2021/3/22
International Workshop on
Quantum Magnets in Extreme Conditions

Development of Multi-extreme THz ESR System and Its Application to Orthogonal Dimer Spin Substance $SrCu_2(BO_3)_2$

T. Sakurai [1], K. Hijii [2], S. Okubo [2], H. Ohta [2], and Y. Uwatoko [3]
[1] *Research Facility Center for Science and Technology, Kobe University, Kobe 657-8501, Japan*
[2] *Molecular Photoscience Research Center, Kobe University, Kobe 657-8501, Japan*
[3] *Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan*

Outline

1. Outline of our multi-extreme THz ESR system

2. Introduction of $SrCu_2(BO_3)_2$

3. Result and discussion of multi-extreme THz ESR measurements

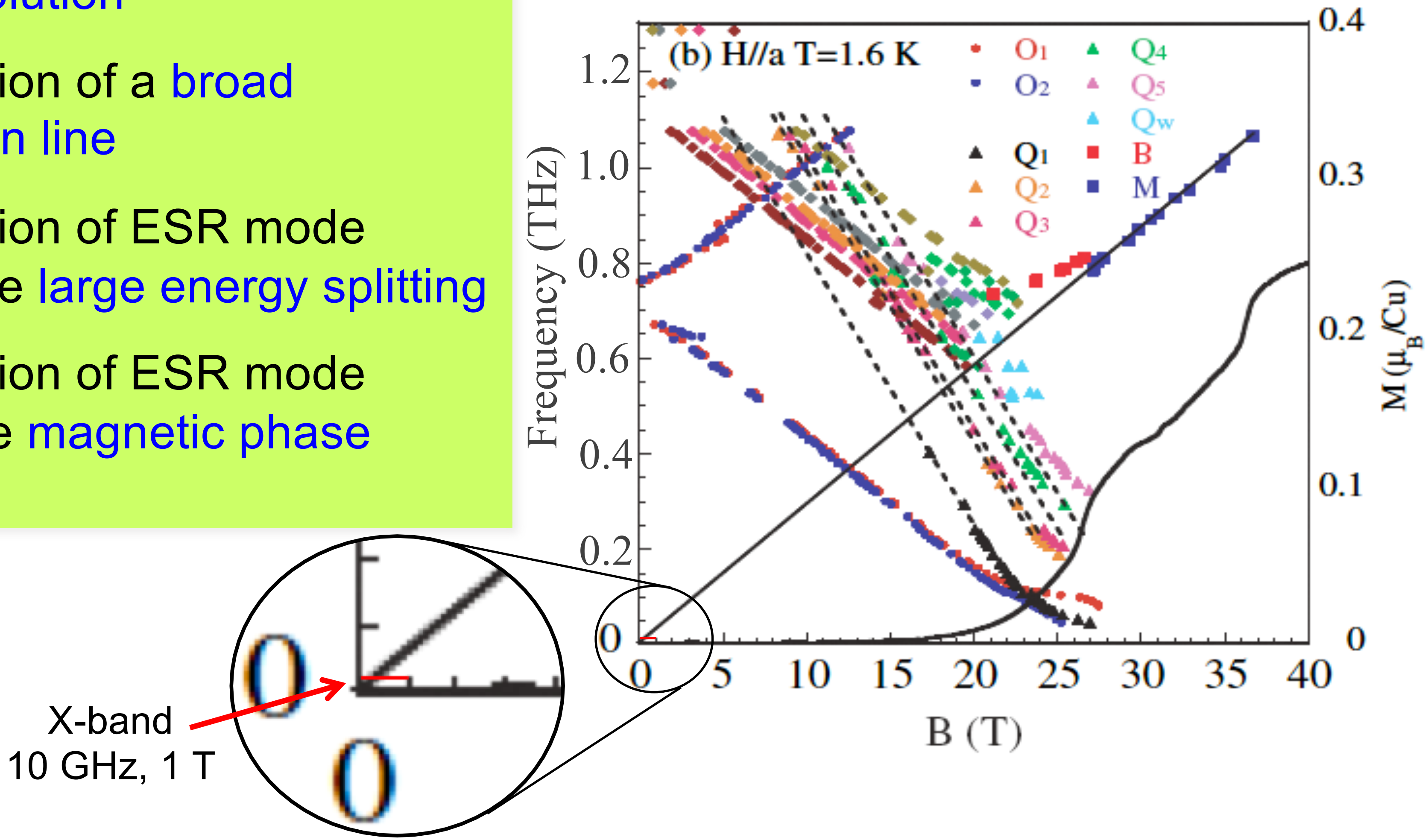
4. Summary

Advantage of High Field THz ESR Measurement

- # Strong ESR absorption intensity
- # High resolution
- # Observation of a broad absorption line
- # Observation of ESR mode across the large energy splitting
- # Observation of ESR mode above the magnetic phase transition

Frequency-field diagram of $SrCu_2(BO_3)_2$ at ambient pressure

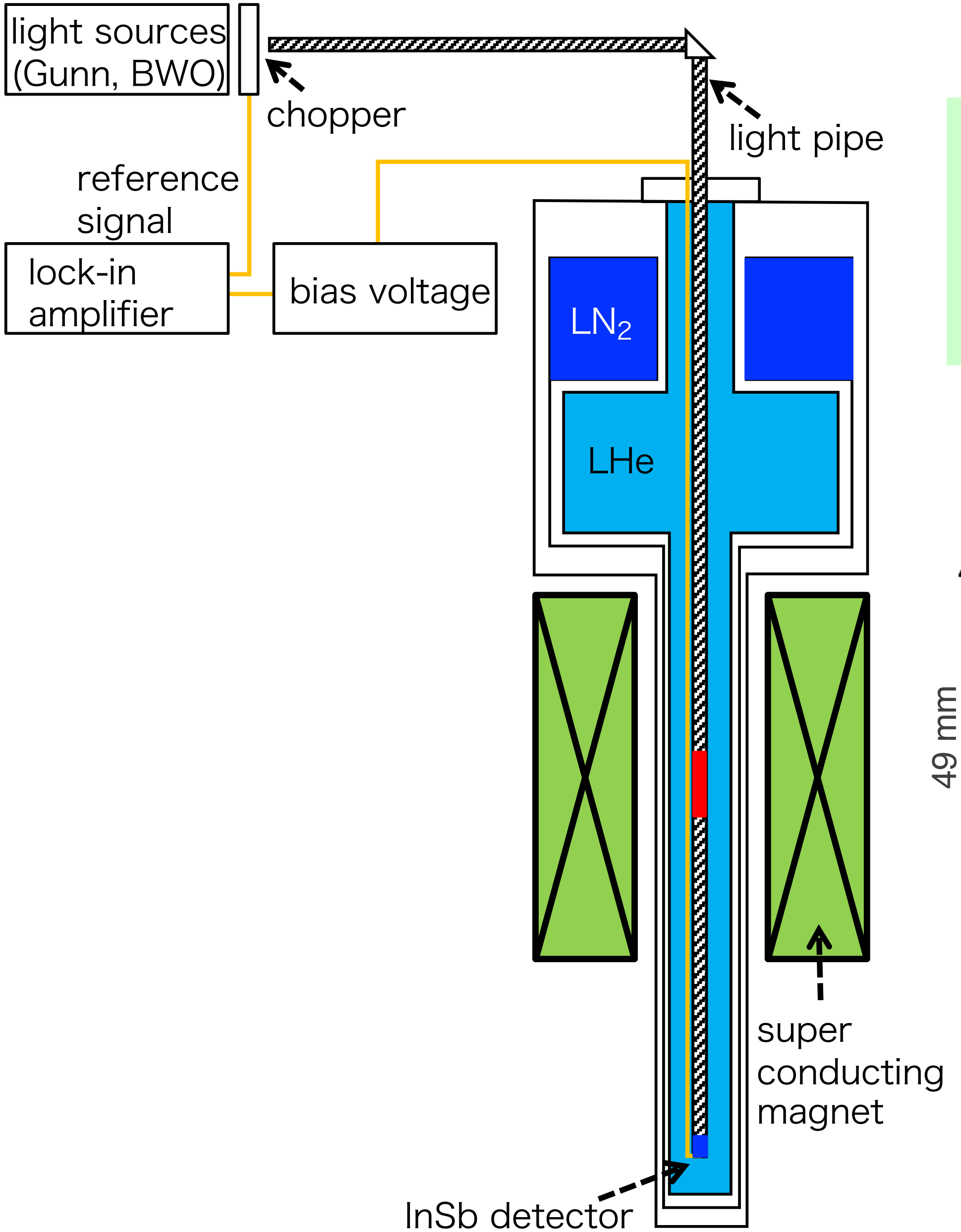
H. Nojiri *et al.*, J. Phys. Soc. Jpn. **72** (2003) 3243.



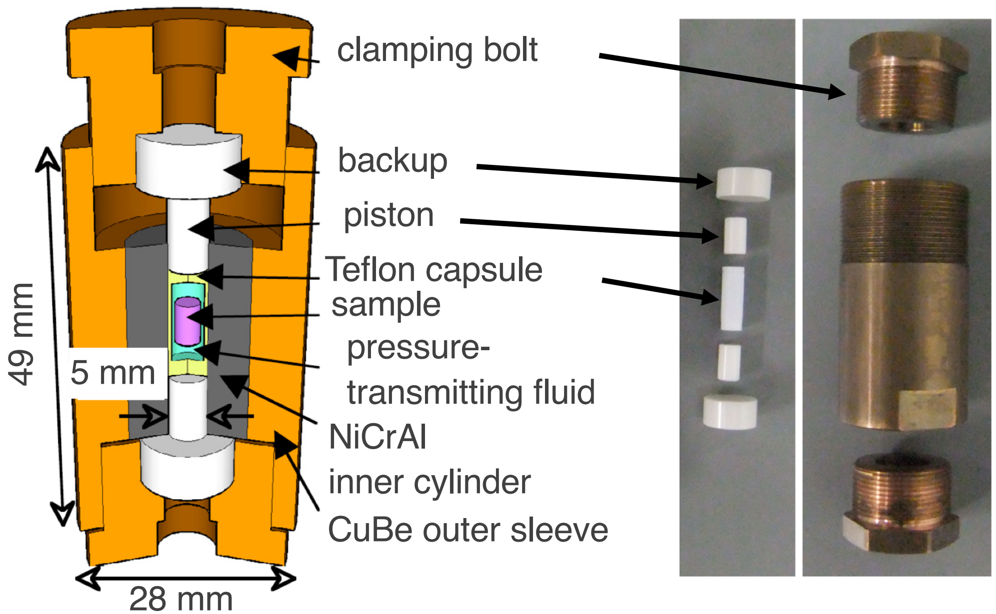
High field THz ESR is a powerful means to study quantum magnets!

High pressure THz ESR system-1

10 T cryogen-free super conducting magnet; T. Sakurai *et al.*, J. Magn. Reson. **259** (2015) 108.

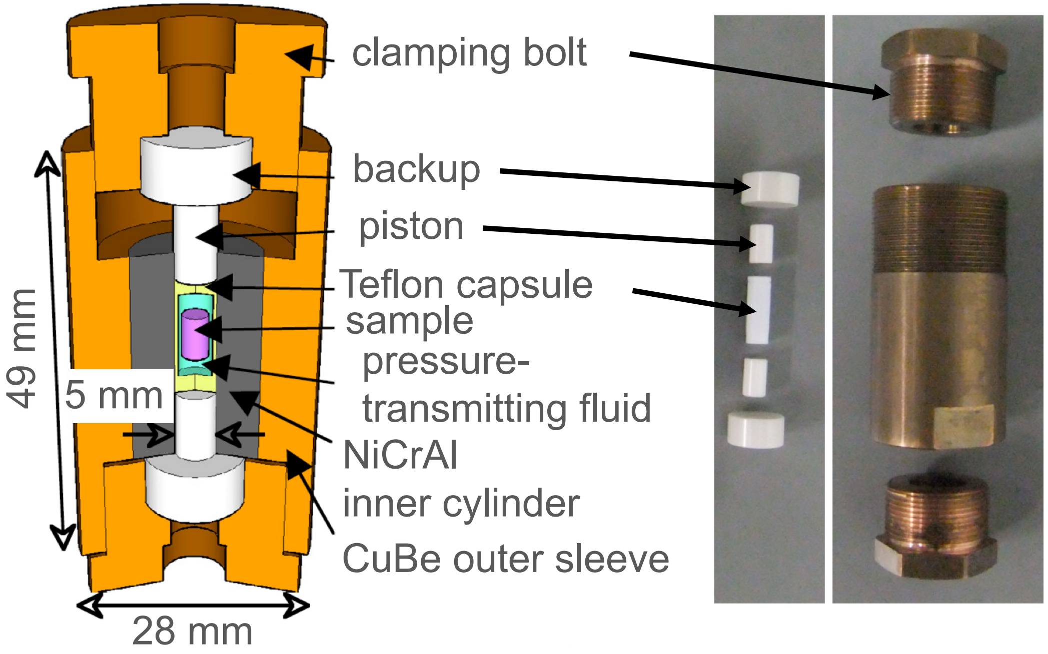


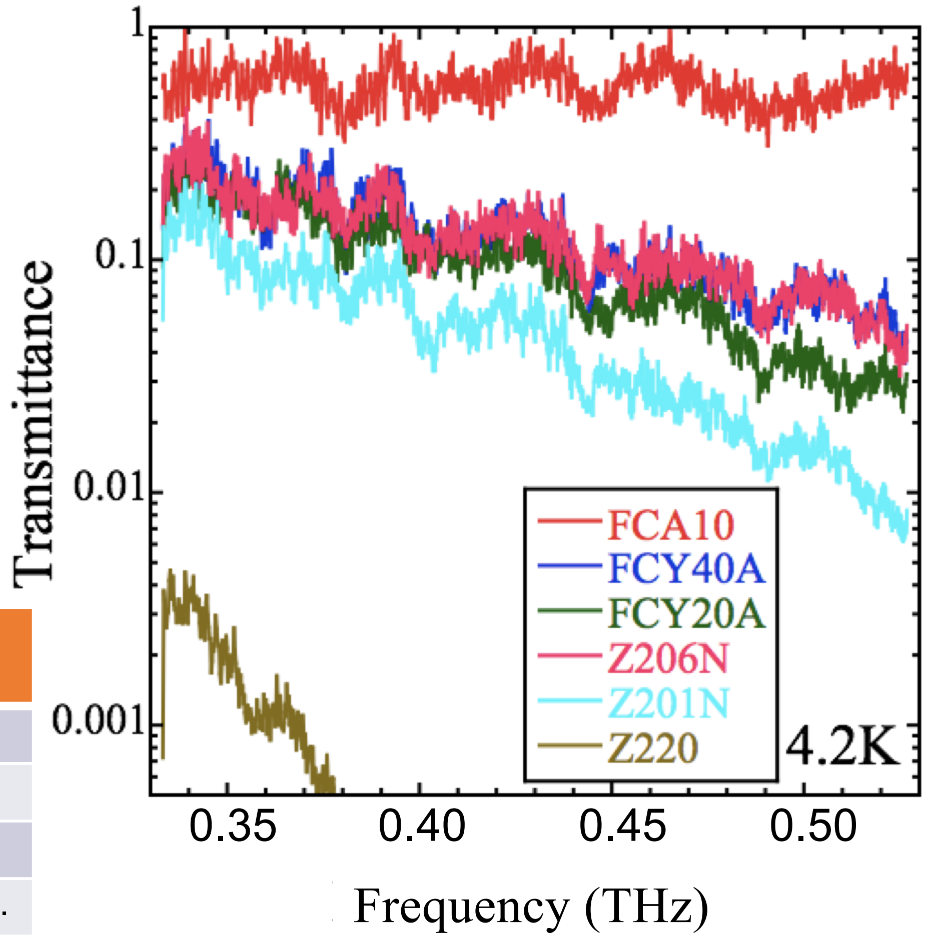
#	Frequency	0.05 – 0.8 THz
#	Magnetic field	≤ 10 T
#	Temperature	2 – 4.2 K
#	Pressure	≤ 2.5 GPa



Pressure cell for THz ESR

T. Sakurai *et al.*, J. Magn. Reson. **259** (2015) 108.





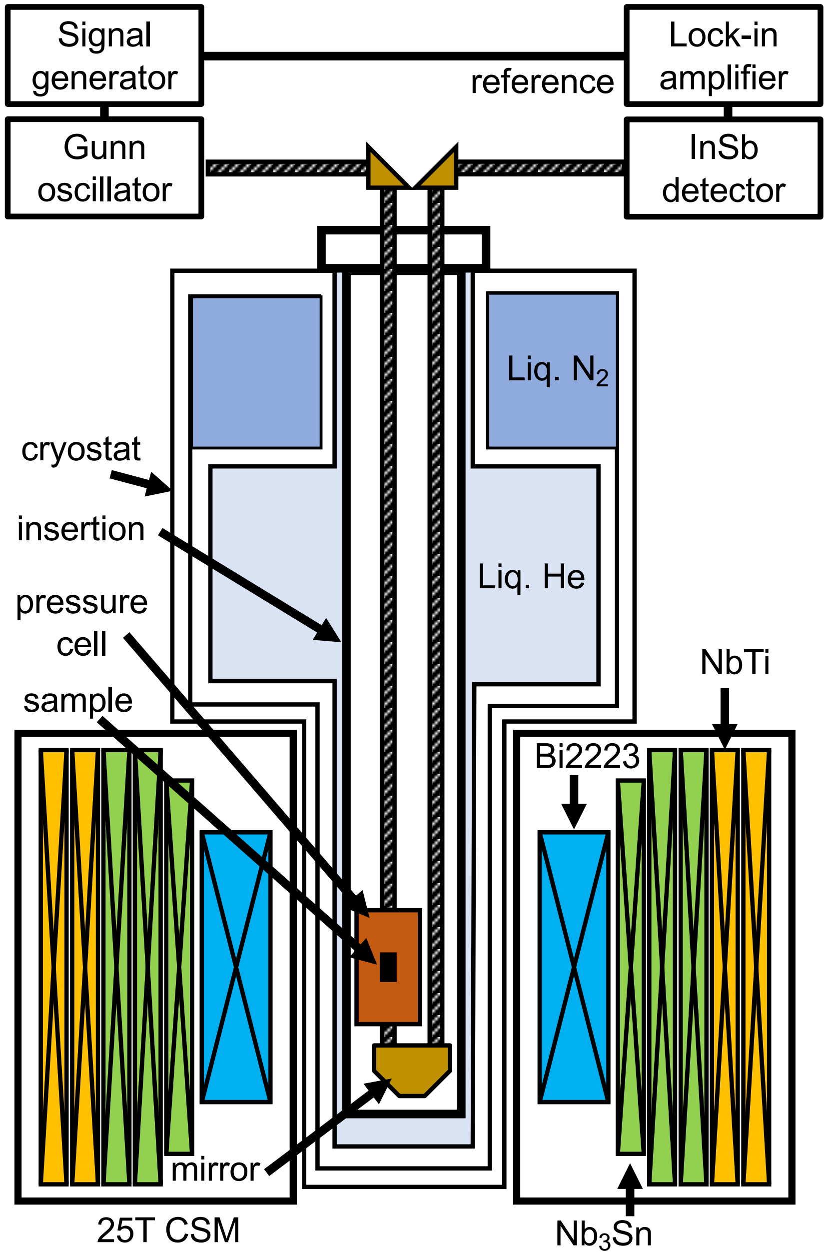
product name	main component	K_{1c} ($MPa \cdot m^{1/2}$)	company
FCA10	Al_2O_3	3.1	Fuji Die Co. Ltd.
FCY40A	Al_2O_3:ZrO_2 = 40:60	5.3	Fuji Die Co. Ltd.
FCY20A	Al_2O_3:ZrO_2 = 20:80	6.2	Fuji Die Co. Ltd.
Z206N	ZrO_2:Y_2O_3 = 95:5	6 ~ 7	KYOCERA Corp.
Z201N	ZrO_2:Y_2O_3 = 93:7	4 ~ 5	KYOCERA Corp.
Z220	ZrO_2:MgO = 95:5	7.8	KYOCERA Corp.

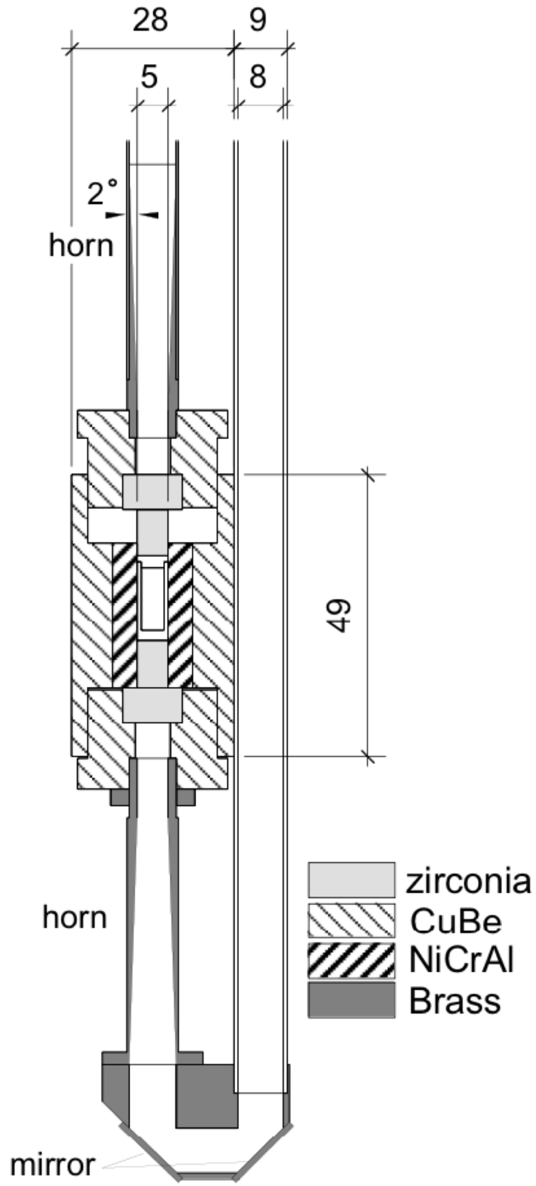
FCY20A is well balanced in toughness, transmittance, etc.

High pressure THz ESR system-2

25 T cryogen-free super conducting magnet; T. Sakurai *et al*., J. Magn. Reson. **296** (2018) 1.
15 T super conducting magnet; R. Okuto *et al*., Appl. Magn. Reson. **50** (2019) 1059.

25T-CSM
Institute for Materials Research (IMR), Tohoku Univ.
Time to maximum field: 60 min
Effective bore: 52 mm RT
S. Awaji *et al*., Supercond. Sci. Technol. **30** (2017) 065001.



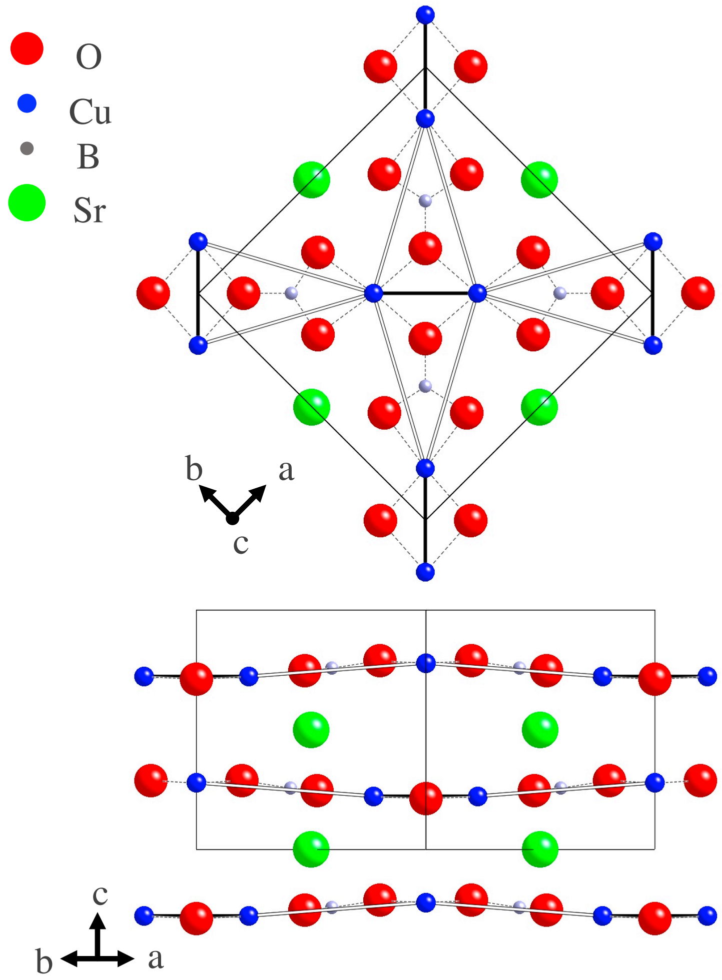


Application example;
Pressure-tuning the quantum spin Hamiltonian of the triangular lattice antiferromagnet Cs_2CuCl_4
S. A. Zvyagin *et al*.,
Nat. Commun. **10** (2019) 1064.

Orthogonal Dimer Spin System $SrCu_2(BO_3)_2$

Crystal structure

R. W. Smith and D. A. Keszler,
J. Solid State Chem. **93** (1991) 430.

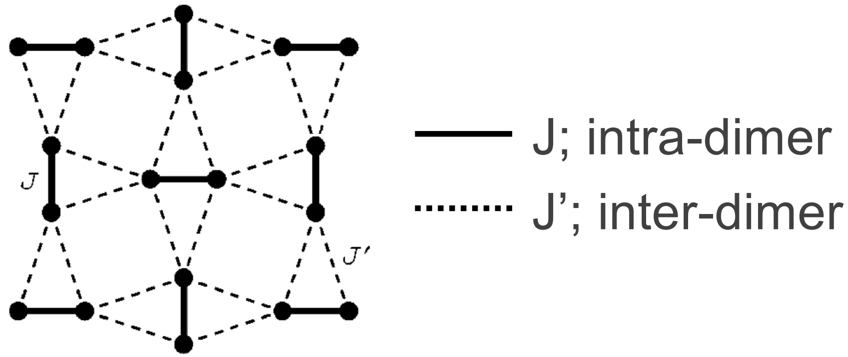


space group: tetragonal $I\bar{4}2m$

a = 8.995 Å

c = 6.649 Å

Magnetic model



Orthogonal dimer system

H. Kageyama *et al.*, PRL **82** (1999) 3168.

Shastry-Sutherland lattice (1981)

S. Miyahara and K. Ueda, PRL **82** (1999) 3701.

$$\mathcal{H} = J\sum_{nn} \mathbf{s}_i \cdot \mathbf{s}_j + J'\sum_{nnn} \mathbf{s}_i \cdot \mathbf{s}_j$$

Exact eigenstate $|\Psi\rangle = \prod_a |s\rangle_a$

Localization of the triplet

J = 85 K, α = J'/J = 0.64

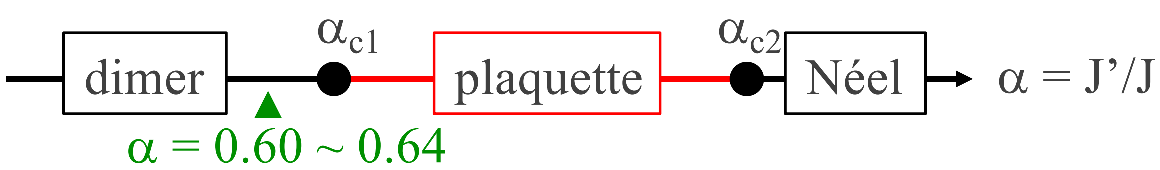
S. Miyahara and K. Ueda, JPSJ **69** Suppl. B (2000) 72.

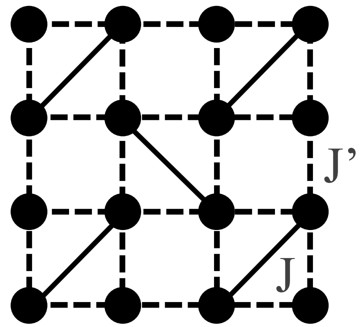
J = 71 K, α = J'/J = 0.60

C. Knetter *et al.*, PRL **85** (2000) 3958.

Existence of Intermediate Phase

[1] A. Koga and N. Kawakami, Phys. Rev. Lett. **84** (2000) 4461.





Main method	α_{c1}	α_{c2}	
Plaquette expansion [1]	0.677(2)	0.86	
Infinite projected entangled-pair states [2]	0.675(2)	0.765(15)	
Numerical diagonalization [3]	0.675	0.76	α_{c3} at ~ 0.70
Infinite density matrix renormalization group method [4]	0.675	0.77	

[1] A. Koga and N. Kawakami, Phys. Rev. Lett. **84** (2000) 4461.
[2] P. Corboz and F. Mila, Phys. Rev. B (2013) 115144.
[3] H. Nakano and T. Sakai, J. Phys. Soc. Jpn. **87** (2018) 123702.
[4] J. Y. Lee et al., Phys. Rev. X 9 (2019) 041037.

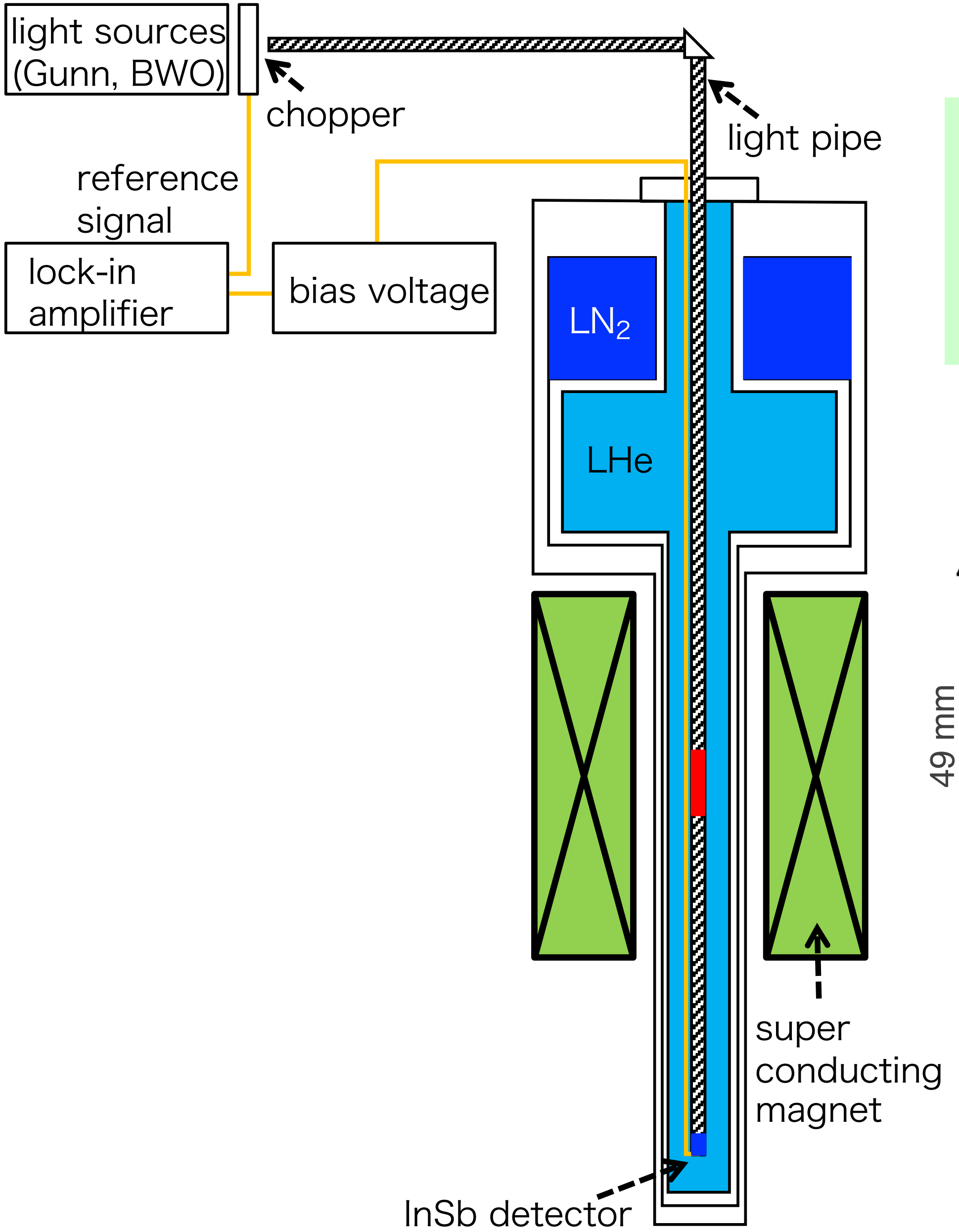
Pressure Effect

Method	P_{max}	Remarks	year
χ-T [1]	0.7 GPa	Suppression of gap	2003
X-ray [2]	23 GPa	Structural phase transition at 4.7 GPa (300 K) tetragonal -> monoclinic	2005
χ-T [3]	1.44 GPa	Kink at 4 K (1.44 GPa)	2007
NMR [3]	2.4 GPa	Loss of four-fold symmetry below 30 K (2.4 GPa) Spatial order of two types of dimers below 3.6 K (2.4 GPa)	2007
ESR [4]	1.2 GPa	Suppression of gap	2009
X-ray [5]	8 GPa	Collapse of gap at 1.93 ± 0.07 GPa No structural phase transition up to 4 GPa at 4 K	2012
MH (TDO) [6]	2.2 GPa	New phase at 2.2 GPa	2016
INS [7]	2.15 GPa	Phase transition between 1.6 and 2.15 GPa at 0.5 K dimer singlet -> plaquette singlet	2017
ND [7]	4.0 GPa	Phase transition from plaquette to AFM at 4.0 GPa	2017
ESR [8]	2.13 GPa	Phase transition between 1.85 GPa ± 0.10 GPa dimer singlet -> plaquette singlet	2018
Specific heat [9]	4.9 GPa	Phase transition to plaquette singlet at 1.7 GPa Phase transition to AF state in 3 ~ 4 GPa	2020
Raman [10]	3.4 GPa	Sign switching at ~ 2.2 GPa	2020

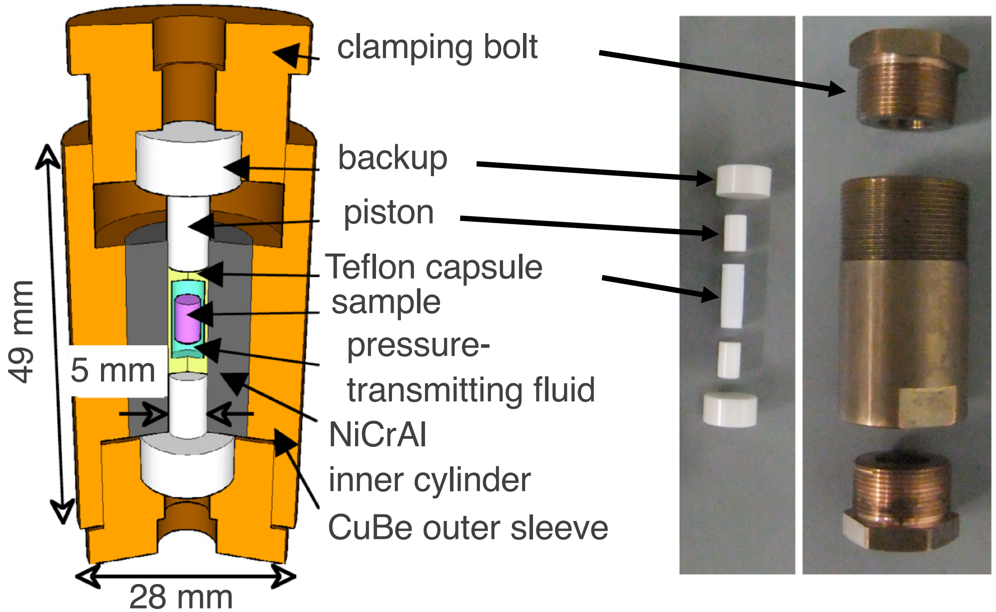
[1] H. Kageyama *et al*., Physica **329-333** (2003) 1020.
[2] I. Loa *et al*., Physica B **359-361** (2005) 980.
[3] T. Waki *et al*., JPSJ **76** (2007) 073710.
[4] T. Sakurai *et al*., J. Phys. Conf. Ser. **150** (2009) 042171.
[5] S. Haravifards *et al*., Proc. Natl. Acad. Sci. USA **109** (2012) 2286.
[6] S. Haravifard, *et al*., Nat. Commun. **7** (2016) 11956.
[7] M. Zayed *et al*., Nat. Phys. **13** (2017) 962.
[8] T. Sakurai *et al*., J. Phys. Soc. Jpn. **87** (2018) 033701.
[9] J. Guo *et al*., Phys. Rev. Lett. **124** (2020) 206602.
[10] S. Bettler *et al*., Phys. Rev. Res. **2** (2020) 012010.

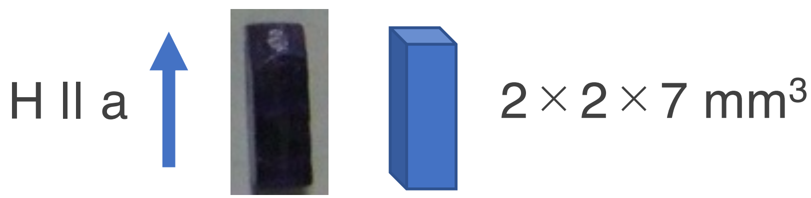
Experimental

T. Sakurai *et al.*, J. Magn. Reson. **259** (2015) 108.



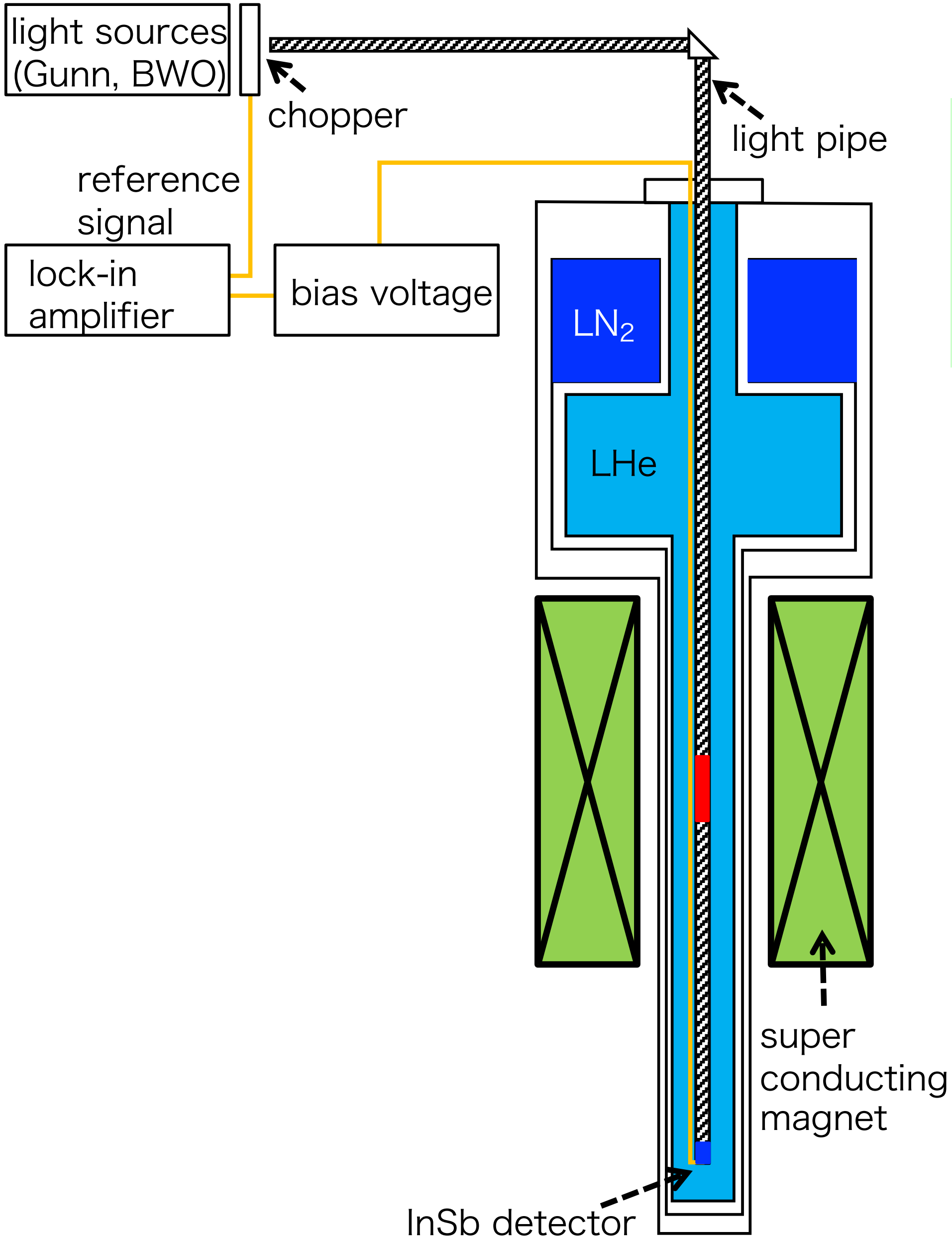
#	Frequency	0.05 – 0.8 THz
#	Magnetic field	≤ 10 T, 25 T
#	Temperature	< 2 K
#	Pressure	≤ 2.5 GPa





Experimental

T. Sakurai *et al.*, J. Magn. Reson. **259** (2015) 108.



#	Frequency	0.05 – 0.8 THz
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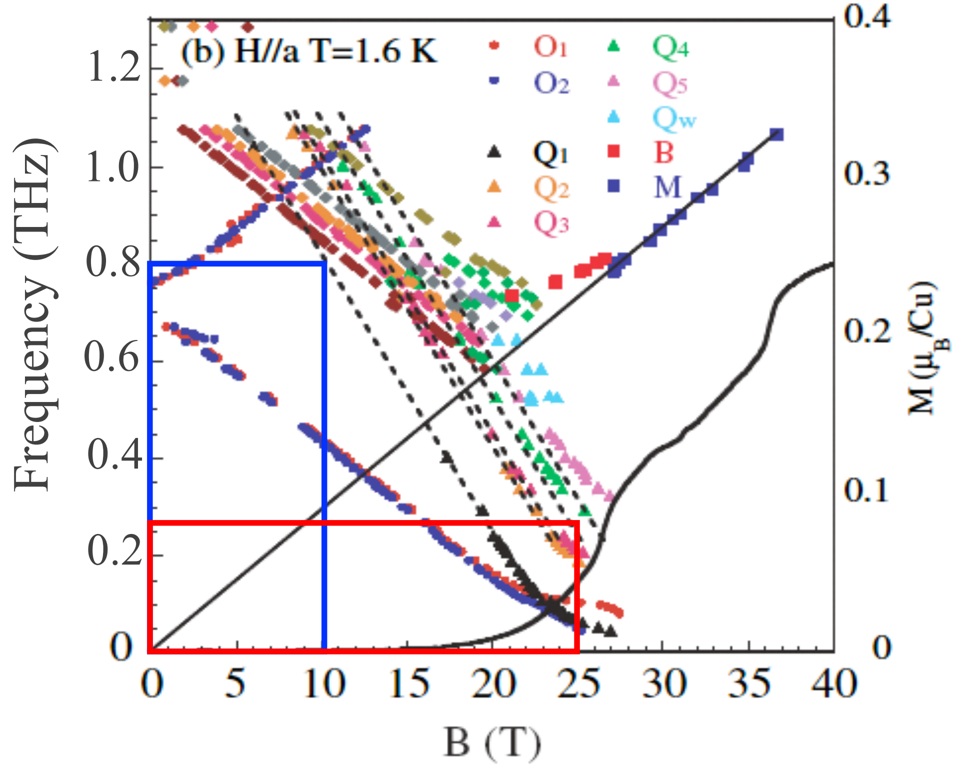
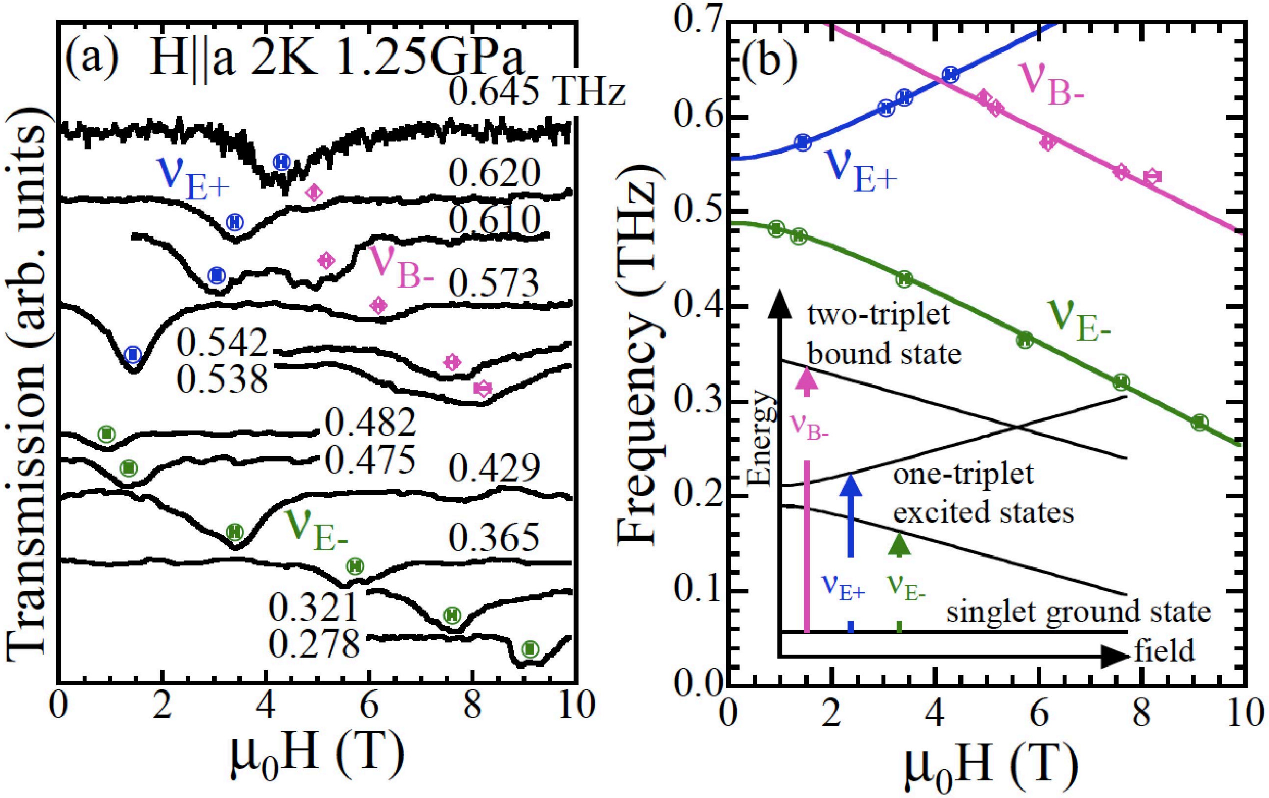


Results of HP THz ESR Measurement 1

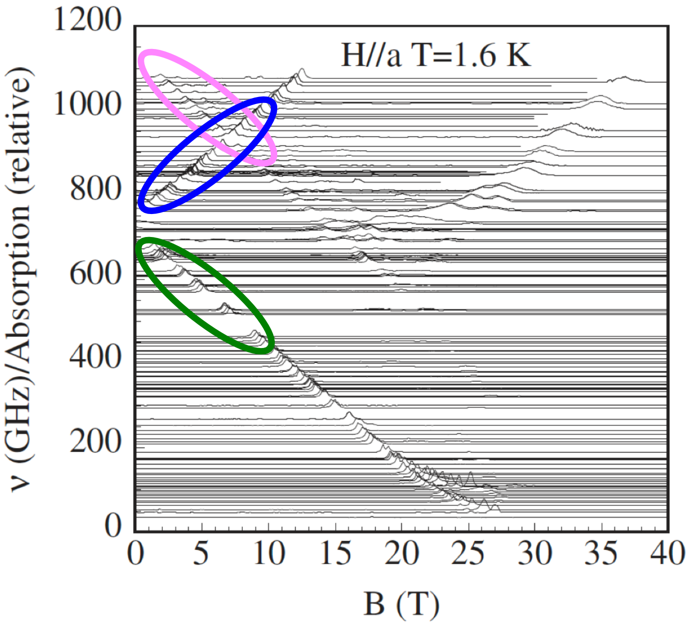
T. Sakurai *et al*., JPSJ **87** (2018) 033701.

ESR spectra obtained at 1.25 GPa



ESR spectra at ambient pressure

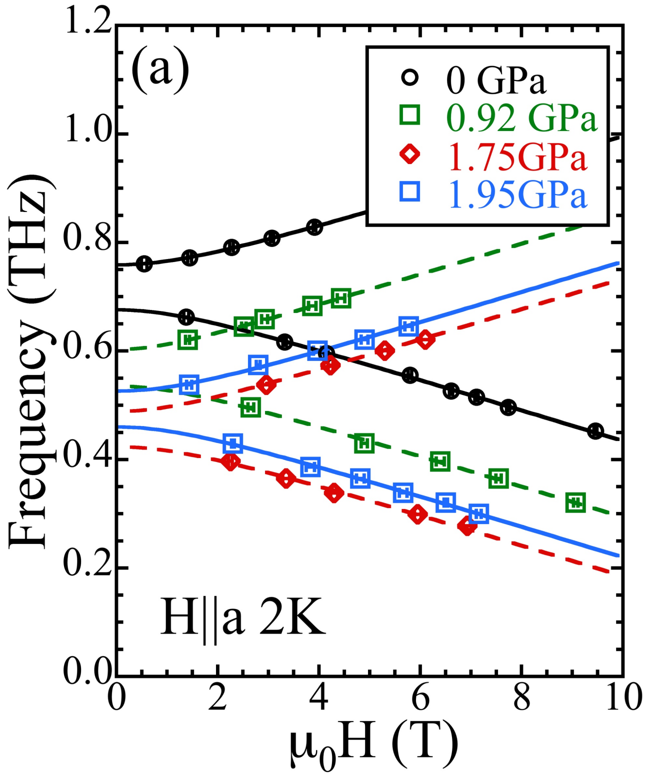
H. Nojiri *et al*., J. Phys. Soc. Jpn. **72** (2003) 3243.



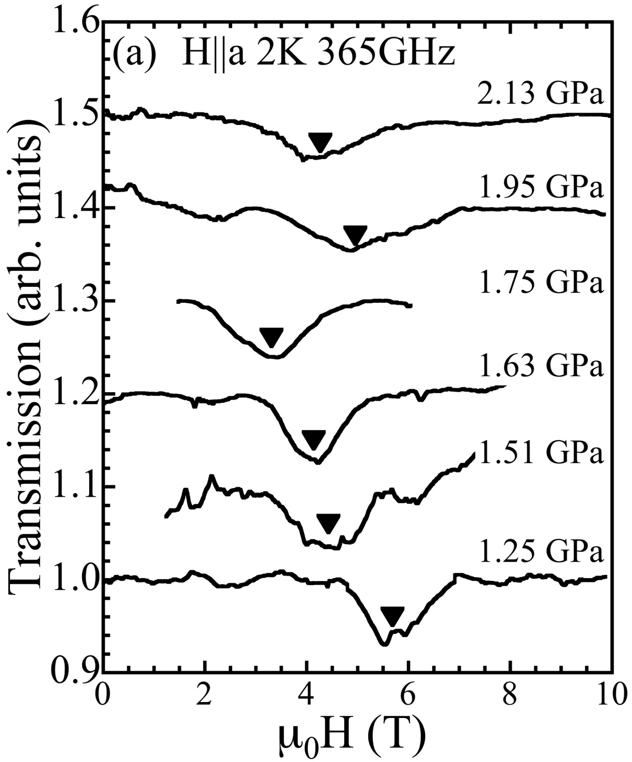
- \# We succeeded in observing ESR under pressure in the wide frequency region.
- \# We observed ESR modes due to the direct transition between the singlet ground state to the first excited triplet states and the bound triplet states.

Results of HP THz ESR Measurement 2

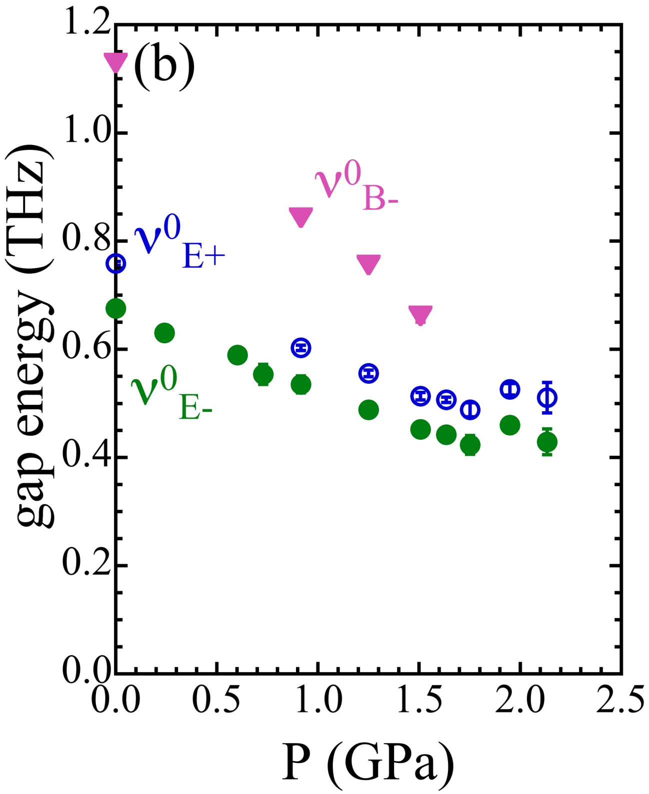
FH diagram for ν_E modes



P dependence of spectrum

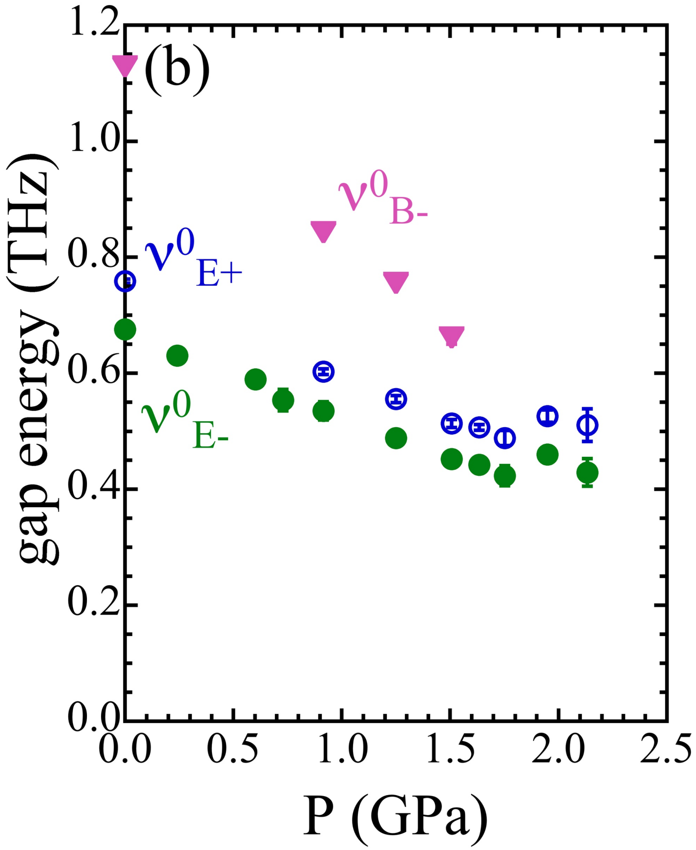


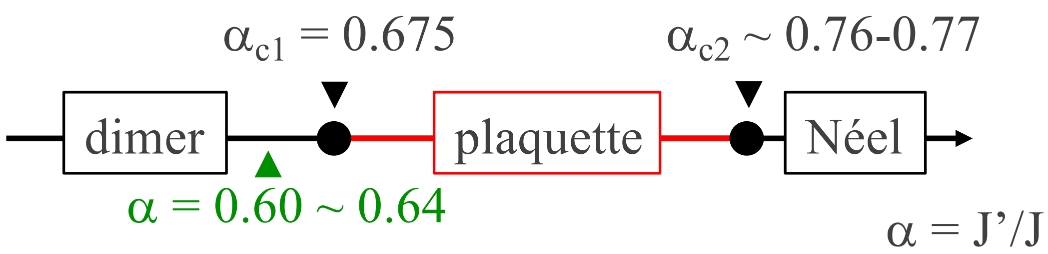
P dependence of gap energy

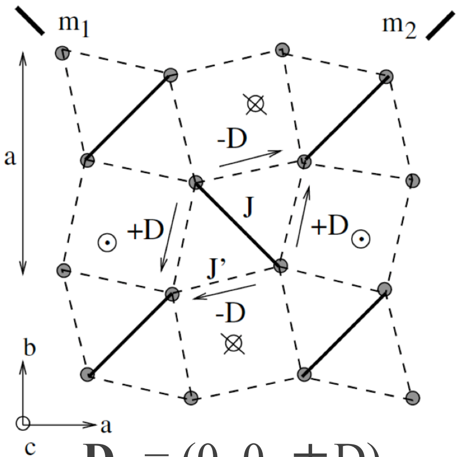


\# The gap energy is suppressed by applying pressure.
\# We observed the phase transition at 1.85 GPa ± 0.10 GPa.
\# The phase transition occurs with remaining gap.

Analysis 1







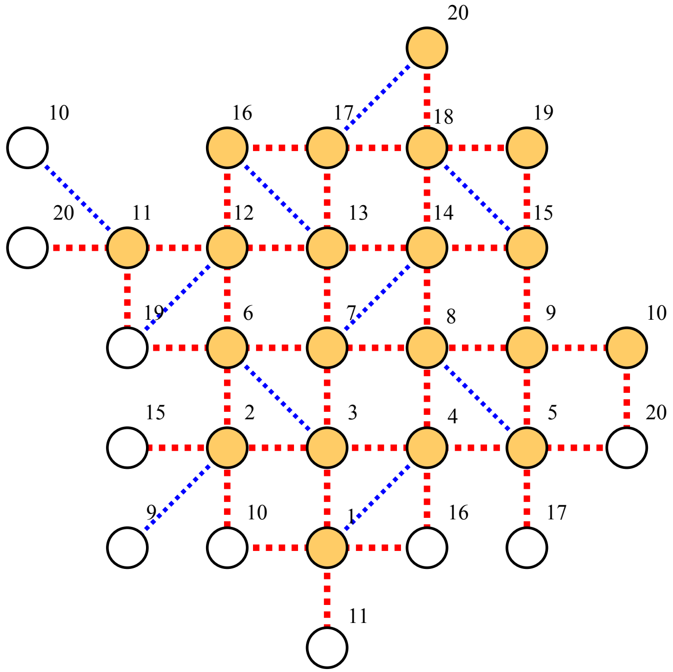
$$\mathcal{H} = J\sum_{nn} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + J'\sum_{nnn} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \sum_{nnn} \boldsymbol{D}_{ij} \cdot (\boldsymbol{S}_i \times \boldsymbol{S}_j)$$

$\mathbf{D}_{ij} = (0, 0, \pm D)$

O. Cépas *et al.*, Phys. Rev. Lett. **87** (2001) 167205.

Analysis 2

Exact diagonalization for Shastry-Sutherland lattice
with DM interaction;
20 sites under periodic boundary condition



$$\mathcal{H} = J\sum_{nn} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + J'\sum_{nnn} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \sum_{nnn} \boldsymbol{D}_{ij} \cdot (\boldsymbol{S}_i \times \boldsymbol{S}_j)$$

$$\mathcal{H} = J\left\{\sum_{nn} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \alpha\sum_{nnn} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \alpha k \sum_{nnn} (-1)^{i+j} \left(S_{ix}S_{jy} - S_{iy}S_{jx}\right)\right\}$$

$$\alpha = \frac{J'}{J}$$

$$D = kJ'$$

Obtained parameters

ν^0_{B-}, ν^0_{E+}, ν^0_{E-}

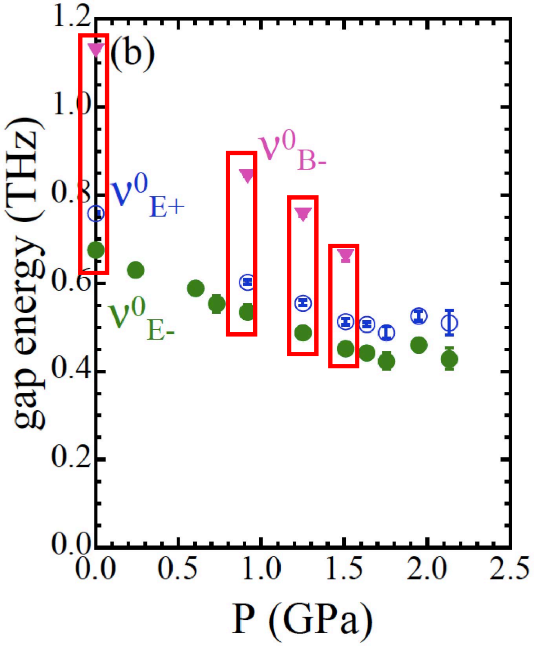
⇕

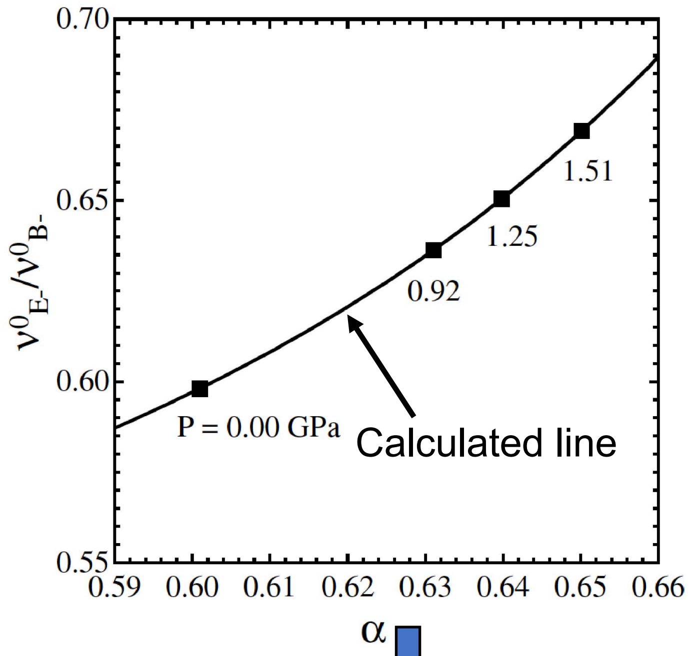
Unknown parameters

J, J', D

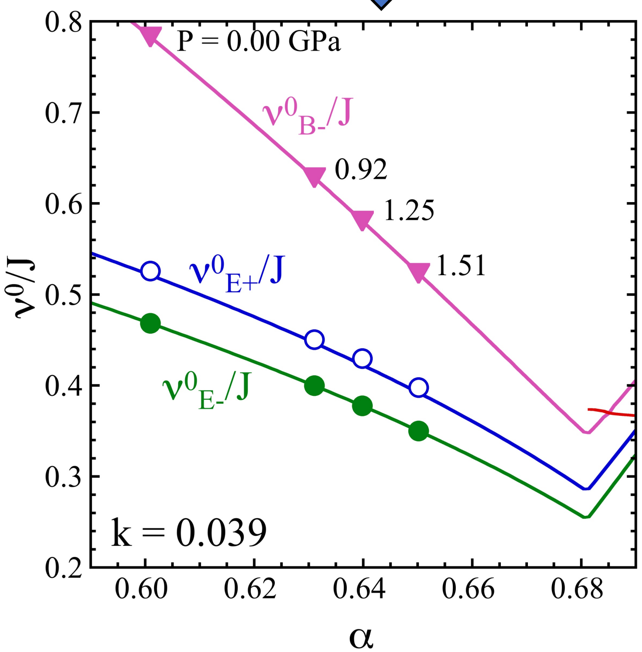
(J, α, k)

Analysis 3

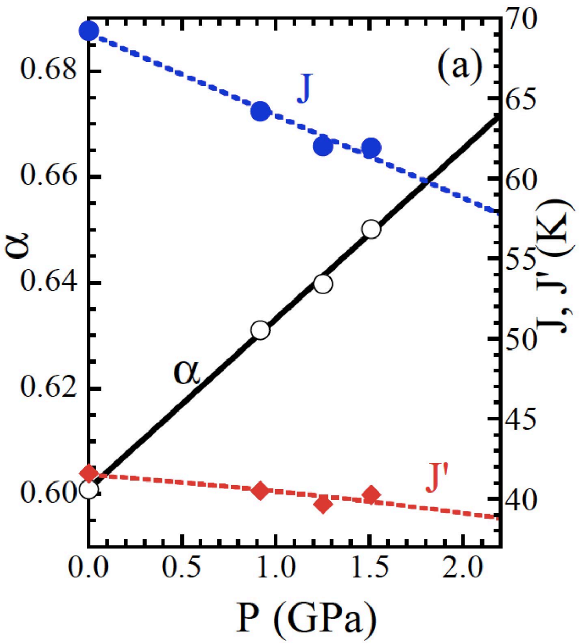




α = J'/J is determined at each pressure.



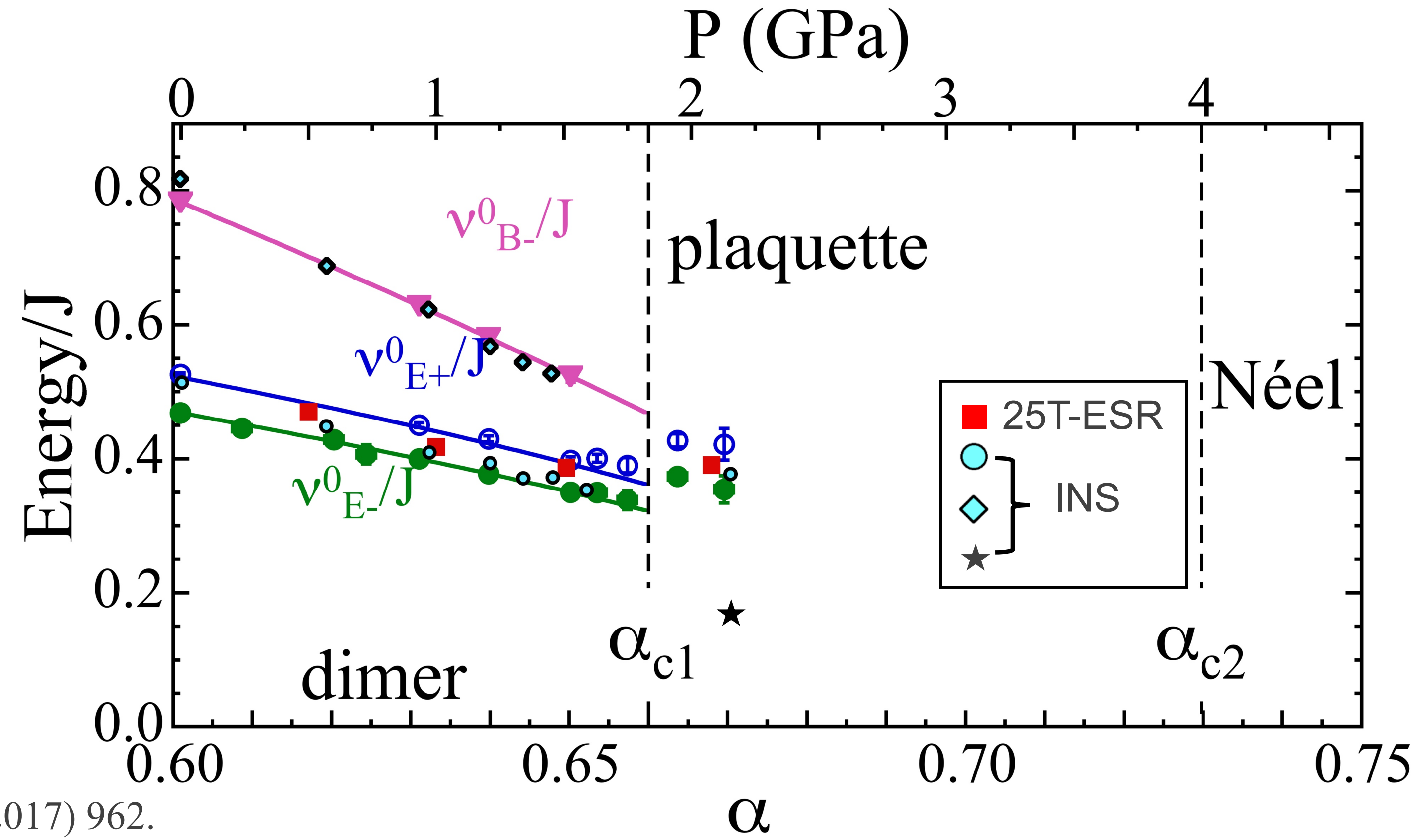
J is determined at each pressure.
k is determined.



α(P) and J(P) are obtained from the fitting.

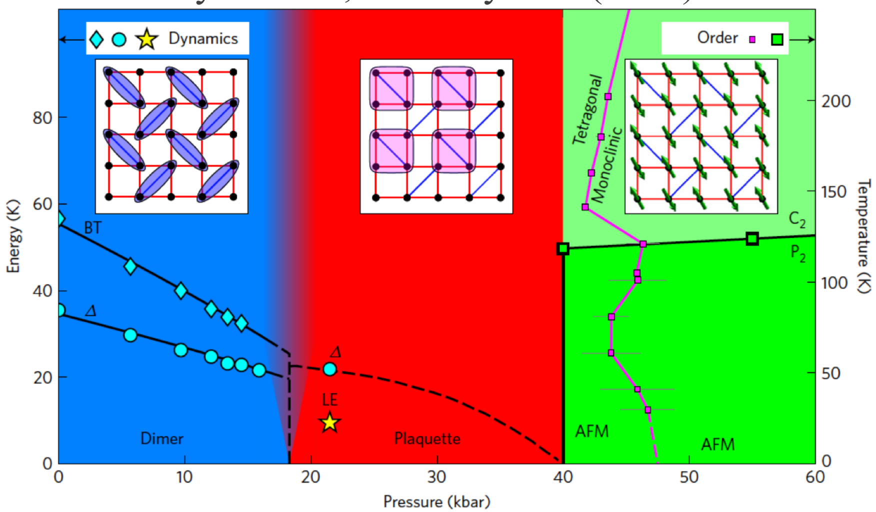
Discussion

J/k_B = -5.14 P + 69.1
α = 0.0322 P + 0.601



INS

M. Zayed *et al.*, Nat. Phys. **13** (2017) 962.



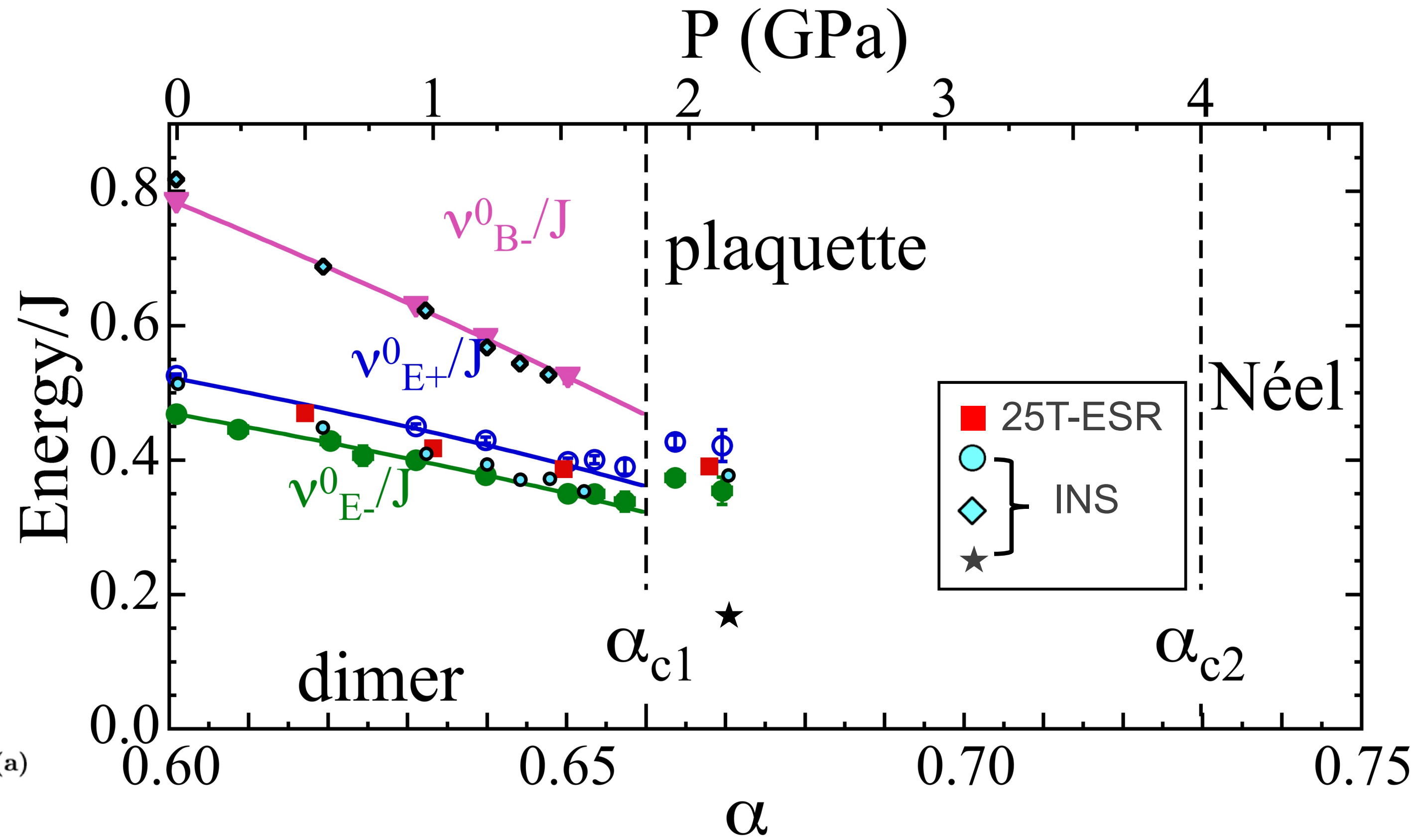
We observed the first-order phase transition accompanied with discontinuous excitation energy change at α = 0.66.

The transition points are consistent with the theoretical prediction.

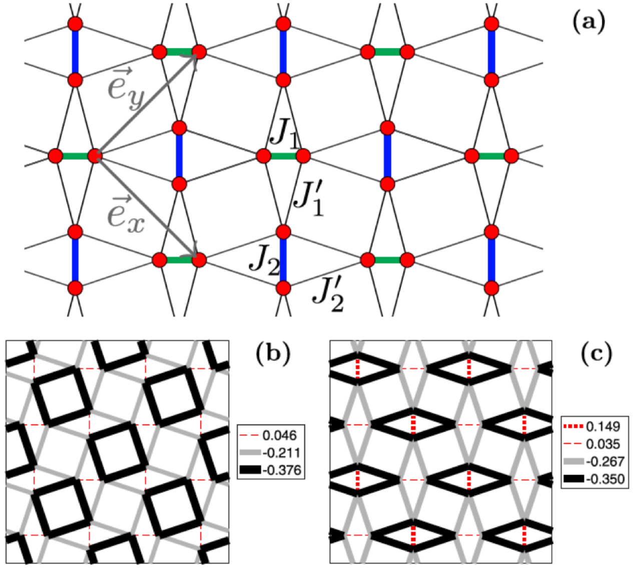
cf $\alpha_{c1} = 0.675$
$\alpha_{c2} = 0.76\text{-}0.77$

Discussion

J/k_B = -5.14 P + 69.1
α = 0.0322 P + 0.601

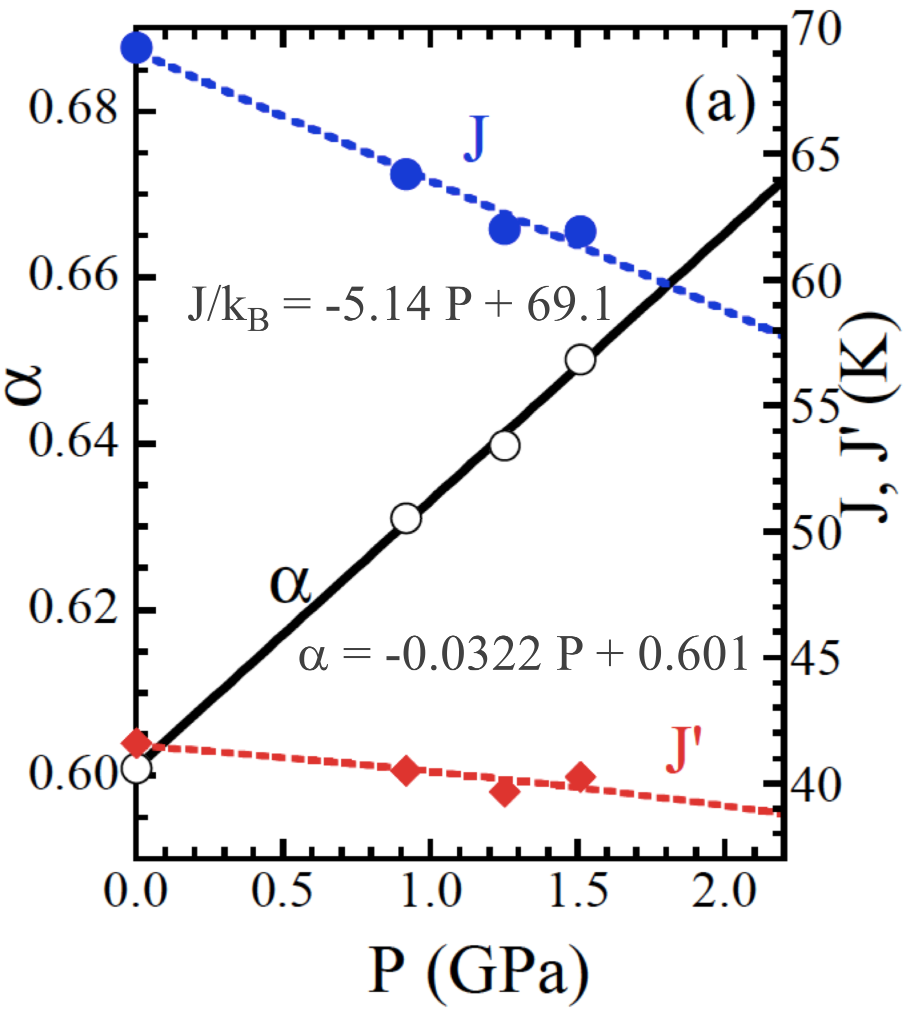


C. Boos et al., Phys. Rev. B **100** (2019) 140413.



Phase transition from the dimer phase to the full plaquet phase accompanies the appearance of two types of intra- and/or interdimer interactions.

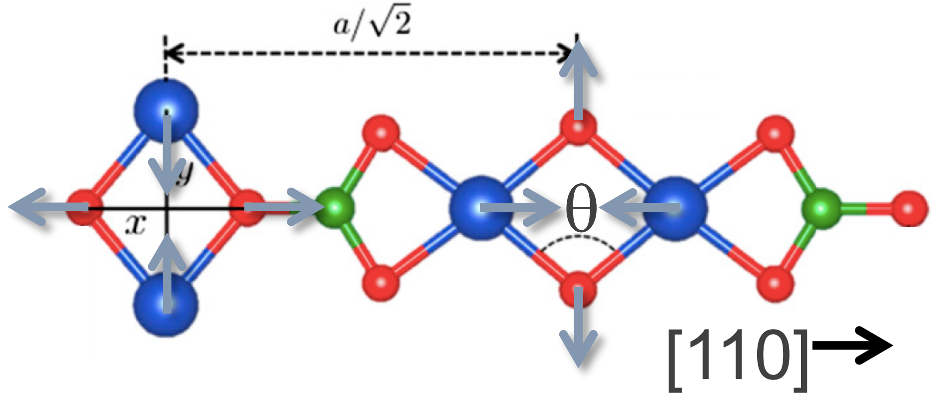
Discussion



\# Slight lattice reduction in ab plane can yield large reduction of J by changing the Cu-O-Cu angle.

Nanopantograph mechanism

G. Radtke *et al.*, Porc. Natl. Acad. Sci. USA **112** (2015) 1971.



$$\theta \simeq 35 \frac{\Delta a}{a}$$

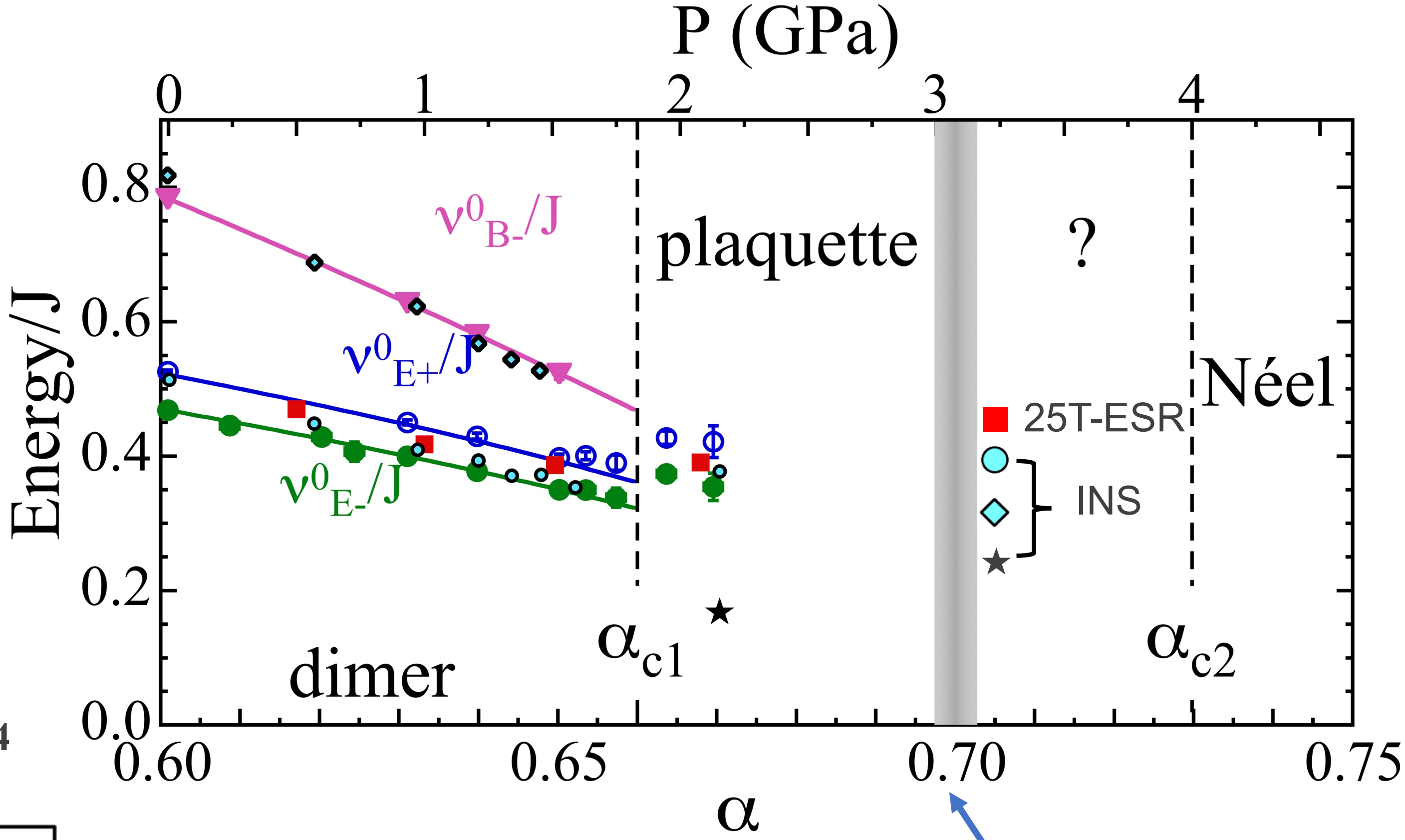
S. Haravifarda *et al.*, Porc. Natl. Acad. Sci. USA **109** (2012) 2286.

$$\frac{\Delta a(P)}{a} = -1.18 \times 10^{-3} P$$

97.6º at 0 GPa
⇩
93.2º at 1.85 GPa

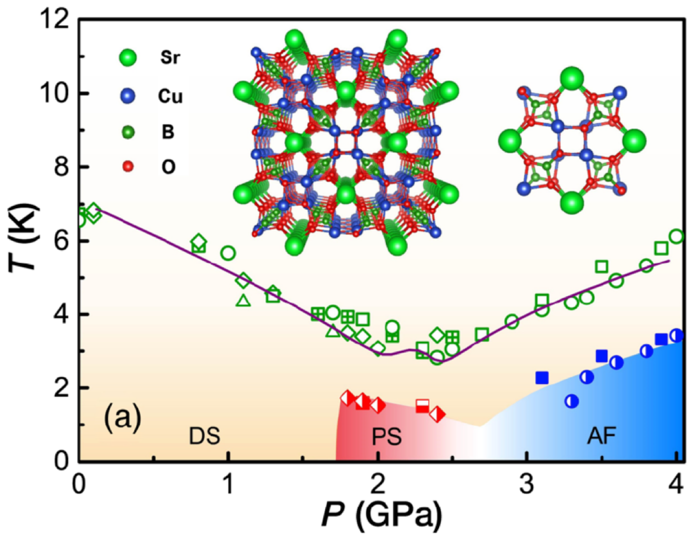
Discussion

J/k_B = -5.14 P + 69.1
α = 0.0322 P + 0.601



α_{c3} = 0.70
H. Nakano and T. Sakai,
J. Phys. Soc. Jpn. **87** (2018) 123702.

specific heat
J. Guo *et al.*, Phys. Rev. Lett. **124** (2020) 206602.



\# Anomaly found in specific heat measurement in 3 – 4 GPa corresponds to the third boundry α_{c3} found in the numerical diagonalization calcuration???

Summary

We have developed unique multi-extreme THz ESR systems using the piston-cylinder type pressure cells with THz window.
We applied this ESR system to the 2D orthogonal dimer spin system $SrCu_2(BO_3)_2$ and we succeeded in observing that the gap energy was reduced by applying the pressure.
We observed the first-order phase transition at 1.85 GPa ± 0.10 GPa. It occurs with remaining gap.
The pressure was successfully converted to α and we concluded that the system undergoes the phase transition from dimer singlet phase to plaquette singlet phase at $\alpha = 0.66$.

Future challenges

Observation of the signature of full plaquette.
ESR measurement under higher pressure region.