Molecule-based chiral manets

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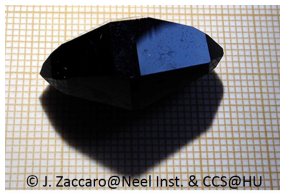
Core-to-Core Program, A. Advanced Research Networks.

9/4, 2019

Single chiral domain crystal growth Inorganic materials

1. "Monochiral helimagnetism in homochiral crystals of CsCuCl3", Y. Kousaka, T. Koyama, K. Ohishi, K. Kakurai, V. Hutanu, H. Ohsumi, T. Arima, A. Tokuda, M. Suzuki, N. Kawamura, A. Nakao, T. Hanashima, J. Suzuki, J. Campo, Y. Miyamoto, A. Sera, K. Inoue and J. Akimitsu. Phys. Rev. Materials 1, 071402(R)/5 (Dec 12, 2017) , DOI:10.1103/PhysRevMaterials.1.071402

2. "Magnetic Properties and Magnetic Phase Diagrams of Trigonal DyNi3Ga9", Hiroki Ninomiya, Yuji Matsumoto, Shota Nakamura, Yohei Kono, Shunichiro Kittaka, Toshiro Sakakibara, Katsuya Inoue, and Shigeo Ohara, J. Phys. Soc. Jpn. , 86, 124704 (2017) Published November 7, 2017, DOI:10.7566/JPSJ.86.124704



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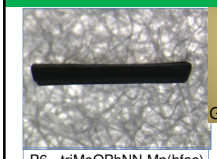
Chiral Magnets



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Design of Chiral Crystals

1. Chiral Induction for Molecule-based crystals
   Chiral Ligand
2. Spontaneous crystallization
   Unsaturated intercalation of layered materials
   Tetrahedrals design

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New Molecule-based magnets

1. "Magnetic phase diagram and chiral soliton phase of antiferromagnetic chiral magnets [NH4][Mn(HCOO)3]", Yoji Ichiraku, Rikuho Takeda, Seiya Shimono, Masaki Mito, Yoshiki Kubota, Katsuya Inoue, and Yusuke Kato, J. Phys. Soc. Jpn. 88, 094710 (2019), Published August 22, DOI:10.7566/JPSJ.88.094710

2. "Crystal structures and magnetic properties of nitroxide radical-coordinated copper(II) and cobalt(II) complexes", Yan-Li Gao, Katsuya Inoue, Transition Metal Chemistry, 44, 3, 283-292 (Apr 2019) , DOI: 10.1007/s11243-018-00297-w

3. "Synthesis, crystal structures and magnetic properties of six coordination compounds constructed with pyridine iminomethyl-TEMPO radicals and [M(hfac)2] (M = CuII and MnII)", Yan-Li Gao, Sadafumi Nishihara and Katsuya Inoue, CRYSTENGCOMM Volume: 20 Issue: 21 Pages: 2961-2967 Published: JUN 7 2018, DOI: 10.1039/c8ce00061a

4. "Coupling of Magnetic and Elastic Domains in the Organic–Inorganic Layered Perovskite-Like (C6H5C2H4NH3)2FeIICl4 Crystal", Yuki Nakayama, Sadafumi Nishihara, Katsuya Inoue, Takashi Suzuki, and Mohamedally Kurmoo. Angew. Chem. Int. Ed. 2017, 56, 9367–9370 (Jul 7, 2017), DOI:10.1002/anie.201703898

5. "Biomimetic Transformation by a Crystal of a Chiral Mn-II-Cr-III Ferrimagnetic Prussian Blue Analogue", Y. Yoshida, K. Inoue, K. Kikuchi, M. Kurmoo. CHEMISTRY OF MATERIALS, 28, 19, 7029-7038 (Oct 11 2016), DOI:10.1021/acs.chemmater.6b02852

6. "Progressive Transfromation between Two Magnetic Ground States for One Crystal Structure of a Chiral Molecular Magnet", Li Li, Sadafumi Nishihara, Katsuya Inoue, Mohamedally Kurmoo, Inorganic Chemistry, 55 (6), 3047–3057 (Mar 21 2016) , DOI:10.1021/acs.inorgchem.5b02956

7. "Synthesis, Crystal Structure, and Magnetic Properties of a Chiral Cyanide-Bridged Bimetallic Framework K3[MnII(L-asp)]6[CrIII(CN)6]·2H2O", Li Li, Sadafumi Nishihara, Katsuya Inoue, Mohamedally Kurmoo, Inorganic Chemistry , 55, 300-306 (Jan 4 2016) , DOI:10.1021/acs.inorgchem.5b02399

8. "High Magnetic Hardness for the Canted Antiferromagnetic, Ferroelectric and Ferroelastic Layered Perovskite-like (C2H5NH3)2[FeIICl4]", Jing Han, Sadafumi Nishihara, Katsuya Inoue, and Mohamedally Kurmoo, Inorg. Chem., 54, 2866-2874 (Mar 16 2015) , DOI: 10.1021/ic5030229

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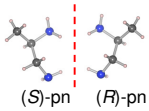
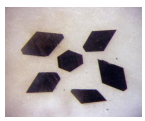
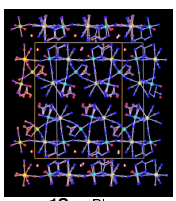
Molecule Based Chiral Magnet

$[Cu\{(S)\text{-pn}\}H_2O]_4[Cu\{(S)\text{-pn}\}]_2[W(CN)_8]_4 \cdot 2.5H_2O$

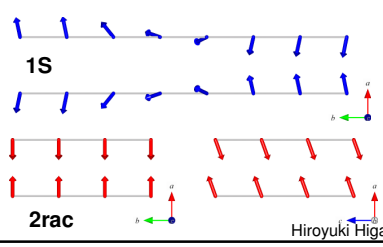
1,2-diaminopropane (pn)
$CuSO_4 \cdot 5H_2O$
$Cs_3[W^V(CN)_8] \cdot 2H_2O$
} Chiral Ligand







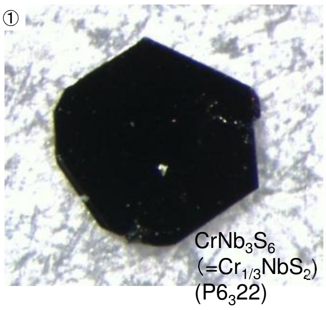
1S : Blue
2rac : Red

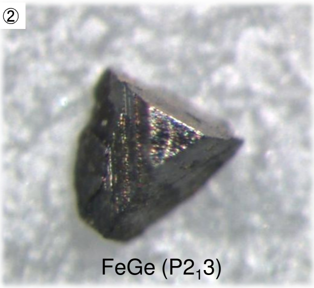


1 mm

Hiroyuki Higashikawa

Inorganic chiral magnets

① 

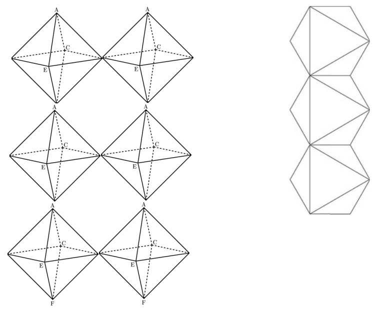
② 

M. Miyagawa, Y. Kousaka (HU)

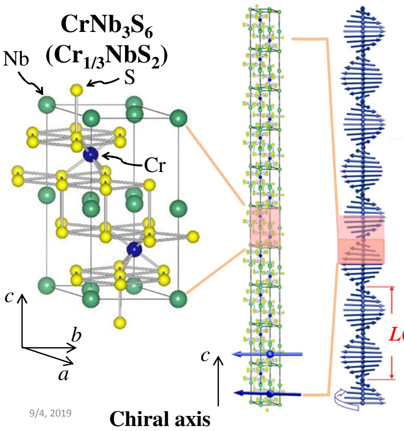
① T. Moriya and T. Miyadai: Solid State Communications **42** (1982) 209
② Ohoyama, Yasukochi, , Kanematsu, K , J. Phys. Soc. Jpn, 18, 589 (1963)

Spontaneous Resolution

対称性の低いユニットを結晶化させる



Chiral Magnet



Exchange interaction

$- J\, S_1 \cdot S_2$

v.s.

$- D \cdot S_1 \times S_2$

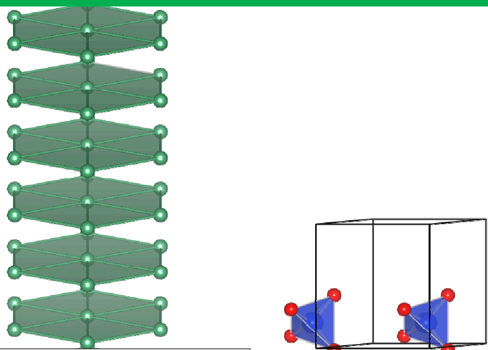
Dzyaloshinskii-Moriya (DM) interaction

$$L_0 = \frac{2\pi}{Q_0} = \frac{a_0}{\arctan(D/J)} \simeq \frac{J}{D} a_0$$

Typically $10a_0 \sim 100\, a_0$
CrNb$_3$S$_6$: ~ 40 a_0
(~ 48 nm)

I. E. Dzyaloshinskii, Sov. Phys. JETP **5**, 1259 (1957) .
T. Moriya, Phys.Rev.**120**, 91 (1960).

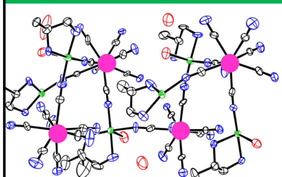
無機キラル磁性体の合成指針（模式図）



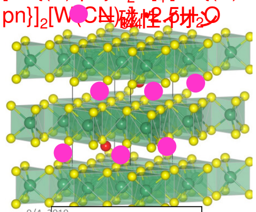
層状化合物に不飽和にインターカレートする。インターカレート可能サイトが3箇所の場合に1つ等。
例：C NbS (=CrNb S)

四面体型配位ユニットが積層した場合。
例：水晶

Targeted Chiral Magnets



[Cu{(*S*)-pn}H$_2$O]$_4$ [Cu{(*S*)-pn}]$_2$[W(CN)$_8$]$_4$・2.5H$_2$O



MM'$_3$S$_6$ (=M$_{1/3}$M'S$_2$)

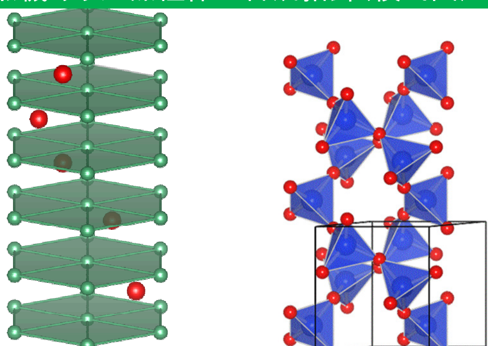
Molecule based chiral magnets

- Chiral Induction by ligands

Inorganic chiral magnets

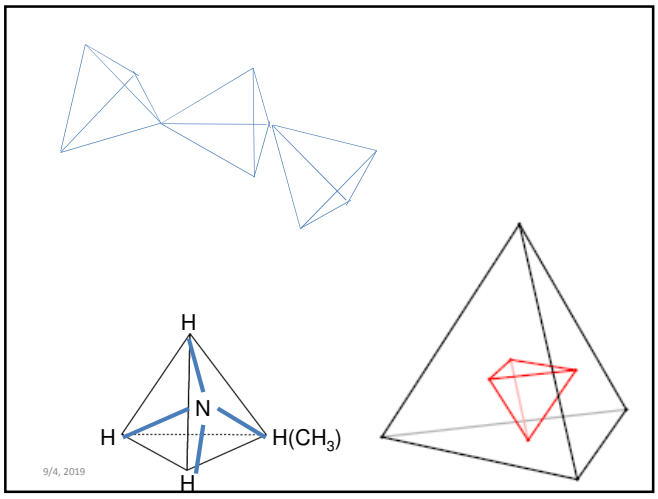
- Intercaleted Layered materials
  MM'$_3$S$_6$ (=M$_{1/3}$M'S$_2$), CsCuCl$_3$
- Tetrahedral coordinated based materials(contain 14, 15, 16 group elements and perovskites)
  GeFe, MnSi, MnP, CsCuCl3, Ferrites

無機キラル磁性体の合成指針（模式図）



層状化合物に不飽和にインターカレートする。インターカレート可能サイトが3箇所の場合に1つ等。
例：C NbS (未知のキラル無機磁性体へと研究対

四面体型配位ユニットが積層した場合。
例：水晶



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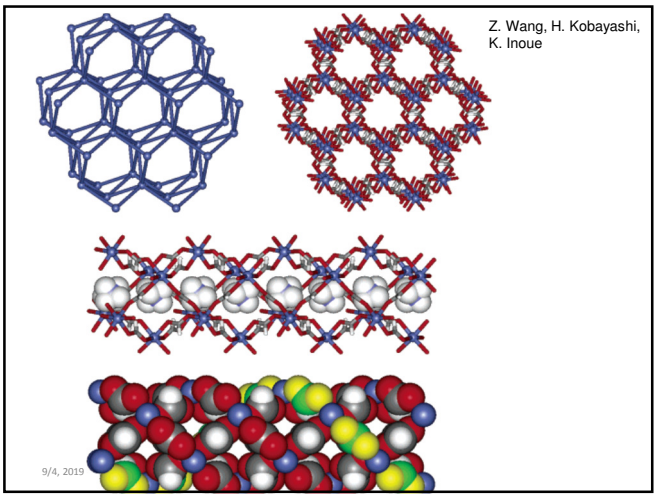

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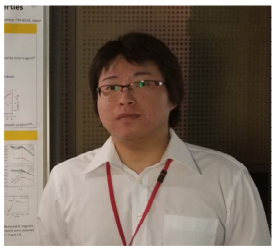
[ANH3][M(RCOO)2] systems
Work with Y. Ichiraku, R. Takeda, Y, Kato(U T), S. Shimono, Y. Kubota (OPU), M. Mito(KIT), D. Smirnykh, K. Hirono, Y, Sawada, Kida, M. Hagiwara(Osaka U)



Yoji Ichiraku DMITRII SMIRNYKH Keita Hirono

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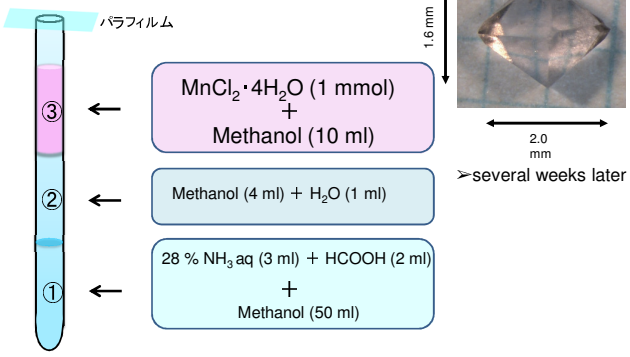
◎$[NH_4][Mn(HCOO)_3]$ Y. Ichiraku, K. Inoue



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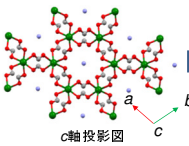
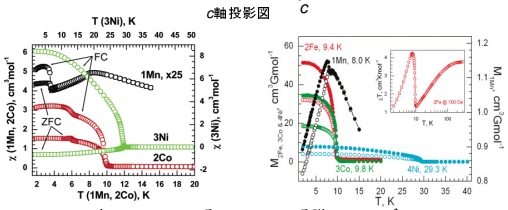
◎$[NH_4][M^{II}(HCOO)_3]$ (M=Mn, Co, Ni) Z. Wang, H. Kobayashi, M. Kurmoo, K. Inoue

☆キラルな空間群：$P6_322$
☆c軸方向にらせん軸



c軸投影図

➡ キラル磁性体に特有な磁気挙動を示す可能性[2]



過去に報告されている粉末試料による磁化率測定データ[1]

例) $[NH_4][Mn(HCOO)_3]$
8.0 K以下の磁気挙動に差異 ➡ 磁気構造？ ➡ 単結晶試料を用いた軸依存の磁気特性の調査

[1] Zheming Wang, Katsuya Inoue *et al.*, *Inorg. Chem.*, 46(2), 437-445, **2007**
[2] L. M. Volkova *et al.*, *J. Supercond. Nov Magn.*, 29, 2931-2945, **2016**

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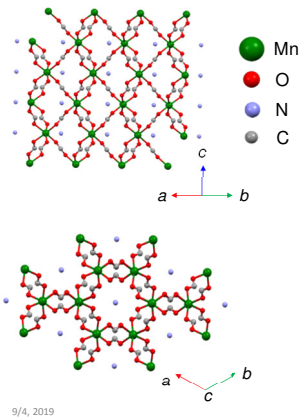
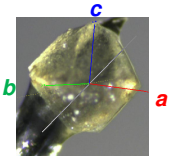
◎Structure Y. Ichiraku, K. Inoue





Formula	$[NH_4][Mn(HCOO)_3]$
Crystal system	hexagonal
Space Group	$P6_322$
a(Å)	7.360(7)
c(Å)	8.486(6)
$R1$	0.0194
$wR2$	0.0635
Flack parameter	0.03(7)
Z	2

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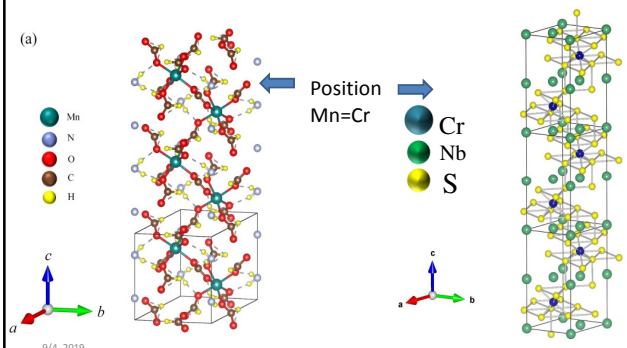
Y. Kato

$[NH_4][Mn(HCOO)_3]$
Hexagonal $P6_322$
a＝7.36 Å
c＝8.48 Å

$CrNb_3S_6$
Hexagonal $P6_322$
a＝5.73 Å
c＝12 Å



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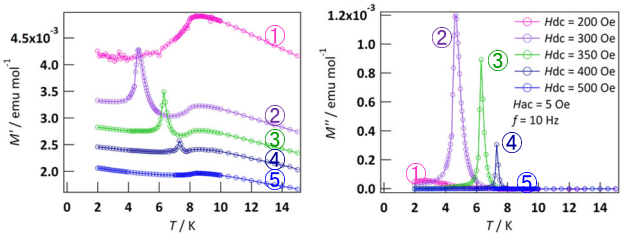
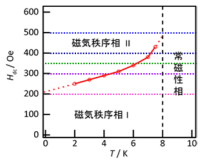
◎ac susceptibility

Y. Ichiraku, K. Inoue



➢領域外(①, ⑤) : 8.0 K未満においてMおよびM'のピークは観測されず
➢領域内(②, ③, ④) : 8.0 K未満においてMおよびM'のピークを観測
➡反強磁性転移温度以下に相境界の存在を確認
➢磁場増大に伴いピーク強度が大幅に減少
➡高調波解析による比較



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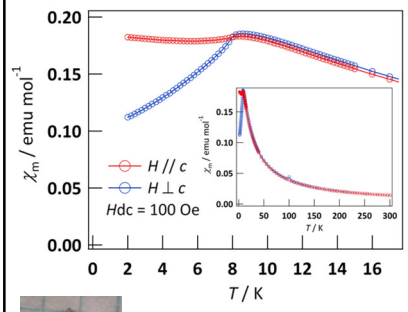
◎dc magnetizations

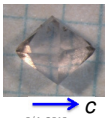
Y. Ichiraku, K. Inoue



H // c
C = 4.243 emu K mol^{-1}
θ_p = -10.76 K

H ⊥ c
C = 4.402 emu K mol^{-1}
θ_p = -11.77 K

◎C = 4.368 emu K mol^{-1}
(S = 5/2の時の理論値)



TN=8.0K

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◎ac susceptibility

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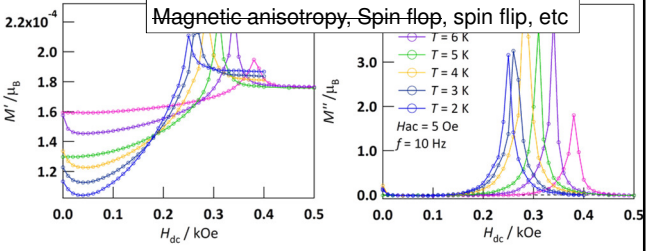
Possibilities:
~~Magnetic anisotropy, Spin flop~~, spin flip, etc



➢低温になるほどピークが低磁場側にシフト
➢8.0 K未満で特定の磁場領域においてのみ観測される磁気挙動
➡反強磁性転移温度以下において相境界の存在を示唆

Mのピークトップでの磁場H_{dc}と温度Tとの関係図(H-T 相図)を作成

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◎Field dependence

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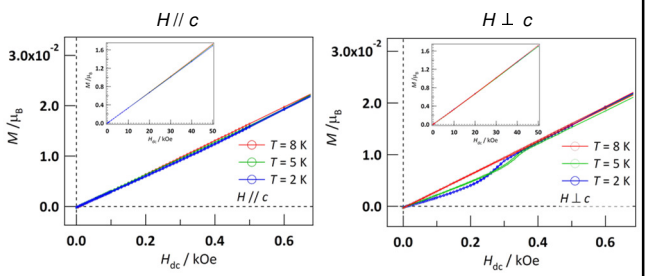

Possibilities:
Magnetic anisotropy, Spin flop, spin flip, etc

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◎ac susceptibilities

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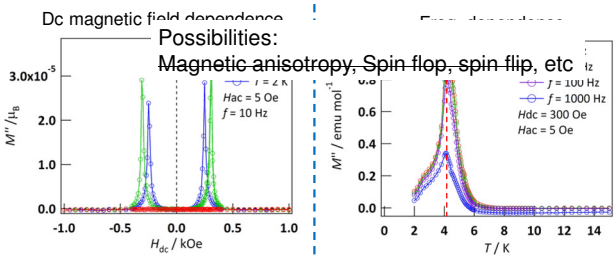
Possibilities:
~~Magnetic anisotropy, Spin flop, spin flip~~, etc



➢T = 5 K と T = 2 K においてM'のピークを観測

↓

転移前後でエネルギーの損失を伴う磁気相転移

➢周波数に依存したピークシフトは観測されず

↓

ある温度に固有な磁気相転移

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◎H_{dc}-T 相図

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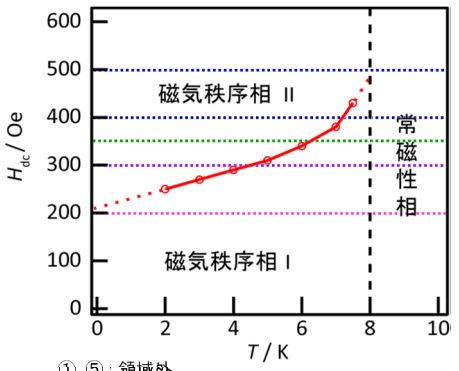

⑤ : H_{dc} = 500 Oe

④ : H_{dc} = 400 Oe
③ : H_{dc} = 350 Oe
② : H_{dc} = 300 Oe

① : H_{dc} = 200 Oe

①, ⑤ : 領域外
②, ③, ④ : 領域内 → 交流磁化率の温度依存性を調査

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M. Mito

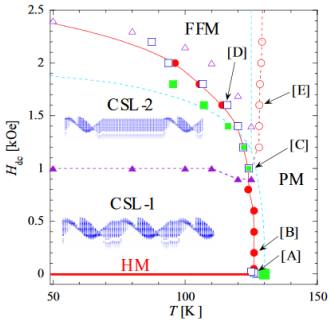

FIG. 8. Phase (region) diagram of $Cr_{1/3}NbS_2$ under the dc magnetic field H_{dc}. A series of anomalies observed in the ac magnetic susceptibility measurements such as $M'_{1\omega}$ (●, ○), $M''_{1\omega}$ (□), and $M_{3\omega}$ (■) is plotted. The intensity of the $M_{3\omega}$ anomaly is symbolized by the size of the symbol. The characteristic changes detected in the M-H curve of Fig. 7, characterized by H_c (△) and H_t (▲), are presented, along with the data on the regional boundary determined by magnetoresistance measurements for the microsample with H_c < 2 kOe (light blue dotted curve and line) [18]. Dotted line connecting the H_t data (▲) marks the crossover from the magnetically

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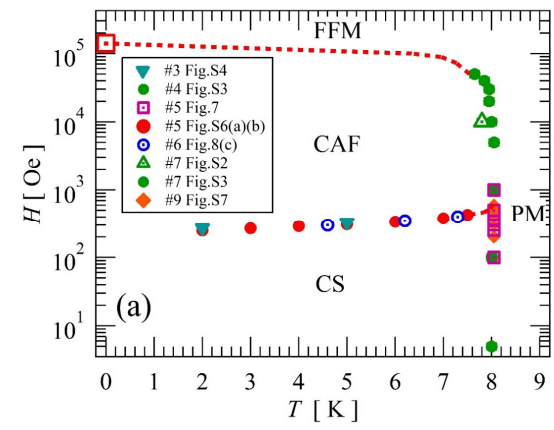

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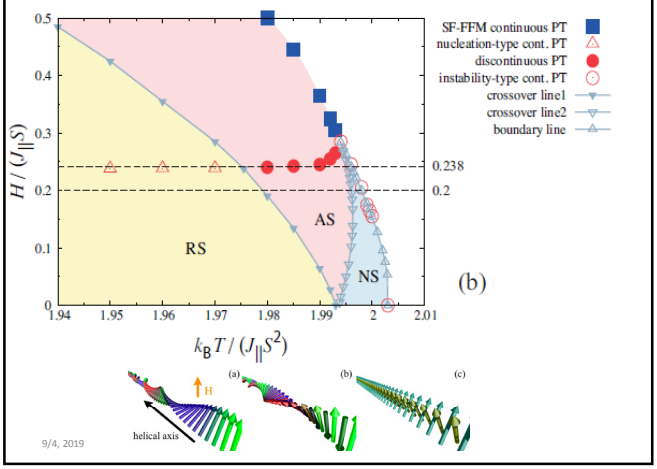
Takeda, Y. Kato



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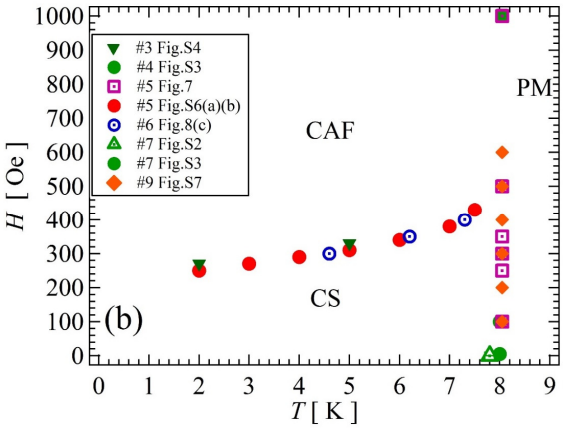
Y. Ichiraku, K. Inoue, Y. Kato



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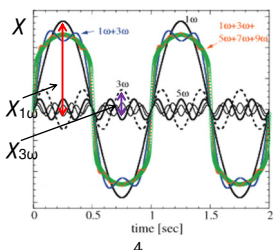
◎non-linear ac susceptibility

M. Mito

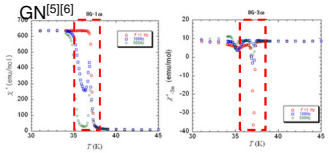


➢ $\chi_{1\omega} = \chi^{(0)} + \frac{4}{3}H_{ac}^2\chi^{(2)} + \frac{5}{8}H_{ac}^4\chi^{(4)} + \frac{35}{64}H_{ac}^6\chi^{(6)} + \cdots$

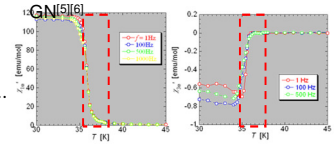
➢ $\chi_{3\omega} = \frac{1}{4}H_{ac}^2\chi^{(2)} - \frac{5}{16}H_{ac}^4\chi^{(4)} + \frac{21}{64}H_{ac}^6\chi^{(6)} + \cdots$

➡非線形成分

➢ $R-$GN[5][6]



➢ $rac-$GN[5][6]

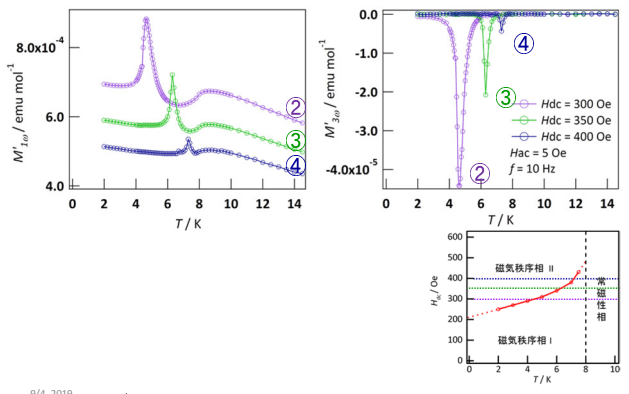


➢キラル体においてのみ$\chi_{3\omega}$の巨大な応答が観測されている

[5] Katsuya Inoue *et al.*, *Angew. Chem. Int. Ed.*,42, 4810-4813, **2003**
[6] Masaki Mito *et al.*, *Phys. Rev. B*, 79, 012406, **2009**

◎ non-linear ac susceptibility

M. Mito, Y. Ichiraku, K. Inoue



※解析プログラムは九州工業大学の美藤教授より提供

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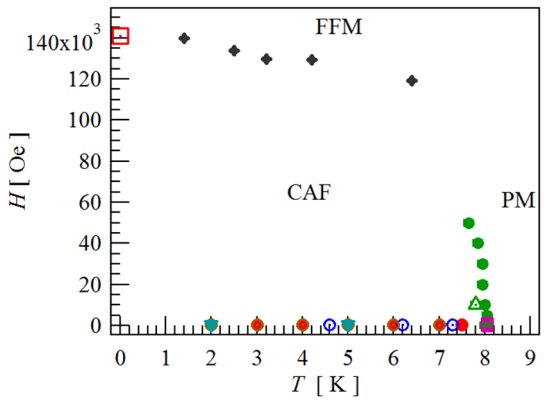


◎ non-linear ac susceptibility

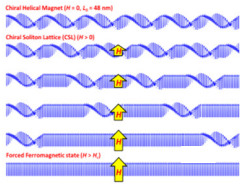
M. Mito, Y. Ichiraku, K. Inoue

➢$Cr_{1/3}NbS_2$ [7]

$\frac{M''_{1\omega}}{M'_{1\omega}}$ ≒ 10 %, $\frac{M'_{2\omega}}{M'_{1\omega}}$ ≒ 0.2 %, $\frac{M'_{3\omega}}{M'_{1\omega}}$ ≒ 8 ~ 10.8 %

➢$[NH_4][Mn(HCOO)_3]$

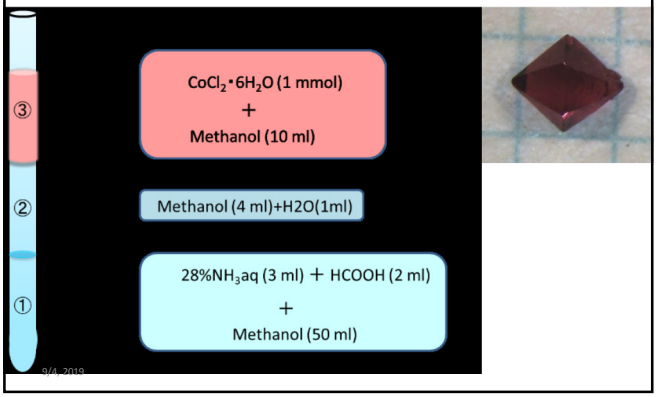
	$M''_{1\omega}/M'_{1\omega}$	$M'_{2\omega}/M'_{1\omega}$	$M'_{3\omega}/M'_{1\omega}$
300 Oe	32.2 %	0.13 %	5.0 %
350 Oe	29.6 %	0.32 %	2.9 %
400 Oe	15.6 %	0.054 %	0.81 %



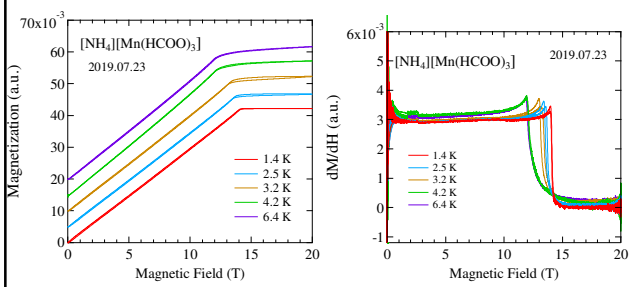
[7] Kazuki Tsuruta *et al.*, *Phys. Rev. B*, 93, 104402, **2016**

Y. Ichiraku, K. Inoue

[NH4][Co(HCOO)3]



High Field (Pulse) measurement



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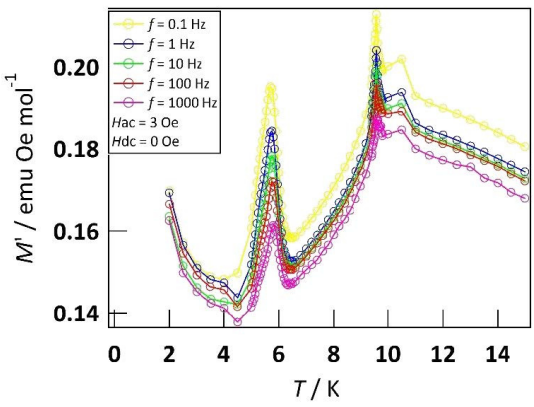
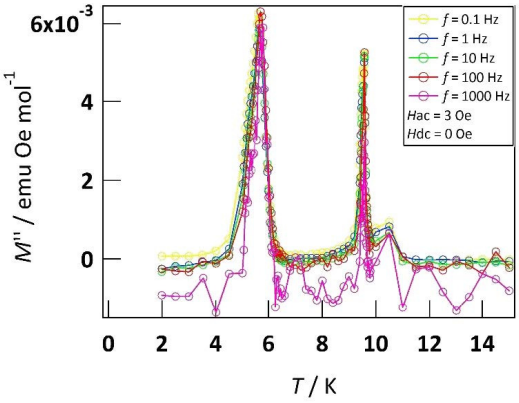


Y. Ichiraku, K. Inoue



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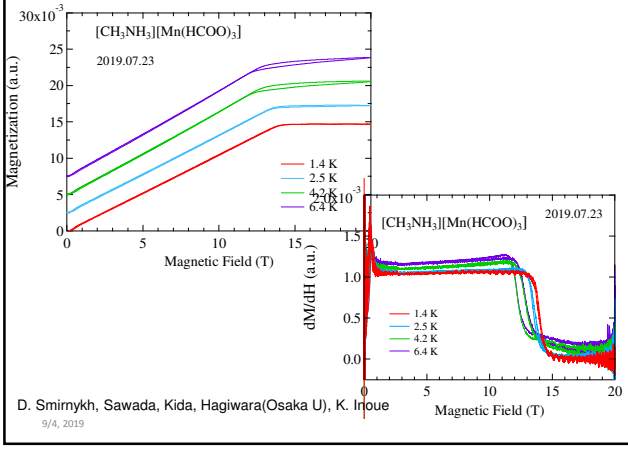
High Field (Pulse) measurement



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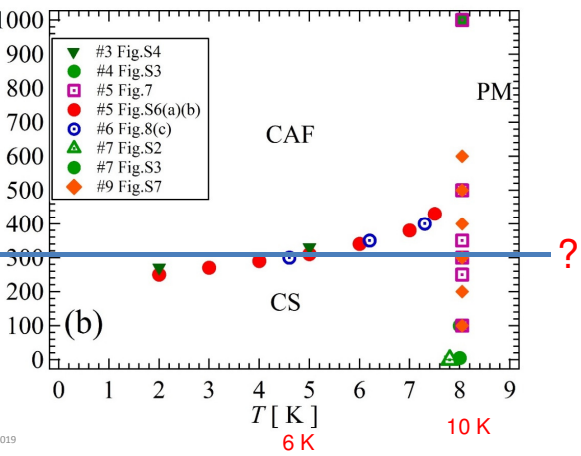

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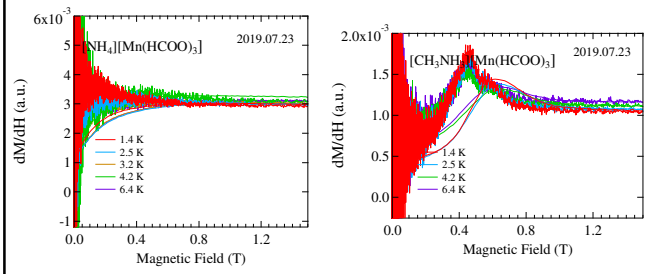

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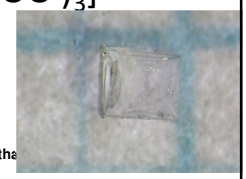
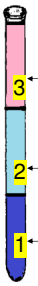
CH3NH3+[Mn(HCOO-)3]





3rd Layer
MnCl2 0,1 mMol in metha
solution

2nd layer
methanol 2ml with water 1ml

1st layer
8 ml methanol solution containing
0.80 M NH4OH and 0.40 M HCOOH

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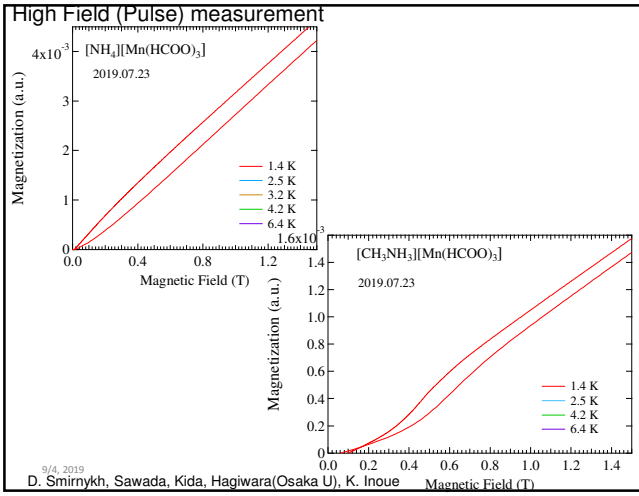
High Field (Pulse) measurement



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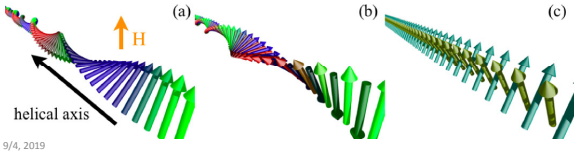
summary

- Successful growth of a series of new chiral magnets, P6322, [NH3A][M(RCOO)3], A=H, CH3; M=Mn, Co; R=H
- There is a possibility of growing new chiral magnets, A and R=organic substituents, M=transition metals, Lanthanoids.



Inoue Lab.

Platform for Advanced Material Research Centered around Spin Chirality

Advanced materials for new-generation telecommunication technologies

Proof of chiral control of material properties and establishment of basic science

Educating young researchers for their international efforts

England

Building the base of international networks for the future

University of Glasgow
Base institution

Ural Federal University
Base institution

Institute of Metal Physics, Russian Academy of Science

PNPI
Sankt-Peterburg

Russia

Measurement of physical properties
Prove theoretically estimated chiral properties

Create a new integral field about spin chirality

Japan

Material production
Large expansion of chiral magnetic crystals

Theory
Establish basic science for creating functions of chiral magnetic material

Australia

Monash University
Collaborating institutions in England

Expansion of organic consortium

+ α

Future consortium base

Hiroshima University
URA support・financial support

- Collaboration with international standard education program
- Formation of base for international education and research
- Improvement of university's international reputation

Chirality Research Center, Hiroshima University

The Open University of Japan	Hiroshima University Base Institution	The University of Tokyo
Osaka University Collaborators	Osaka Prefecture University Collaborators	Kyushu Institute of Technology Collaborators
Zaragoza University Collaborators	University of Lyon 1 Collaborators	Yamanashi University Collaborators

Hiroshima University center activity support staff
Specially appointed substitute professors and designated administrative assistants

Institute for Molecular Science
Collaborating institutions

Operation direction of the consortium

(1) Build relationships for naive idea exchanges between researchers of different cultural backgrounds.
(2) Provide young researchers with opportunities to test their flexible ideas, not confined to conventional ideas

Research collaboration (combination of theory and experiment), continuous multilateral seminars, and exchanges between researchers (20 people/year)

(1) Monthly brainstorming (2) Small visiting seminars (3) Regular seminars at bases (semiannual) (4) International seminars (annual) (5) Support for seminars and

Google

Hiroshima chiral

Thank you !

研究拠点形成事業
Core-to-Core Program

RSF Russian Science Foundation

University of Glasgow

Ural Federal University
named after the first President of Russia B.N.Yeltsin

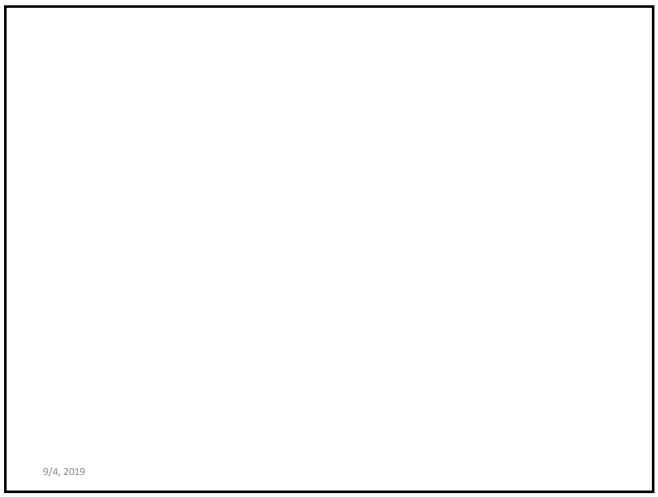
Japan Society for the Promotion of Science
日本学術振興会

科研費 KAKENHI

EPSRC
Engineering and Physical Sciences Research Council

Today's Dinner

At same restaurant with Lunch from 20:45!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