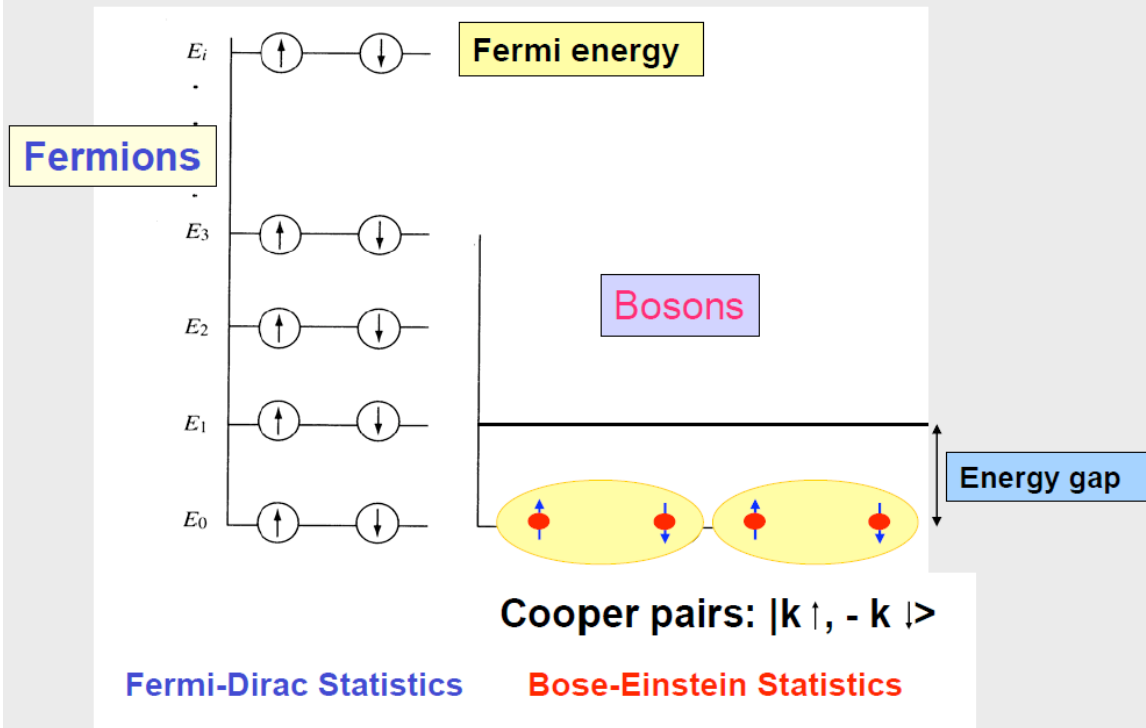


超伝導(BCS理論)の概念



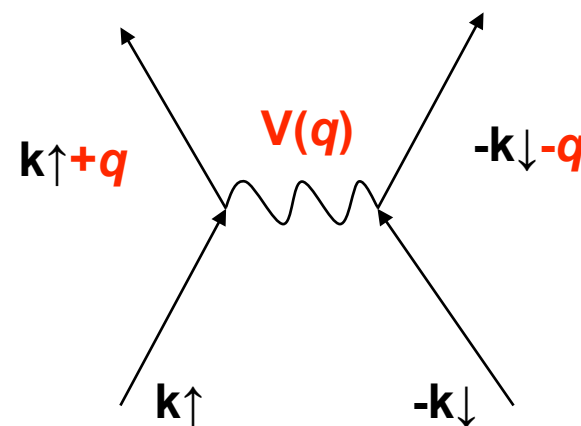
常伝導状態

電子は基底状態からフェルミ統計に従い状態を占めていく

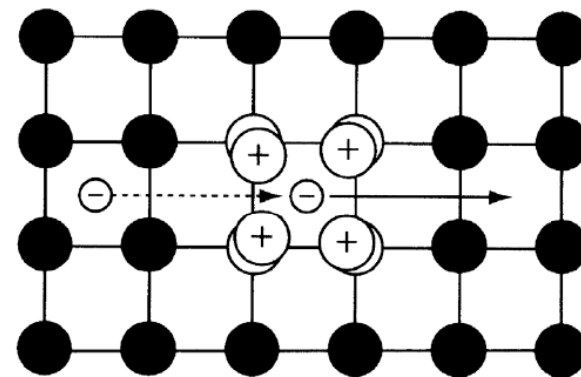
超伝導状態

$k \uparrow$ と $-k \downarrow$ がボーズ粒子となる対を組み基底状態に落ち込む

2電子 $|k \uparrow, -k \downarrow\rangle$ 間の引力

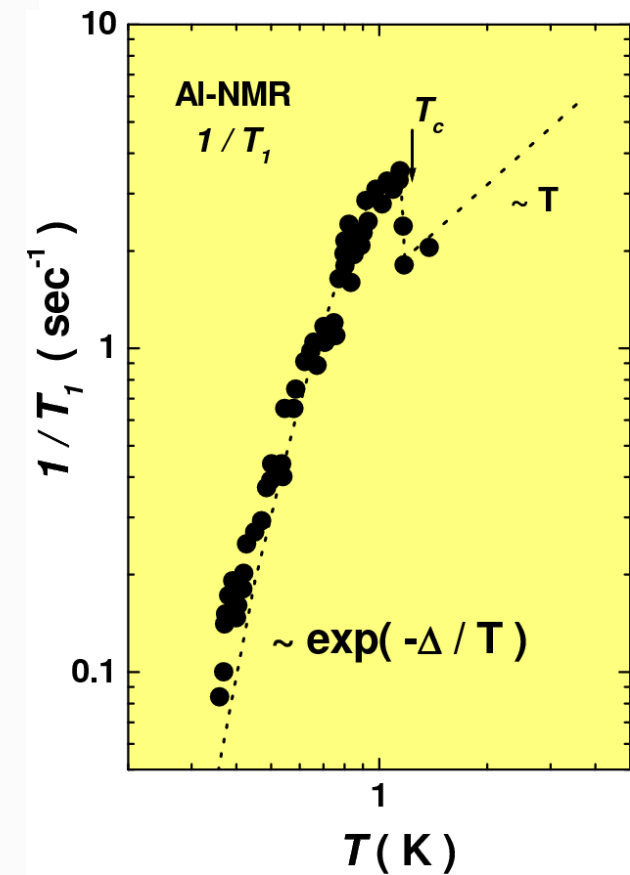
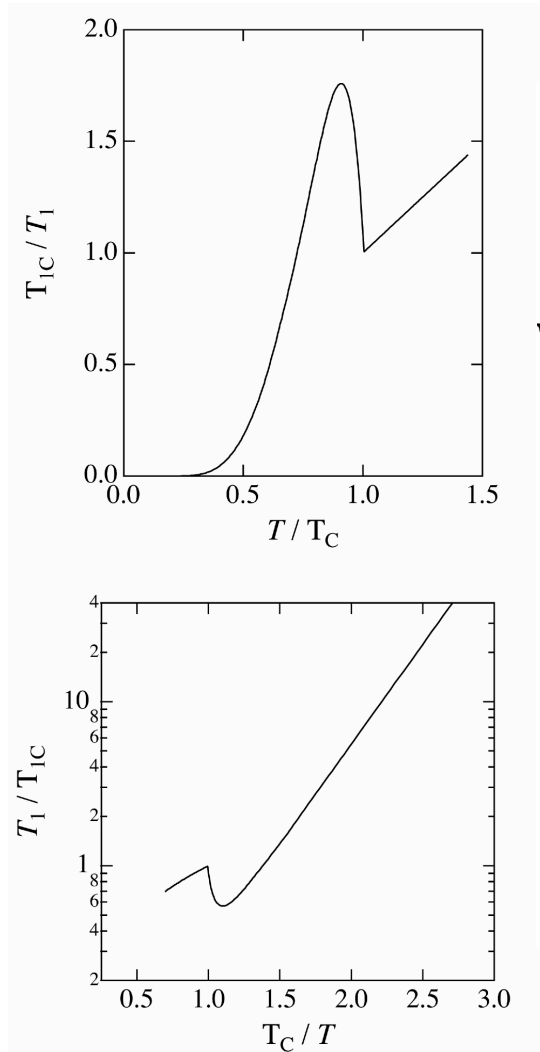
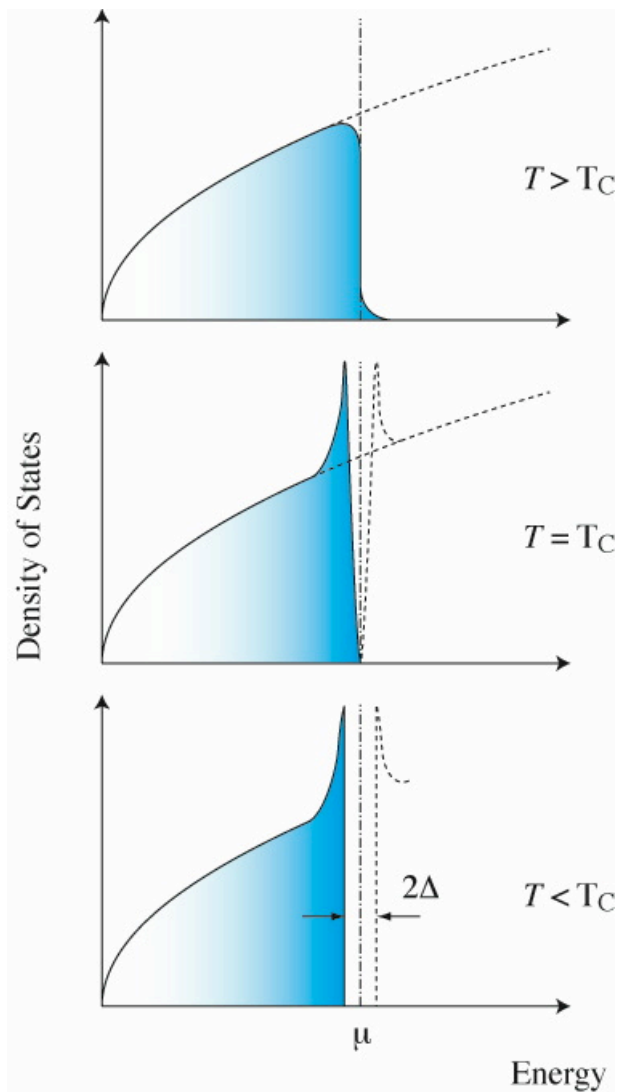


2電子間に働く引力の概念図



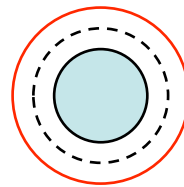
量子化された格子振動(フォノン)

BCS-Type



$$T \ll T_c: 1/T_1 \propto \exp\left(-\frac{2\Delta_0(0)}{k_B T}\right)$$

$$2\Delta_0(0) \cong 3.5 k_B T_c$$



**Uniform gap
formation
Isotropic gap**

**Y. Masuda and A.
Redfield, Phys. Rev.
133 A944 ('64)**

**→ s-wave super-
conductor**

超伝導対の波動関数

P.W. Anderson and P. Morel, *PR* 123
1911('61) "Generalized BCS State..."

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) = \chi(\sigma_1, \sigma_2) \cdot \psi(\mathbf{r}_1, \mathbf{r}_2)$$

Spin part **Orbital part**

Spin part: $S = 0$ スピン一重項

$$\chi^{S=0} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

$S = 1$ 三重項

$$\chi^{S=1} = |\uparrow\uparrow\rangle, \quad \left(1/\sqrt{2}\right)(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad |\downarrow\downarrow\rangle$$

スピン三重項超伝導

Orbital part: $\psi(\mathbf{r}_1, \mathbf{r}_2)$ $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ $\psi(\mathbf{r})$

$$\left(-\frac{\hbar^2}{m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$V(r)$ が異方的な場合、超伝導対の波動関数も異方的になる

$$\psi(r) \propto \underline{Y_l^m(\theta, \varphi)}$$

球面調和関数

$$\Delta_l = \Delta_0 \sum_{m=-l}^l \lambda_{lm} Y_l^m(\theta, \varphi)$$

$$l = 0, \quad l = 1, \quad l = 2, \quad l = 3, \dots\dots$$

s -波, p -波, d -波, f -波

異方的な超伝導ギャップ

異方的超伝導対

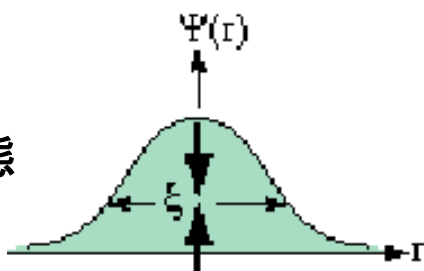
スピン状態

一重項

軌道状態

s 波

スピン状態

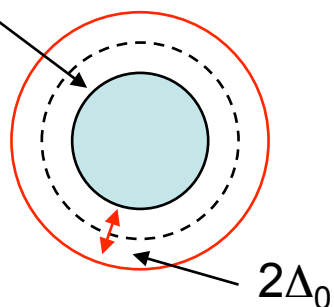


波動関数の広がり



フェルミ面

ギャップ関数



原点に振幅を持たない

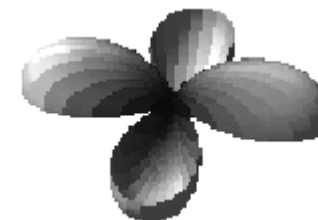
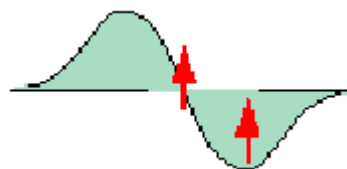
強相関電子系
の特徴

三重項

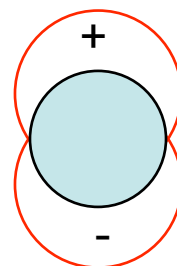
一重項

p 波

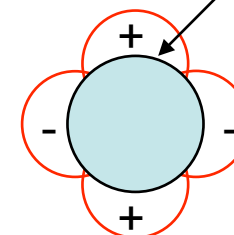
d 波



2D フェルミ面

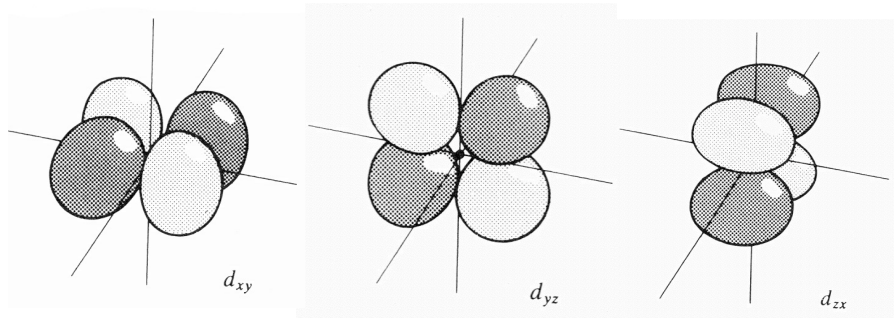
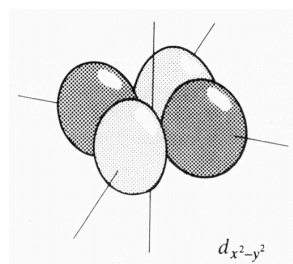
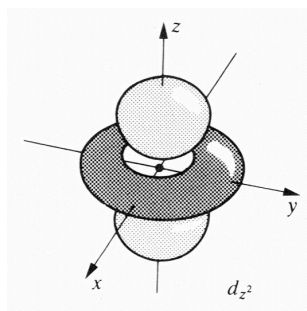
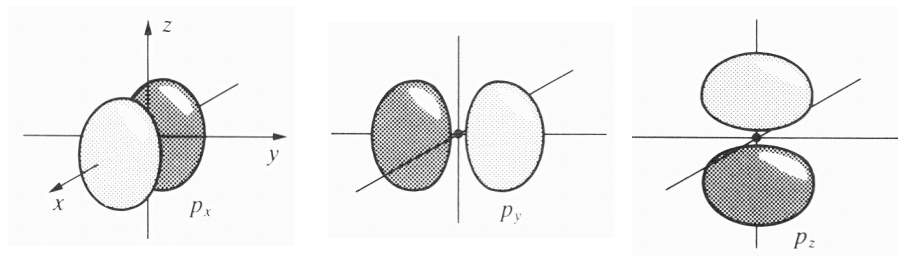


$$\Delta(\theta) = \Delta_0 \cos \theta$$

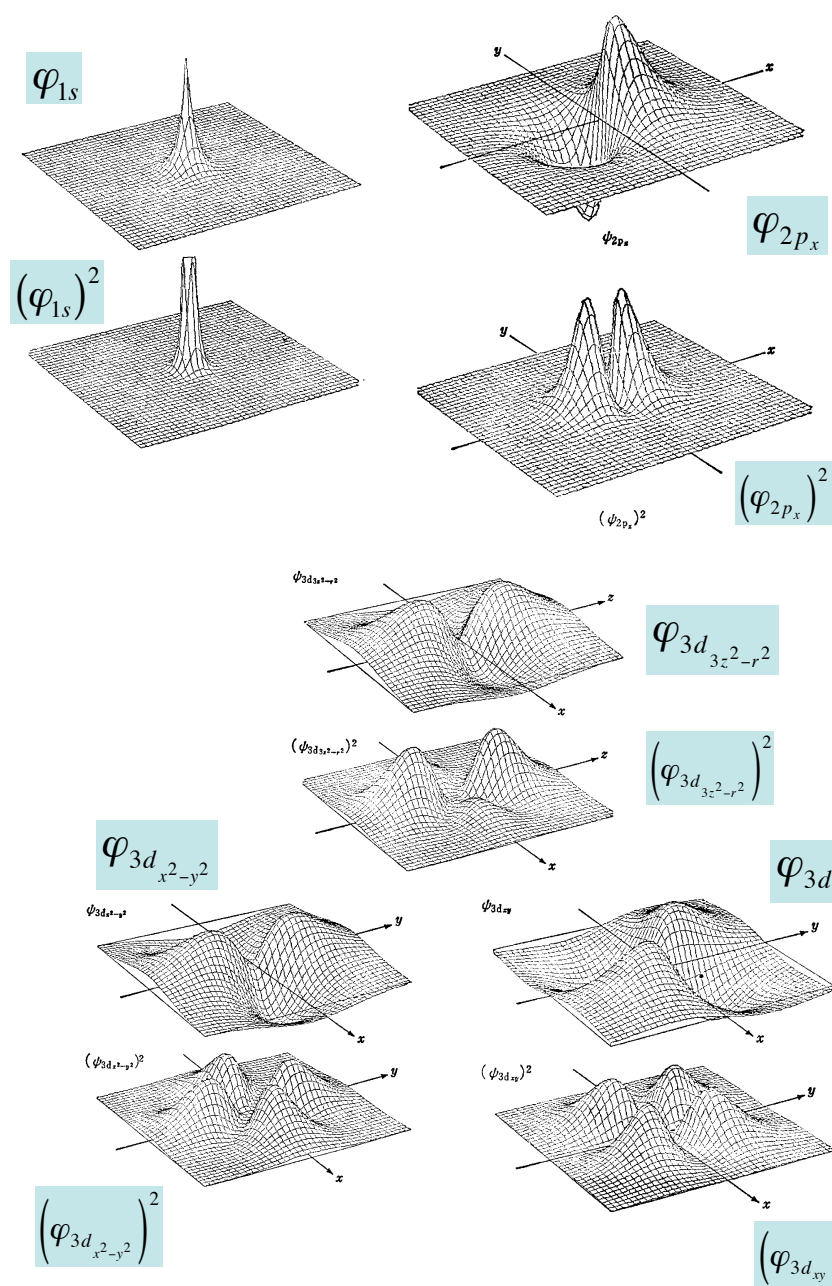


$$\Delta(\theta) = \Delta_0 \sin(2\theta)$$

電子軌道

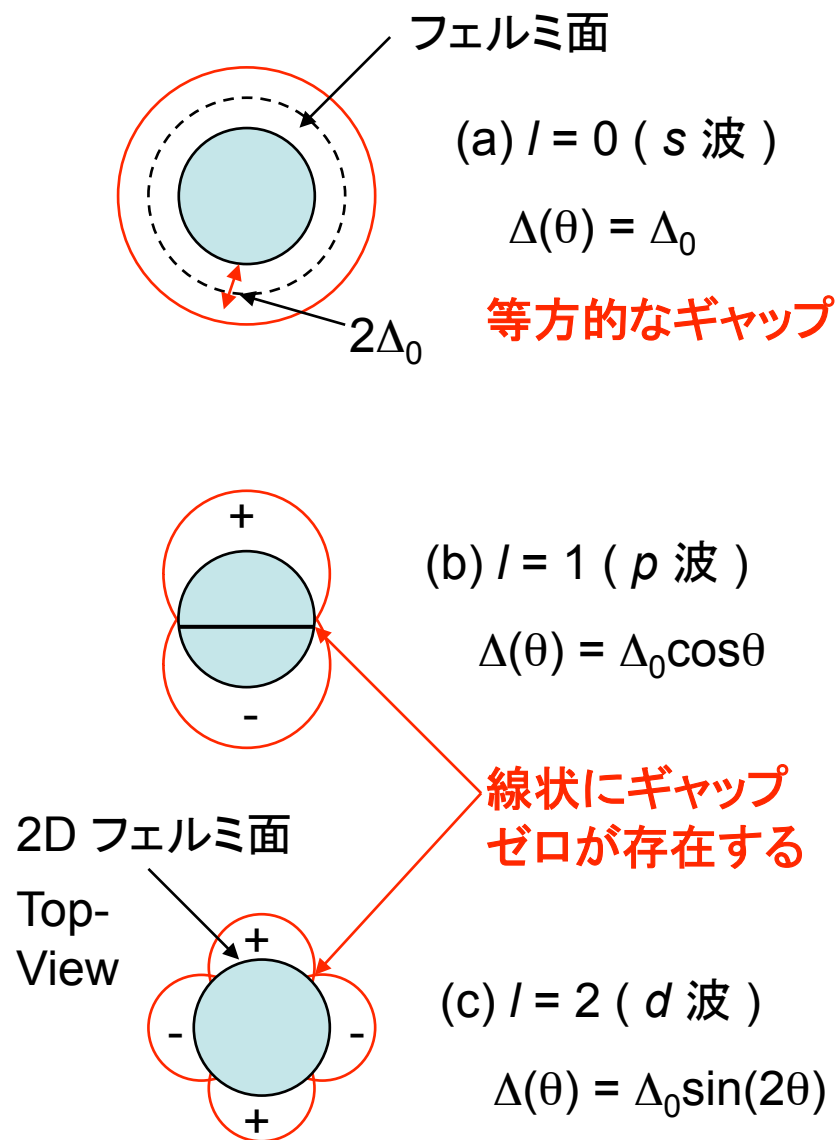


波動関数の角度依存

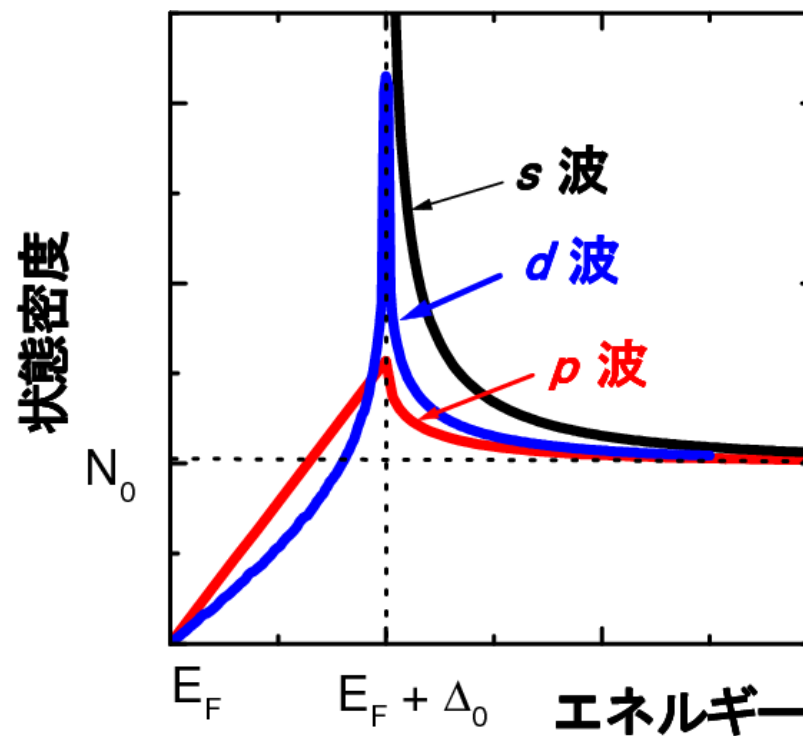


波動関数の形

異方的超伝導ギャップ



超伝導状態状態の状態密度



異方的超伝導ギャップの特徴

超伝導ギャップ内に連続的に状態を持つ $N(E) \propto E$

➡ 超伝導状態の物理量が温度のべき乗となる。

強相関電子系超伝導の相図

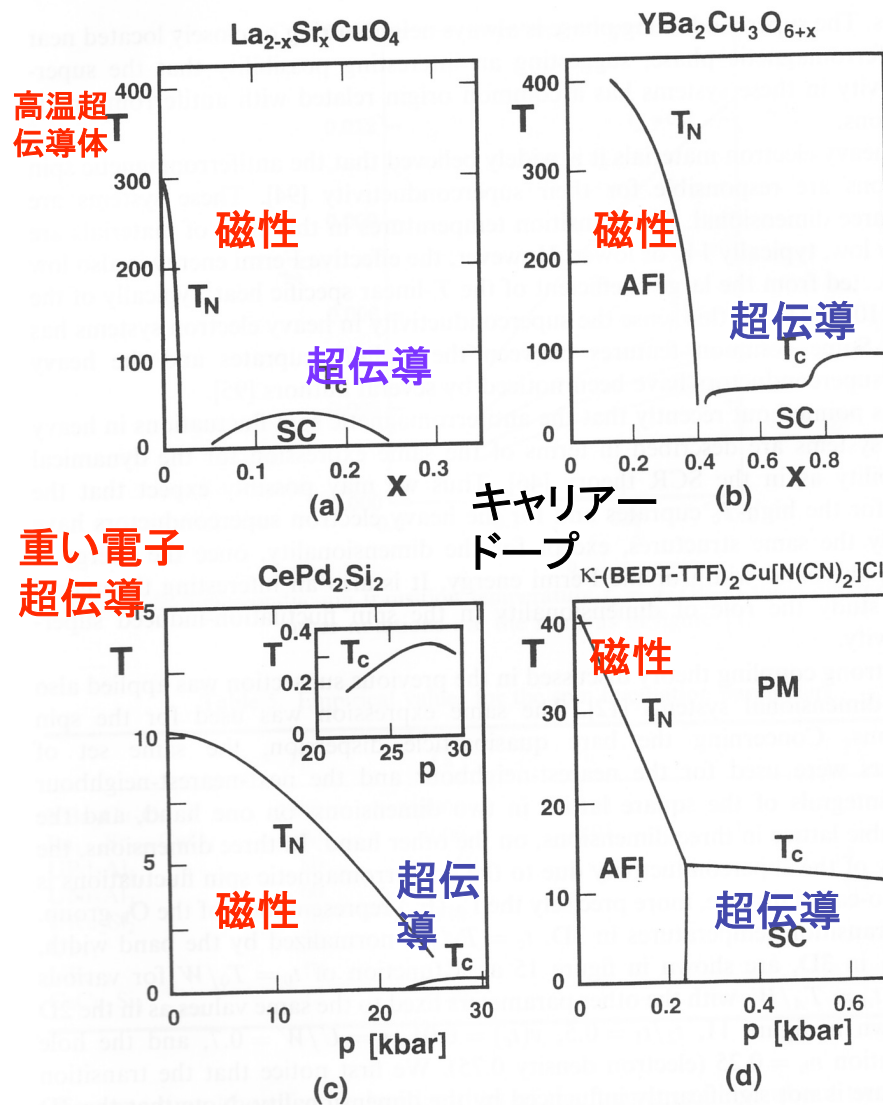


Figure 14. Phase diagrams of high- T_c cuprates, (a) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and (b) $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, (c) a heavy electron superconductor CePd_2Si_2 under pressure p and (d) an organic superconductor $\text{K}-(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ under pressure. T_N : Néel temperature, AFI: antiferromagnetic insulator, SC: superconductor, PM: paramagnetic metal.

強相関電子系物質

電子間のクーロン相互作用が強い系
磁気転移、モット転移(金属-絶縁体転移)近
傍の電子状態

共通点

- 異方的超伝導体である。
超伝導対の対称性(性質)が従来の
BCS超伝導体と性質を異にする

- 磁気相と超伝導が競合
(共存)している。

磁性と超伝導が密接に関係

$\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ の超伝導

“磁氣的Frustration”

Pyrochlore Oxide ($A_2B_2O_7$),
Spinel Oxide (AB_2O_4),
C15 Laves Phase (AB_2)

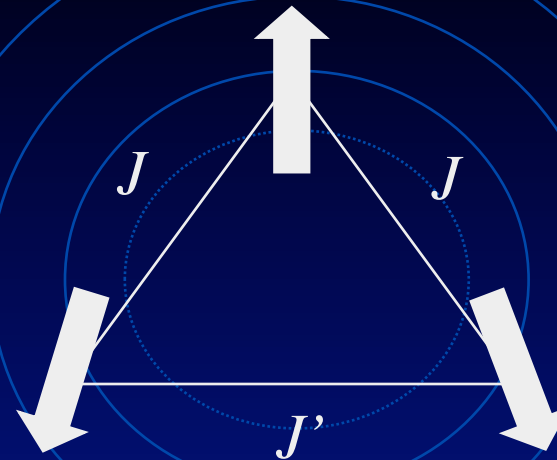
Geometrical Frustration
Spin Frustration
Charge Frustration

Magnetite Fe_3O_4 (Fe^{2+} and Fe^{3+})

Spinel Oxide AlV_2O_4
($V^{2.5-\delta}$ and $V^{2.5+3\delta}$)

High Degeneracy

Lattice Distortion, Spin-Ice, Spin-Singlet,
Heavy Fermion

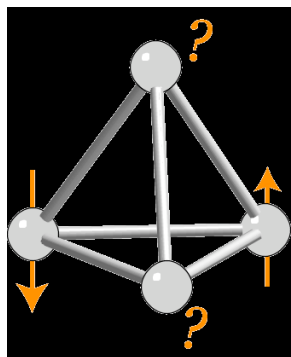
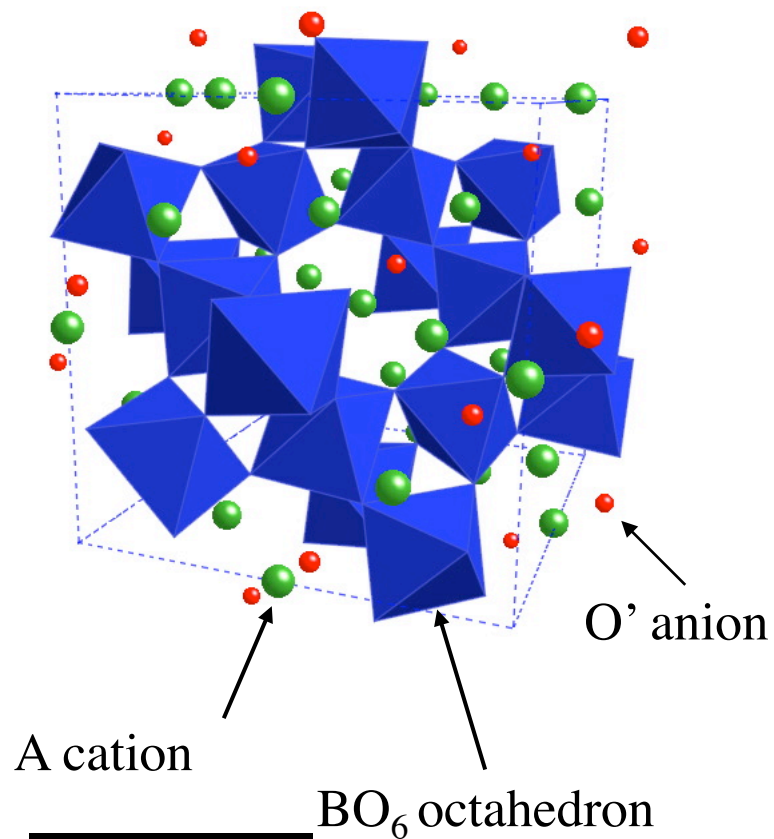


P. Laccore (1987)

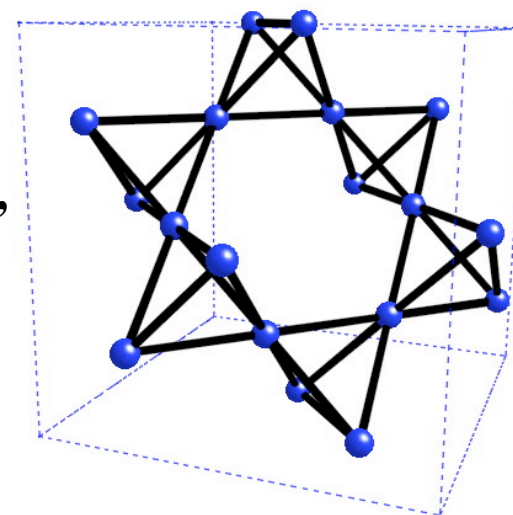
AF Triangular platelet < AF Pyrochlore

“低次元性 (Low Dimensionality)”

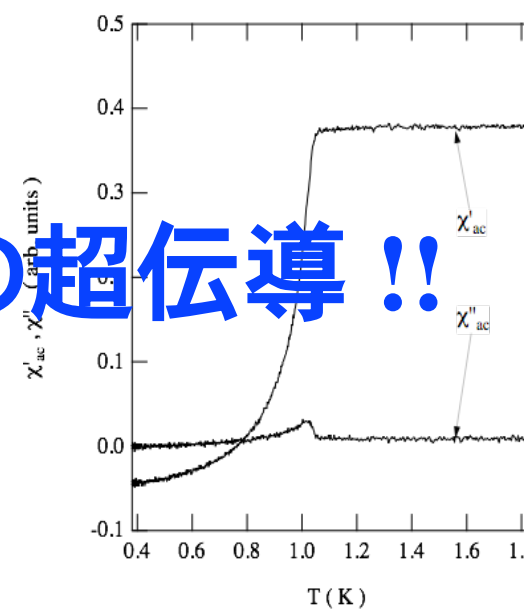
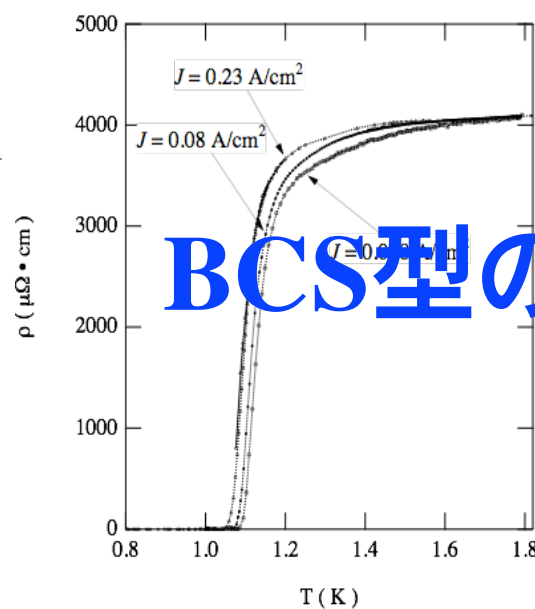
Pyrochlore $A_2B_2O_6O'$



“Pyrochlore Lattice”
of B Cation



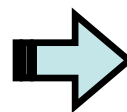
$Cd_2Re_2O_7$ の超伝導



BCS型の超伝導 !!

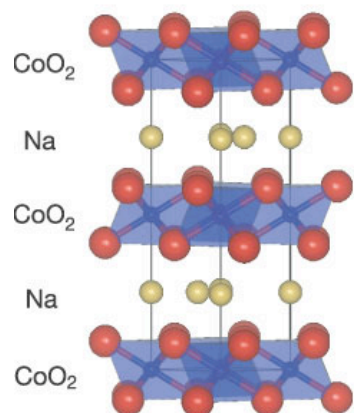
H. Sakai, K. Yoshimura et al., J. Phys. Condens. Matter 13 (2001) L785.

Introduction Takada, Sakurai *et al.* Nature **422** (2003) 53

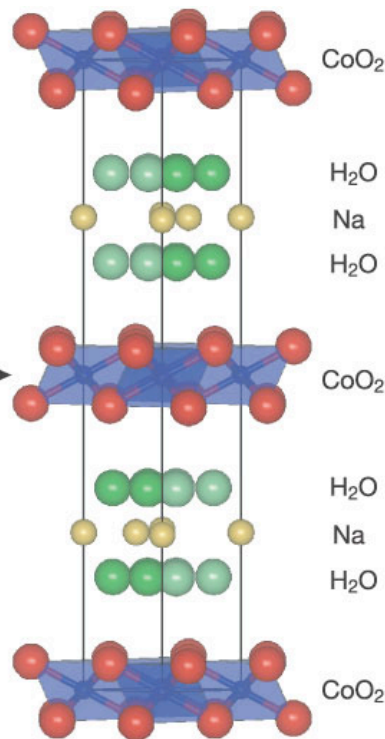


Bulk Superconductivity in
Layered structure with
CoO₂ layer, double H₂O layers and
partially occupied Na layer

Na_xCoO_2 ($x \sim 0.7$)
(mother compound)



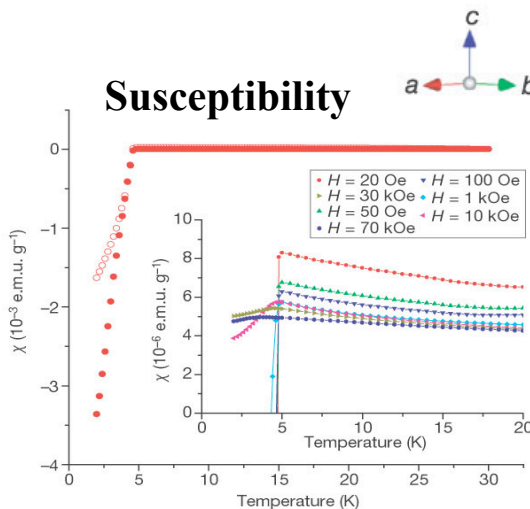
Oxidation
Process



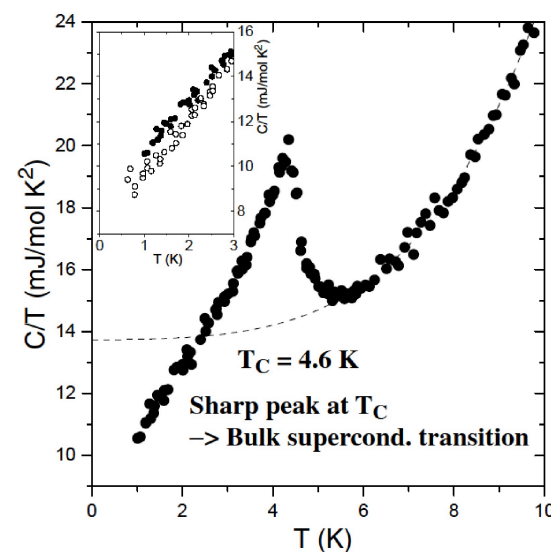
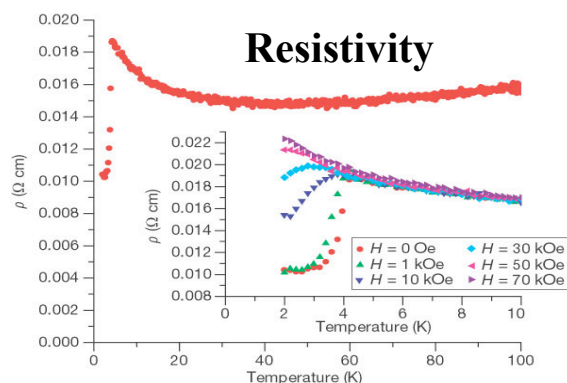
Co ions form **triangular lattice** in CoO₂ layer.

Crystal structure is different
from Cuprate and Ruthenate
superconductors.

Susceptibility



Resistivity

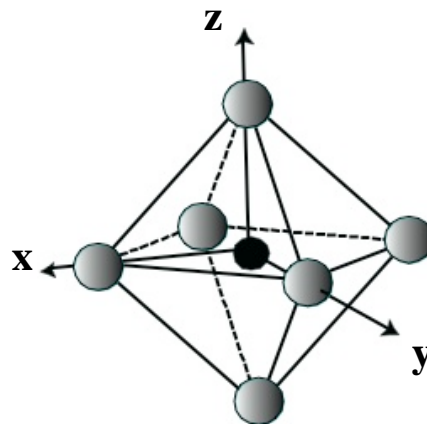
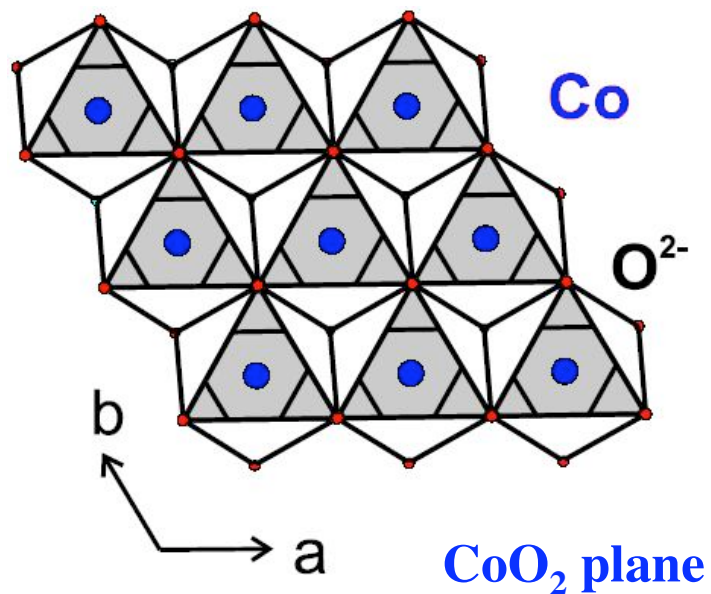


Specific Heat

$T_C = 4.6 \text{ K}$

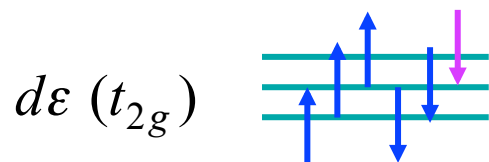
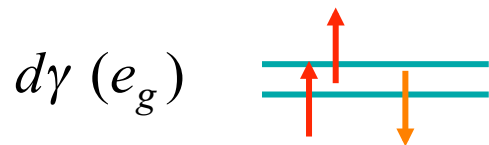
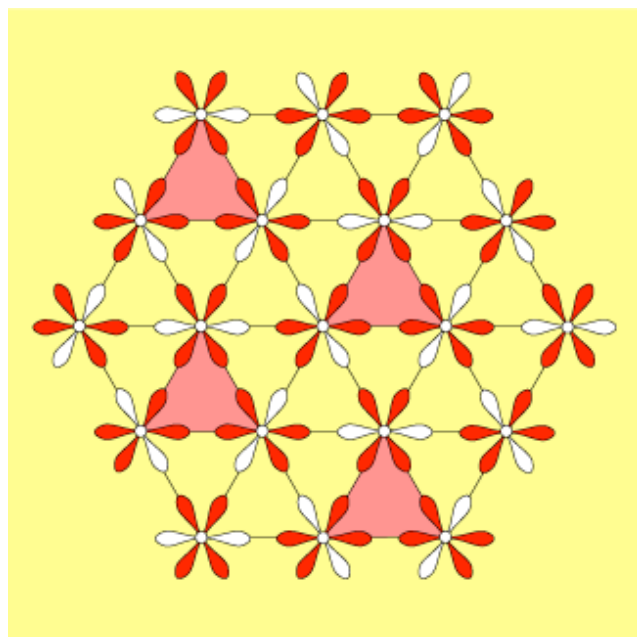
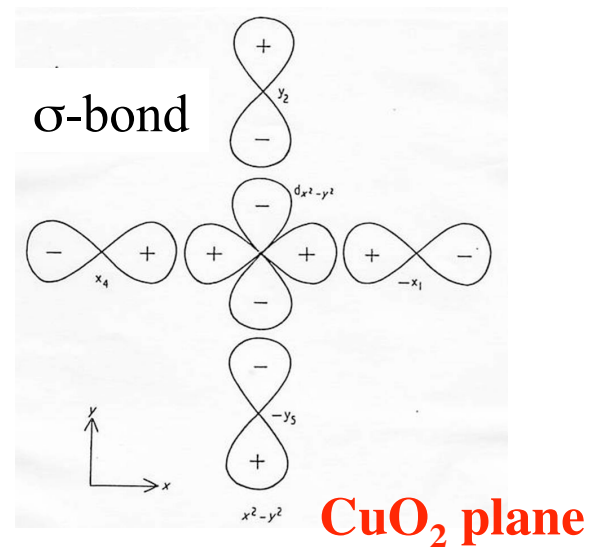
Sharp peak at T_C
→ Bulk supercond. transition

Cobaltate Superconductor



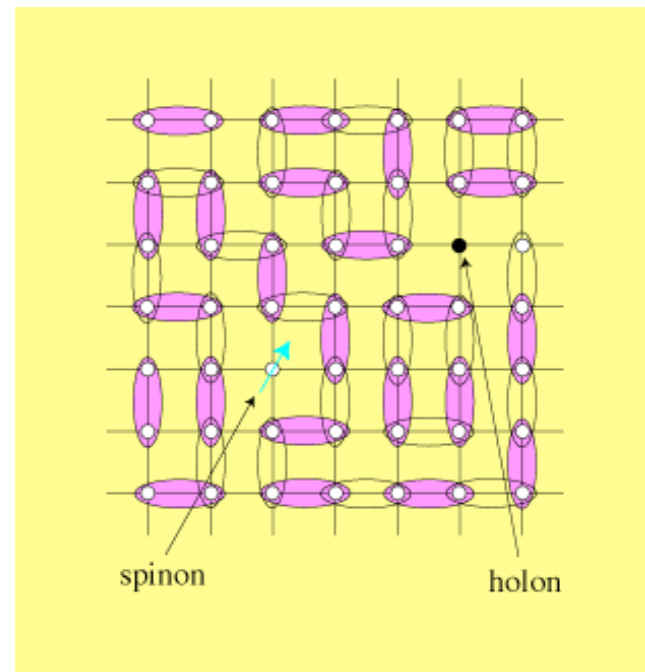
Superconductivity in
the strongly correlated
electron system

Cuprate Superconductor



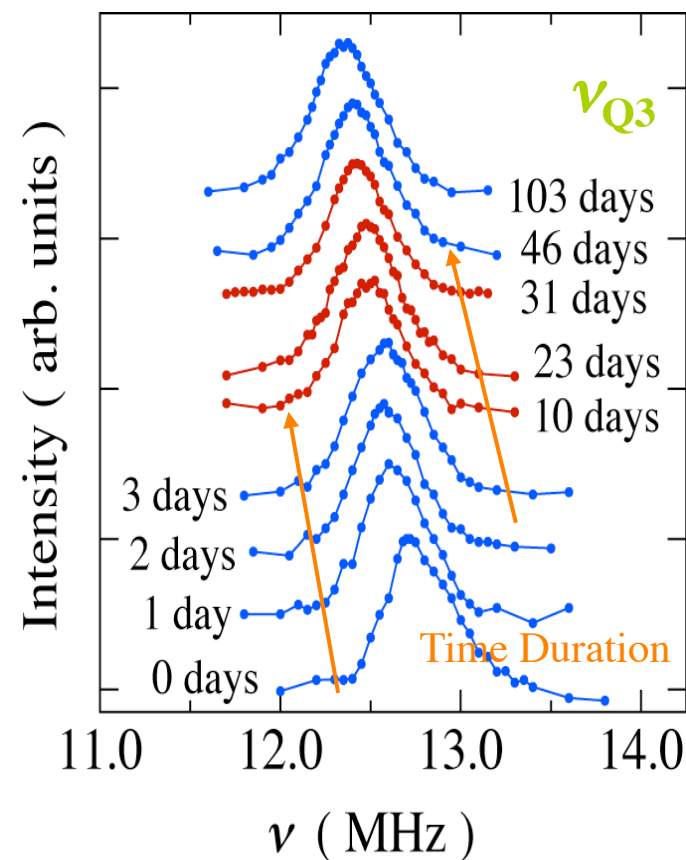
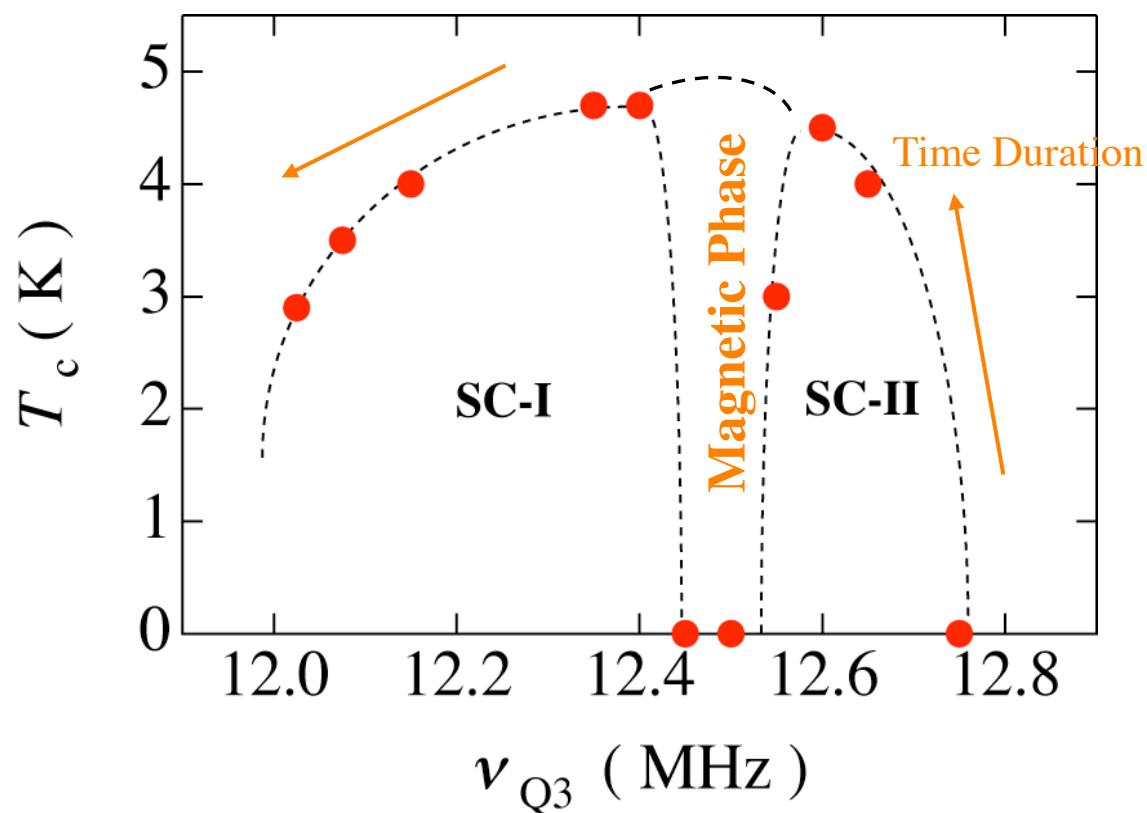
$Co^{4+}: 3d^5$
 $Co^{3+}: 3d^6$

$Cu^{3+}: 3d^8$
 $Cu^{2+}: 3d^9$



T_c vs. ν_{Q3} Phase Diagram of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

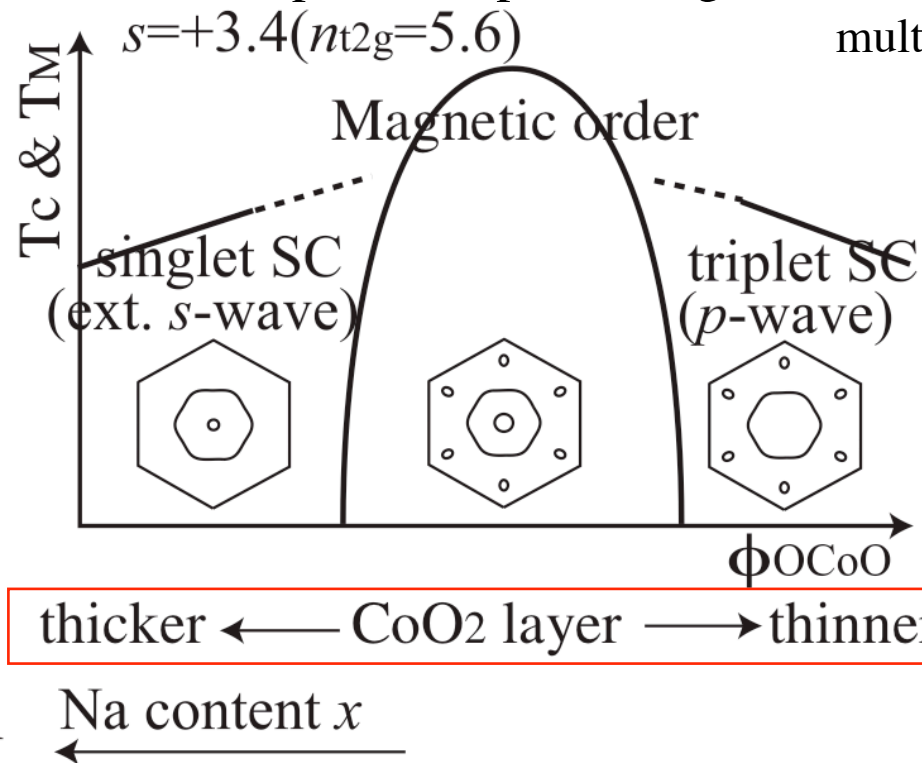
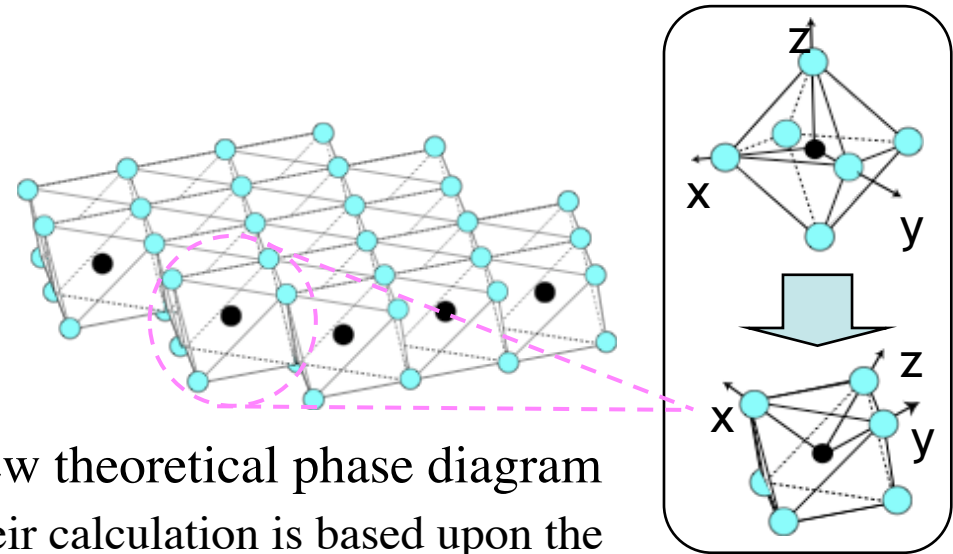
Reentrant Behavior of Superconductivity



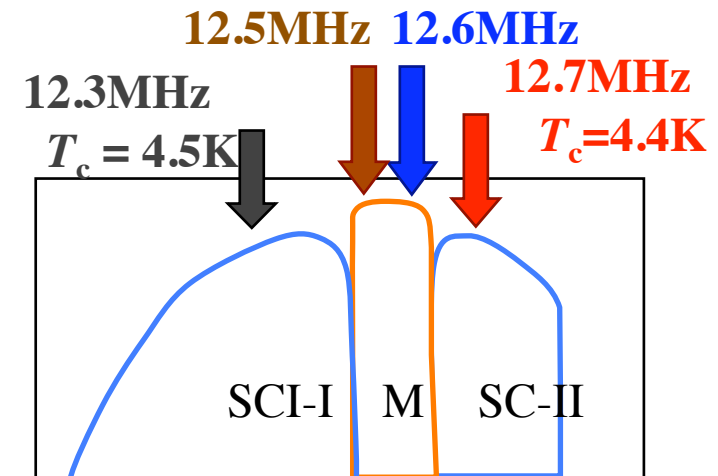
^{59}Co NQR Spectra at 77K

The Phase Diagram of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

Recently, Mochizuki & Ogata proposed new theoretical phase diagram in order to explain our phase diagram. Their calculation is based upon the multi-orbital model and RPA.



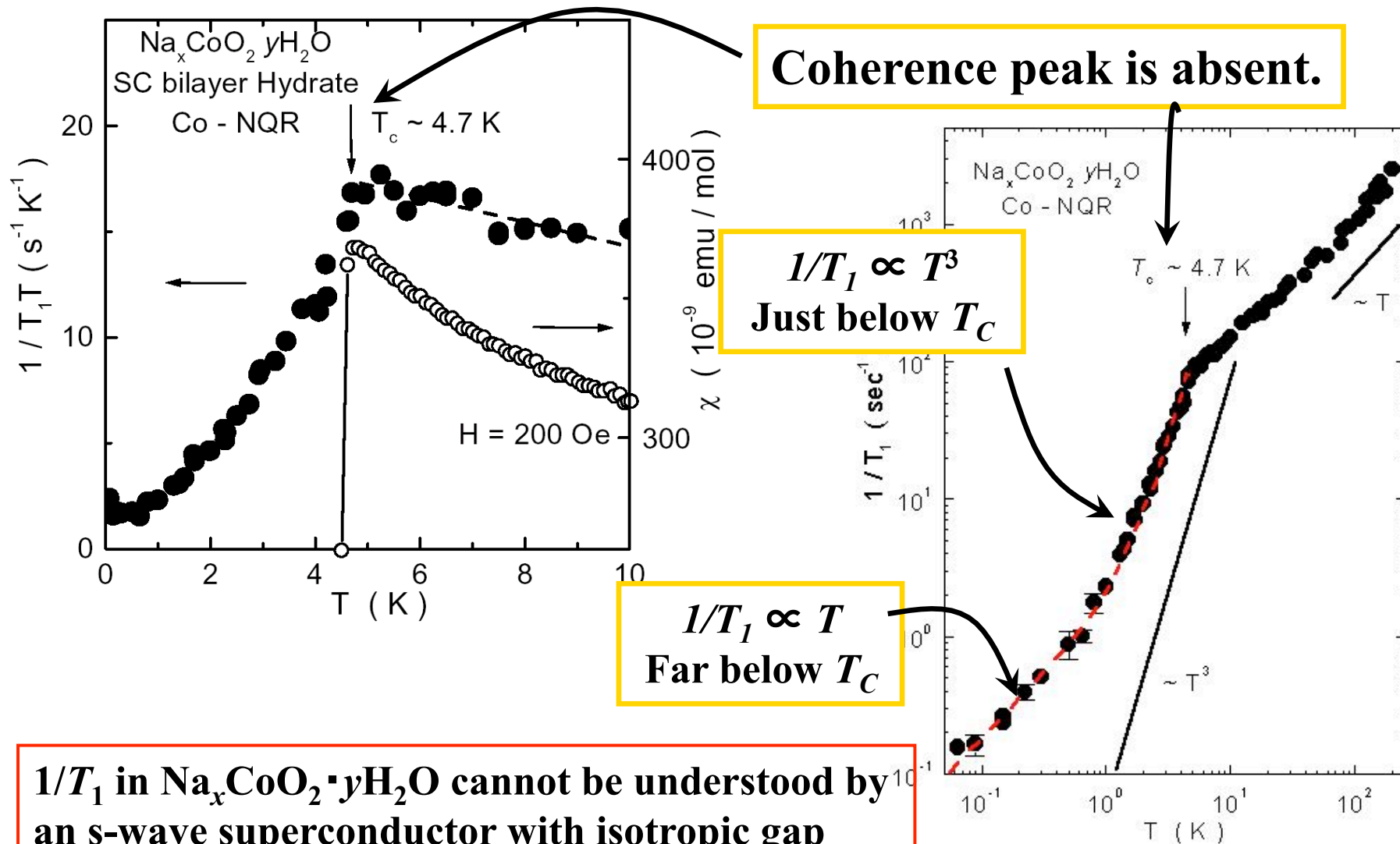
It is important to compare to the real phase diagram.



M. Mochizuki & M. Ogata: JPSJ 76 (2007) 013704.

Nuclear Spin-Lattice Relaxation Rate $1/T_1$: SC state

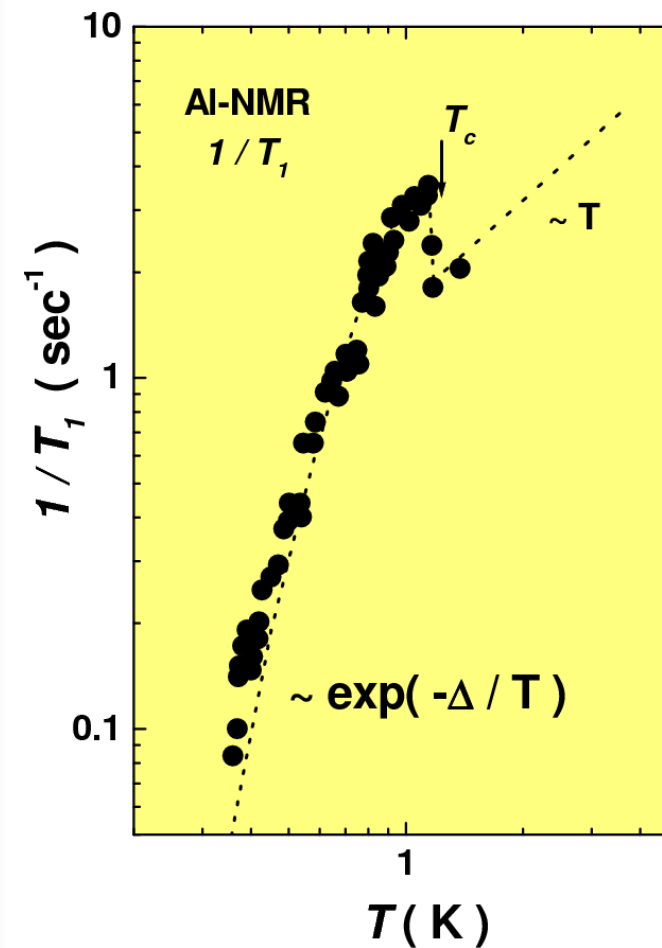
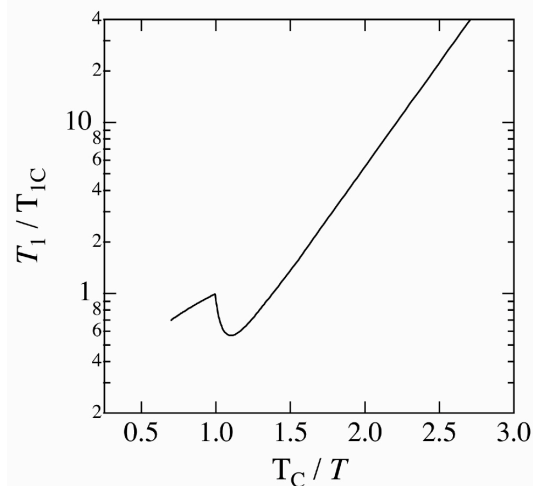
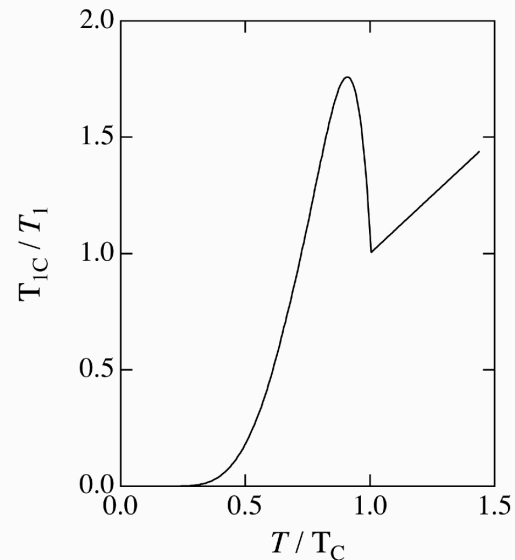
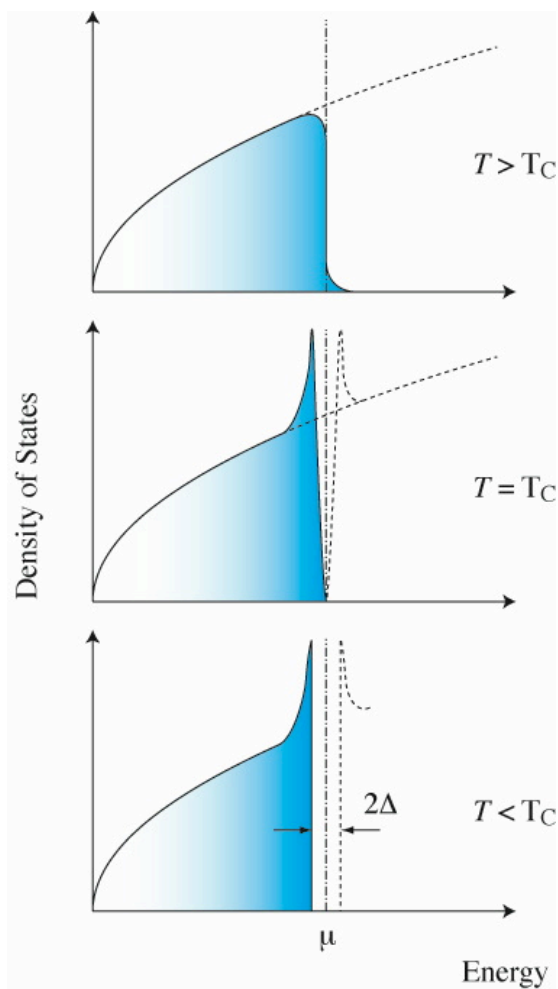
K. Ishida *et al.* J. Phys. Soc. Jpn 72 3041 (2003)



$1/T_1$ in Na_xCoO₂·yH₂O cannot be understood by an s-wave superconductor with isotropic gap

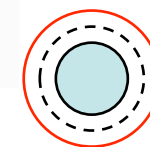
the same conclusion by Fujimoto *et al.* PRL 97 047004 (2004)

BCS-Type



$$T \ll T_c: 1/T_1 \propto \exp\left(-\frac{2\Delta_0(0)}{k_B T}\right)$$

$$2\Delta_0(0) \approx 3.5 k_B T_c$$

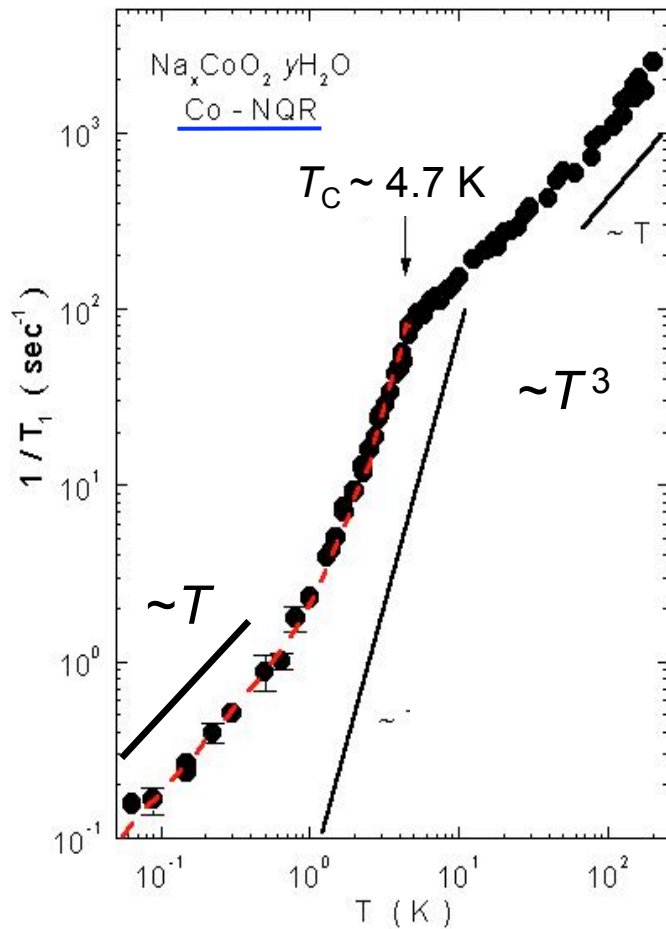


Uniform gap formation → s-wave super-conductor
Isotropic gap

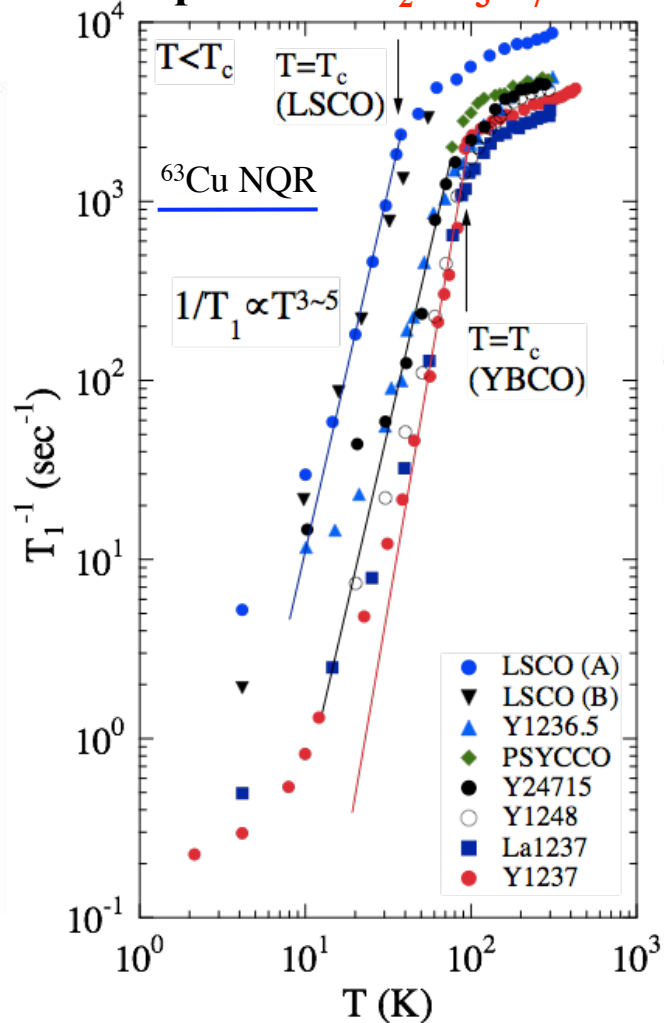
Y. Masuda and A. Redfield,
Phys. Rev. 133 A944 ('64)

Nuclear Spin-Lattice Relaxation Rate $1/T_1$: SC state

BLH Cobaltate $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

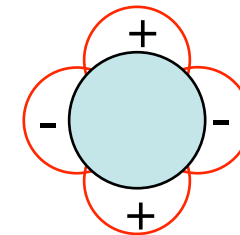
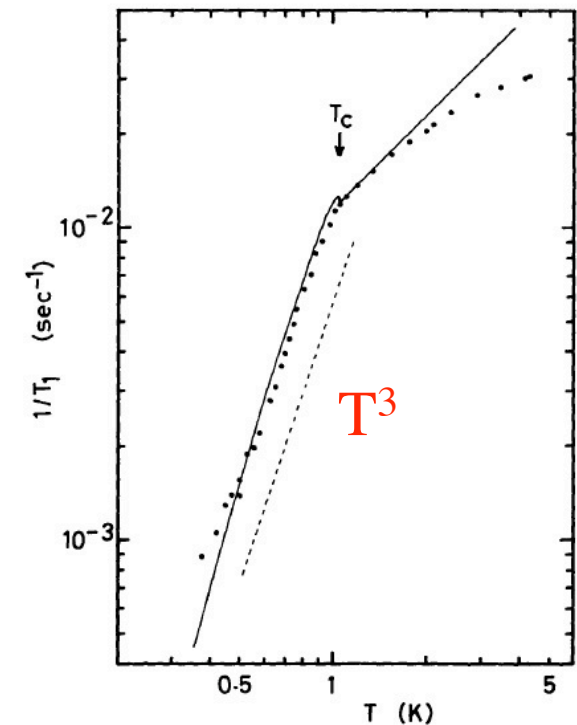


Cuprate $\text{YBa}_2\text{Cu}_3\text{O}_7$



Organic System

TMTSF ^1H NMR

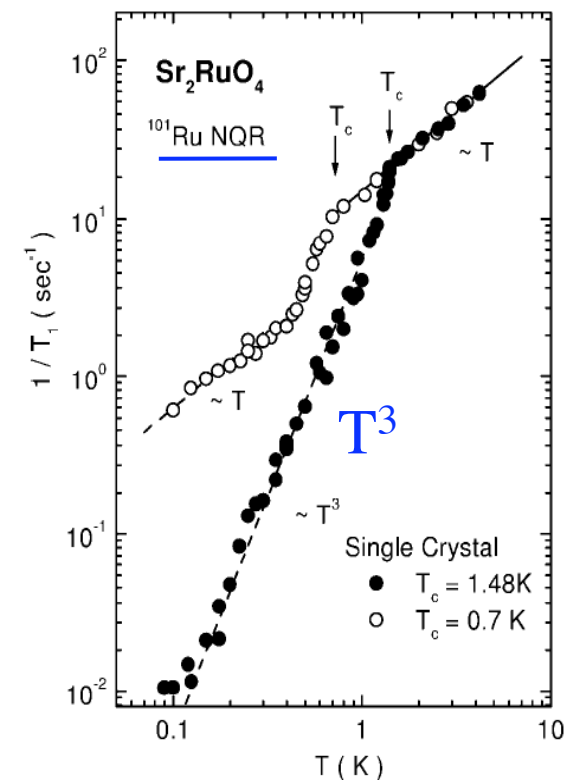
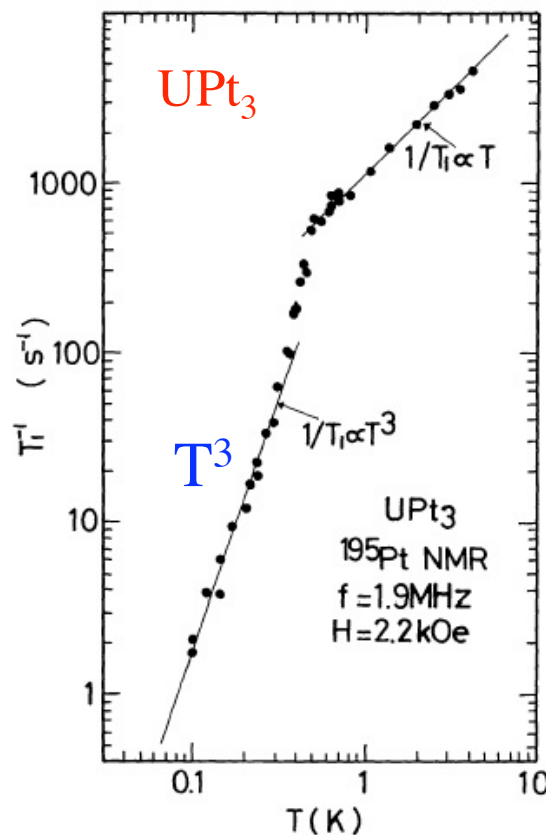
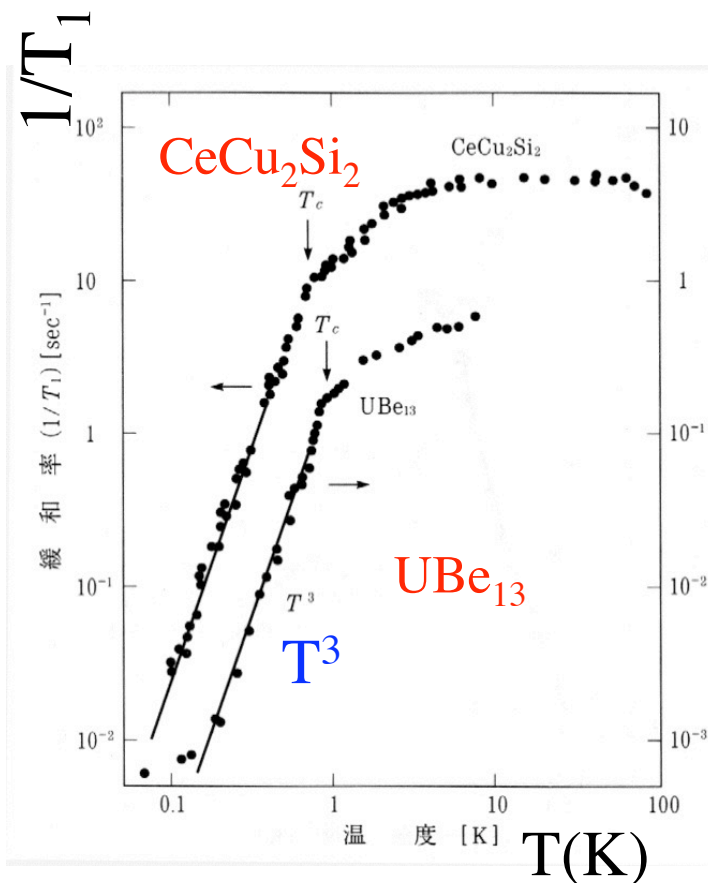


K. Ishida, Y. Ihara, K. Yoshimura *et al.*
JPSJ 72 3041 (2003)
Fujimoto *et al.* PRL 97 047004 (2004)

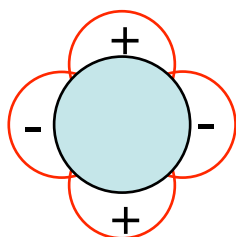
$\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is classified to be
an **unconventional superconductor**.

Heavy-Fermion Superconductors

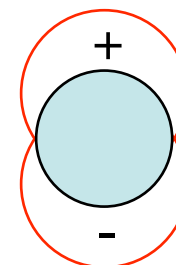
Ruthenate Sr_2RuO_4



K. Ishida *et al.*
PRL 84 5387 (2000)



$\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is classified to be an **unconventional superconductor**.



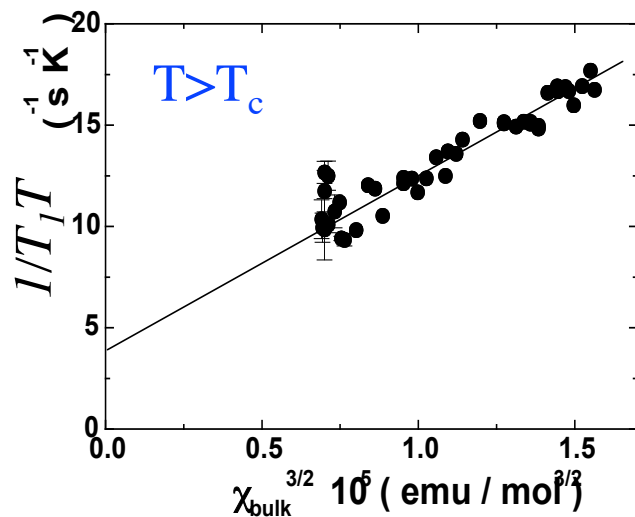
Magnetic Excitations in BLH, MLH and Unhydrated

Magnetic fluctuations above 100 K are similar in these cobaltate.

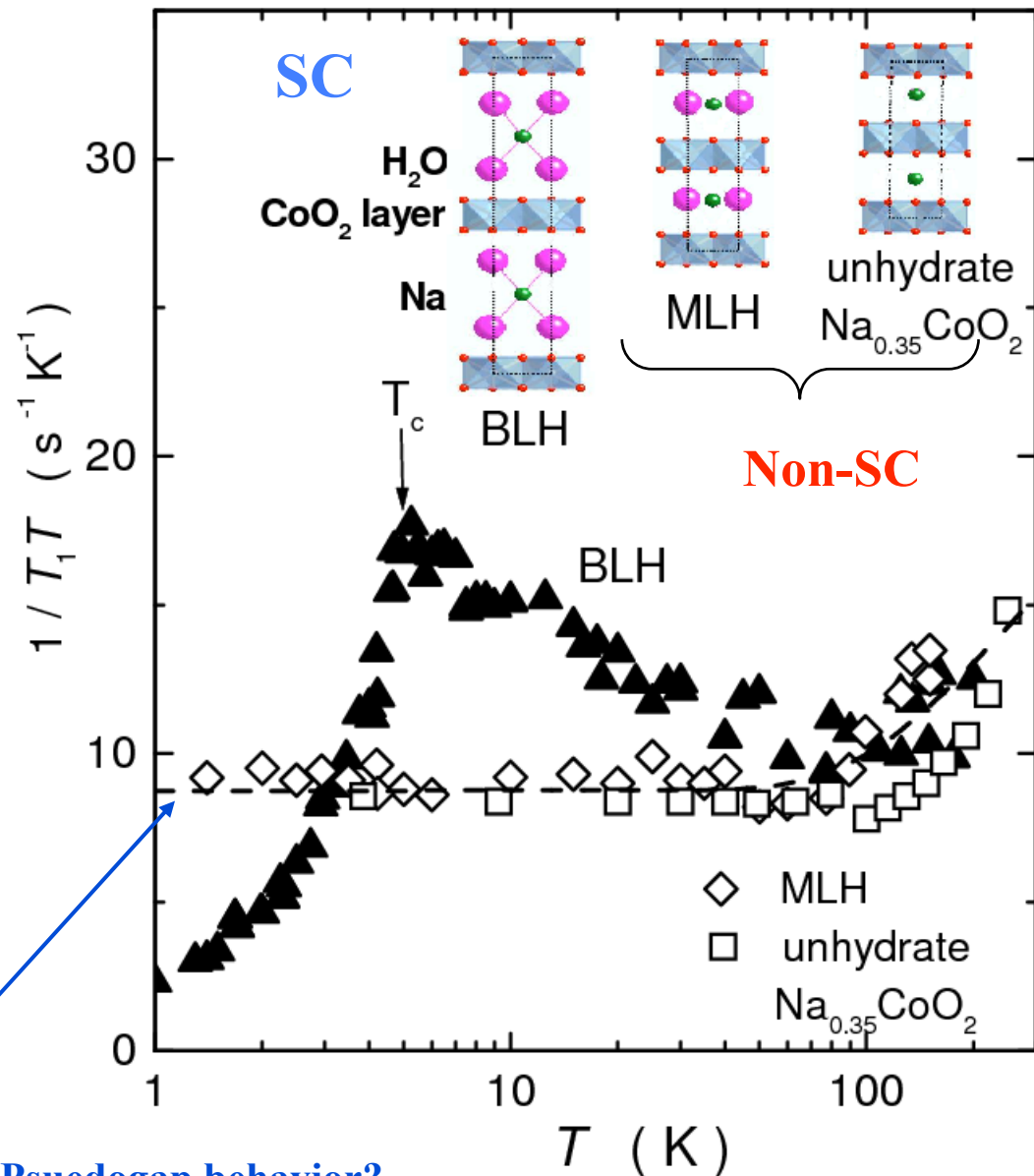
SC BLH shows the increase of $1/T_1T$ below 70 K

Two kinds of magnetic fluctuations in BLH

Ferromagnetic Fluctuation ($q \sim 0$)



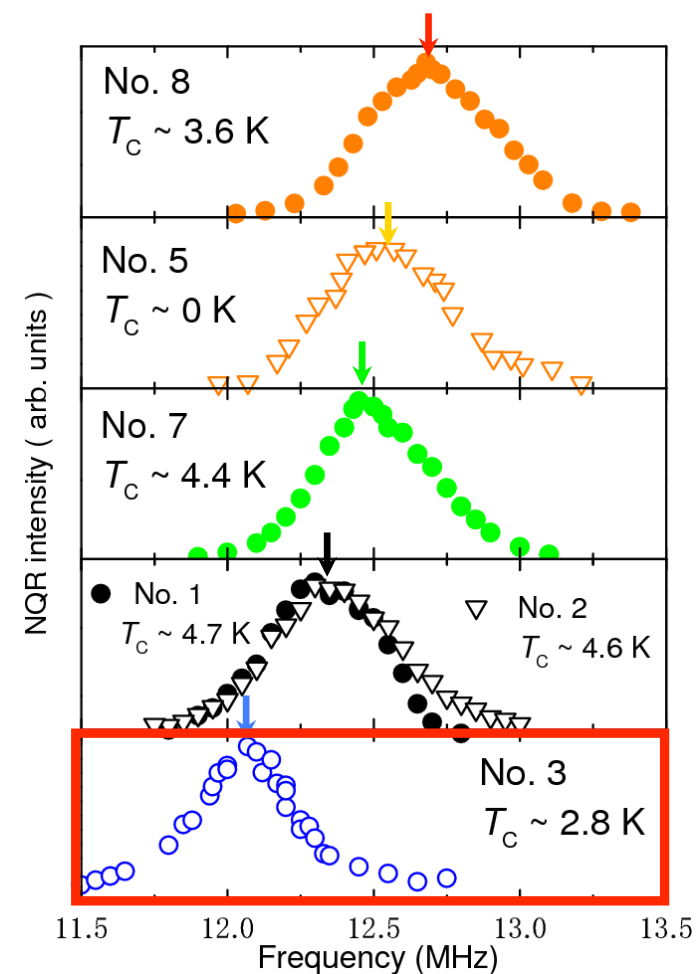
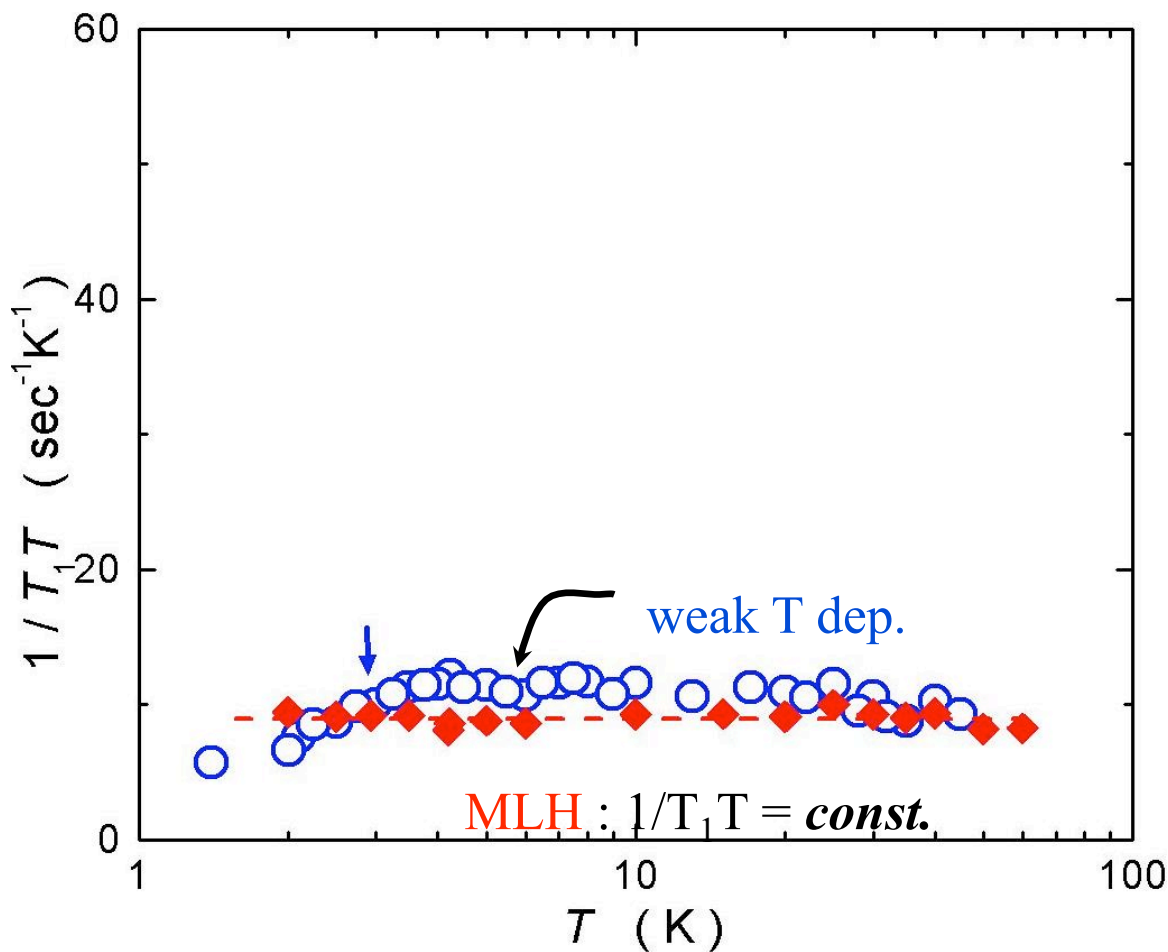
$$\left(\frac{1}{T_1T} \right)_{\text{MLH}} = 8.75 + 15 \exp \left(-\frac{\Delta}{T} \right) \quad (\text{sec}^{-1} \text{K}^{-1})$$



Pseudogap behavior?

$1/T_1T$: Nuclear spin-Lattice relaxation Rate

NQR Spectrum



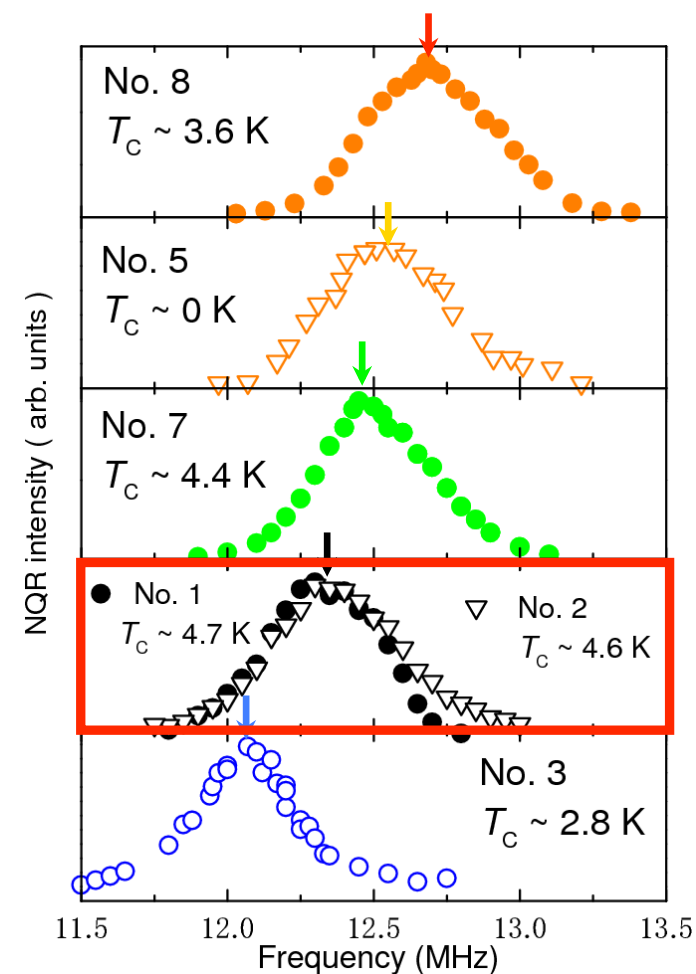
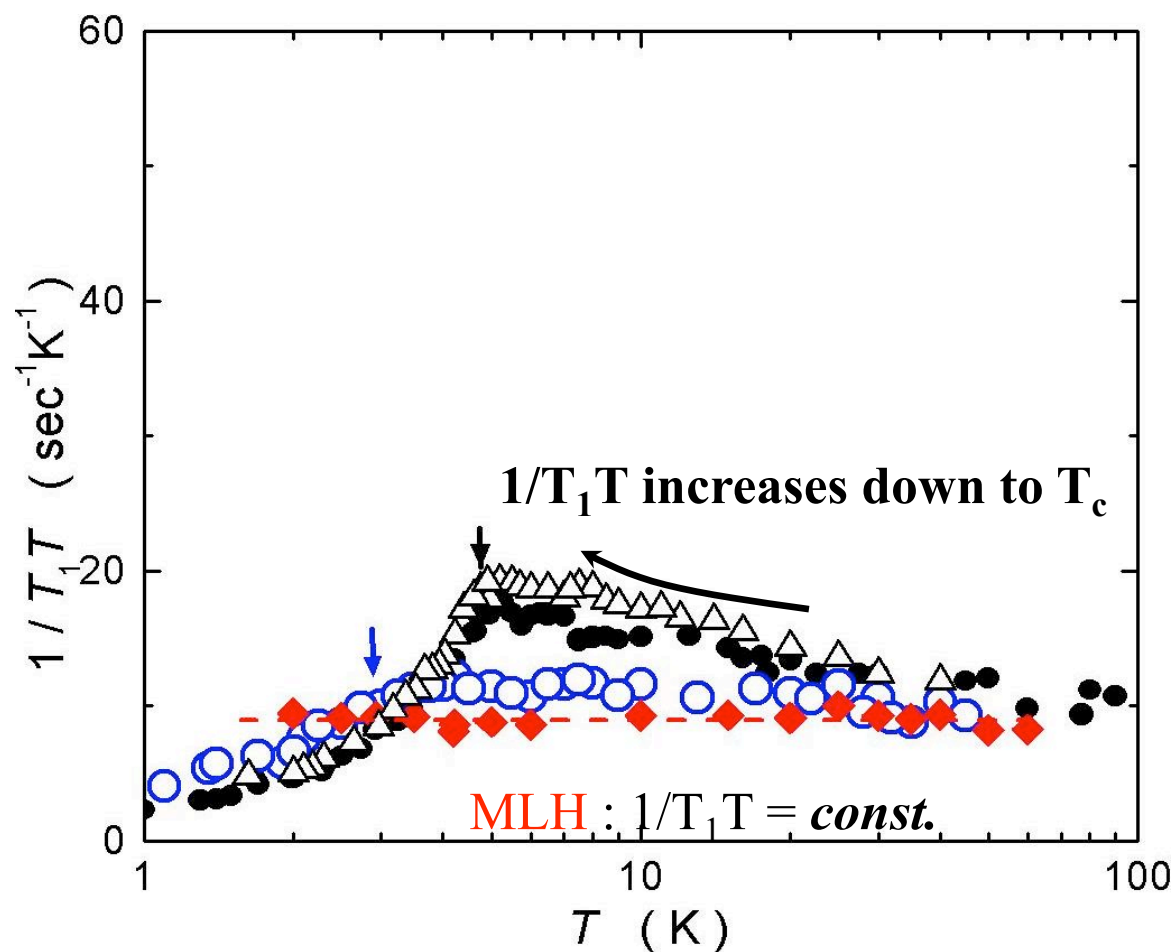
MLH $\text{Na}_{0.3}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$

non-SC down to 1.5 K

$1/T_1T$ is constant below 100 K

$1/T_1T$: Nuclear spin-Lattice relaxation Rate

NQR Spectrum



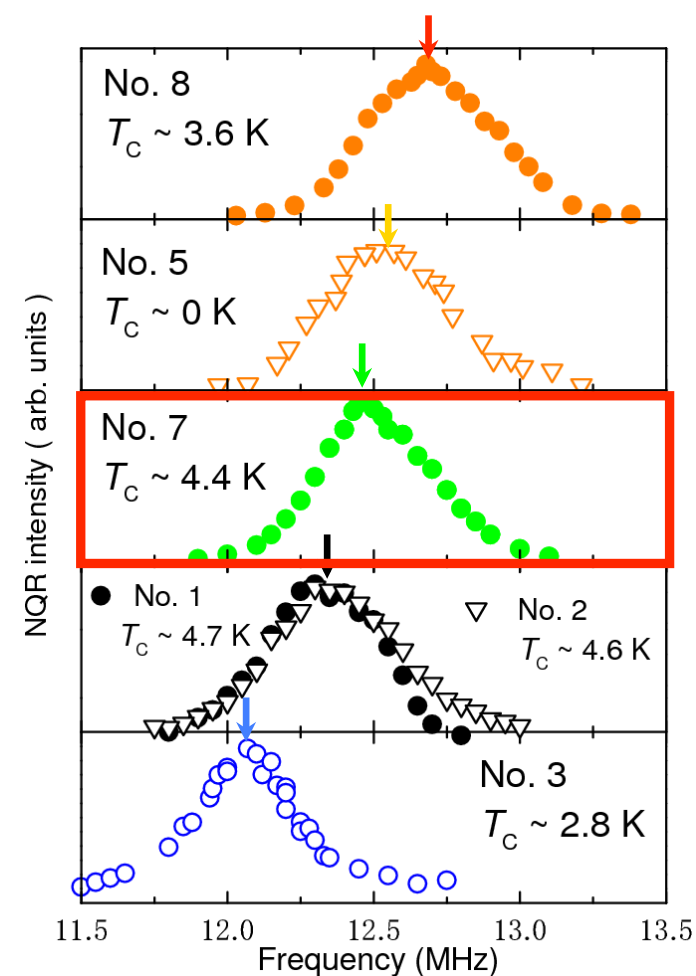
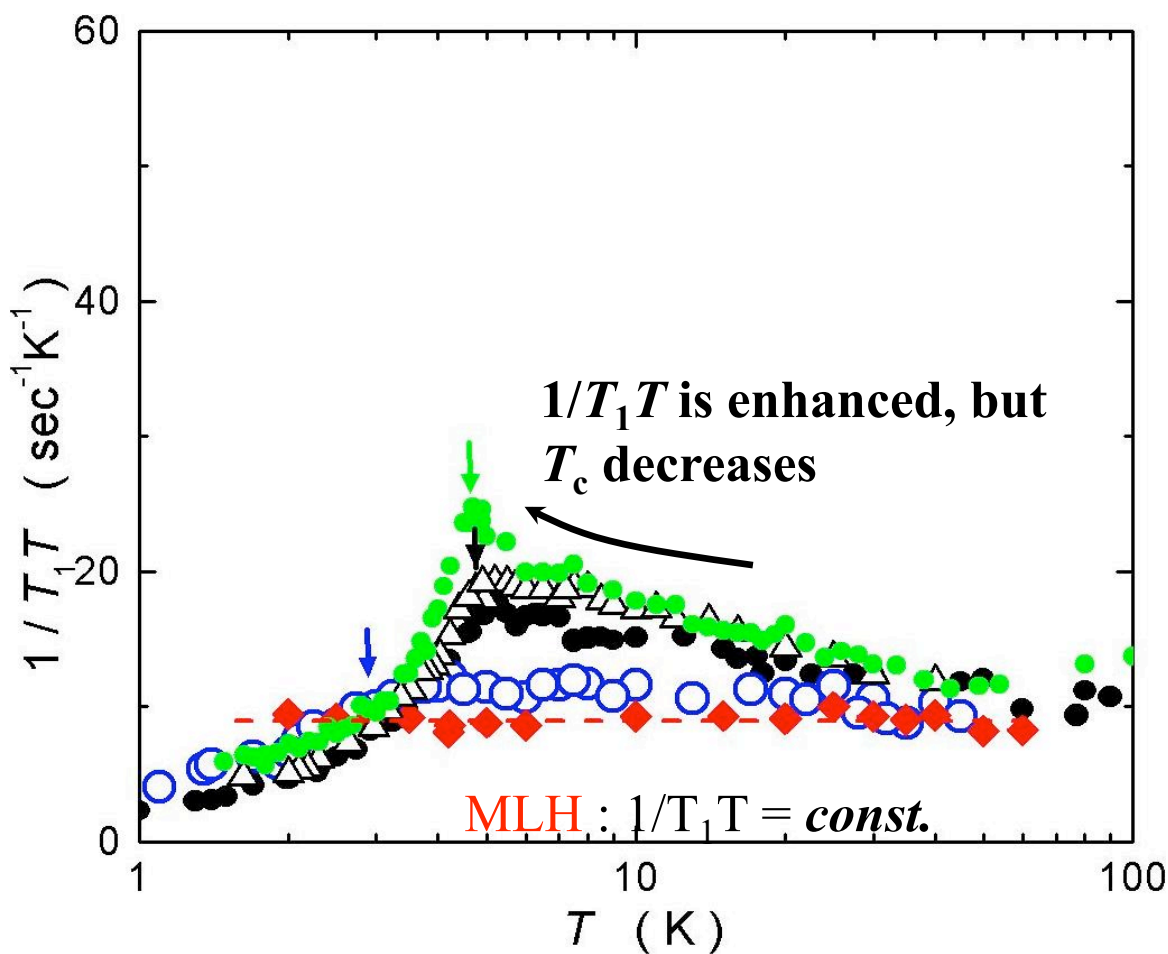
MLH $\text{Na}_{0.3}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$

non-SC down to 1.5 K

$1/T_1T$ is constant below 100 K

$1/T_1T$: Nuclear spin-Lattice relaxation Rate

NQR Spectrum



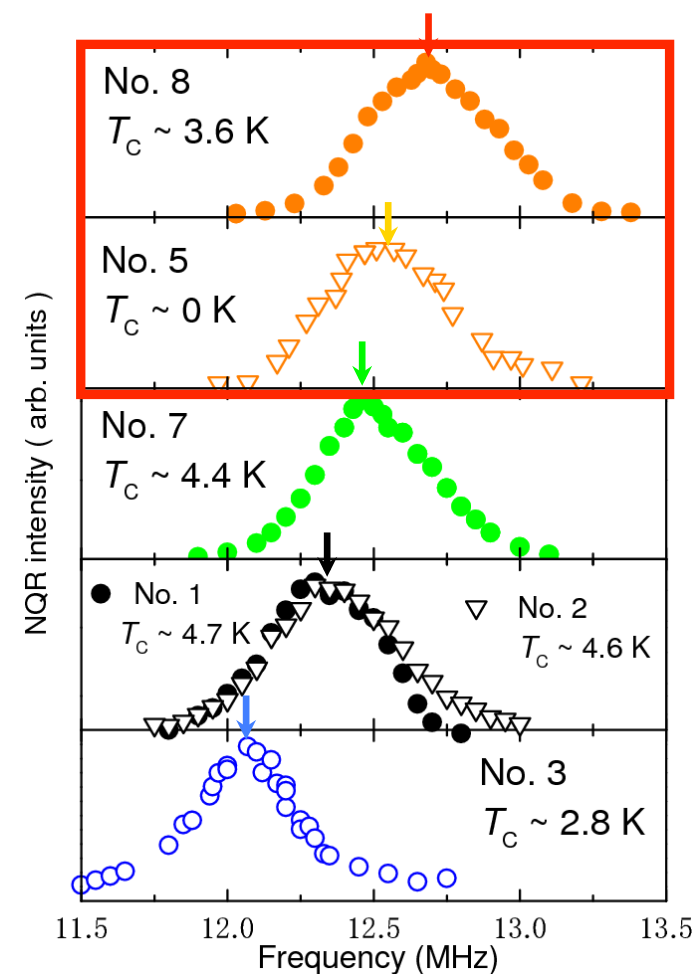
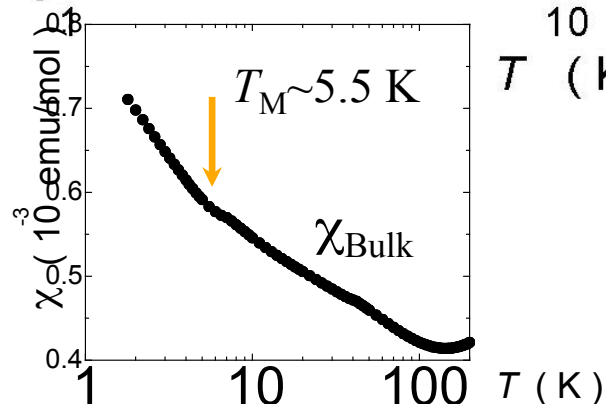
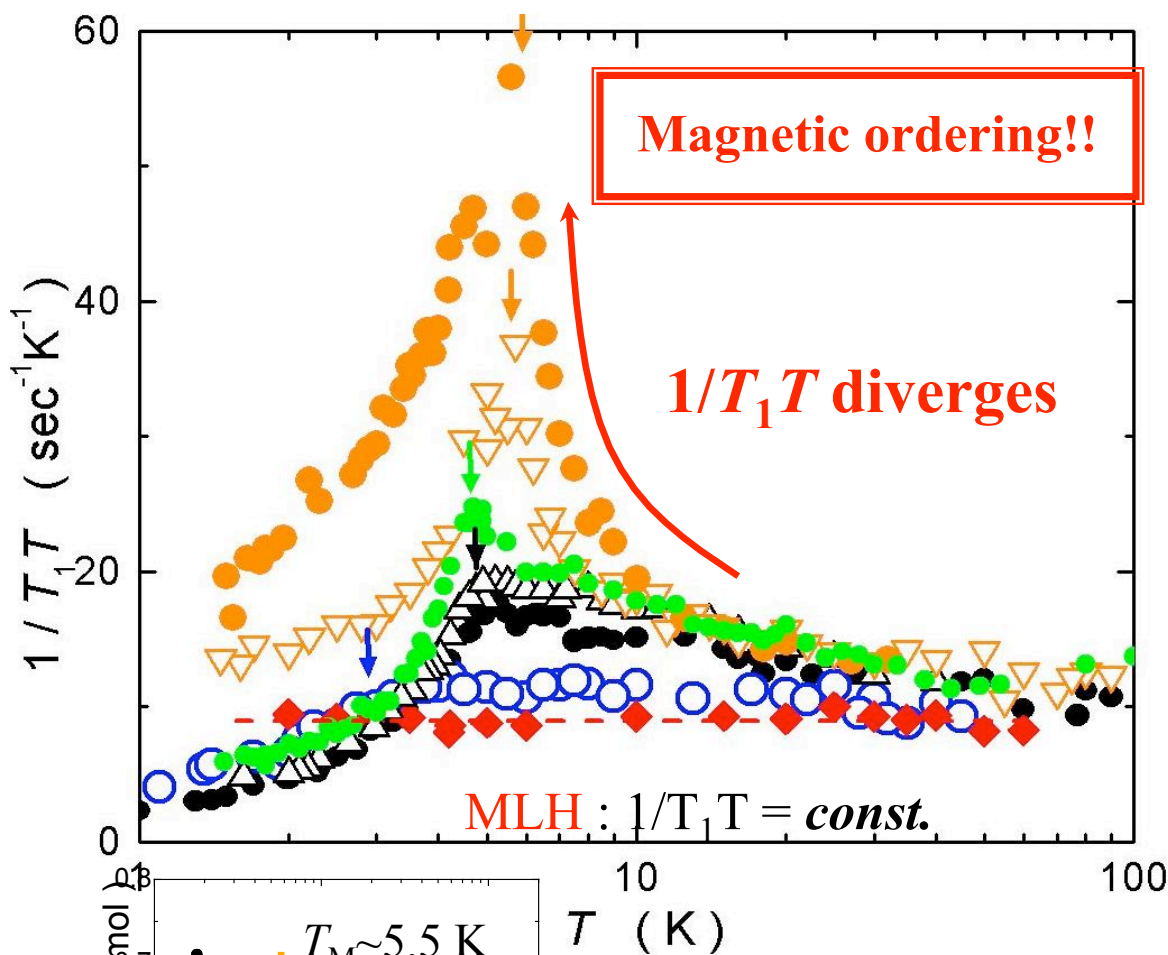
MLH $\text{Na}_{0.3}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$

non-SC down to 1.5 K

$1/T_1T$ is constant below 100 K

$1/T_1T$: Nuclear spin-Lattice relaxation Rate

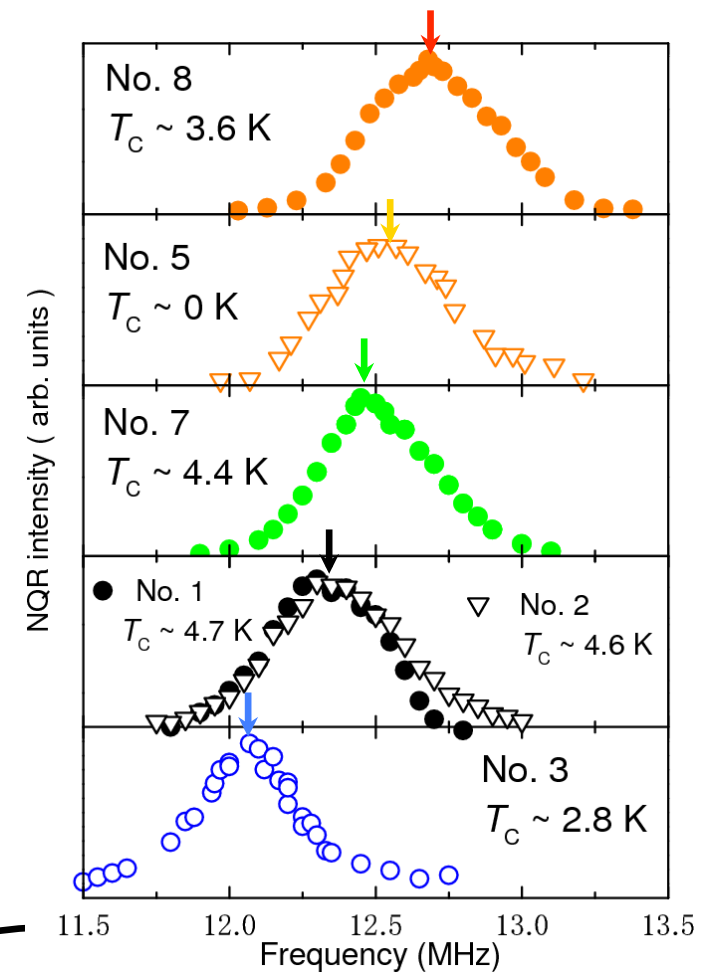
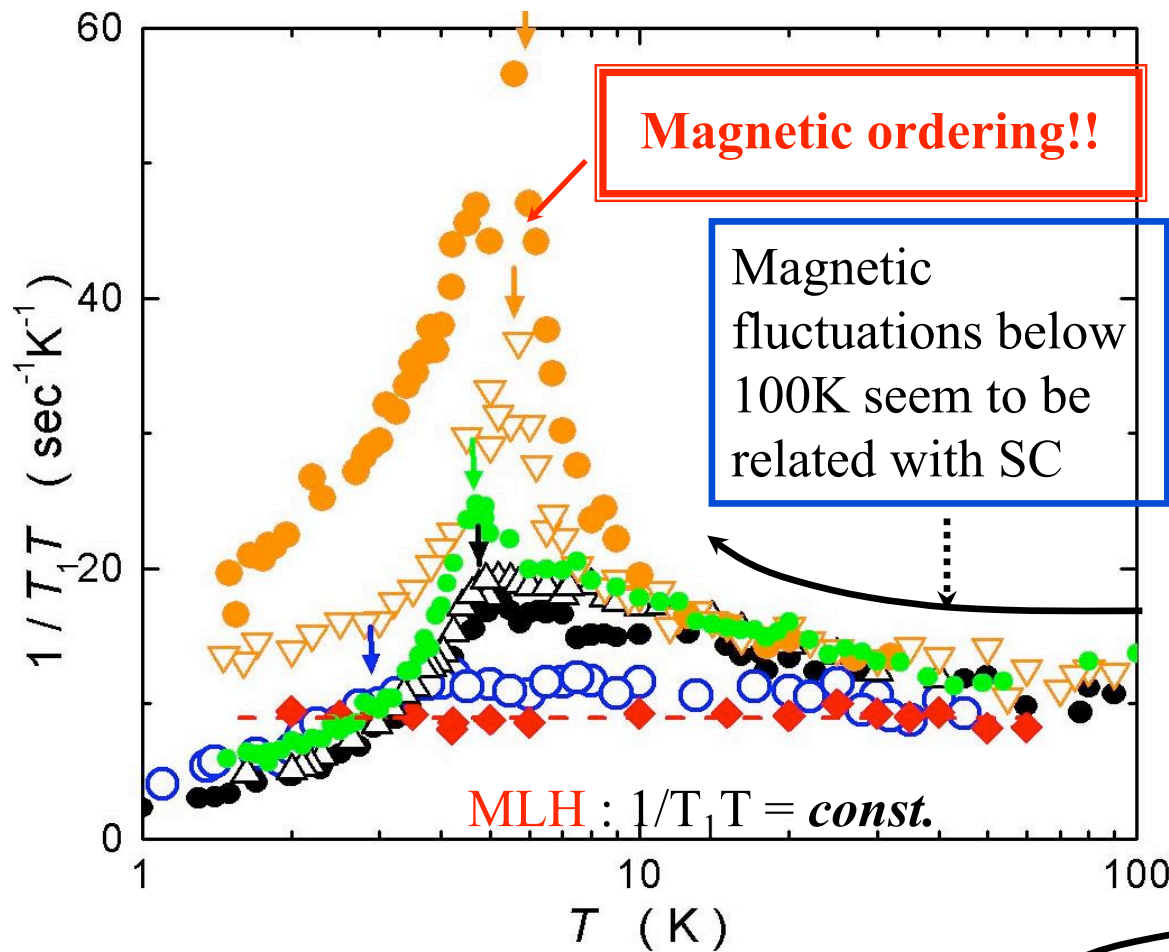
NQR Spectrum



The samples with higher ν_Q show magnetic ordering.

$1/T_1T$: Nuclear spin-Lattice relaxation Rate

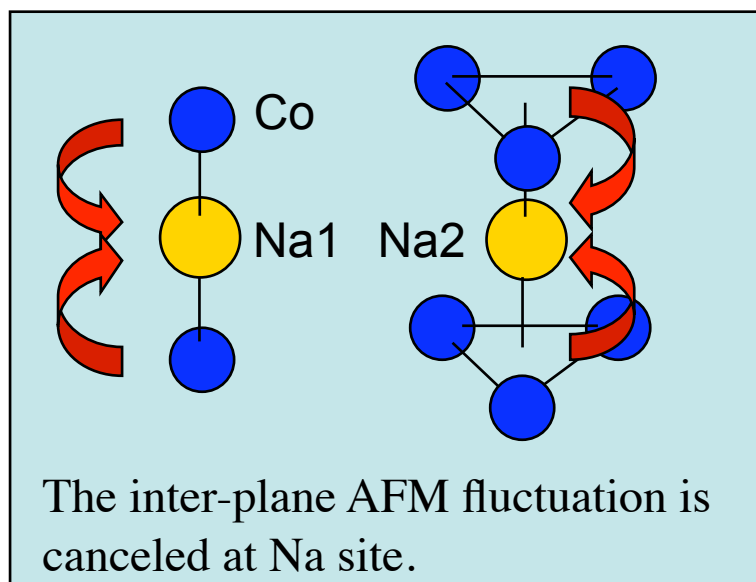
NQR Spectrum



SC is observed in the vicinity of QCP of magnetic fluctuations.

NQR frequency has relation with S.F.

Magnetic fluctuation in BLH

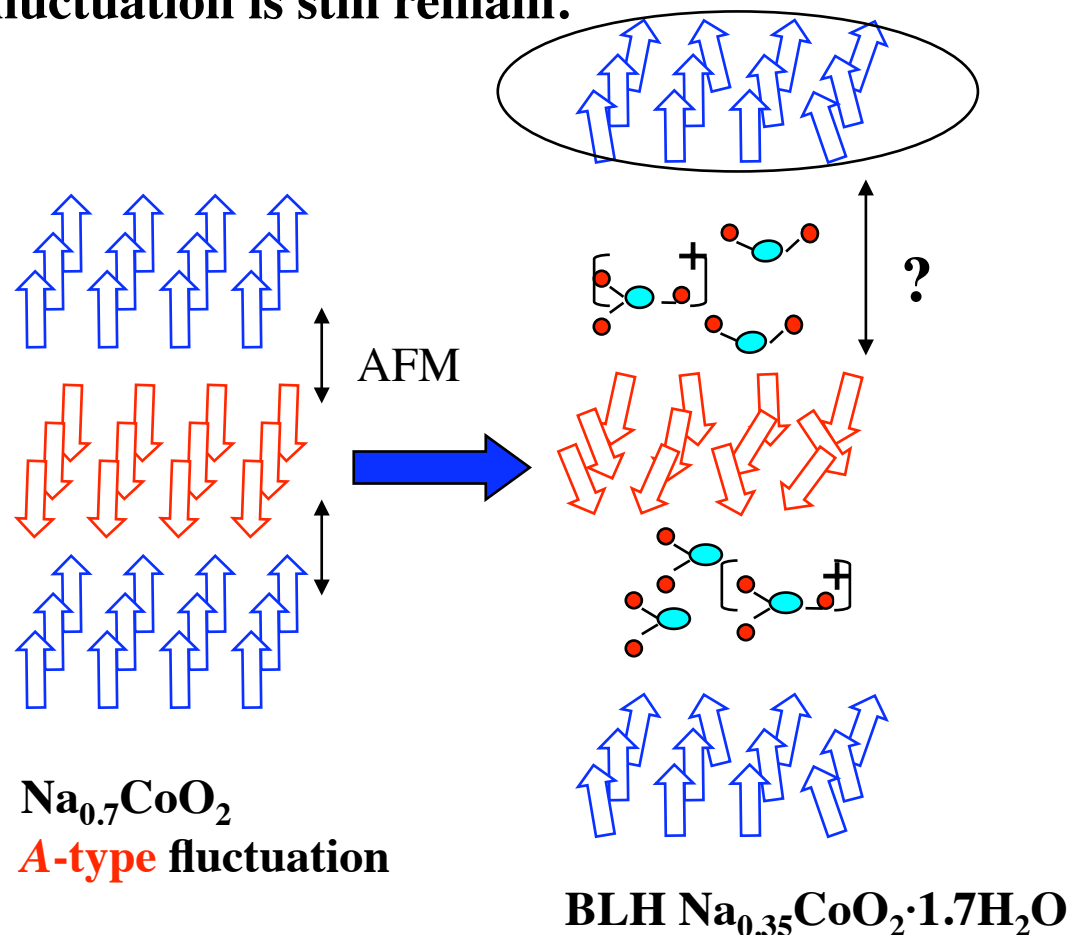


The T^n relation seen in $^{23}\text{Na}/T_1$ of $\text{Na}_{0.7}\text{CoO}_2$ below 40K is due to FM spin fluctuations. ($\rightarrow \text{Co}^{3.3+}$)

Similar relation seen in $^{23}\text{Na}/T_1$ of $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.7\text{H}_2\text{O}$ indicates the existence of FM spin fluctuations in the SC $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$.

($\rightarrow \text{Co}^{3.65+} ? \rightarrow \text{Co}^{3.4+}$ in the presence of H_3O^+)

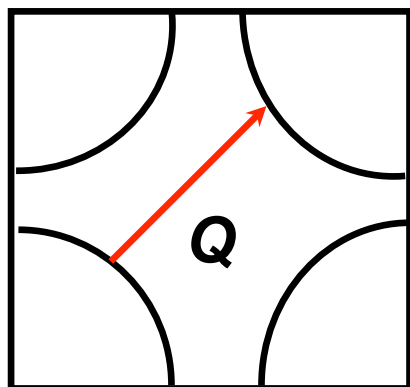
In-plane ferromagnetic fluctuation is still remain.



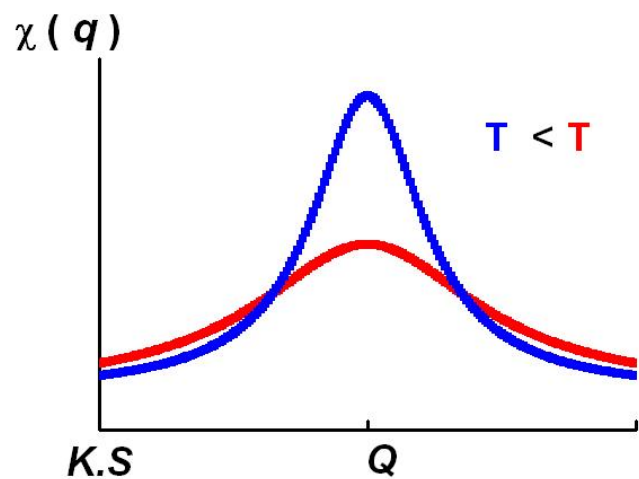
Superconductivity
in the vicinity of QCP
of A-type fluctuation ?

Comparison

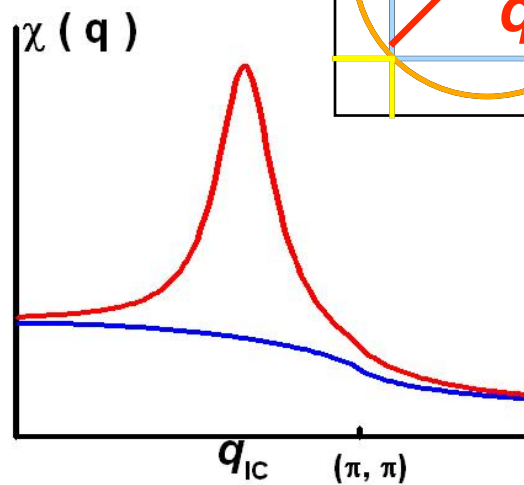
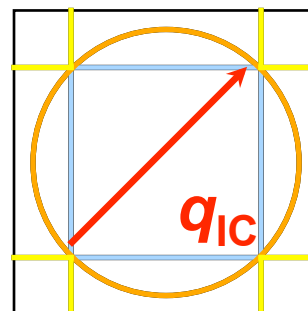
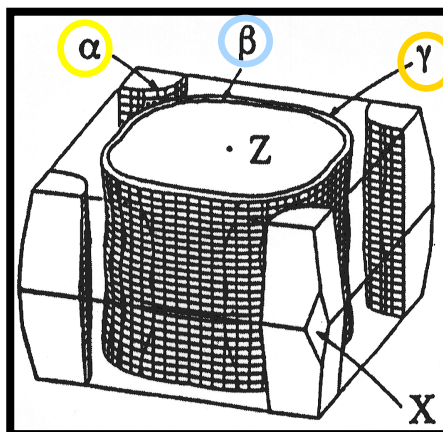
Cuprate



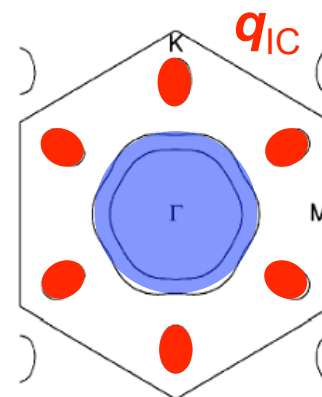
One component



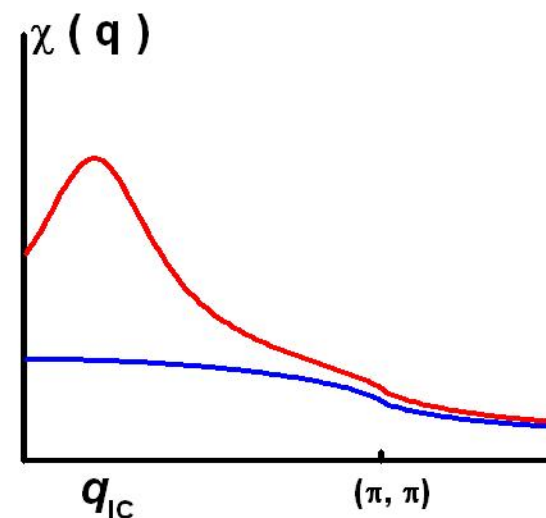
Ruthenate



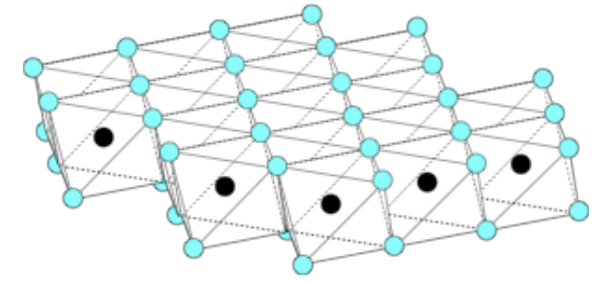
Cobaltate



Multi bands



Conclusion ($\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$)



1. Universal Phase Diagram: T_c vs. ν_Q of ^{59}Co NQR
→ Superconducting Phases appear in **both sides** of Magnetic Phase !
→ **Strong Relation** between Superconducting and Magnetic Phases

2. Magnetic Correlation: $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is **Unconventional Superconductor**
← $1/T_1$ of ^{59}Co NQR
Superconductivity appears in the vicinity of
Unconventional Quantum Critical Point !

3. Only SC BLH has **spin fluctuations at $q \sim 0$** ! ← ^{59}Co NQR
The ***A-type* spin fluctuation** is important ! ← ^{23}Na NMR

