron

low-D conductor, metal

the introduction of localized d-electrons

\[
\begin{cases}
\text{donor } \pi\text{-electron } \rightarrow \text{free carriers} \\
\text{acceptor: anions with 3d transition metal } \rightarrow \text{localized spins}
\end{cases}
\]

$\pi$-d interaction

strong magnetic interaction mediated by $\pi$-conduction carriers

molecule-based metal magnetic systems

cf. Fe metal $s$-d interaction
\( \pi\text{-d interaction system} \)

- \( -2J_{\pi d}\delta(r)s_{\pi}S_{d} \)

\( \text{cond. } \pi\text{-electron} \rightarrow \text{localized spin (d-electron)} \)

RKKY interaction

\[ J_{dd} = \frac{3N}{16\pi^2} \frac{J_{\pi d}^2}{E_F} I(R)S_iS_j \]

\[ I(R) = \frac{16\pi k_F^3}{(2k_F R)^4} (2k_F R \cos 2k_F R \sin 2k_F R) \]

ferro

antiferro

decaying with an oscillation

conduction electron-mediated interaction
$\pi$-carriers ___ e^- ___ e^- ___ e^- ___ $\pi$-d interaction

d-spins

interplay of electron transport and magnetism
organic version of metal magnet

new type of molecular magnet
(4) $U \gg 4t$ + localized d-spins

**Mott insulator with $\pi$-spins**

- donor $\pi$-spins
- anion $\pi$-spins

$\pi$-$d$ composite magnets

- ferrimagnetism, weak ferromagnetism, helical magnetism, etc.

**Band insulator with no $\pi$-spins**

$\pi$-electron-mediated superexchange path for interaction between d-spins

Superexchange interaction

[Diagram showing superexchange interaction with wave function overlap]
Overview of magnetism appearing in organic charge transfer complexes

- **π-based system**
  - low-D Heisenberg antiferromagnet quantum spin system
  - high correlated metal

- **π-d system**
  - superexchange-mediated π-d composite magnet ferrimagnet/helical spins
  - magnetic superconductor
  - π-d metal magnet

Graphical representation with axes labeled $t/U$ and $J_{\pi-d}$.
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   four categories
Low-dimensional magnet of localized $\pi$-electrons

$\text{(C}_1\text{TET} \cdot \text{TTF)}_2\text{Br}$
\[(C_1\text{TET} \cdot \text{TTF})_2\text{Br}\]

2D triangular AF magnet

\[J_1: \text{square lattice} \quad J_2 \Rightarrow \text{spin frustration}\]

\[
\begin{align*}
J_1 &\sim -t_{b1}^2/U \sim -t_c^2/U \\
J_2 &\sim -t_{b2}^2/U \\
J_2 &\sim 0.5J_1
\end{align*}
\]
1 spin/2 donors $\theta = -17.3$ K
short range order (SRO) $\sim 12$ K
Néel temperature $T_N = 3.0$ K

small apparent value of $T_N$
compared with $J$'s for ordinary complexes

Magnetization: weak concave feature
quantum $\rightarrow$ classical

spin frustration effect
Coexistence of metallic conduction and localized spin magnetism in the vicinity of Mott MI transition
Correlation between conductivity and magnetic susceptibility

low resistivity and large magnetic susceptibility in the vicinity of Mott MI transition
(EDO-TTFBr$_2$)$_3$I$_3$

coeistence of metallic conductivity and localized spins
$(\text{EDO-TTFBr}_2)_3\text{I}_3$

<table>
<thead>
<tr>
<th>Transfer integral $S / 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$</td>
</tr>
<tr>
<td>$q$</td>
</tr>
<tr>
<td>$r$</td>
</tr>
</tbody>
</table>

Donor molecules: equivalent 1/6 filled

$|t_r/t_q| \sim 0.27$

**Quasi-1D structure**
Conductivity (1D-direction)

$T \geq 150K$
metallic (quasi-1D metal)
$\rho_{rt} \lesssim 10^{-2} \ \Omega \text{cm}$
considerably high conductive

$T \leq 150K$
semiconductive $E_a = 400K$
still highly conductive

$$\rho(T) = \rho_0 \exp(J_{a} / k_B T)$$

$T(K)$
$\log \rho (\Omega \text{cm})$
**magnetic Susceptibility**

$T \sim 70K$  short range order peak

1D Heisenberg antiferromagnet

$\sim 0.2$ spin / donor

(fractional moment)

$\frac{t_r^2 + t_q^2}{t_p^2} \sim 0.1$

3D long range order

$T_N \sim 15K$

presence of localized spins apparently inconsistent with metallic conduction

Mott M-I boundary
$\pi$-d composite magnets
interaction between d-spins in $MX_2$ ($M=$Mn, Fe, Co, Ni, Cu; $X=$F, Cl, Br, I)

- halogen species dependence
  $F > Cl > Br > I$ except Cu

- transition metal dependence for $X=Br$
  $Mn < Fe < Co < Ni << Cu$

- # strongest exchange interaction
  $CuBr_2$: magnetic d-electron wave function extended to Br sites
Overview on the strengths of $\pi$-d interaction ($\Theta_d$) and the d-d direct interaction ($\Theta_{\pi d}$) in $\pi$-d composites


A variety of competitions between $\pi$-d interaction and d-d interaction in various electronic states of $\pi$-electron
(C_{1}TET-TTF)FeBr_{4}

c_{1} TET-TTF

triangle-based spin ladder
$\text{(C}_1\text{TET-TTF)}\text{FeBr}_4$

$\text{Fe-Br} \cdots \text{Br-Fe} \to J_1$ (path 1)

$\text{Fe-Br} \cdots \text{D} \cdots \text{Br-Fe} \to J_2$ (path 2)

$\text{Fe-Br} \cdots (\text{D}_2) \cdots \text{Br-Fe} \to J_3$ (path 3)

Mutual angle between two FeBr$_4$ anions: 30°
magnetic susceptibility and magnetization curves

(a) Magnetic susceptibility ($\chi$) vs. temperature ($T$)
- $T_N = 4.2$ K
- $\Theta = -18$ K
- $C = 4.6$ emu K/mol

(b) Magnetization ($M$) vs. magnetic field ($H$)
- Weak ferromagnetism ($H_{\text{wf}} = 2.3$ T)
- Spin flop ($H_{\text{sf}} = 2.3$ T)

Easy axis $\parallel a$-axis
- $A = \frac{2z_1J_1}{N/2 \cdot (g\mu_B)^2}$
- $\Gamma = \frac{2z_2J_2}{N/2 \cdot (g\mu_B)^2}$

$J_1 \sim -1.76$ K, $J_2 \sim -0.5$ K
spin-canted weak ferromagnetism under magnetic field

\[ H < H_{wf} \]

\[ H > H_{wf} \]

\[ E_1 = 2J_1SS + 2J_2SS - 3J_3SS \]
\[ E_h = 2J_1SS + 2J_2SS + 3J_3SS \]

weak ferromagnetic transition

\[ \Delta M_{wf} B_{wf} = E_h - E_1 = 6J_3SS \text{ at } H_{wf} \]

\[ J_3 \sim 9 \times 10^{-3} \text{ K } \sim 6 \times 10^{-3} J_1 \]

weak inter-ladder interaction
(BDH-TTF)[Cr(isoq)$_2$(NCS)$_4$]
(BDH-TTF)[Cr(isoq)$_2$(NCS)$_4$]

M(isoq)$_2$(NCS)$_4$

Two Cr$^{3+}$ spin sites with ligand axes tilted by 5.5°

Magnetic anisotropy

Ferrimagnetism

$\pi$-spin $s=1/2$ and Cr$^{3+}$ d-spin $S=3/2$

1D ferrimagnetic chain
magnetic susceptibility and magnetization curves

\[ \chi / \text{emu mol}^{-1} \]

\[ T / \text{K} \]

\[ B = 0.1 \text{T} \]

- \( B / / a \)
- \( B / / b \)
- \( B / / c \)

\[ M / \mu_B \]

\[ B / \text{T} \]

\[ T = 2 \text{K} \]

- \( B / / b \)
- \( B / / c \)

\( T_N = 7.6 \text{ K} \) antiferromagnetic transition accompanied by
- weak ferromagnetic features (∥ b)
- spin-flop transition \( B = 1 \text{ T} \) (∥ c)

small spontaneous magnetization with hysteresis at low field (∥ b)

weak ferromagnetism

\[ \Delta M = 0.10 \mu_B \]

canting angle \( \theta = 2.9^\circ \)

d-spin
magnetization under high pressures

- $T_N$ elevated
- weak ferromagnetic moment $\Delta M_{wf}$ reduced

\[ M_R / 10^{-2} / 4_B \]
\[ T / K \]

\[ B = 0 \text{ mT} \]

\[ T_N \]
\[ p / \text{kbar} \]
\[ T_C = 100 \text{K at 100 kbar} \]

exchange interaction $-JSS$
competing with the magnetic anisotropy

Pressure $\theta$
j increases $\rightarrow$ antiparallel arrangement preferred
$\Delta M_{wf}$ reduced
$\pi$-d conducting magnets
Organic metal interacting with ferromagnetic spin systems

\[(\text{EDO-TTFI}_2)_2\text{M(mnt)}_2\]

\[\text{M=Ni, Pt}\]
(EDO-TTFI₂)₂M(mnt)₂ (M=Ni, Pt)

EDO-TTFI₂

M(mnt)₂

Electrical resistivity
metal-insulator transition

<table>
<thead>
<tr>
<th>M</th>
<th>ρ₉₀ (Ω cm⁻¹)</th>
<th>TMI (K)</th>
<th>Eₐ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M=Ni</td>
<td>110</td>
<td>88</td>
<td>700</td>
</tr>
<tr>
<td>M=Pt</td>
<td>170</td>
<td>96</td>
<td>800</td>
</tr>
</tbody>
</table>

Donor 1D metal (∥c) 3/4 filled
strong interaction (Br-CN)
Magnetic behavior

$\chi T$ vs $T$

- $\chi T (M=\text{Ni})$
  - isotropic
- 1D Heisenberg ($J=18K$)
  - ferromagnetic

Ni(mnt)$_2$-chain
- 1D ferromagnetic
  - $\uparrow \uparrow \uparrow \uparrow \uparrow$

intra-chain: $J_1 \sim 18K$
inter-chain: $J_2 \ll J_1$

coexistence of metallic conductivity and ferromagnetic interaction
M = Pt

Magnetic susceptibility

\[ \chi \text{(emu mol}^{-1}) \]

\[ T \text{(K)} \]

\[ 0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \]

\[ 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1 \]

1D Ising \((J=22K)\)

Magnetization curve \((H//a-b)\)

\[ M \text{ (\textmu B)} \]

\[ 0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \]

\[ 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1 \]

1D metal interacting with ferromagnetic spins

anion chain \(\rightarrow\) 1D Ising ferromagnet

Metamagnet \(T_C = 5.5K\)

\[ J_{\text{intra}} \sim 22K \quad J_{\text{inter}} \sim -0.05K \]
Donor conduction electron

Interacting

Acceptor localized spin

Metallic state interacting with ferromagnetic spins
π-d interaction systems

\[
(D\text{MET})_2\text{FeBr}_4 \\
(ED\text{TDM})_2\text{FeBr}_4 \\
(ED\text{S-TTF})_2\text{FeBr}_4
\]

isostructural

interplay of magnetism and electron transport
Crystal structure

Alternate stacking

D:A = 2:1

1D-column of EDTDM molecules

2D-lattice of FeBr$_4^-$ anions
Crystal structure

$d_{\text{Br-Br}} = 3.87 \text{ Å (v.d.W. 3.9 Å)}$

$d_{\text{S-Br}} = 3.75 \text{ Å (v.d.W. 3.8 Å)}$

Close intermolecular contacts: 3D magnetic interaction
resistivity

$I \parallel \text{Inter-plane}$

- $(\text{EDTDM})_2\text{FeBr}_4$
- $(\text{DMET})_2\text{FeBr}_4$

$(\text{DMET})_2\text{FeBr}_4$
$(\text{EDTDM})_2\text{FeBr}_4$
$(\text{EDS-TTF})_2\text{FeBr}_4$

donor $\pi$-electrons

metal-insulator (MI) transition
Pauli susceptibility
incomplete discontinuous drop

$^{13}\text{C-NMR, ESR}$
SDW feature
(spin density wave)

$T_{\text{MI}} \sim 40\,\text{K}$
$T_{\text{SDW}} \sim 25\,\text{K}$
$T_{\text{SDW}} \sim 15\,\text{K}$

$\rho(T) = \rho_0 \exp\left(\frac{E_a}{k_B T}\right) \quad \rightarrow \quad E_a = k_B \frac{d \ln \rho}{d(1/T)}$

donor $\pi$-electrons
Fe$^{3+}$ ($S=5/2$) mainly contributing

<table>
<thead>
<tr>
<th></th>
<th>$T_N$ (K)</th>
<th>$\theta$ (K)</th>
<th>easy axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS-TTF</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DMET</td>
<td>3.7</td>
<td>-6</td>
<td>$// a$</td>
</tr>
<tr>
<td>EDTDM</td>
<td>3</td>
<td>-2.8</td>
<td>$// a$ ($T &lt; T_N$)</td>
</tr>
</tbody>
</table>

※ EDTDM: anisotropy appears below ~50K reversed at $T_N$
magnetization of (DMET)$_2$FeBr$_4$

- Spin flop transition (∥$a$)
  \[ B_{sf} = 2T \]
- Anomalous features:
  - Extrapolated to a negative value at $B=0T(∥a)$
  - Shoulder around $B_2 \approx 5T(∥b)$
- Participation of donor electrons
- $\pi$-$d$ interaction
magnetoresistance
(DMET)$_2$ FeBr$_4$

$magnetoresistance$ $(DMET)_2$ FeBr$_4$

\[ \Delta \rho \left( \frac{B}{\rho(0)} \right) \]

$T=1.64 K$

\[ \Delta \omega \left( \frac{B}{\omega(0)} \right) \]

\[ B_{sf} \]

\[ I// \text{in-plane} \]

inter-plane hopping frequency $\omega_{\perp}$

negative magnetoresistance

magnetism-related anomalies

- spin easy axis ($//a$)
- spin flop transition ($B_{sf}$)
- spin hard axis ($//b$)

excellent correlation with magnetization
interplay between magnetism of d-electron spins and transport of $\pi$-electron carriers

$\pi$-d interaction
Mechanism of negative MR

\( P < 9.2 \text{ kbar}: \) SDW state below \( T_N \)

\( H \neq 0 \)

- conduction
- \( \pi \)-electron
- magnetism
- \( d \)-spins

Disappearance of periodic potential:
- Periodic potential by AF spin configuration
  - reduction of effective SDW gap

↓

- increase of effective SDW gap by Fe\(^{3+}\)
- Field induced high conductive state
magnetoresistance anomaly induced by electronic instability of low-dimensional system
(EDTDM)$_2$FeBr$_4$ high pressure conductivity

- $I//in-plane$
- $T(K)$
- $E_A(K)$

- Giant anomaly at 4K
- Magnetic origin
- Effect of AF order in Fe$^{3+}$ spins
- Metal-insulator (SDW) transition
- $\rho_c \sim 9$ kbar
- Largest anomaly
- Strong $\pi$-d interaction

- Activation energy $E_A$
- 9.2 kbar
- 13.5 kbar
- 17.6 kbar
Magnetoresistance under various pressures

$H \parallel b$-axis, $T \sim 1.8$ K

$P < P_{SDW} \sim 9.2$ kbar: 
|MR| increases with increasing $P$

$P > P_{SDW} \sim 9.2$ kbar: 
|MR| decreases with increasing $P$

$P_{SDW} \sim 9.2$ kbar:

The largest negative MR ($\sim 58\%$)

$\rightarrow$ boundary between SDW and metal
Pressure dependence of magnetoresistance

$T \sim 1.8 \text{ K}$

Singularity

at around $P_c \sim 9.2 \text{ kbar}$

(MI boundary)

$|\Delta \rho/\rho(0)|_{\text{max}}$

$P_c$

$P / \text{kbar}$

$0 \quad 5 \quad 10 \quad 15 \quad 20$

$0 \quad 0.2 \quad 0.4 \quad 0.6$

$|\text{MR}|$ increases toward the MI boundary.

Once the metallic state is stabilized,

the observed MR rapidly decreases again.
Detailed mechanism of negative MR

Effective field by the $d$-spins:

$$H_{\pi d}(Q_d) = -\frac{2z_{\pi d}J_{\pi d}S_d(Q_d)}{g\mu_B}$$

mean field approx.

Induced moment of $\pi$-electron spins by $d$-spins:

$$g\mu_B\delta s_\pi(Q) = -\chi(Q)H_{\pi d}(Q)$$

SDW gap

$$E_g = E_0 + \Delta E_{\pi d}$$

$$= E_0 + \frac{1}{2}J_{\pi \pi}[\delta s_\pi(Q)]^2$$

$$= E_0 + \frac{1}{2}\chi(Q)^2\frac{J_{\pi \pi}J_{\pi d}^2S(Q)}{(g\mu_B)^2}$$

For $Q_d = Q_\pi$ (present case)

Antiferromagnetic arrangement of $d$-spins can work as additional potential to $\pi$-electron system
Pressure effect on $E_g$ and $\chi(Q)$ in the $\pi$-electron system

- Tight binding calculation with on-site $U$
  \[ \chi(Q) \propto \sum_k \frac{f_k + Q - f_k}{E_k - E_{k+Q}} \]

- Pressure application
  \[ \alpha \]
  Increase of $\alpha$

Reduction of $E_g$ $\rightarrow$ Metallic above $\alpha > 1.6$

Divergent behavior of $\chi(Q)$ toward $\alpha \sim 1.6$
$(VT)_2FeBr_4$

field-induced magnetoresistance anomaly
Structure

Close contacts between donors and anions

1D-donor chain
2D-anion sheet

Alternate stacking

No close contacts between anion molecules

$D:A = 2:1$

$d_{S-Br} \sim 3.5 \text{ Å}$

$d_{\text{Br-Br1}} \sim 4.0 \text{ Å}$

$d_{\text{Br-Br2}} \sim 4.3 \text{ Å}$

$d_{\text{Br-Br1}}$ and $d_{\text{Br-Br2}}$ distances refer to the distances between bromine atoms in the anion sheet.
Band Structure

$t_{\text{intra}} = 0.2 \text{ eV}$

$t_{\text{inter}} = 0.02 \text{ eV}$

Quasi-1D metal

$Q \sim c^*/2 + a^*/8$

Nesting vector
Electronic state of $\pi$-electron system

# Metal-insulator transition  
**Matallic above ca. 150 K**

**AF long range order below ca. 20 K**

**SDW transition**

# $T>T_{SDW}$: temperature dependence of Pauli susceptibility

Large electron correlation

**1D Heisenberg AF feature**

spin degree of freedom

\[
\begin{align*}
    s_\pi &= 0.55 \, \mu_B \\
    J_{\pi\pi} &= -31 \, K
\end{align*}
\]
Magnetic properties of (VT)$_2$FeBr$_4$ (d-spins)

- Magnetic transition at 4 K
- Strong interaction
- $\Theta = -4.3$ K
- $\Theta = -4.3$ K
- Long distances between anions
- Helical magnetism

Saturation field: $B_{\text{sat}} \approx 14$ T

Susceptibility along the three directions don’t tend to zero when $T \rightarrow 0$. 
Magnetoresistance of $\text{(VT)}_2\text{FeBr}_4$

\[ \Delta R(\text{B}=0 \text{T}) \]

$T \sim 1.94 \text{ K}, I \parallel \text{in-plane}$

Large positive MR
\[ \Delta R_{\text{max}} \sim 160 \% \text{ at } B_{\text{max}} \sim 10.6 \text{ T} \]

(Small positive MR for GaBr$_4$)

Rapidly decrease of MR above $B_{\text{max}}$
\[ \Delta R \sim 0 \% \text{ at } B \sim 15 \text{ T} \]

Large positive MR is caused by the Fe$^{3+}$ spins.
Mechanism of positive MR

Periodicity $Q_\pi$ modulated by the Fe$^{3+}$ spins to $Q_{\pi d}$

Application of field compensates the effect of the $d$-spins. ($Q_\pi = Q_{\pi d}$)

Large positive magnetoresistance is observed.
\[(EDCh-TTFBr_2)_2FeY_4 (Ch=O, S, Y=Cl, Br)\]

Strong donor-anion bonding through halogen atoms (Br-Y)

$\pi$-d interaction enhanced
(EDCh-TTFBr$_2$)$_2$FeY$_4$ (Ch=O, S, Y=Cl, Br)

**Donor layer**

**Anion layer**

*Quasi-1D donor π-electron system*

*Quasi-1D Fe$^{3+}$ (S=5/2) localized spin system*

*Br-Y semi-covalent bond*

*Strong donor-anion interaction*
### Intermolecular atomic distance (Å)

<table>
<thead>
<tr>
<th></th>
<th>Br-Y</th>
<th>Y-Y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d(d(_{vdw}))</td>
<td>d/d(_{vdw})</td>
</tr>
<tr>
<td>Y=Br Ch=0</td>
<td>3.52 (3.70)</td>
<td>0.951</td>
</tr>
<tr>
<td>Y=Cl Ch=0</td>
<td>3.40 (3.60)</td>
<td>0.944</td>
</tr>
<tr>
<td>Y=Br Ch=S</td>
<td>3.66 (3.99)</td>
<td>0.938</td>
</tr>
</tbody>
</table>

**extremely short Br-Y distance**

**strong π-d interaction**
Fe$^{3+}$ ($S=5/2$) d-spin system

**antiferromagnetic transitions**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_N$(K)</th>
<th>$\Theta$(K)</th>
<th>easy axis</th>
<th>$H_s$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DMET)$_2$FeBr$_4$</td>
<td>3.7</td>
<td>-6</td>
<td>$a$ (in-plane)</td>
<td>2.5</td>
</tr>
<tr>
<td>(EDTDM)$_2$FeBr$_4$</td>
<td>3.0</td>
<td>-2.8</td>
<td>$a$ (in-plane)</td>
<td>2</td>
</tr>
<tr>
<td>(EDT-TTFFBr$_2$)$_2$FeBr$_4$</td>
<td><strong>11.0</strong></td>
<td>-3.6</td>
<td>$b$ (in-plane)</td>
<td><strong>5.5</strong></td>
</tr>
<tr>
<td>(VT)$_2$FeBr$_4$</td>
<td>4K</td>
<td>-4.3</td>
<td><strong>helical?</strong></td>
<td>-</td>
</tr>
</tbody>
</table>

**strongest $\pi$-d interaction in the FeBr$_4^-$ family**
conductivity

metallic with a resistivity minimum at ~ 30 K

anomaly at ca. 15 K
Magnetic susceptibility

- Large Weiss temperature $\Theta = -20 - -30 \text{ K}$
- 3D antiferromagnetic ordering $T_N = 13.5 \text{ K}$
  - Highest $T_N$
- Short range order hump at 30 K $\sim \rho_{min}$
- Strong interaction between $\pi$-carriers and Fe$^{3+}$ spins
Summary

**Magnetic Organic Charge Transfer Complexes**

A large variety of magnetic systems

- **Low-dimensional magnets**
- Conducting magnets with high electron-correlation
- $\pi$-$d$ composite magnets, weak ferromagnets, ferrimagnets
- $\pi$-$d$ conducting magnets, molecular version of metal magnets

intentional molecular design

molecule-based magnets to molecular magnetic devices  \rightarrow  spintronics
anisotropic behavior of susceptibility

\[ \chi (\text{emu/mol}) \]

\[ B = 1 \text{ T} \]

\( T \) (K)

\( a \)- and \( b \)-axes

same finite value at \( T=0 \text{ K} \)

helical spin structure
$J_1$: Fe-Br-Br-Fe

$\pi$-conduction electron mediated

$J_2$: Fe-Br-D-Br-Fe

$J_3$: Fe-Br-D-D-Br-Fe
Exchange energy

\[ E(Q) = -2 \mathcal{J}(Q)SS \]

\[ = -2 \left\{ 2J_1 \cos(q_a/2) + 8J_2 \cos(q_b/2)\cos(q_c/2) \right. \]

\[ + 8J_2 \cos(q_a/2)\cos(q_b/2)\cos(q_c/2) \]

\[ + 8J_3 \cos(q_a/2)\cos(q_c) + 8J_3 \cos(q_c) \}SS \]

\[ Q=(q_a,q_b,q_c) \]

spin structure in ordered state \[ \frac{\partial E(Q)}{\partial Q} = 0 \]
$\mathcal{J}_1 < 0$

$\mathcal{J}(0, 0, 0)$

$\mathcal{J}(0, \pi, 0)$

$\mathcal{J}(\pi, 0, 0)$

$\mathcal{J}(\pi, \pi, 0)$

$\mathcal{J}(\pi, \pi, \pi)$

$\mathcal{J}(0, \pi, \pi)$

$\mathcal{J}(\pi, 0, k)$

$\mathcal{J}(0, 0, k)$

$\mathcal{J}(0, 0, 0)$

$\mathcal{J}(0, 0, k)$

$\cos(k/2) = |J_2|/2|J_3|$