# X-ray and Neutron Analysis of Heusler Alloys

Kanta Ono

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Research Organization (KEK)

# Collaborators

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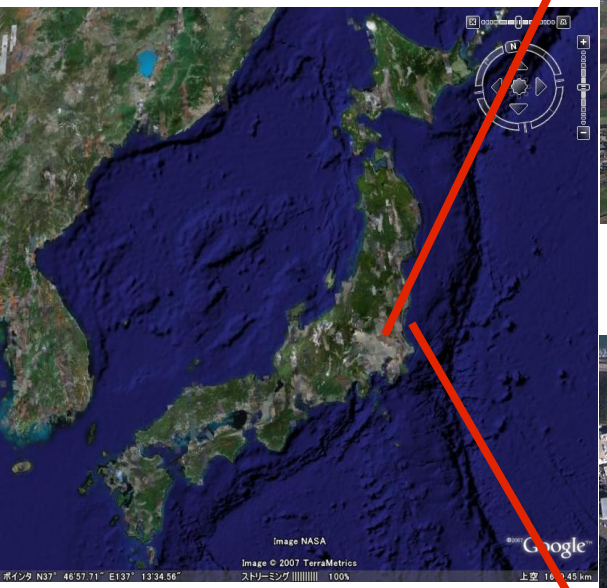
2) High Energy Accelerator Research Organization (KEK)
3) Frontier Research Center for Applied Atomic Sciences, Ibaraki University
4) Department of Materials Science, Tohoku University

# KEK




Tsukuba

Photon Factory

Tokai

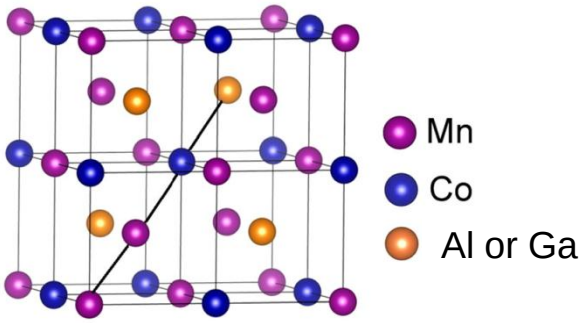
J-PARC/MLF

# Neutron experiment facility at J-PARC/MLF

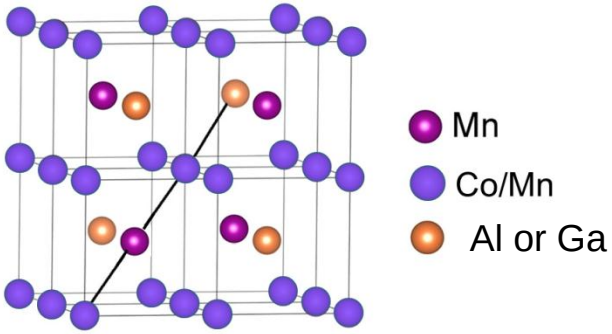
# Outline

1. Structure and magnetic structure analysis of Heusler alloys using x-ray and neutrons

2. Crystal and magnetic structures of $Mn_2CoGa$ Heusler alloy

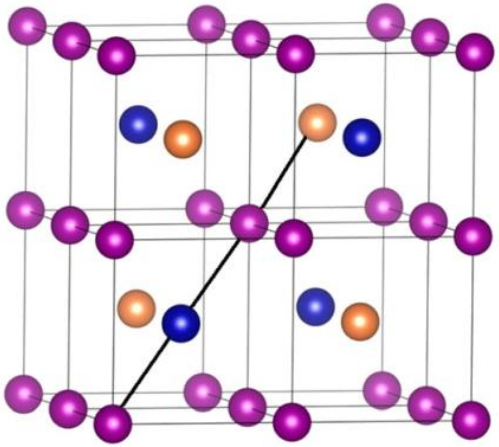



$Hg_2CuTi$-type (Xa)

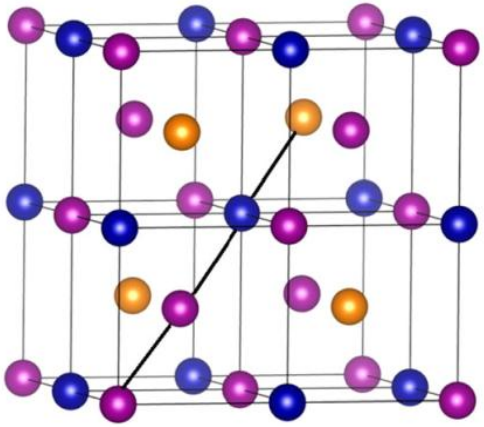



$L2_{1b}$-type (Modified $L2_1$)
（Co, Mn randomly distributed）

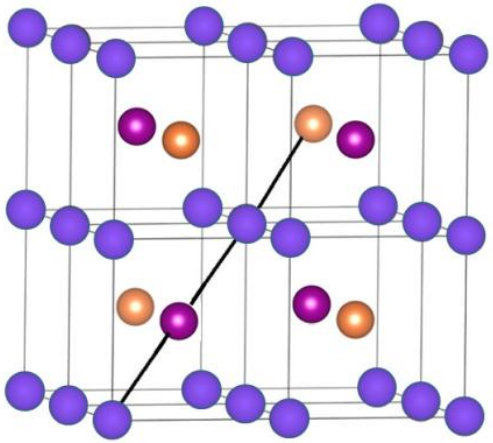
# Structure of Heusler alloys



*L*$2_1$-type
Space group : 225
A – B – A - C



$Hg_2CuTi$ ($X_a$) -type
Space group : 216
A – A – B - C

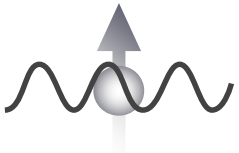


*L*$2_{1b}$-type
Space group : 225
(A,B) – A – (A,B) - C

# Neutron diffraction / scattering

## Neutron

- No charge
- spin 1/2
- meV~Åwavelength



| | X-ray | Neutron |
|---|---|---|
| **Scattering cross section** | Proportional to the number of electrons | Random |
| **Magnetic scattering** | Circular dichroism | spin1/2 |
| **energy** | keV | meV |

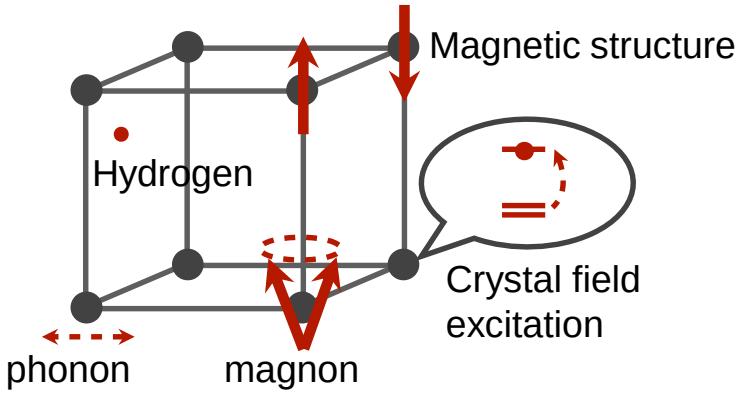
## Advantages

- Sensitive to light elements
- Structure and magnetic structure
- Phonon, magnon dispersion
- Crystal field splitting

| | elastic | inelastic |
|---|---|---|
| **Nuclear** | Crystal structure | phonon |
| **Magnetic** | Magnetic structure | magnon<br>crystal field |

## Disadvantages

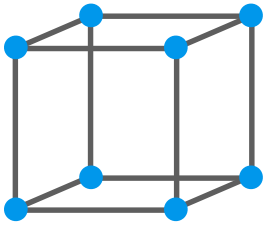
- Research reactor or large accelerator
- mg ~ g samples (difficult for thin films)



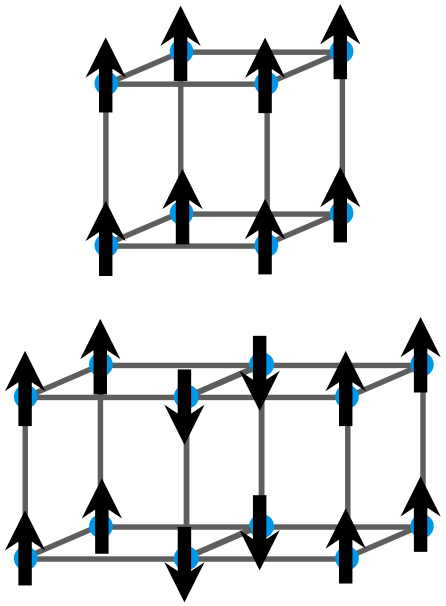
# Magnetic structure

- Magnetic structure analysis
  - Almost identical to x-ray crystal structure analysis
  - Magnetic unit cell is sometimes different from crystals
  - Magnetic scattering can be observed only in large d region for both θ-2θ and Time of flight (TOF)

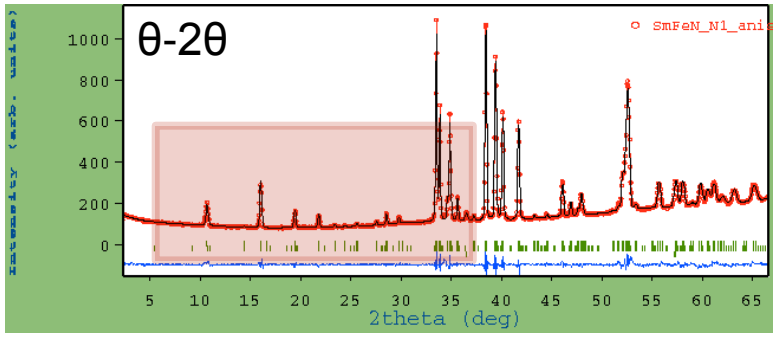
Crystallographic unit cell

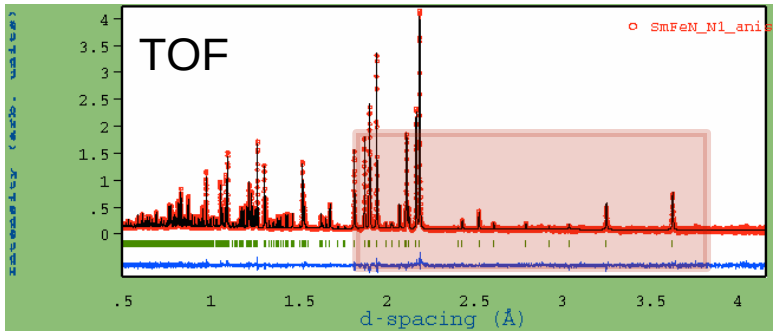


Magnetic unit cell



Region of magnetic scattering contributions

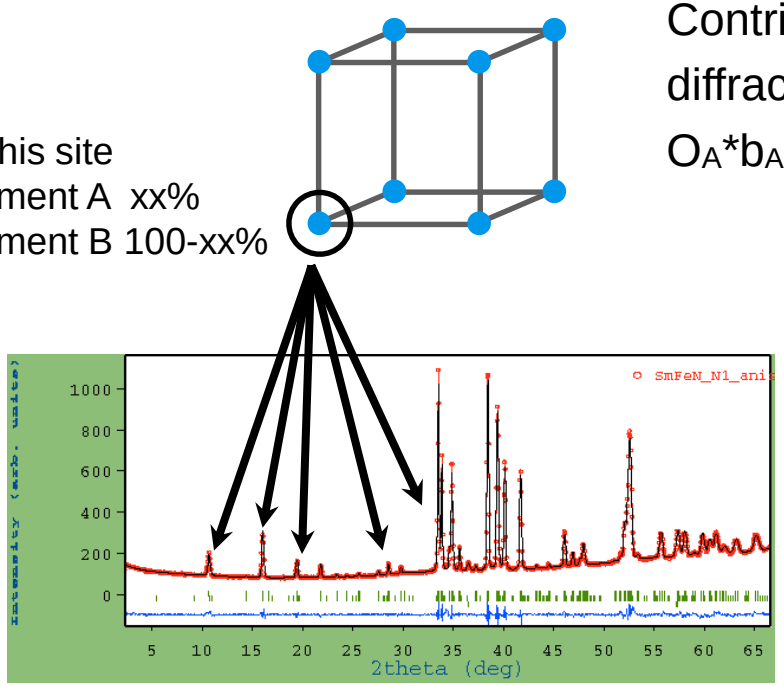


# Site occupancy, degree of order

- Site occupancy
  - Each element (nuclear) has different nuclear scattering length

At this site
Element A xx%
Element B 100-xx%




Contribution of elements A,B at one site to the diffraction peaks

$O_A*b_A*\alpha_A+O_B*b_B*\alpha_B$ , $O_A+O_B=1$

Usually similar

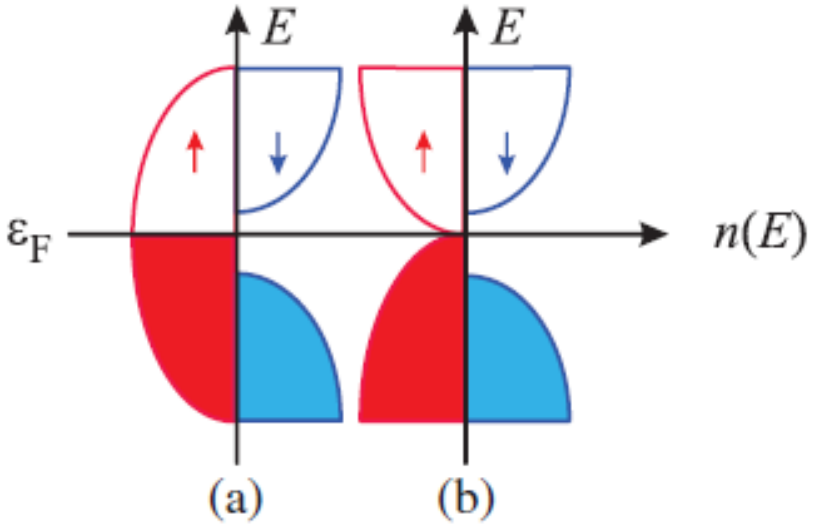
→ scattering length $b_A$、$b_B$ contrast is important

| Neutron scattering length (fm) | |
|---|---|
| Mn | -3.75 |
| Fe | 9.45 |
| Co | 2.49 |
| Cu | 7.72 |
| Al | 3.45 |
| Ga | 7.28 |

# Mn-based Heusler alloys : $Mn_2YZ$

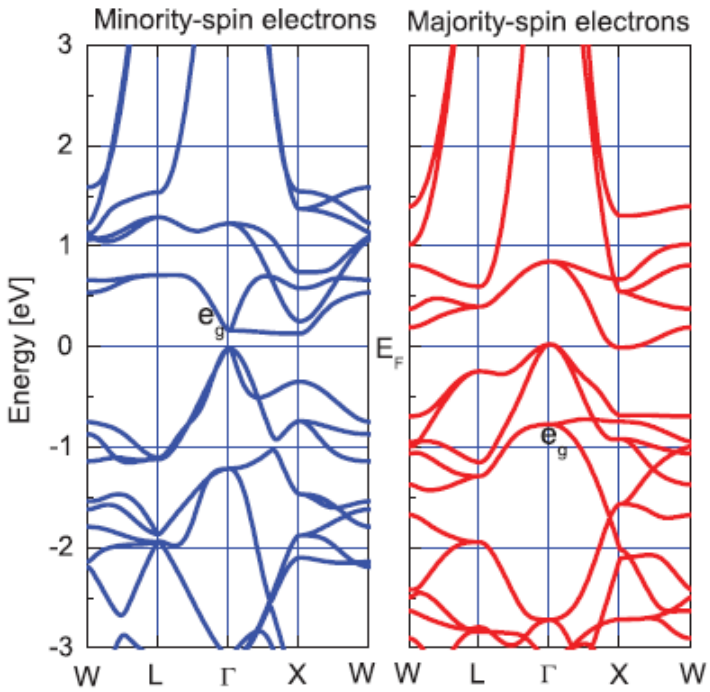
Recently, Mn-based Heulser alloys with a chemical formula of $Mn_2YZ$ have been attracted attention in the field of spintronics because many of them are reported to be half-metallic ferro- or ferri-magnets.

Especially, $Mn_2CoAl$ has been reported to have spin gapless semiconductor-type density of states [1,2], and the physical properties associated to the unique electronic structure are expected to have spintronics applications.




DOS of (a) Half metallic ferromagnet and (b) Spin gapless semiconductor

$Mn_2CoAl$ band structure




S. Ouardi *et al.*, *Phys. Rev. Lett.*, 110 (2013) 100401.


[1] G. D. Liu *et al.*, *Phys. Rev. B*, 77 (2008) 014424.
[2] S. Ouardi *et al.*, *Phys. Rev. Lett.*, 110 (2013) 100401.

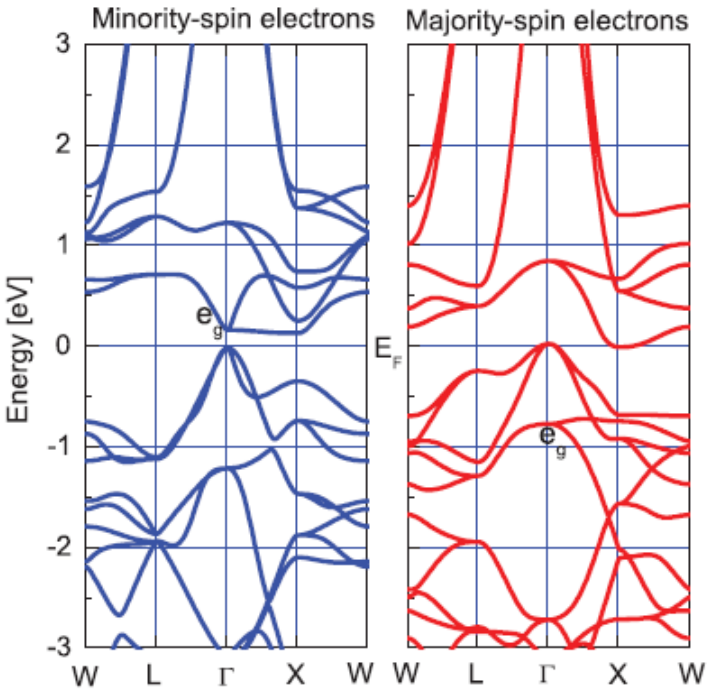
# Mn-based half metallic Heusler alloys

Recent topics

**Spin Gapless Semiconductor (SGS)** ⇒ New material for spintronics

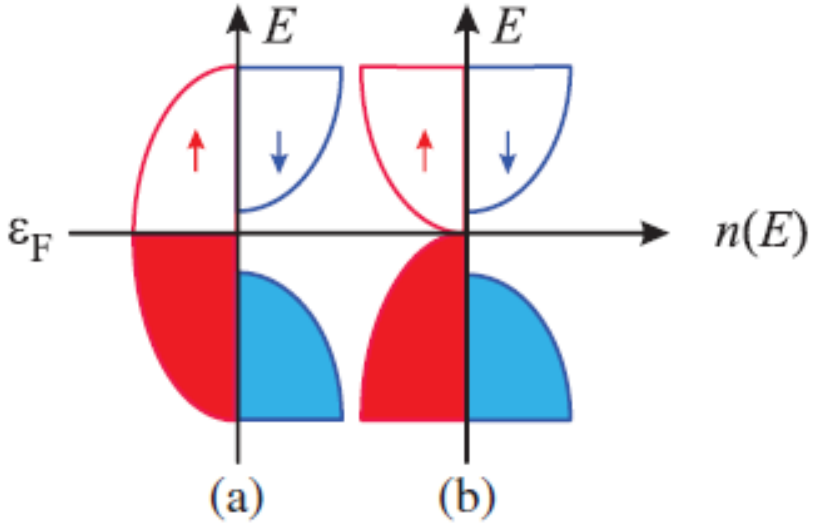
**$PbPdO_2$ :**
**X.L. Wang, Phys. Rev. Lett. (2008).**
**$Mn_2CoAl$ :**
**S. Ouraudi, et al. Phys. Rev. Lett. (2013).**

$Mn_2CoAl$ band structure




S. Ouardi *et al.*, *Phys. Rev. Lett.*, 110 (2013) 100401.

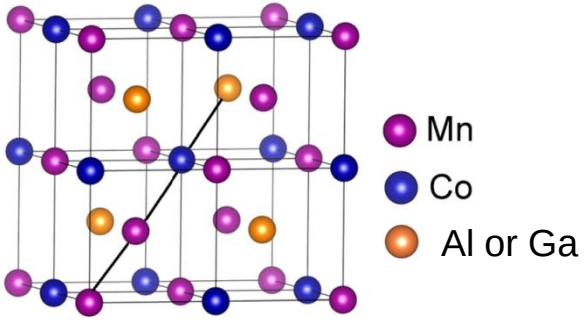
DOS of
(a) Half metallic ferromagnet and
(b) Spin gapless semiconductor



# Crystal structure of $Mn_2CoZ$

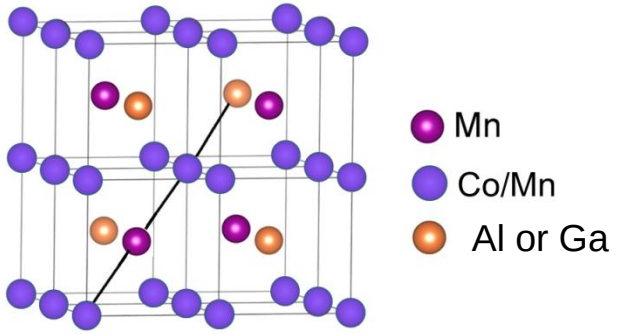
The crystal structure of $Mn_2CoZ$ series is thought to be $Hg_2CuTi$-type [1]

The crystal structure of $Mn_2NiGa$, $Mn_2NiSn$ and $Mn_2CoSn$ was confirmed to be L21b-type structure from neutron diffractions [2,3] and Mössbauer spectroscopy and NMR [4].




**(Mn,Mn,Co,Ga)**

$Hg_2CuTi$-type




**{(Mn/Co), Mn, (Mn/Co), Ga}**

$L2_{1b}$-type (Modified $L2_1$)

（Co, Mn randomly distributed）

[1] G. D. Liu et al., Phys. Rev. B, 77 (2008) 014424.
[2] P. J. Brown et al., J. Phys.: Condens. Matter, 22 (2010) 506001.
[3] R. B. Helmholdt, K. H. J. Buschow, J. Less-Common Metals, 128 (1987) 167-171.
[4] J. Winterlik et al., Phys. Rev. B, 83 (2011) 174448.

Since the atomic configuration closely correlates with the electronic structure, investigations on the crystal structure are very important.

# Introduction : $Mn_2CoGa$

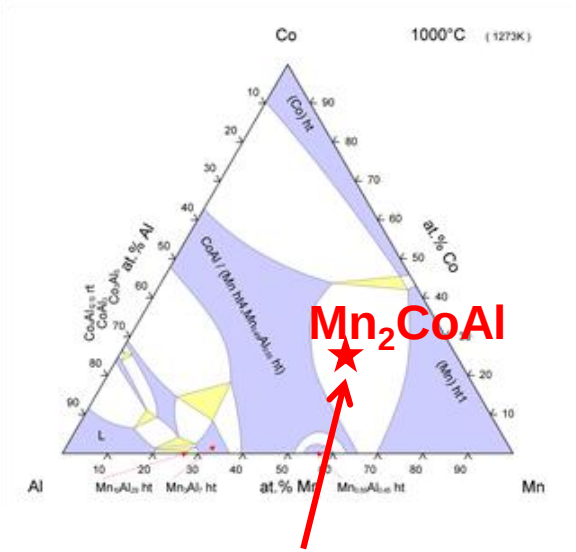
In the phase diagram for Mn-Co-Al ternary alloy, the equilibrium state below 1273 K of the stoichiometric $Mn_2CoAl$ is in two-phase region.

In the present study, we focus on the related material of $Mn_2CoGa$, which has been already reported to indicate half-metallic density of states from theoretical calculations.

Magnetic and powder neutron diffraction measurements were performed in the $Mn_2CoGa$ alloy, and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) observations were also carried out.

# Phase diagrams of Mn-Co-Al and Mn-Co-Ga

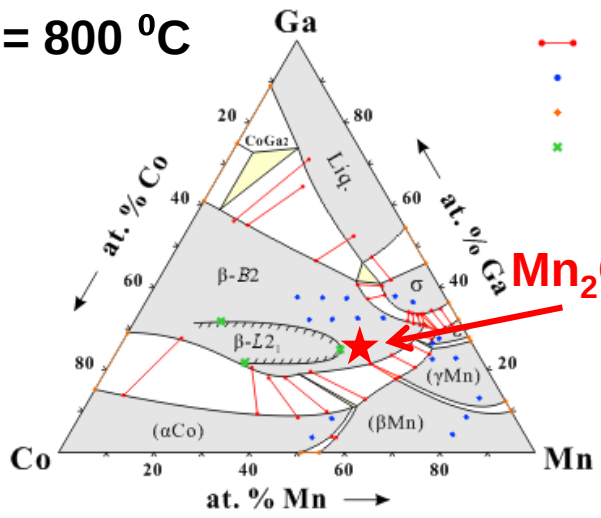
## Phase diagram of Mn-Co-Al

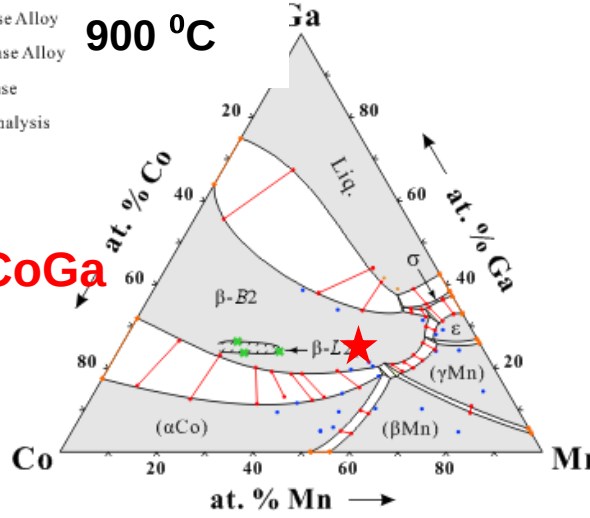


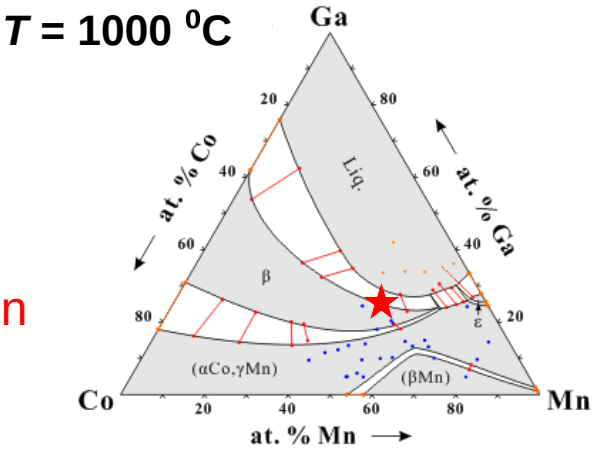

Stoichiometric composition of $Mn_2CoAl$ locates in the two phase region at 1273 K.

R. Kainuma et al., J. Alloys Compds., 269 (1998) 173–180

## Phase diagrams of Mn-Co-Ga



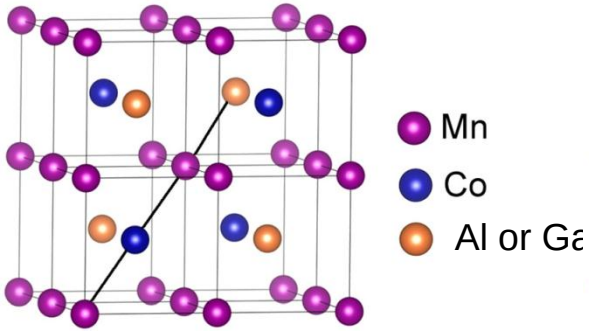




Single phase of stoichiometric composition for $Mn_2CoGa$ is stable at lower temperature.

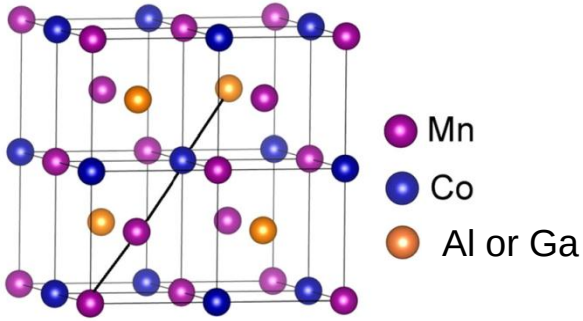
Minakuchi et al., J. Alloys and Compounds 645 (2015) 577

# Possible structure models for $Mn_2CoGa$

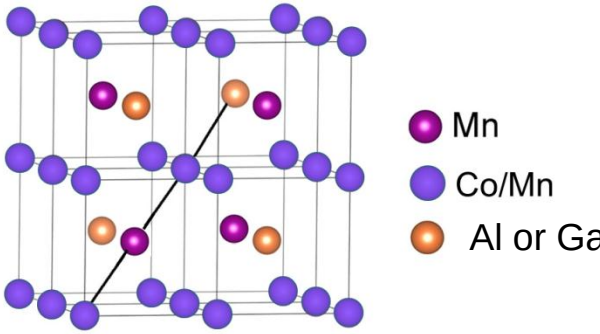
## Only $L2_1$, $Hg_2CuTi$ type structure is considered in previous research




$L2_1$-type



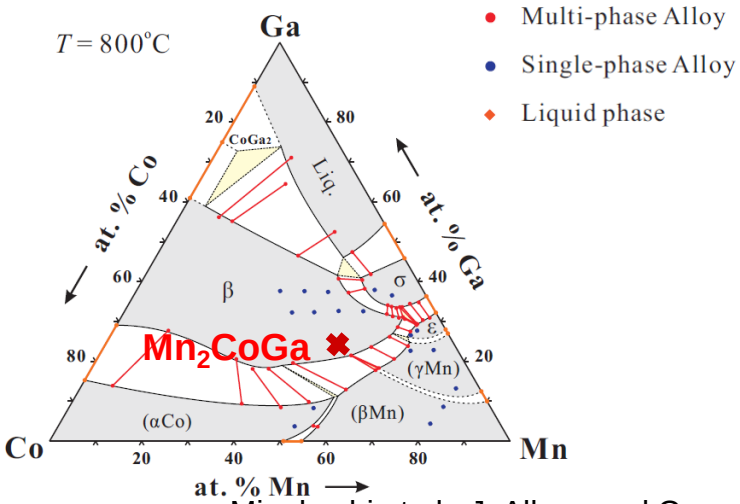

$Hg_2CuTi$-type




$L2_{1b}$-type (Modified $L2_1$)
（Co, Mn randomly distributed）

↓

Possibility of $L2_{1b}$-type?




. Minakuchi et al., J. Alloys and Compounds 645 (2015) 577

# Experimental

Sample preparation:

Induction melting in an argon atmosphere

Annealing at 1173 K for 1 day and 773 K for 7 days

Sample identification:

Optical microscope

X-ray diffraction

ICP-AES (Mn:49.8, Co:24.6, Ga:25.6 at.%)

Thermal analysis: Differential scanning calorimeter (DSC)

Magnetic measurement: SQUID magnetometer

Vibrating sample magnetometer

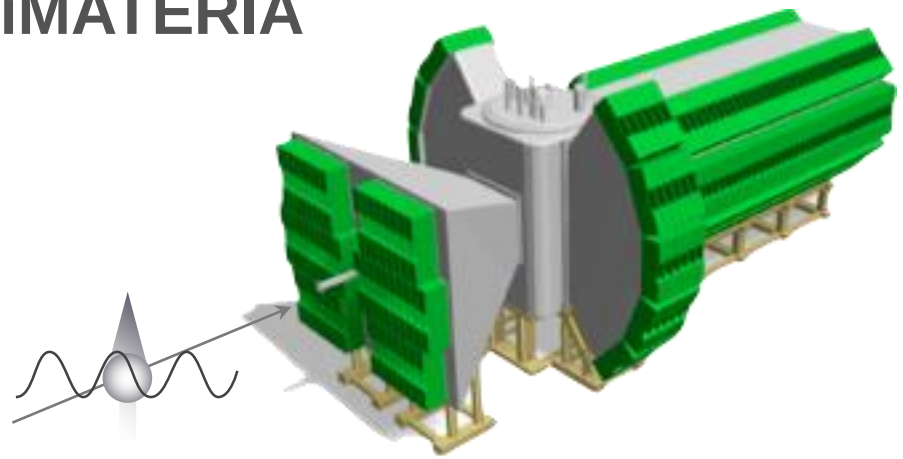
Neutron diffraction:

Ibaraki Materials Design Diffractometer (iMATERIA) in J-PARC

# Experimental

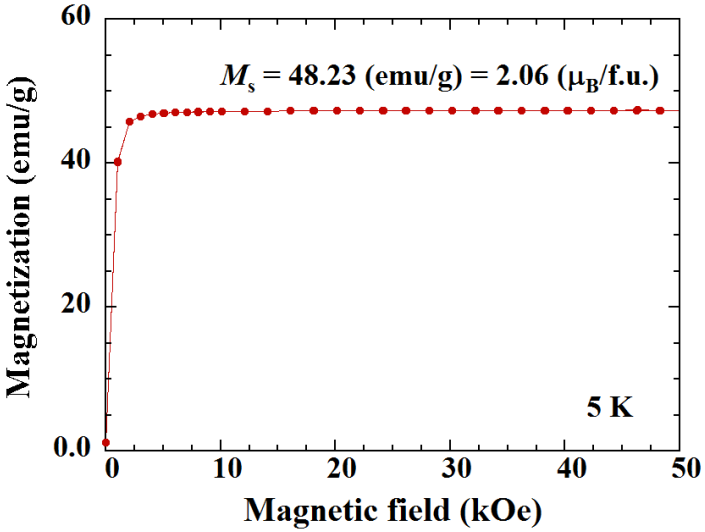
- Sample
  - $Mn_2CoGa$
  - powder, 4g
- Instrument
  - BL20 iMATERIA, J-PARC/MLF
  - 300K
  - d range 0.2-5.1 Å (back scattering, double-frame)

**iMATERIA**

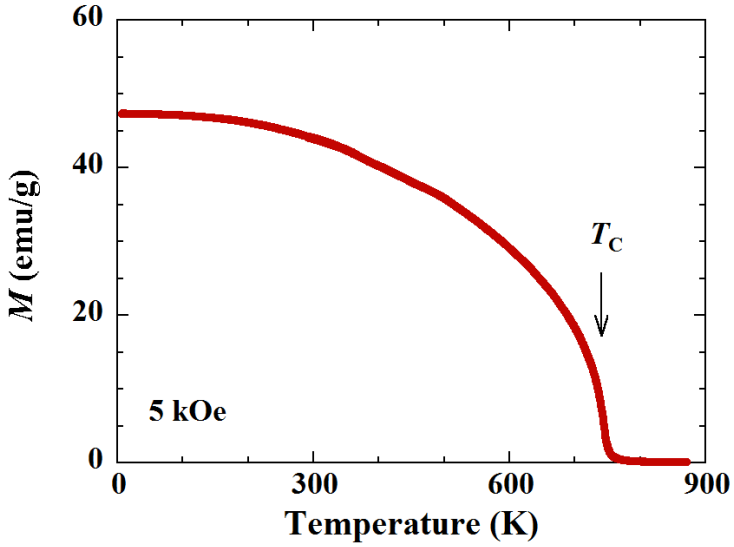


# Magnetic properties of $Mn_2CoGa$

*M-H* curve



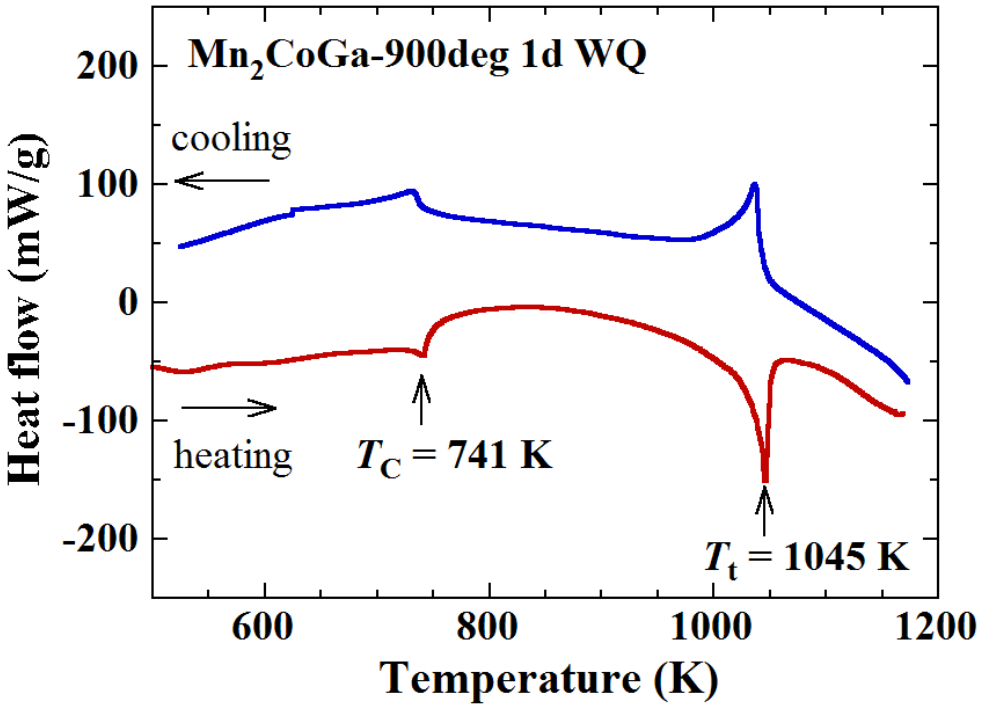

*M-T* curve



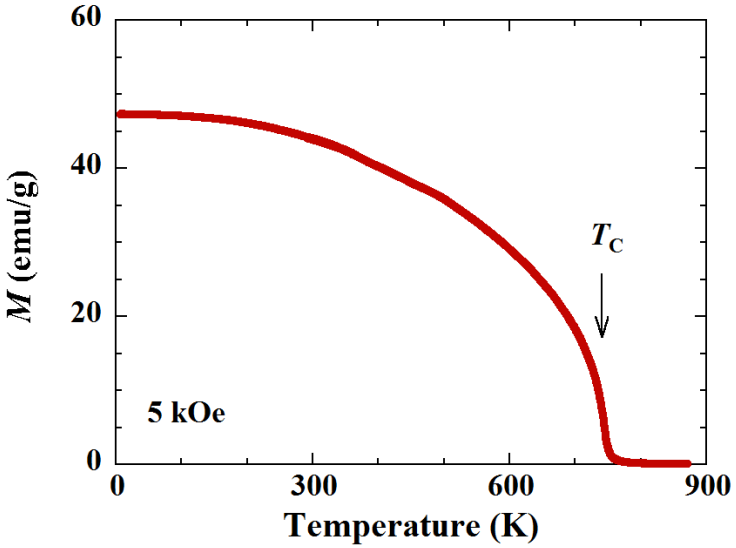

Spontaneous magnetization at 5 K for $Mn_2CoGa$ is 2.06 μB/f.u., and close to the integer number.

# Thermal and magnetic properties of $Mn_2CoGa$

DSC curves



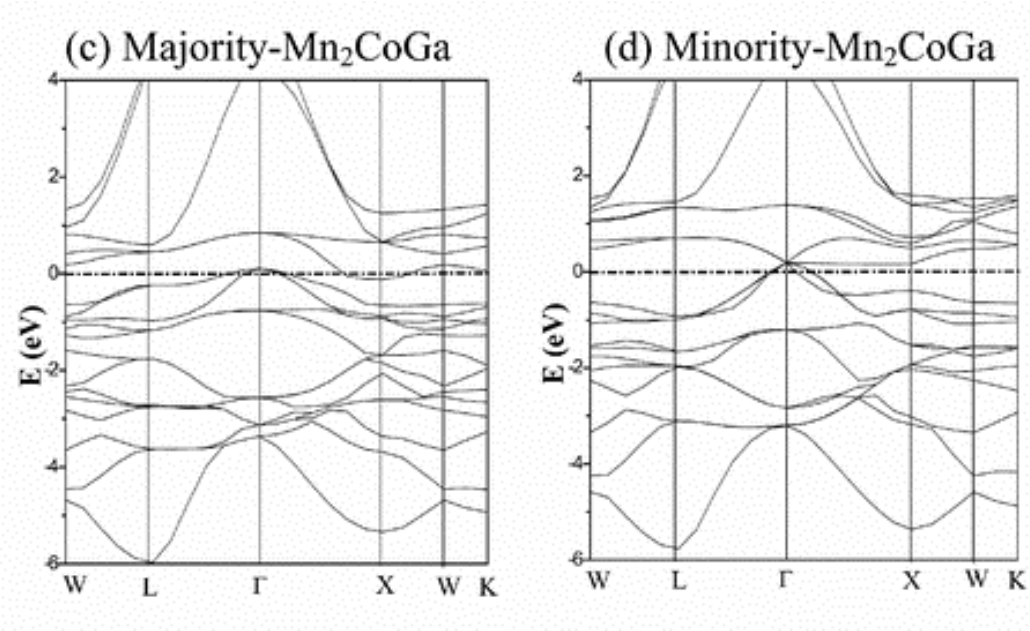

*M-T* curve

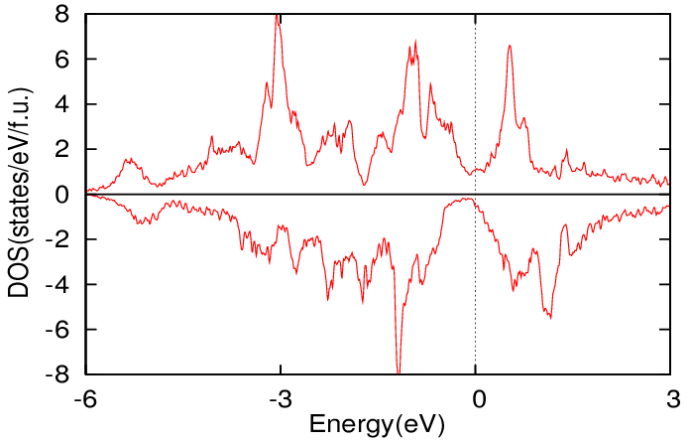



The Curie temperature and order-disorder phase transition temperature are 741 and 1045 K, respectively.

# Electronic structure of $Mn_2CoGa$

DOS of $Mn_2CoGa$ with $Hg_2CuTi$-type

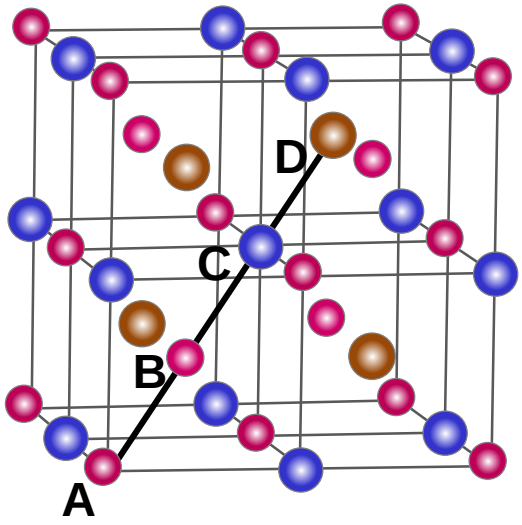



** From M. Tsujikawa (Tohoku University)

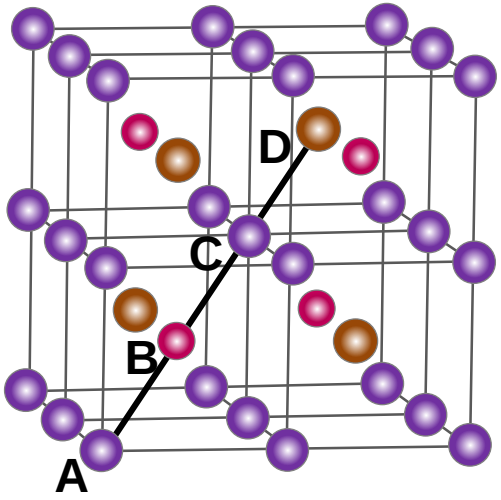
# Structure models of $Mn_2CoGa$

(1) $Hg_2CuTi$-type
216
(Mn,Mn,Co,Ga)



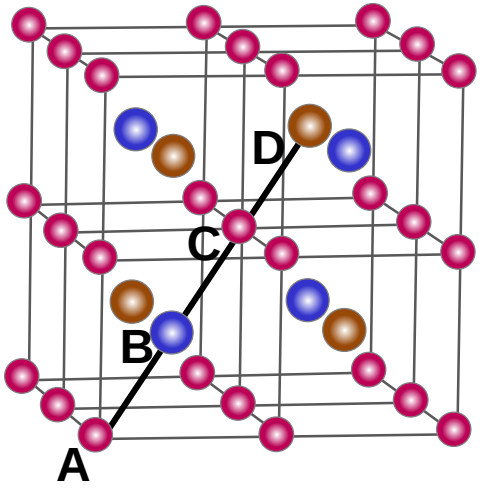

Mn Co Ga

(2) $L2_{1b}$-type (Modified $L2_1$)
225
{(Mn/Co), Mn, (Mn/Co), Ga}




Mn Mn/Co Ga

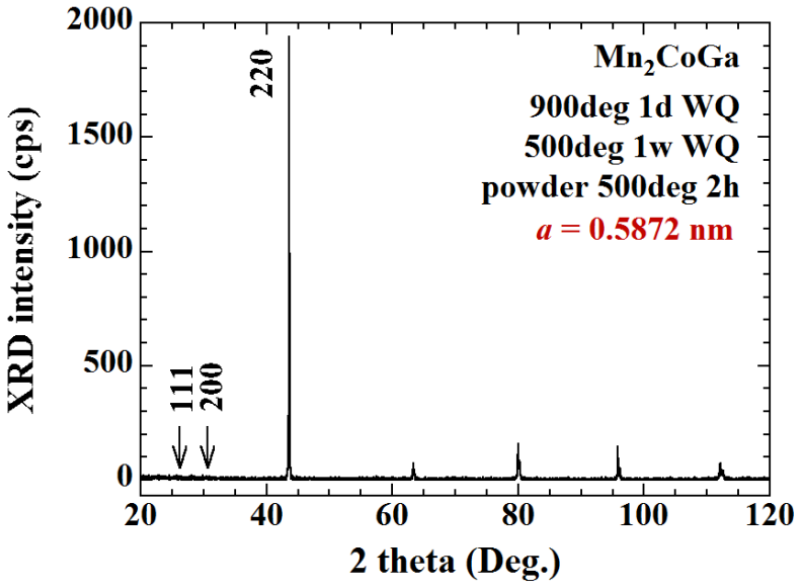
(3) $L2_1$-type,
225
(Mn,Co,Mn,Ga)



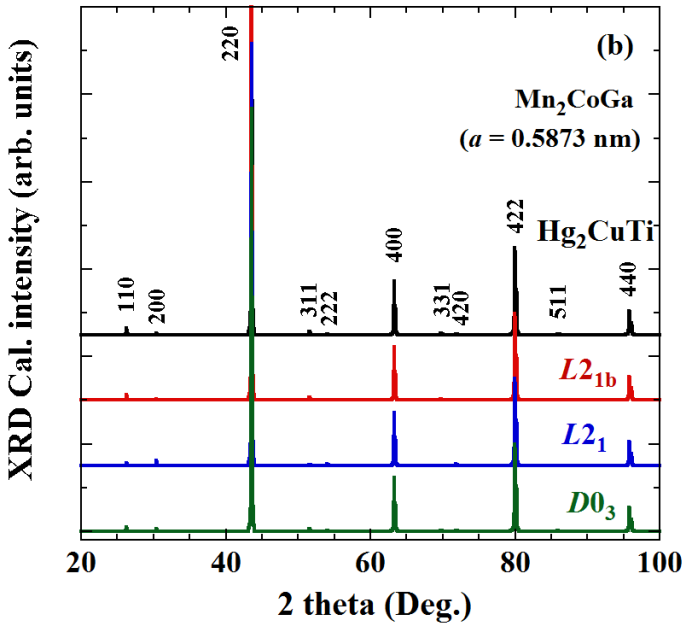

Mn Co Ga

# X-ray diffraction

## Experiment



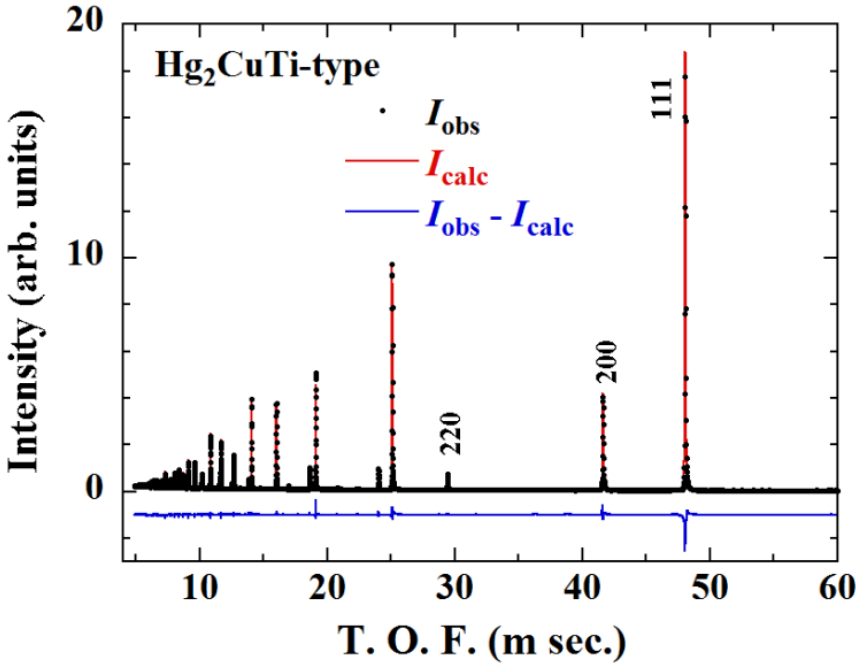

## Simulations



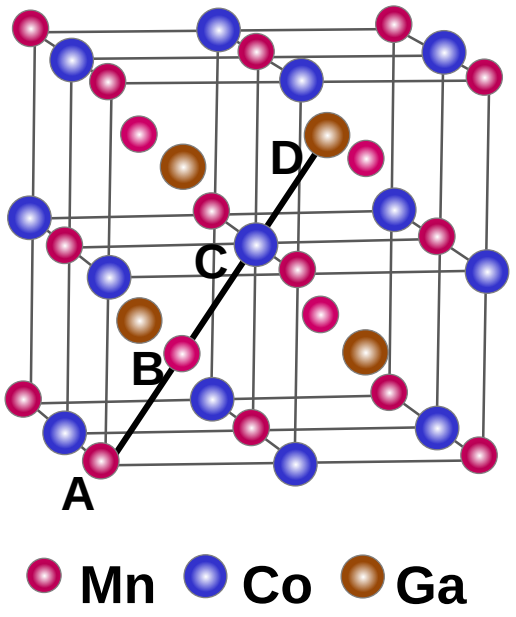

It is very difficult to determine the crystal structure of $Mn_2CoGa$ from XRD

# Powder neutron diffraction of $Mn_2CoGa$

at R.T. iMATERIA BL20 @ J-PARC)




## Model of $Hg_2CuTi$-type




$a$ = 0.6061 nm

$m_{Mn}$ (A site) = -1.46 $\mu_B$ Cal. : (-2.00 $\mu_B$)**

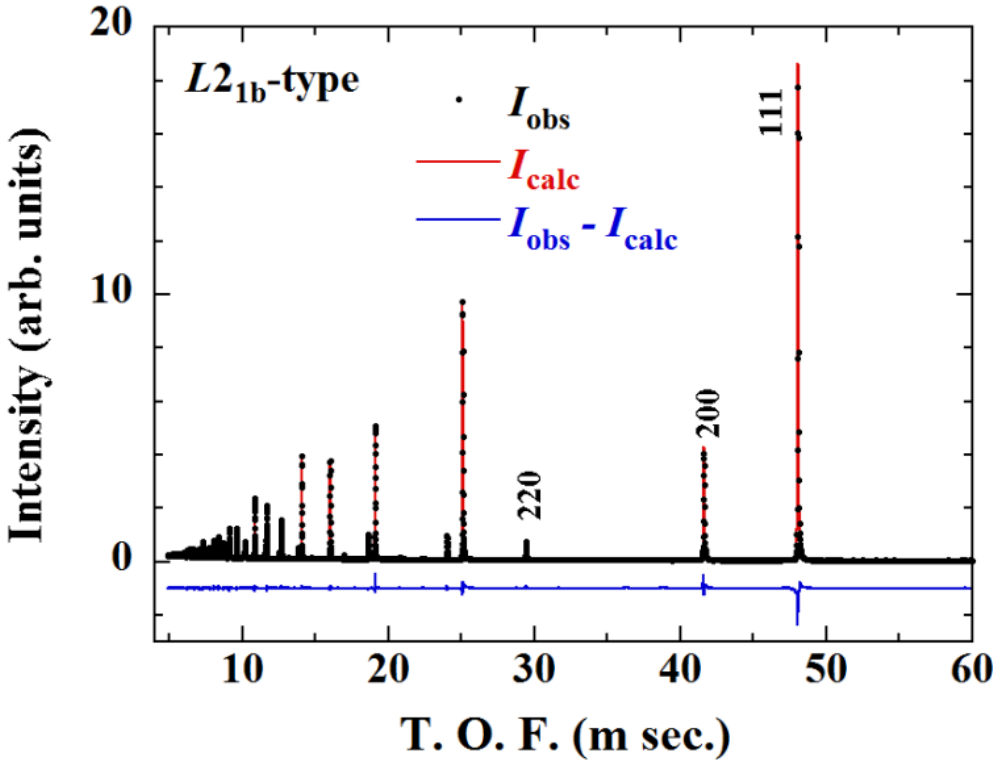
$m_{Mn}$ (B site) = 3.57 $\mu_B$ (3.04 $\mu_B$)

$m_{Co}$ (C site) = 0.31 $\mu_B$ (0.83 $\mu_B$)

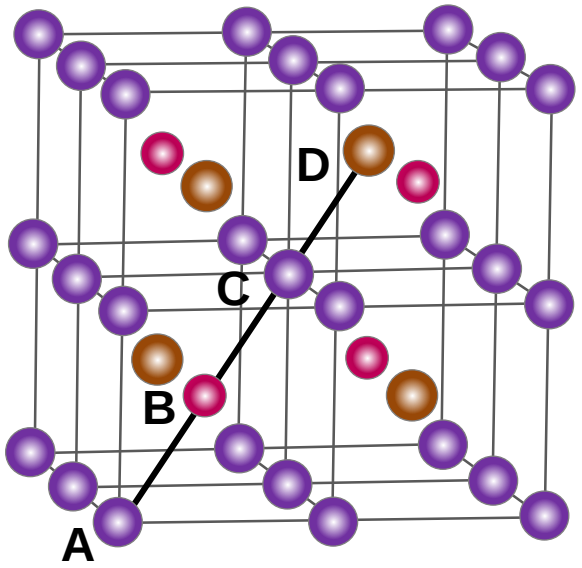
$m_{total}$ = 2.4 $\mu_B$ (1.94 $\mu_B$) (Exp.(5K) = 2.06 $\mu_B$)

$\chi^2$ = 7.43

# Powder neutron diffraction of $Mn_2CoGa$




## Model of $L2_{1b}$-type




Mn  Mn/Co  Ga

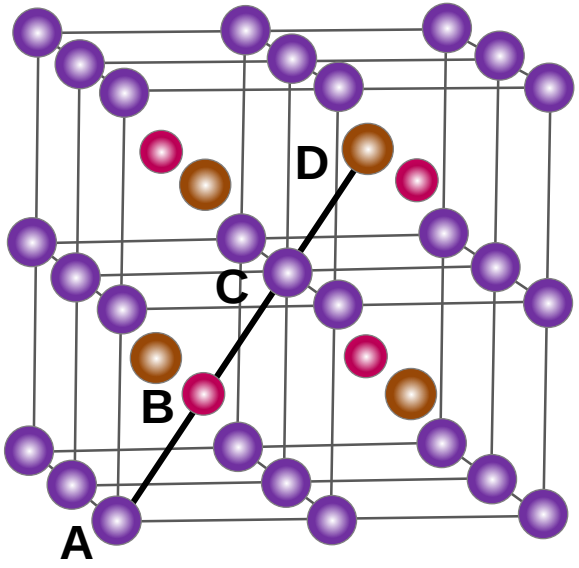
$a$ = 0.6045 nm

| | | |
|---|---|---|
| $m_{Mn}$ (A,C site) = -1.75 $\mu_B$ | Cal. : | (-1.88 $\mu_B$)** |
| $m_{Mn}$ (B site) = 2.81 $\mu_B$ | | (3.01 $\mu_B$) |
| $m_{Co}$ (A,C site) = 0.81 $\mu_B$ | | (0.84 $\mu_B$) |
| $m_{total}$ = 1.9 $\mu_B$ | | (1.99 $\mu_B$) (Exp.(5K) = 2.06 $\mu_B$) |

$\chi^2$ = 6.49

# Magnetic and crystal structure of $Mn_2CoGa$

## Determined structure ($L2_{1b}$-type)




Mn  Mn/Co  Ga

$a$ = 0.6045 nm

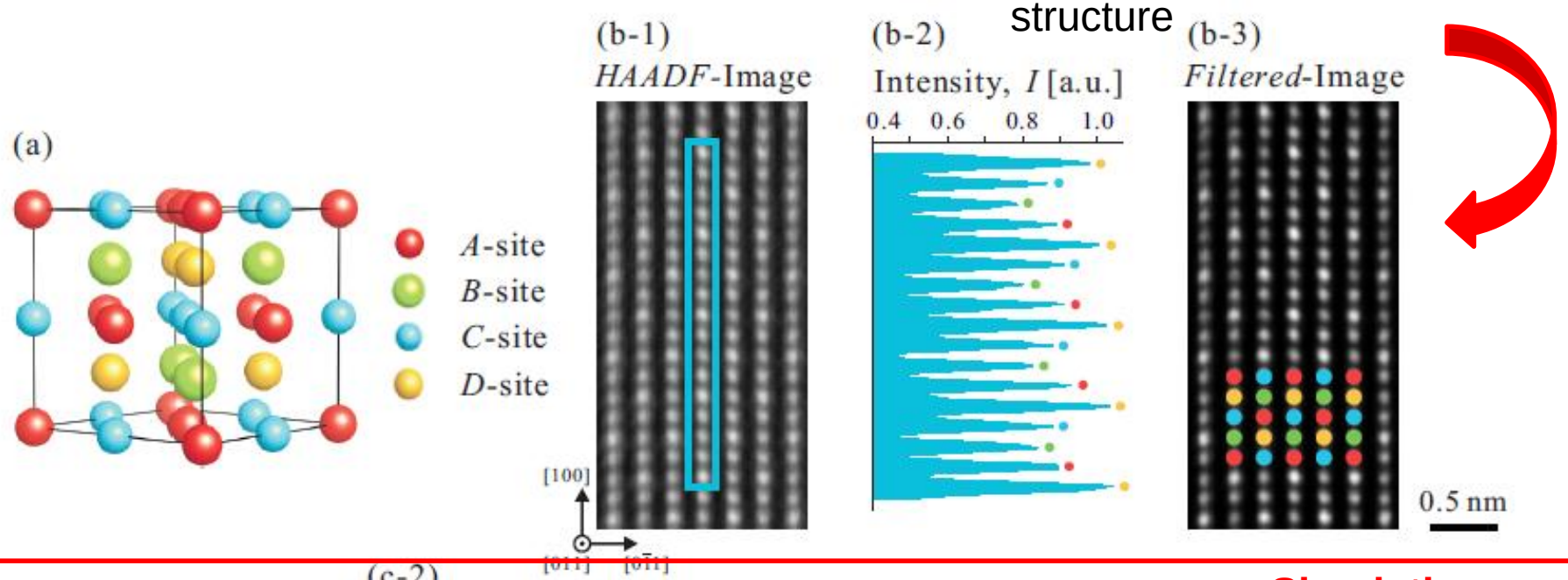
| | |
|---|---|
| $m_{Mn}$ (A,C site) = -1.75 $\mu_B$ | (-1.88 $\mu_B$) |
| $m_{Mn}$ (B site) = 2.81 $\mu_B$ | (3.01 $\mu_B$) |
| $m_{Co}$ (A,C site) = 0.81 $\mu_B$ | (0.84 $\mu_B$) |
| $m_{total}$ = 1.9 $\mu_B$ | (1.99 $\mu_B$) |
| (Exp.(5K) = 2.06 $\mu_B$) | |

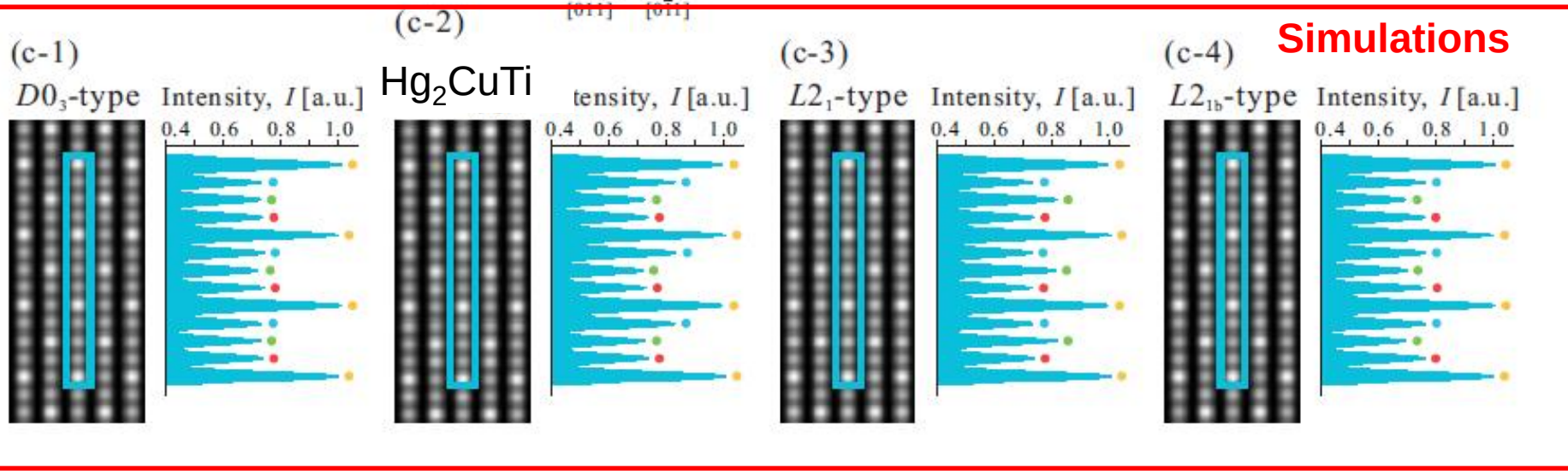
$\chi^2$ = 6.49

The reliability value, $\chi^2$, in the model of $L2_{1b}$-type is smaller than that of $Hg_2CuTi$-type.
Obtained values of the magnetic moments in the $L2_{1b}$-type are also more reasonable than that in the $Hg_2CuTi$-type structure.

# HAADF-STEM image

The obtained HAADF image also suggests the $L2_{1b}$-type structure



# Conclusions

1. Spontaneous magnetization at 5 K for $Mn_2CoGa$ is 2.06 μB/f.u., and close to the integer number. The Curie temperature and order-disorder phase transition temperature are 741 and 1045 K, respectively.
2. Powder neutron diffraction suggests that the atomic configuration of $Mn_2CoGa$ is the $L2_{1b}$-type structure. Obtained magnetic moments in the model of $L2_{1b}$-type are closer to the experimental value from the magnetic measurement.
3. The result of the HAADF-STEM image also supports the $L2_{1b}$-type structure.