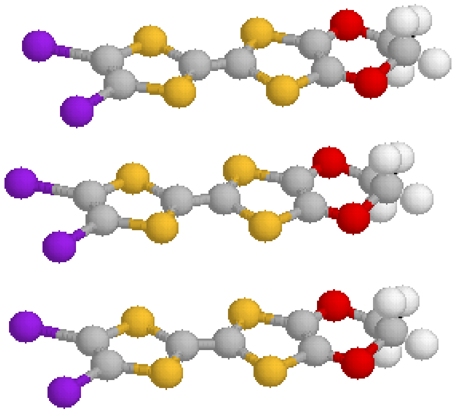
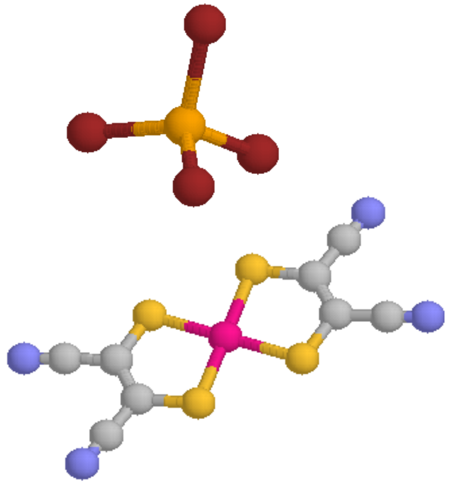
1.Introduction



Organic Donor
(conduction electron)



Transition Metal
Complex
(magnetic moment)

π-d system
coexistence of conductivity and magnetic moment

π-d system is interesting because...

- ***Foundation of molecular devices***

  For example
  conductivity controlled by magnetic field
  magnetization controlled by current

- ***New strong correlated system***

  Organic strong correlated systems have made progress of material science. Creating new such system is effective way to develop the material science.

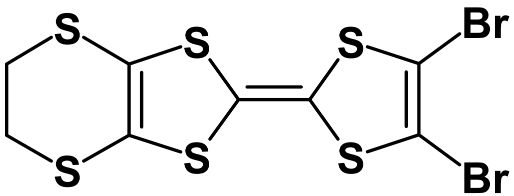
However, π-d interaction is usually very weak!

How To Enhance the Interaction?

There is a simple way!

Shorten Donor-Anion Distance!

For the purpose, we used following donor and anions.



EDT-TTFBr_2

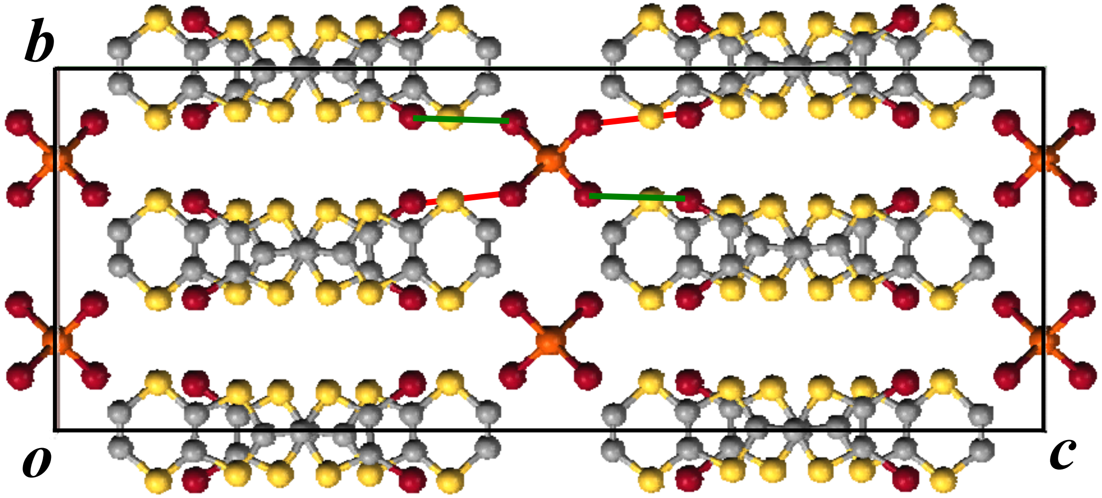
$FeBr_4^-$ *and* $GaBr_4^-$

Halogenated TTF-type donors show strong attractive interaction between the halogen atom of the donor and halogen of acceptors†. Therefor, short donor-anion contacts are easily realized!

† Imakubo, T., Sawa, H. and Kato, R. (1995).

The sizes of these anions are quite similar, while magnetic moments of $FeBr_4^-$ and $GaBr_4^-$ are S = 5/2 and S = 0, respectively. Therefore, we can investigate the effect of π-d interaction by comparing the salt of two kind of anions.

2.Structure



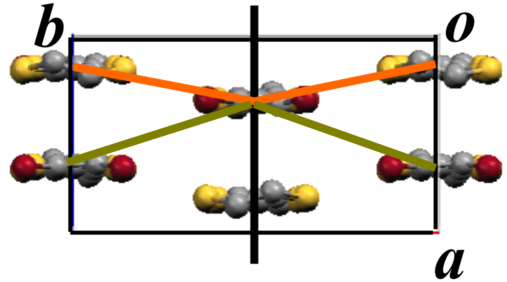
Donor-Anion Br-Br

3.66 Å (short)

3.67 Å (short)

cf. van der Waals radius

Br : 1.95 Å

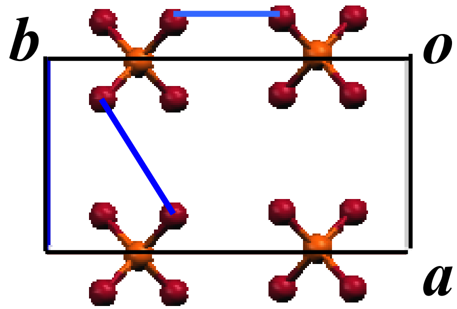


Overlap Integrals

-19.7×10^{-3}

-1.40×10^{-3}

4.26×10^{-3}



Anion-Anion Br-Br

4.01 Å (long)

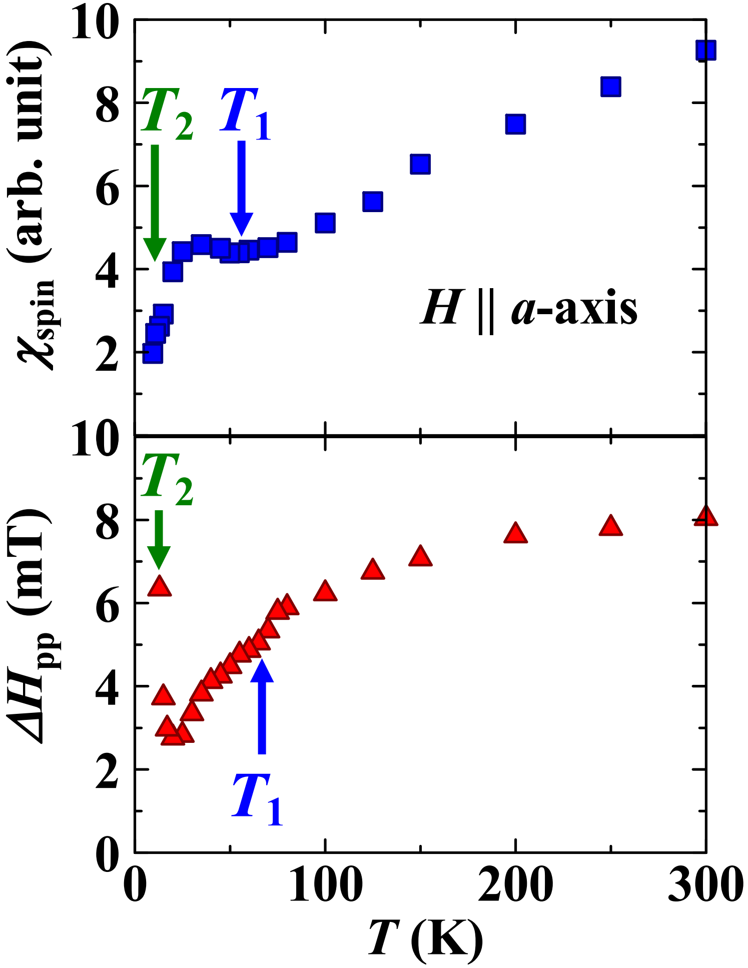
5.08 Å (long)

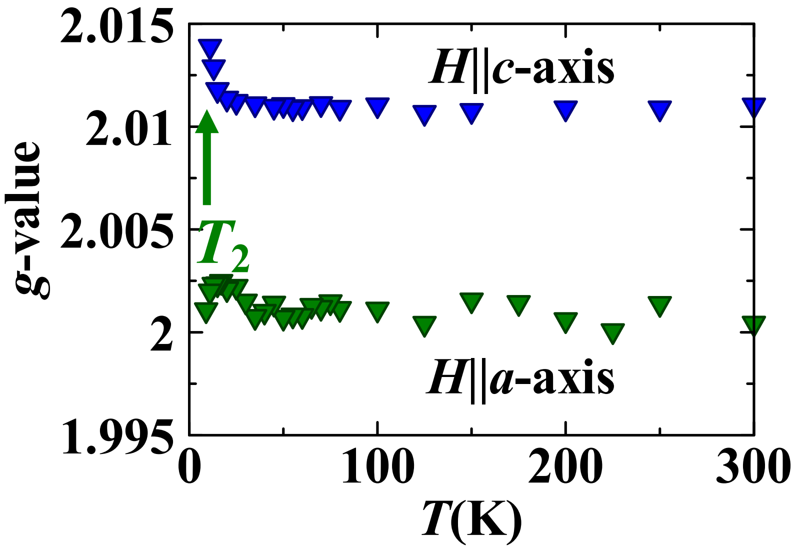
- **Short donor-anion contact**
- **Long anion-anion distance**

⇨ **Magnetic interaction may be mainly caused by π-d interaction**

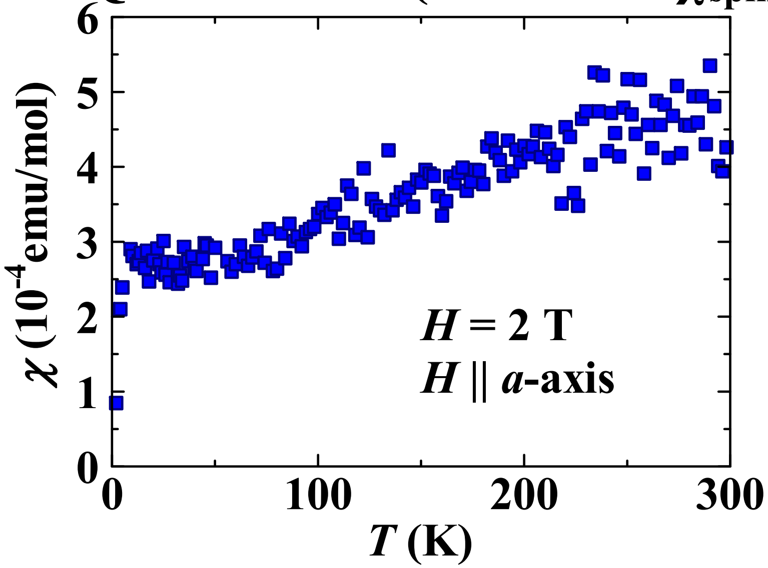
3. ESR and SQUID Results of Ga salt

ESR result

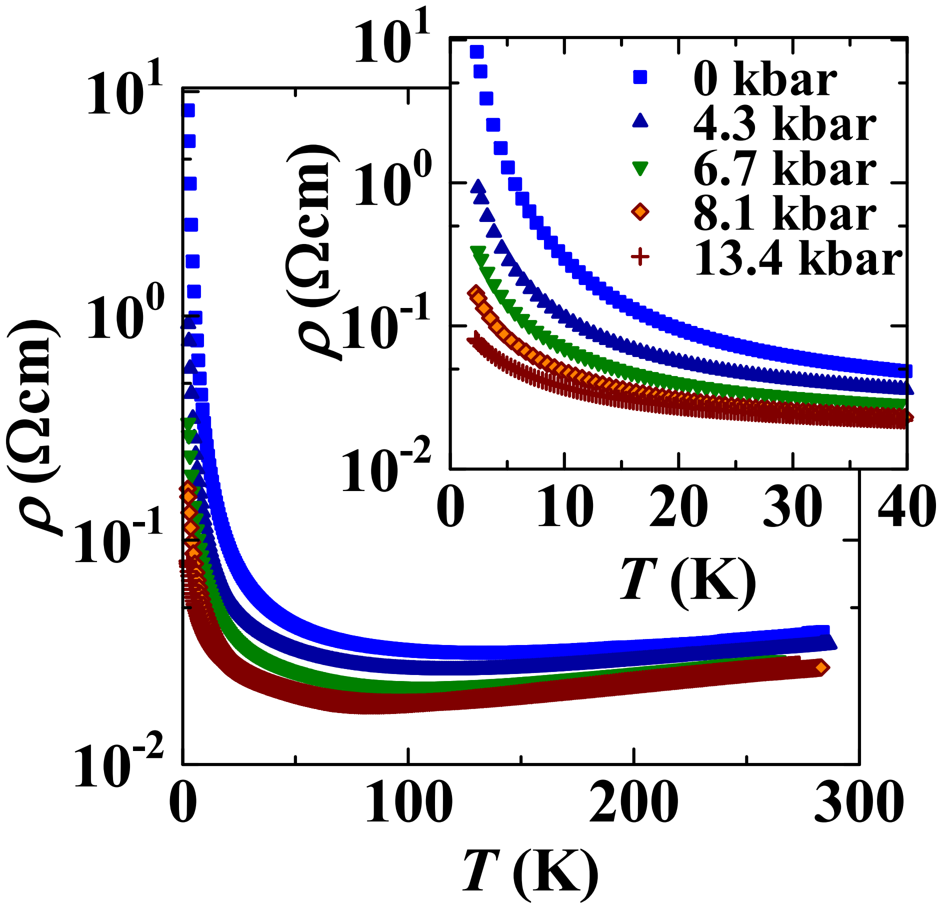


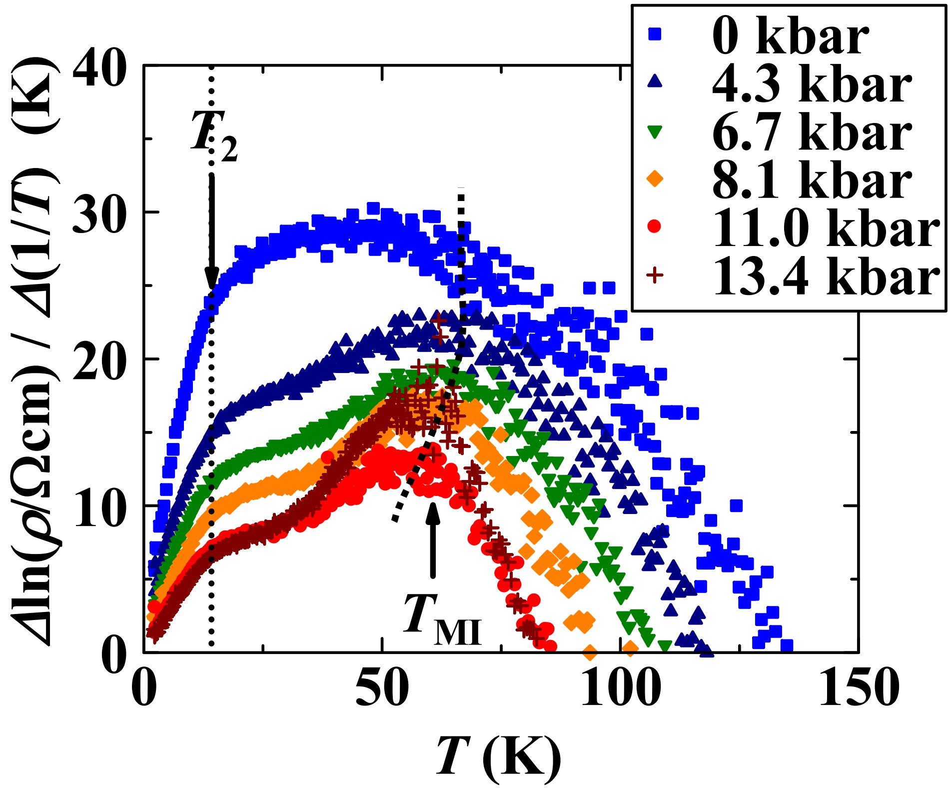


SQUID result (similar to χ_{spin})



4. Resistivity of Ga salt (*I* || *a*)





- Resistivity increases below 140 K
- M-I transition temperature T_{MI} ~ T_1 in ESR result of Ga salt
- Activation energy has anomaly at magnetic order temperature T_2 which estimated from ESR data.

5. Electronic structure of Ga salt

Three Anomalies of Ga salt

T ~ 140 K

Below this temperature, resistivity increases.

T_1 ~ 70 K

ΔH_{pp} changes at the temperature, and below T_1, χ becomes constant

M-I transition temperature.

T_2 ~ 13 K

ΔH_{pp} and g-value increase below 20 K, and they diverge at about 13 K.

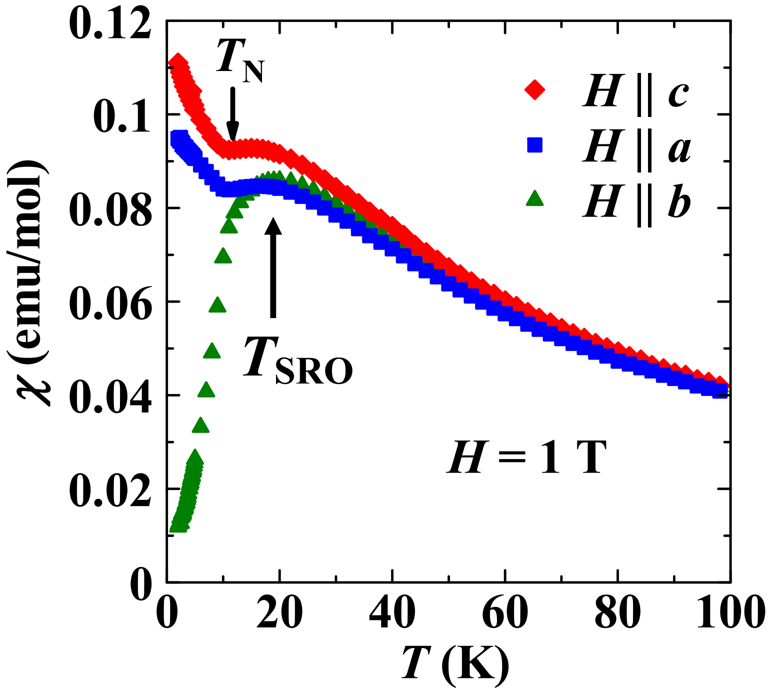
Shoulder of $\Delta \ln(\rho/\Omega \mathrm{cm}) / \Delta(1/T)$

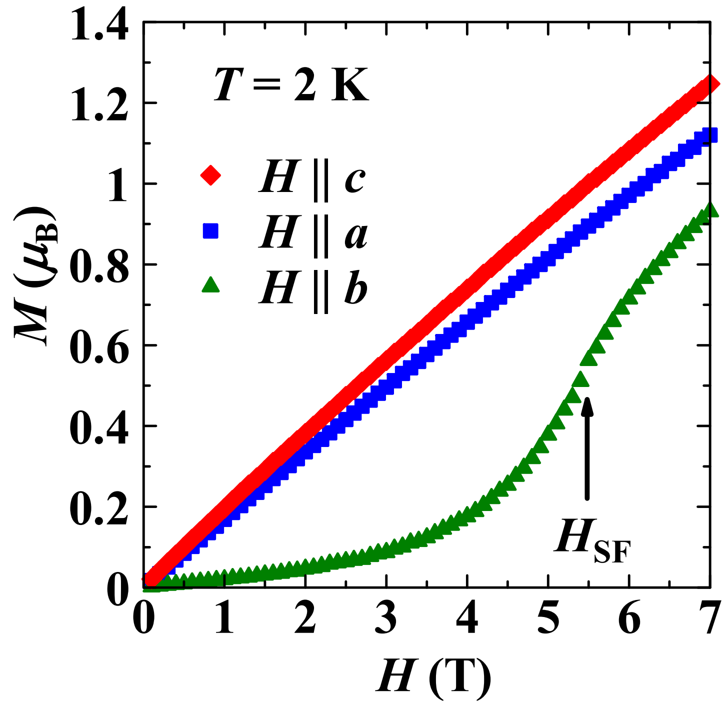
⇩

70 K: Charge ordering (M-I transition)

13 K: Antiferromagnetic transition π-electrons

6. SQUID Results of Fe salt





C = 4.33 emu·K mol^{-1}, Θ = –10.6 K

Quite high Néel temperature: T_N = 11 K

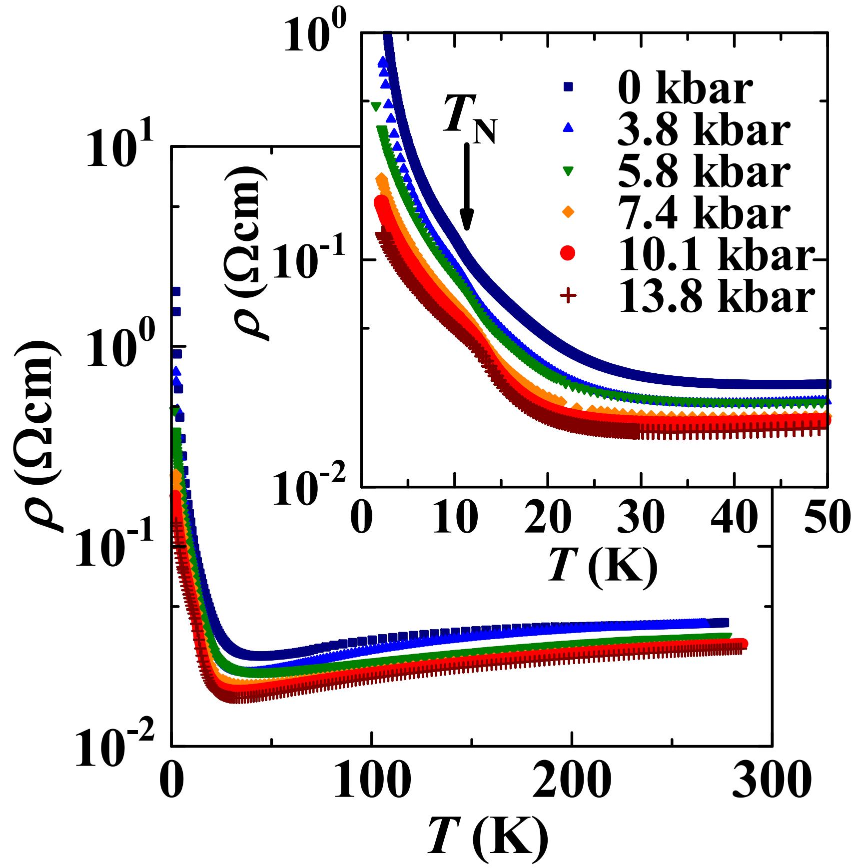
T_{SRO} ~ T_3 of ESR result of Ga salt

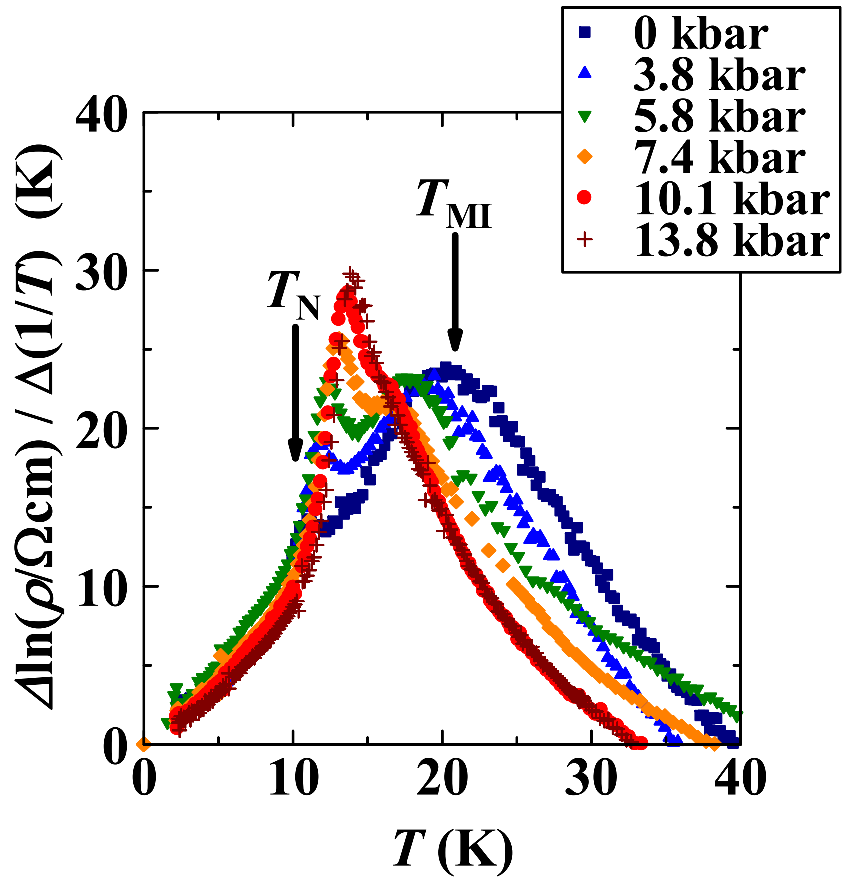
Large Spin Flop Field : H_{SF} = 5.5 T

Despite long anion-anion distances, T_N is surprisingly high.

Strong π-d interaction is suggested!

7. Resistivity of Fe salt (*I* || *a*)





·Anomaly at T_N indicates π-d interaction!
·T_{MI} is lower than that of Ga salt, and it is same as magnetic order temperature of Ga salt.

8. Electronic structure of Fe salt

Three Anomalies of Fe salt

There is no transition at 60 K (T_{MI} of Ga salt)

$T \sim 40$ K

Below this temperature, resistivity increases.

$T_{MI} \sim 20$ K

M-I transition temperature.

Same as Magnetic ordering temperature of Ga salt.

⇨Fe salt also has magnetic ordered insulating π-system?

$T_N \sim 11$ K

Antiferromagnetic (AF) transition temperature of Fe^{3+} ion.

Additional increase of resistivity (π-d interaction)

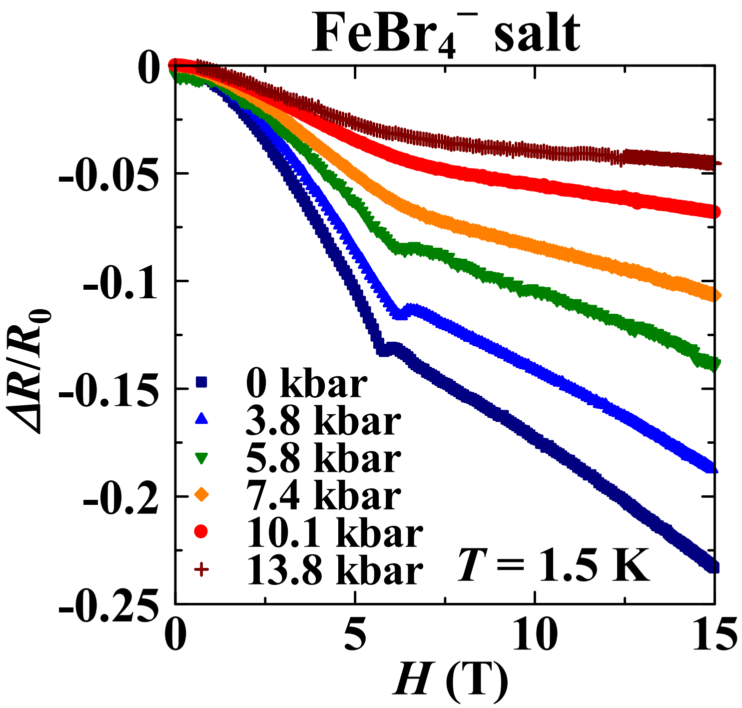
No charge ordering transition?

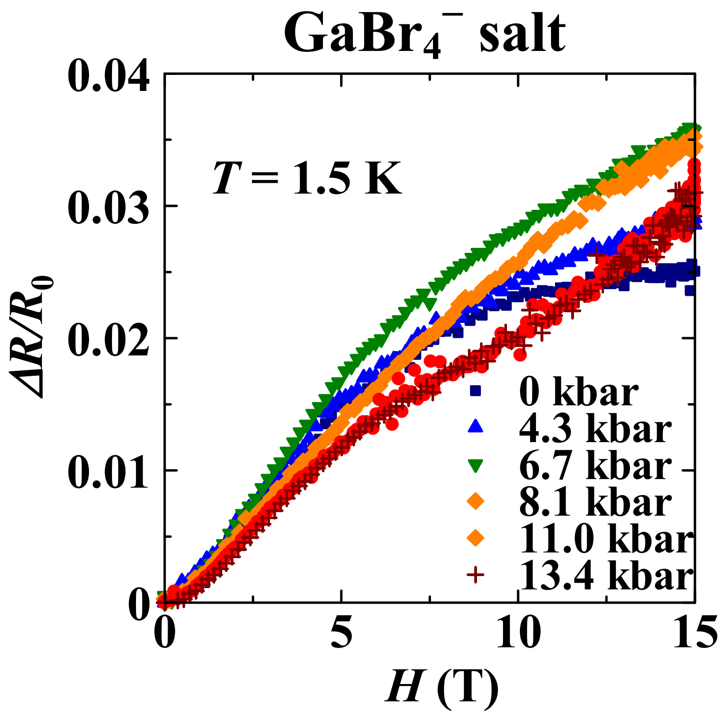
Can electrons move through *d*-orbital of Fe^{3+} ions?

(cf. Ga^{3+}:$(e_g)^4(t_{2g})^6$ closed shell, Fe^{3+} :$(e_g)^2(t_{2g})^3$ open shell)

Increase of path may increase the dimensionality of the system, and metallic state becomes more stable.

9. Magnetoresistances (*I* || *a*, *H* || *b*)





Large negative MR (Fe)
Anomaly at spin flop field (Fe)
Weak positive MR (Ga)

→ **Evidences of Strong π-d interaction!**

10. Origin of large negative magnetoresistance

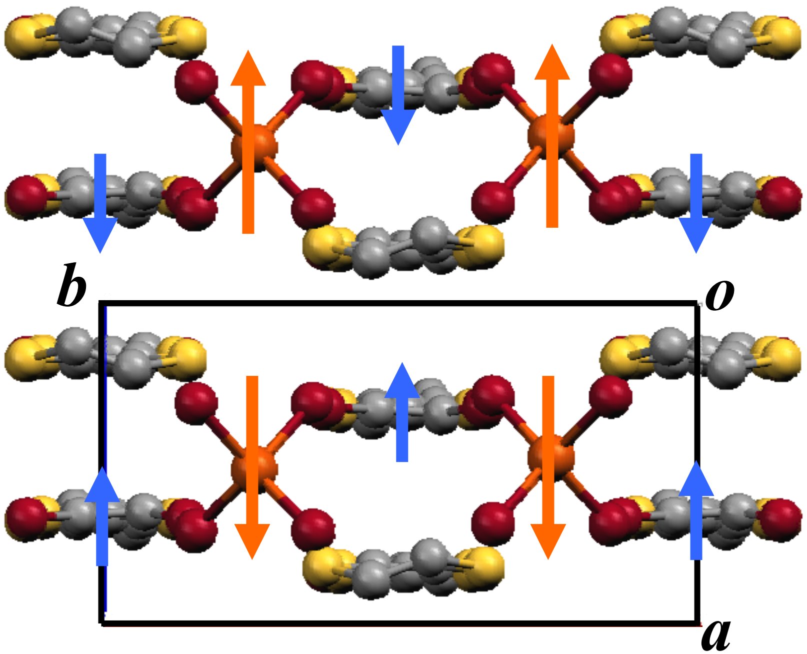
Strong π-d interaction
Magnetic ordered π-system (suggested)

} Combined Magnetic System

Period of AF anion
is equal to
Nesting vector of π-system

AF anions enhance the gap of magnetic ordered π-system

Expected magnetic structure



High magnetic field region
Enhancement of gap disappears.

Large Negative MR

11. Summary

Brominated donor

⇨ **Short donor-anion distances**

⇨ **Strong π-d interaction!**
- **Negative MR**
- **High T_N of $FeBr_4^-$**

Phase Diagram