Neutron & Muon School 2018

Neutron Diffraction

--- Practical Techunique of crystal and magnetic structure refinements by powder diffraction. ---

Prof. Kenji Ohoyama

Ibaraki Univ.

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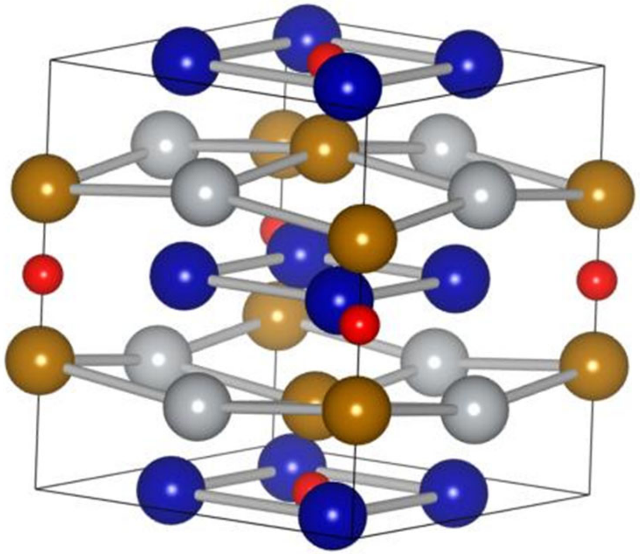
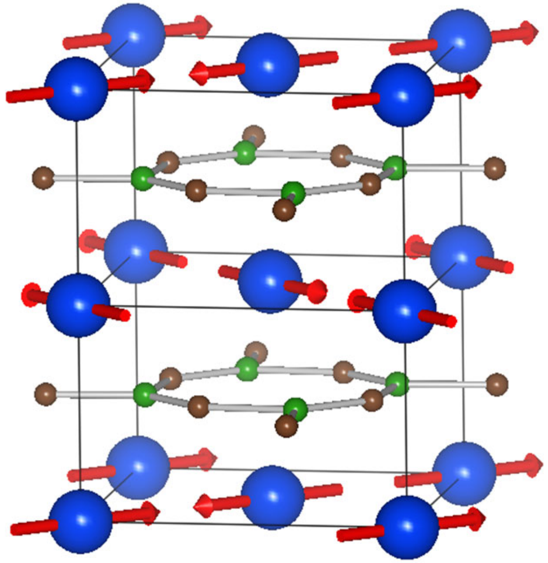
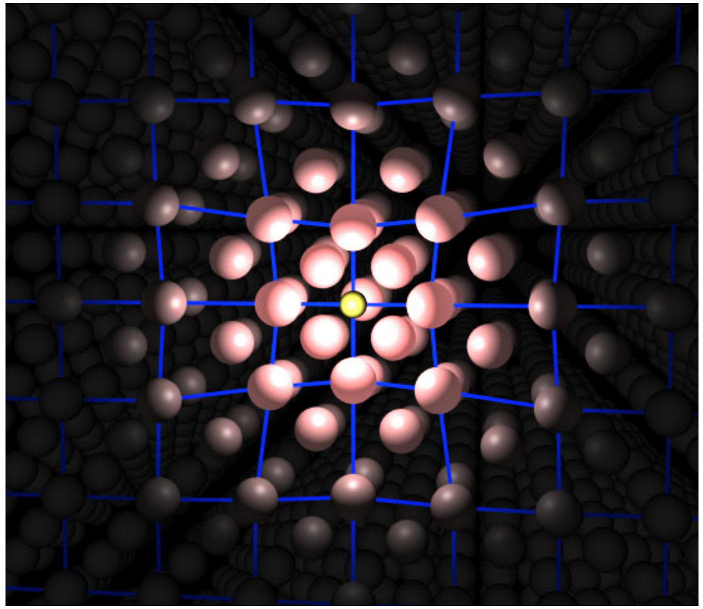
About me





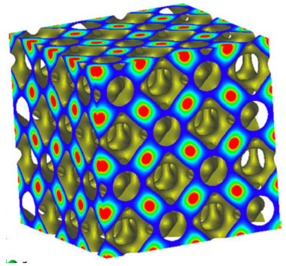
Structural Physics by neutron scattering.



Local structure around dopant by newly developed technique , neutron holography

Advantages of Neutrons

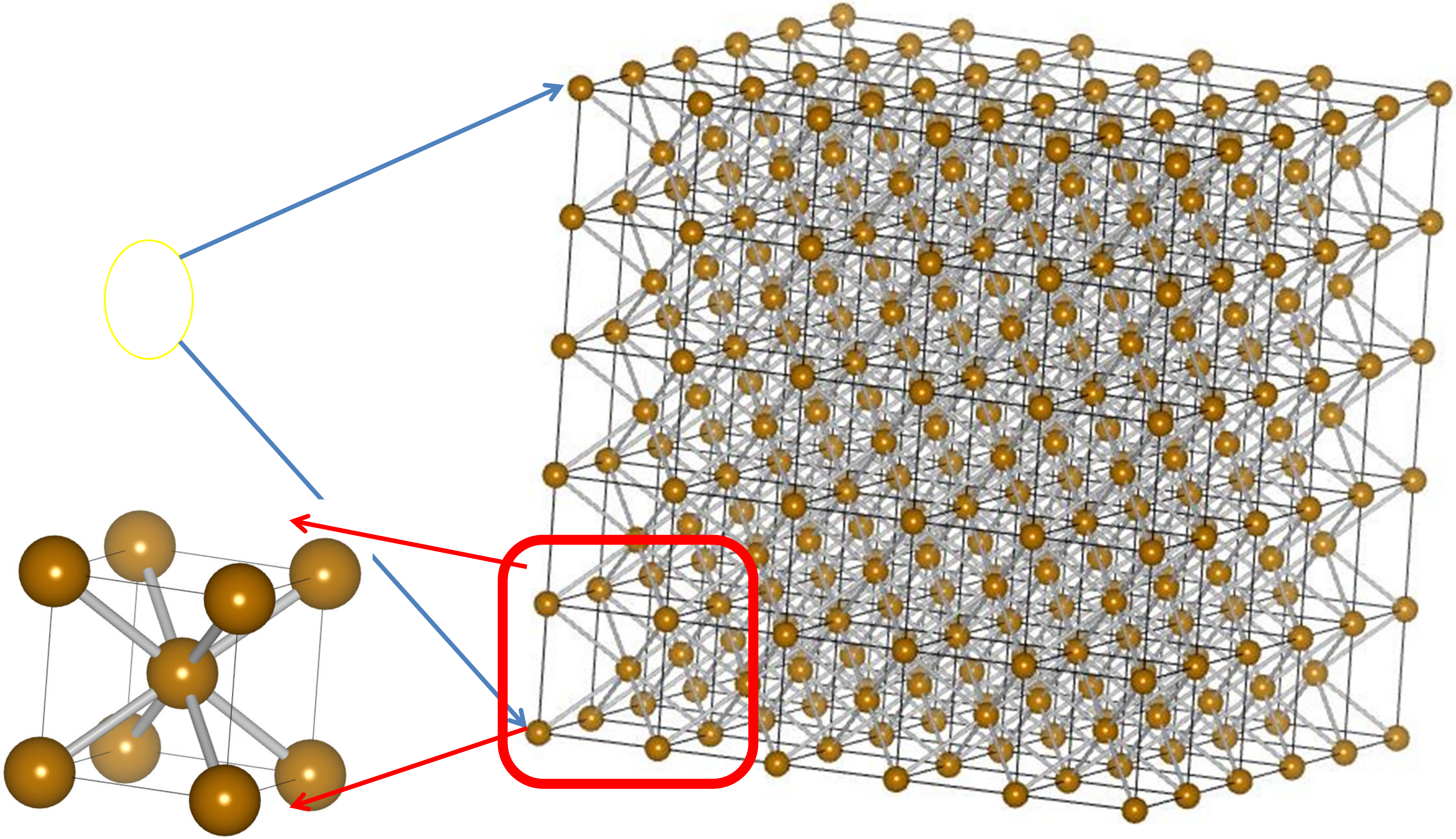
Ion conductor
Yashima et al. 2005



Light elements	Hydrogen Strage Li-Batteries Ion Conductors
Transmission	Radiography Stress
Magnetic Moment	Magnetic Structure Spin wave Magnetic Deveice
Energy-Wave length	Spin wave Phonon Interaction

Contents

Why you have to understand Crystal Structures?



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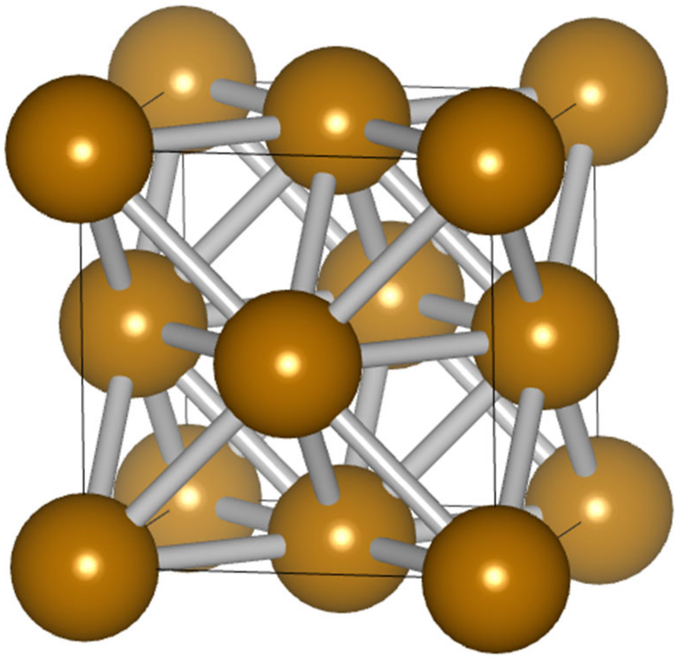
コトバンクから転載https://kotobank.jp/word/磁石-73268

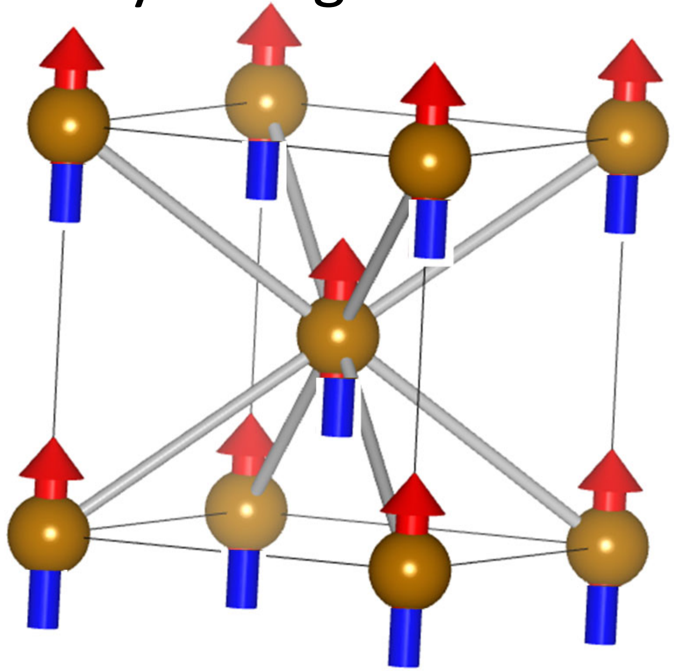
Importance of Crystal Structure

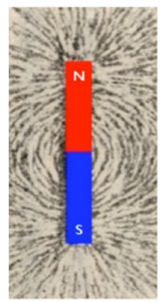
Iron

Iron which is NOT attracted by a magnet.



Iron which is attracted by a magnet at RT.





To understand Macroscopic properties, information on atomic structures is indispensable.

Probe = diffraction

X-ray, electron, and NETURON

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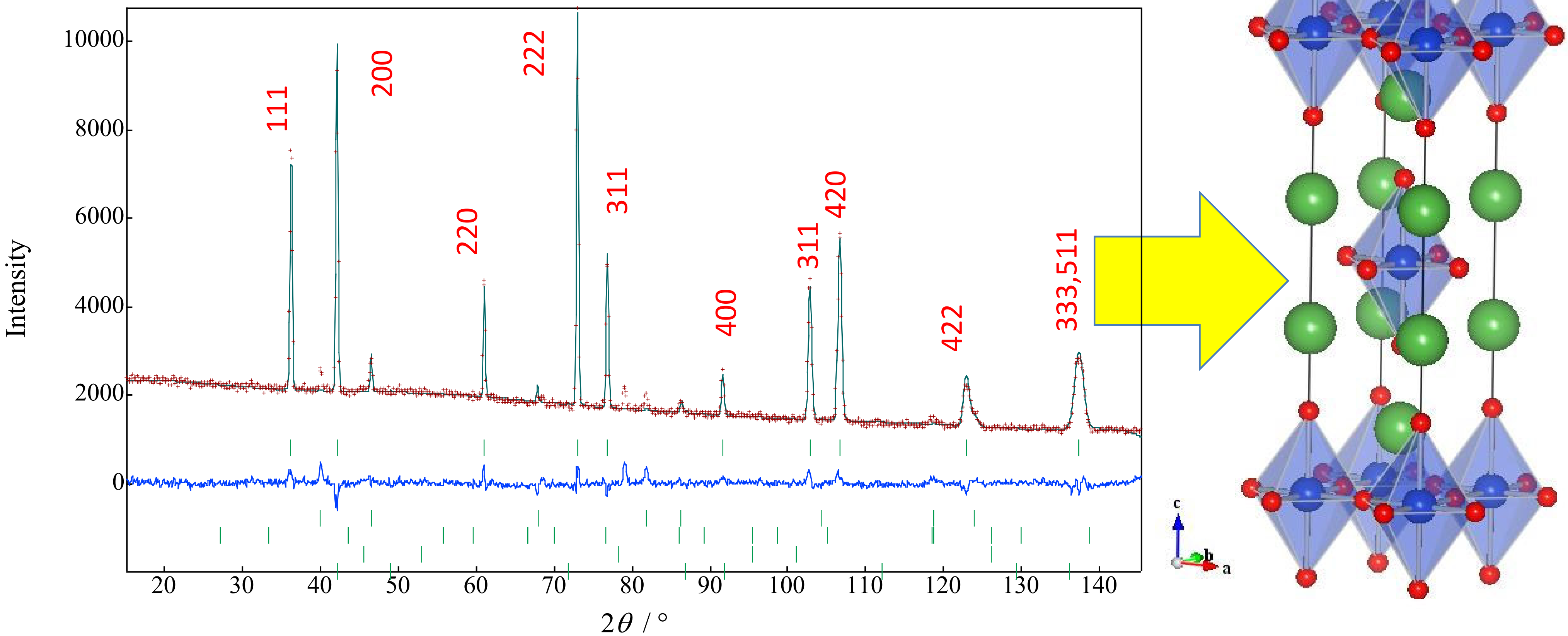
Crystal Structure Refinement?

Powder Diffraction Pattern



Peak Position, Index -> Lattice Parameter, Unit Cell, Space Group

Peak Intensity -> Atomic Position, occupancy, vibration

Intensity of Bragg Peaks

Completely the same as X-ray diffraction

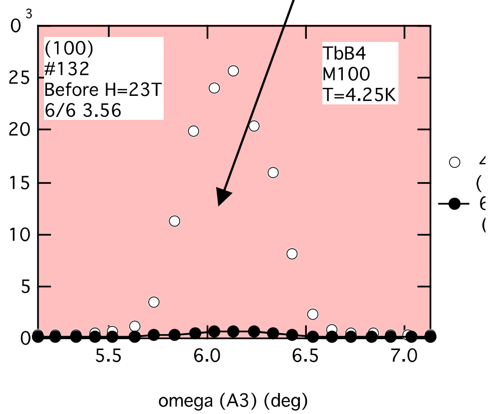
f: atomic scattering factor for X-ray

Integrated Intensity of a Bragg

$$\left(\frac{d\sigma}{d\Omega}\right)_{hkl} = c\left|\sum_i b_i \exp\left(2\pi i\left(\vec{r}_i \vec{\kappa}\right)\right)\right|^2$$

b_i: scattering length

$$\vec{r}_i = \left(x_i, y_i, z_i\right)$$ Position of i-th atom in the unit cell



$$\vec{\kappa} = (h, k, l)$$ Scattering vector or Index

$$= c_{hkl}\left|\sum_i b_i \exp\left(2\pi i\left(x_i h + y_i k + z_i l\right)\right)\right|^2$$

Structure Facoter

This is acutualy Fourier transfer of atomic structure

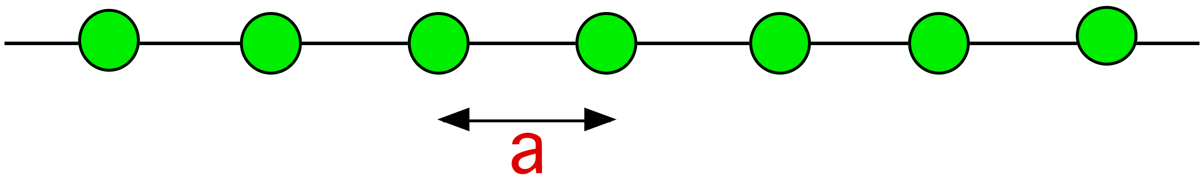
Reciprocal Lattice is “Real”

You can see it.

CaO_7 Al_2O_3 Oikawa et al. 2014

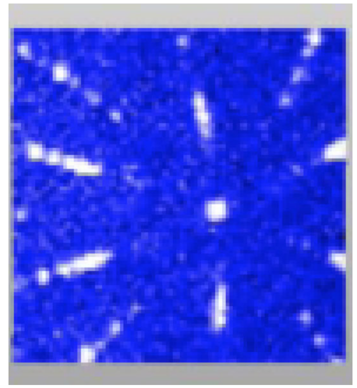
Bragg reflection ＝ Reciprocal lattice point

Reciprocal Space (Lattice) is



Space which indicates Spatial periodicity of materials with points

1/a or 2p/a



Bragg peaks at a reciprocal space.
=Reciprocal Lattice

=

The sample has THE periodicity

Atom, Nucleus
Magnetic moment,
Vacancy

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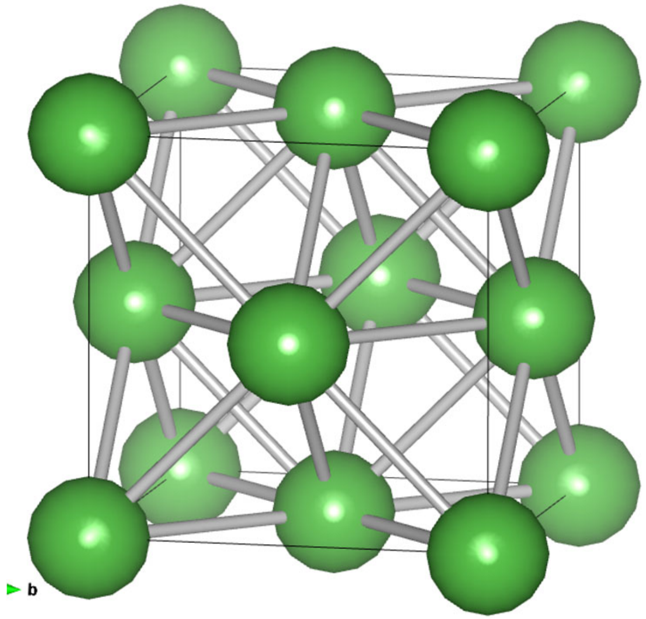
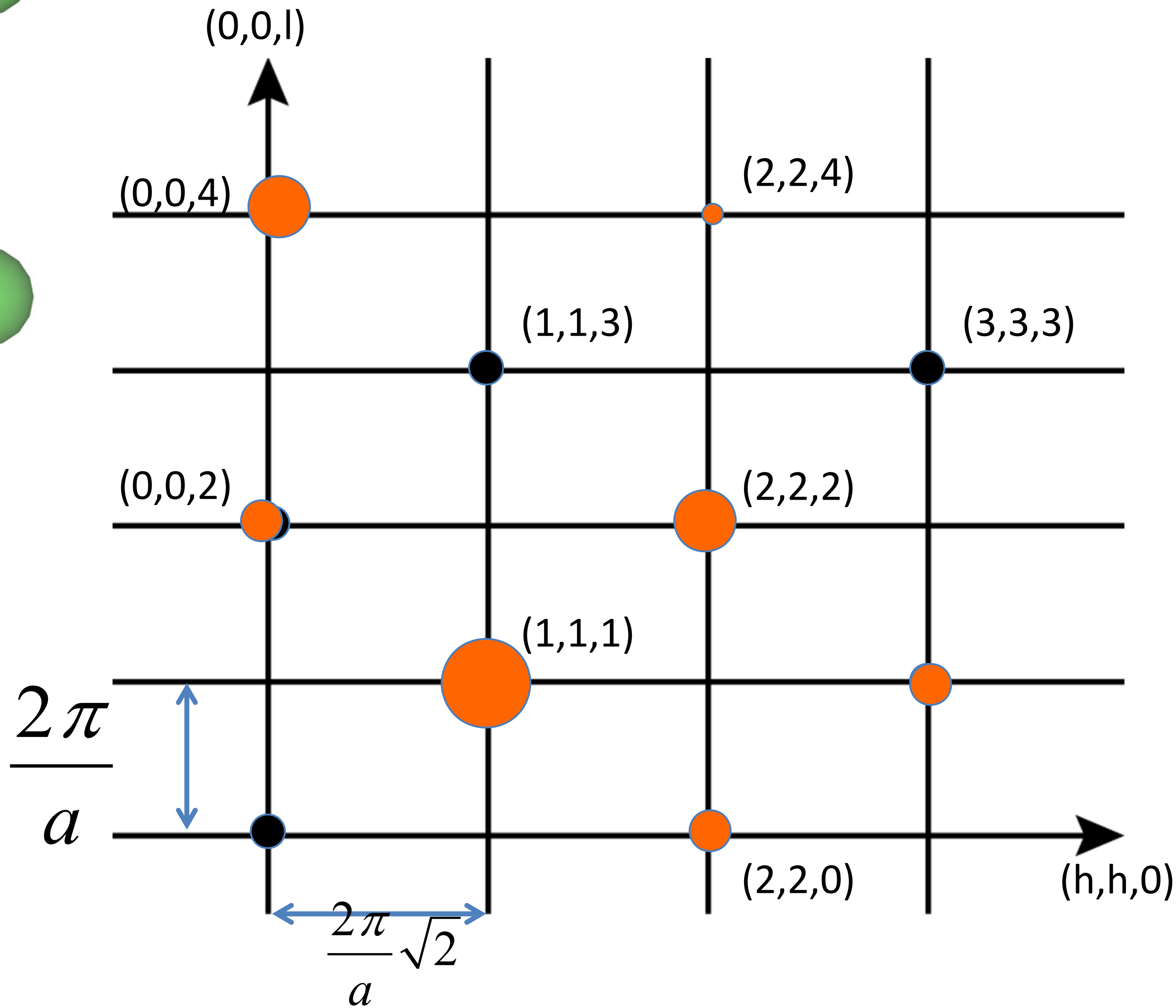
Reciprocal Lattice of FCC



Reflection rule
All even / all odd

= Positions of Bragg Peaks



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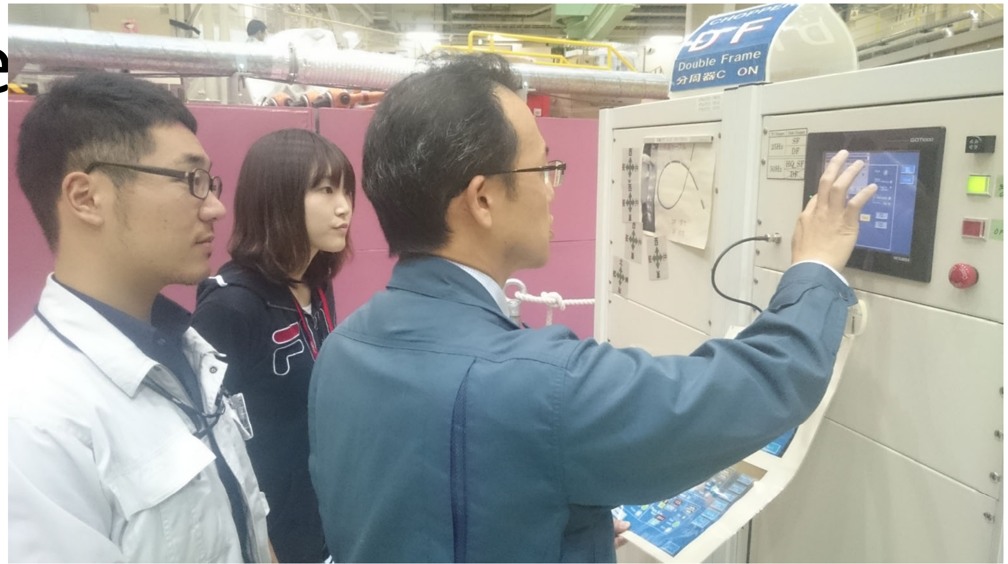

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Hydride in Scoiety

HP of Orimo Lab of IMR< Tohoku Univ

Compact Hydrogen Strage

Storage Materials

Liquid H_2 (-250° C)

High P H_2 Gas (200 atm)

Properties can be changed by Hydrogen

Accurate information on crystal structure of Hydrogen is important

→ Advantage of neutrons

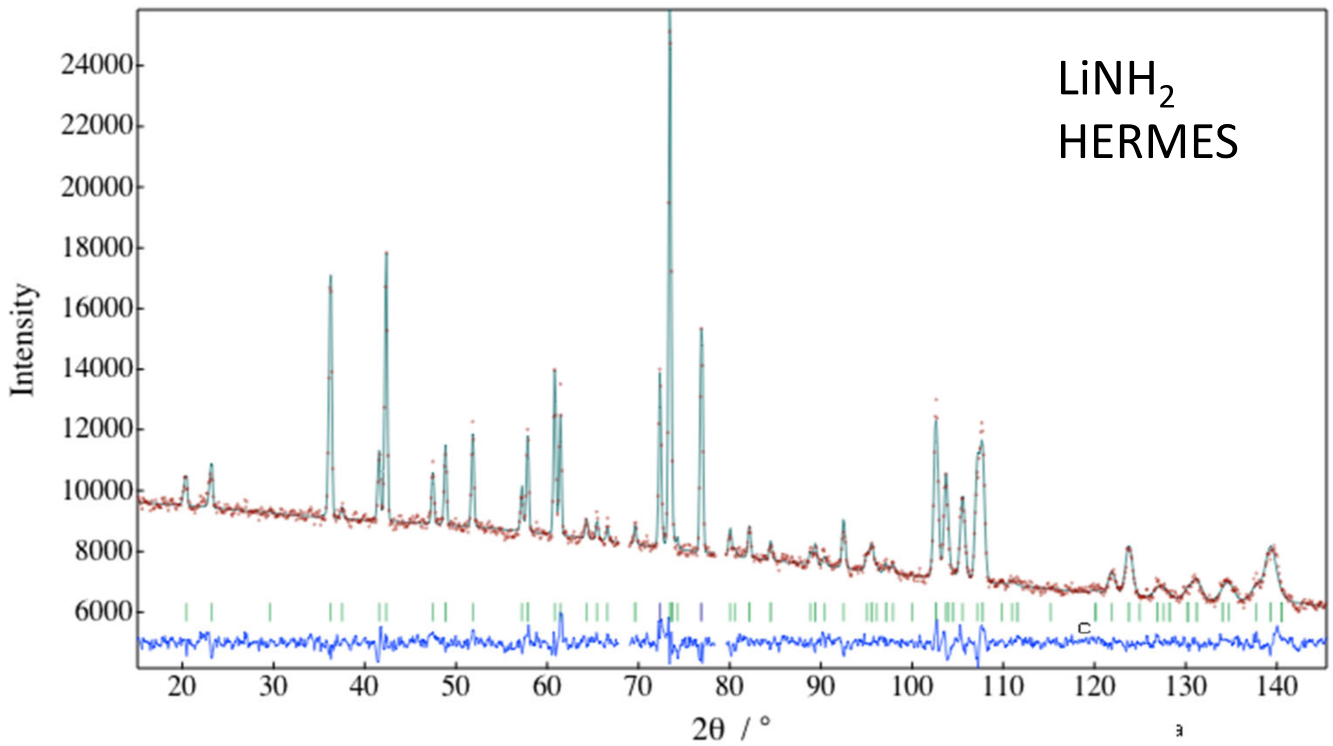
Li-N-H compounds

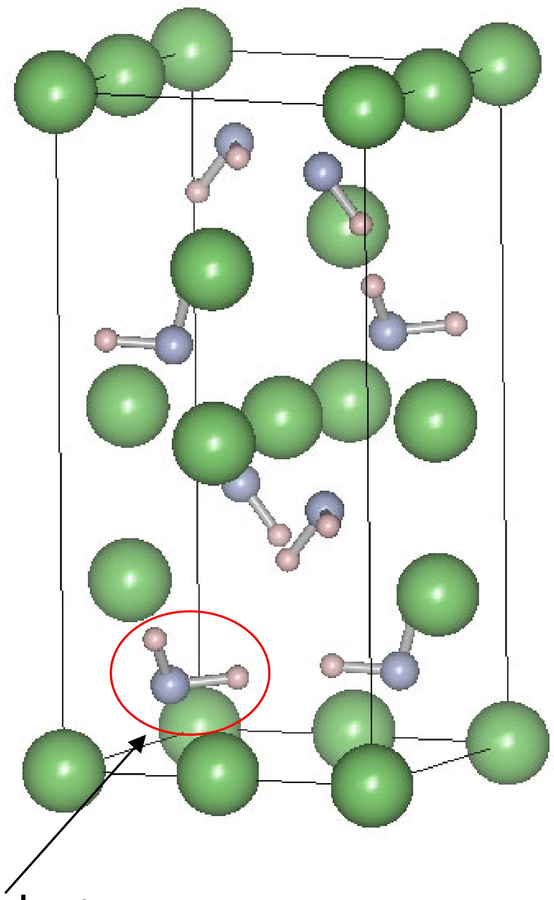
$LiNH_2 + 2LiH \Leftrightarrow Li_2NH + LiH + H_2$ ← 10.4 wt %

$Li_2NH + LiH \Leftrightarrow Li_3N + H_2$

Crystal Structure of $LiNH_2$

Rietveld Analysis





LiNH2

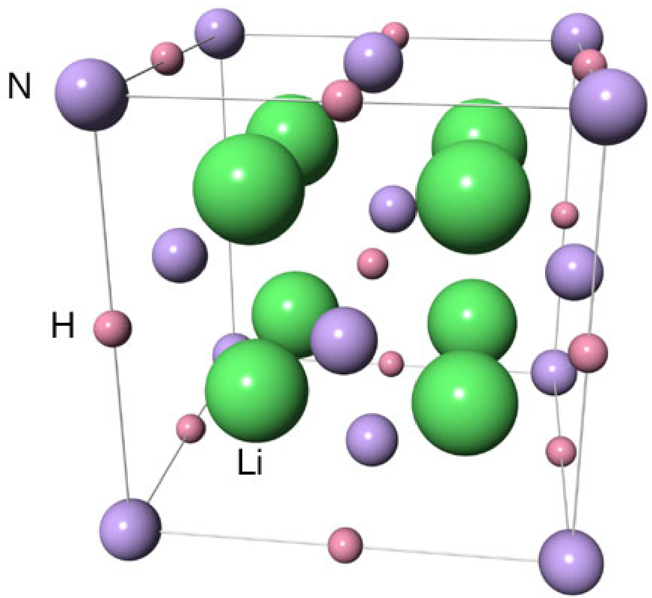
N-H Distance ~ NH_3

H. Jacob and R. Juza, Z. Anorg. Allg. Chem. 391 (1972) 271 .

https://ja.wikipedia.org/wiki/アンモニア

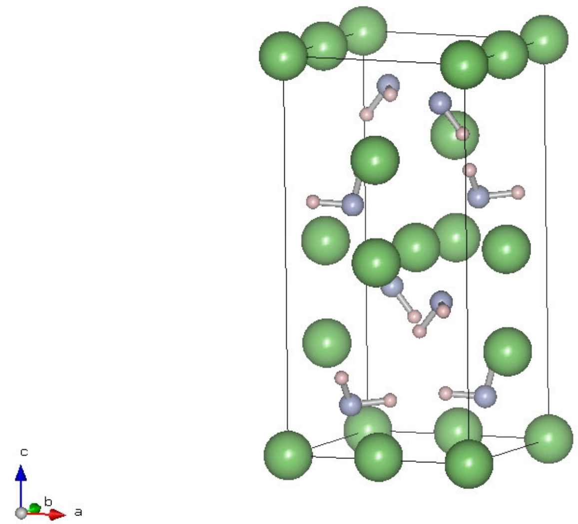
On the other hand, Li_2NH?

The structure in a Dtabase



Fm-3m
A=5.05A

Powder Diffraction File, 6-0417.

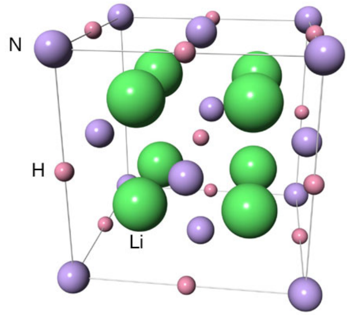


Completely different from $LiNH_2$

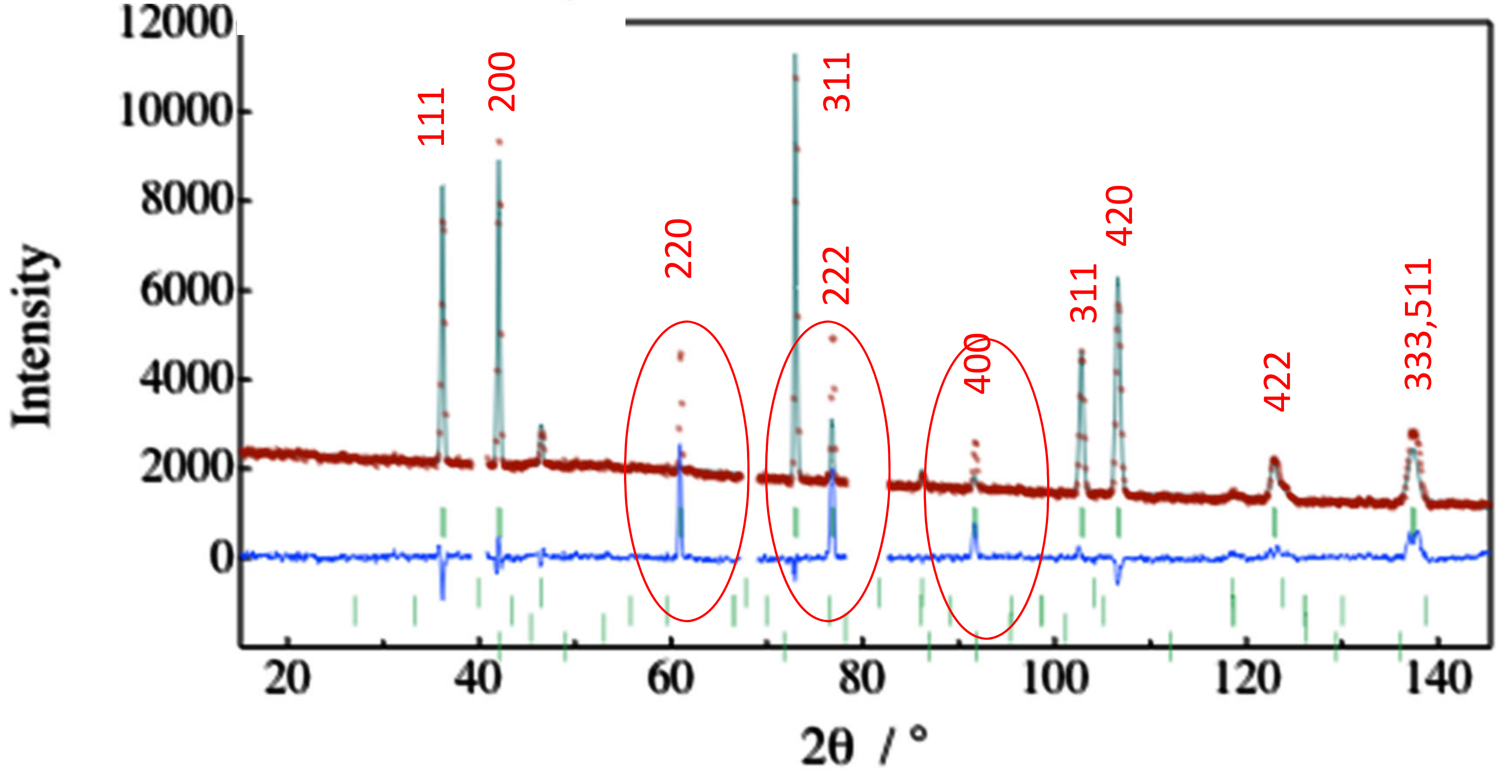
1) N-H ~2.5A (1.03A for $LiNH_2$)
2) No N-H cluster

The structure may be wrong?

Li_2NH: ND patern



This is wrong!



FCC

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What is the structure of Li_2NH？

Basic Conditions
1: FCC (a~5.05A)
2: 4 molecure in a unit cell. (Z=4)

There are only 5 Space Groups allowed.

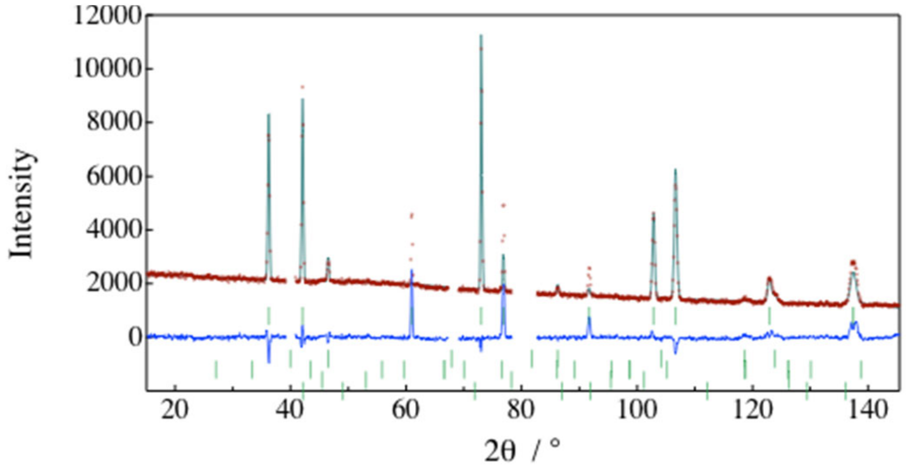
F23, Fm-3, F432, F-43m, Fm-3m

You can check the all the 5 space groups.

However,

However,

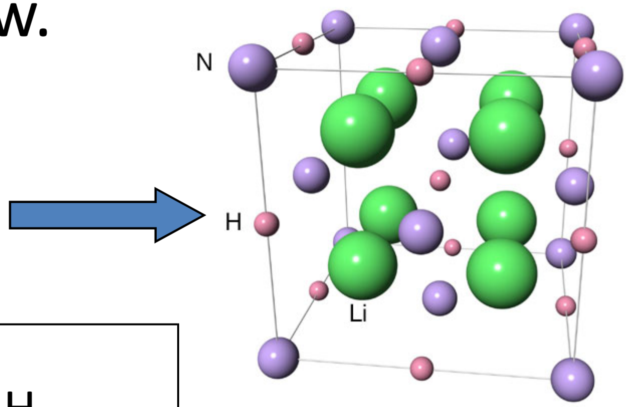
The 5 Space Groups never give good models which can represent the data.

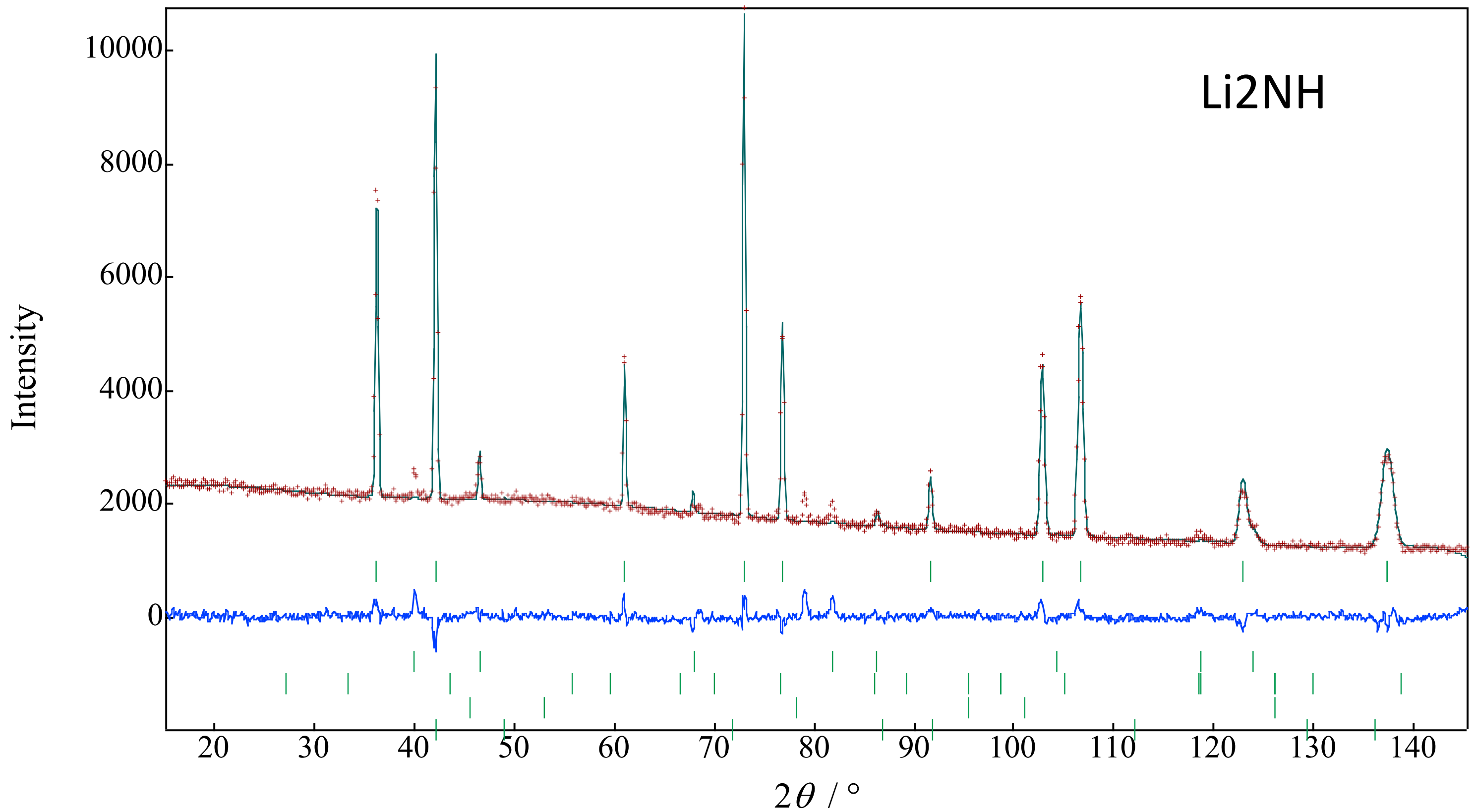


There is no space group for Li_2NH????

If you belive that the hydrogen site is fully occupied.

Model : Occupation of Hydrogen is extremely low.





It represents the data!

But, the occupation of H is only 3%！！

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Partially Occupied Model

Basic COndition
1: FCC (a~5.05A)
2: 4 molecure in a unit cell. (Z=4)

+

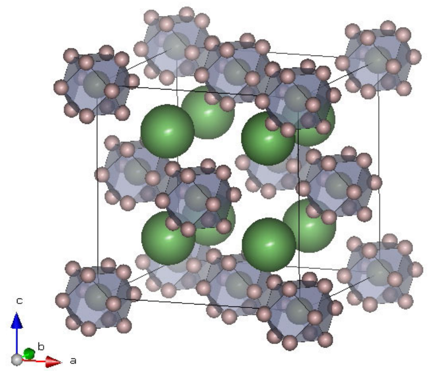
Hydrogen locates at a lower symmetry site.

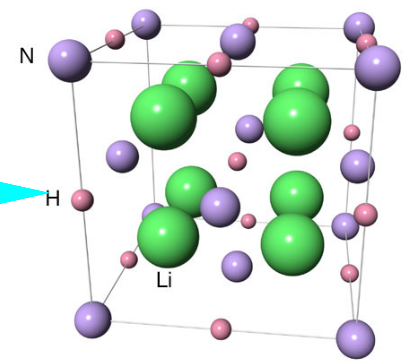
Occupation of H must be 4/m（m：multiplicity）

Low symmetry Site

SP : Fm-3m

Site	Position of H	No. of H
192l	(x,y,z)	192
96k	(x,x,z)	96
96j	(0,y,z)	96
48i	(1/2,y,y)	48
48h	(0,y,y)	48
32f	(x,x,x)	32
24e	(x,0,0)	24
24d		24
8c	Li	
4b	(1/2,1/2,1/2)	4
2a	N	





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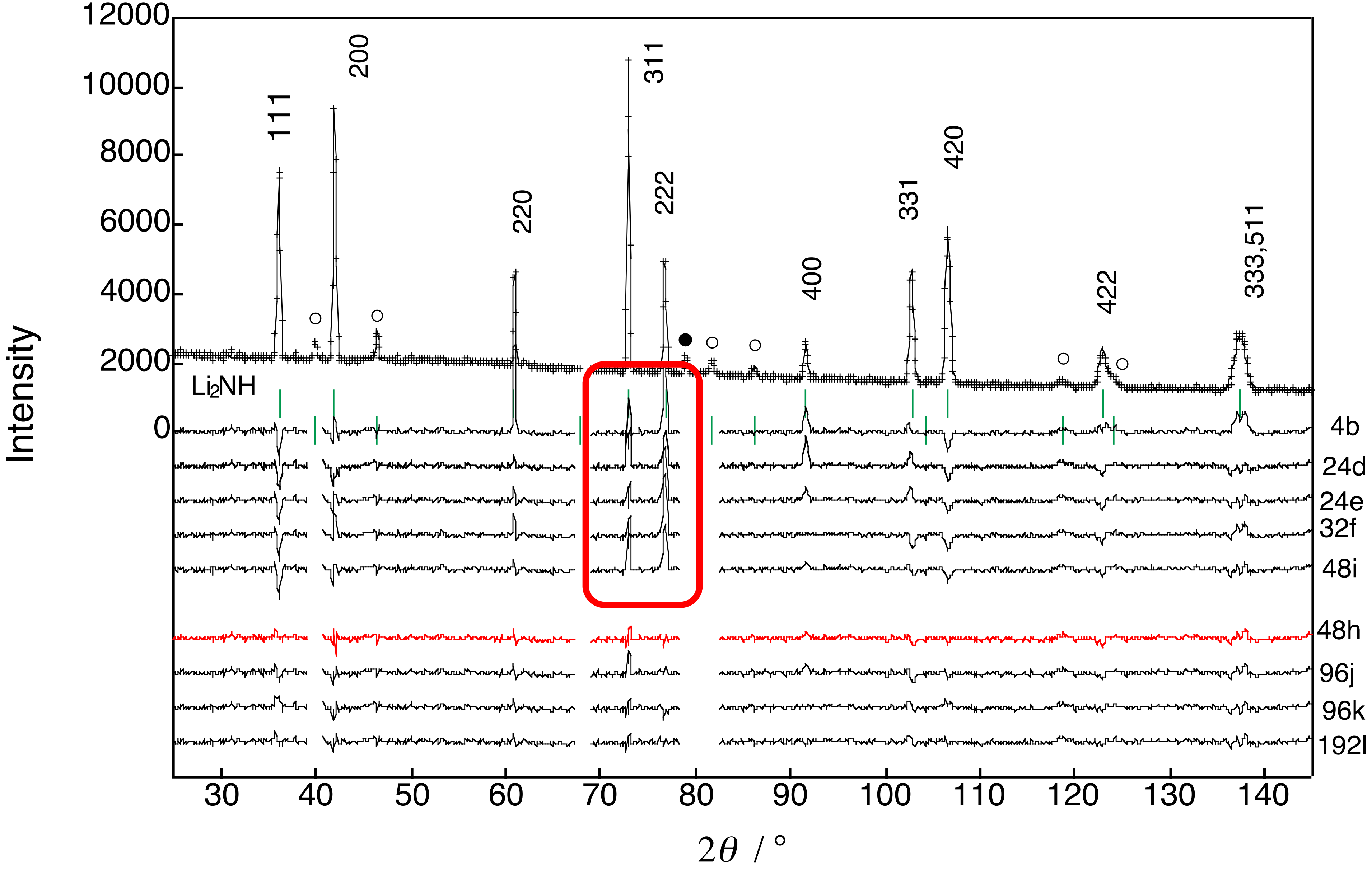
Fm-3m



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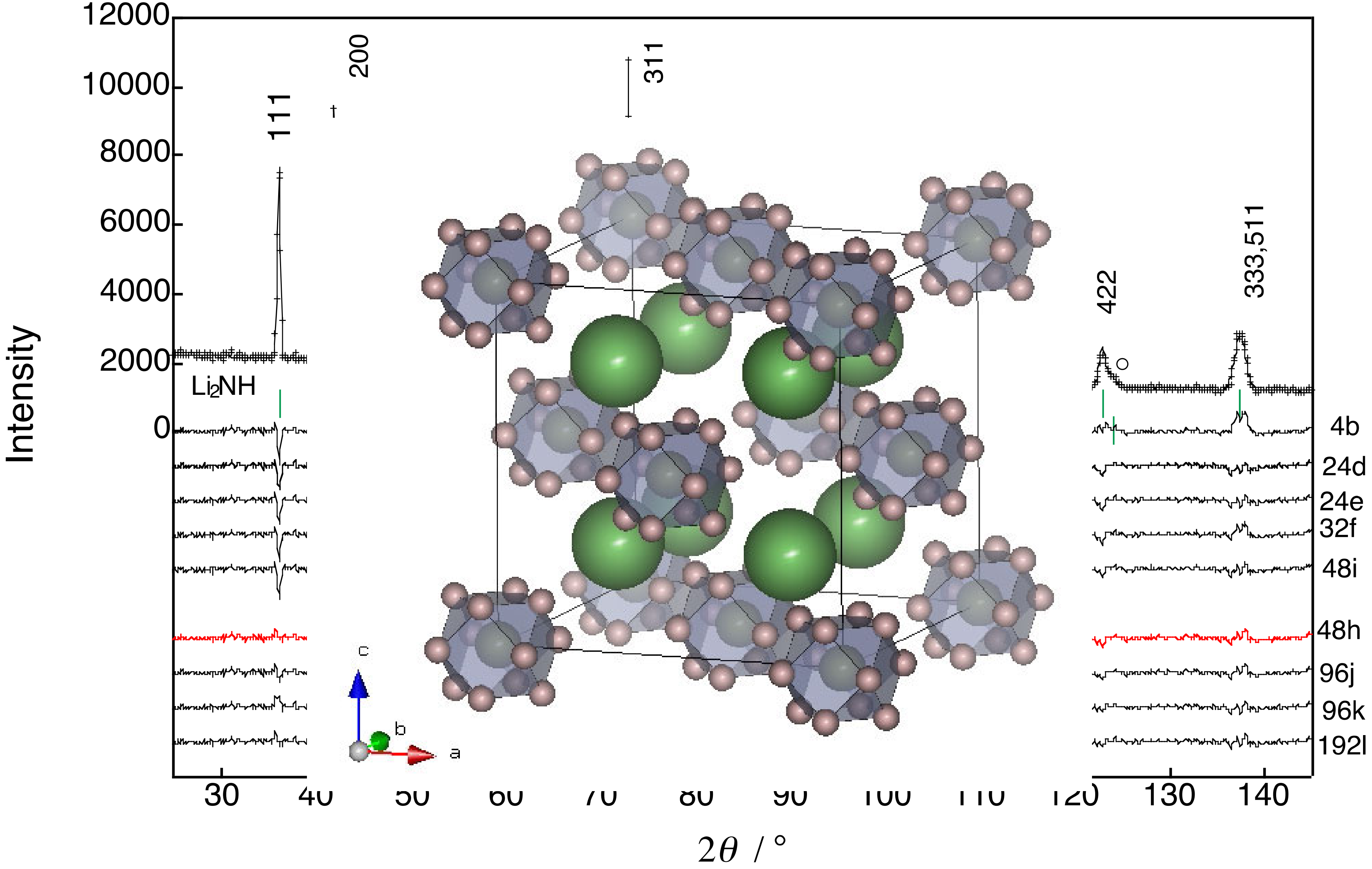
Fm-3m 48h model is the best

Occupancy : g= 8.7(5)% ～4/48=1/12

Fm-3m



Fm-3m 48h model is the best

Occupancy: g= 8.7(5)% ～4/48=1/12

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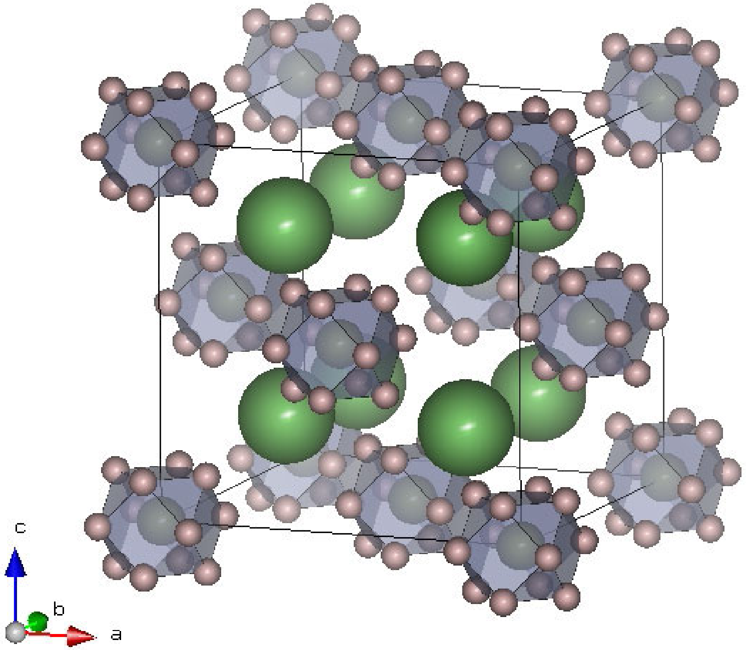
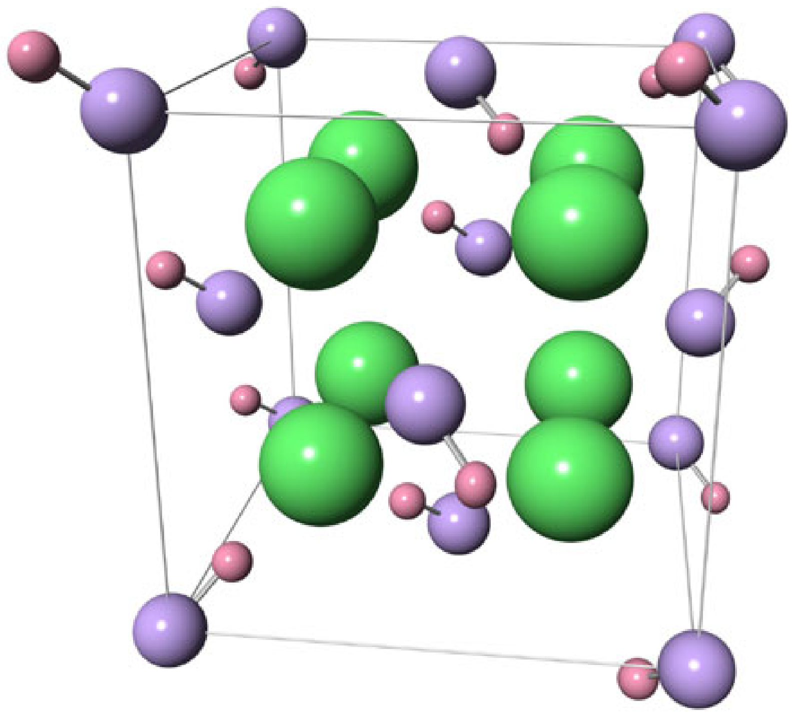
Li2NH : Average and Local structure

Only One H around a N

Fm-3m
g=8.3%





Local Structure

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Magnetic Structure

Why you have to understand magnetic structure?

How it can be observed by Neutron

Magnetic structure refinement

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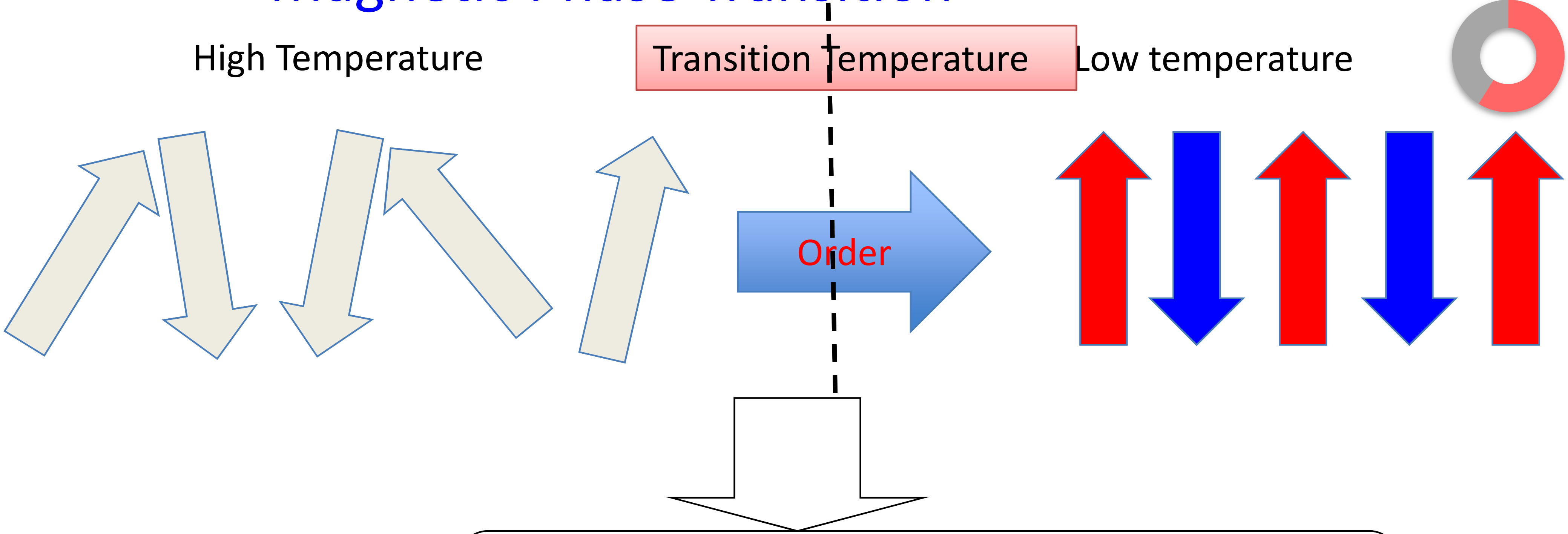
Magnetic Phase Transition



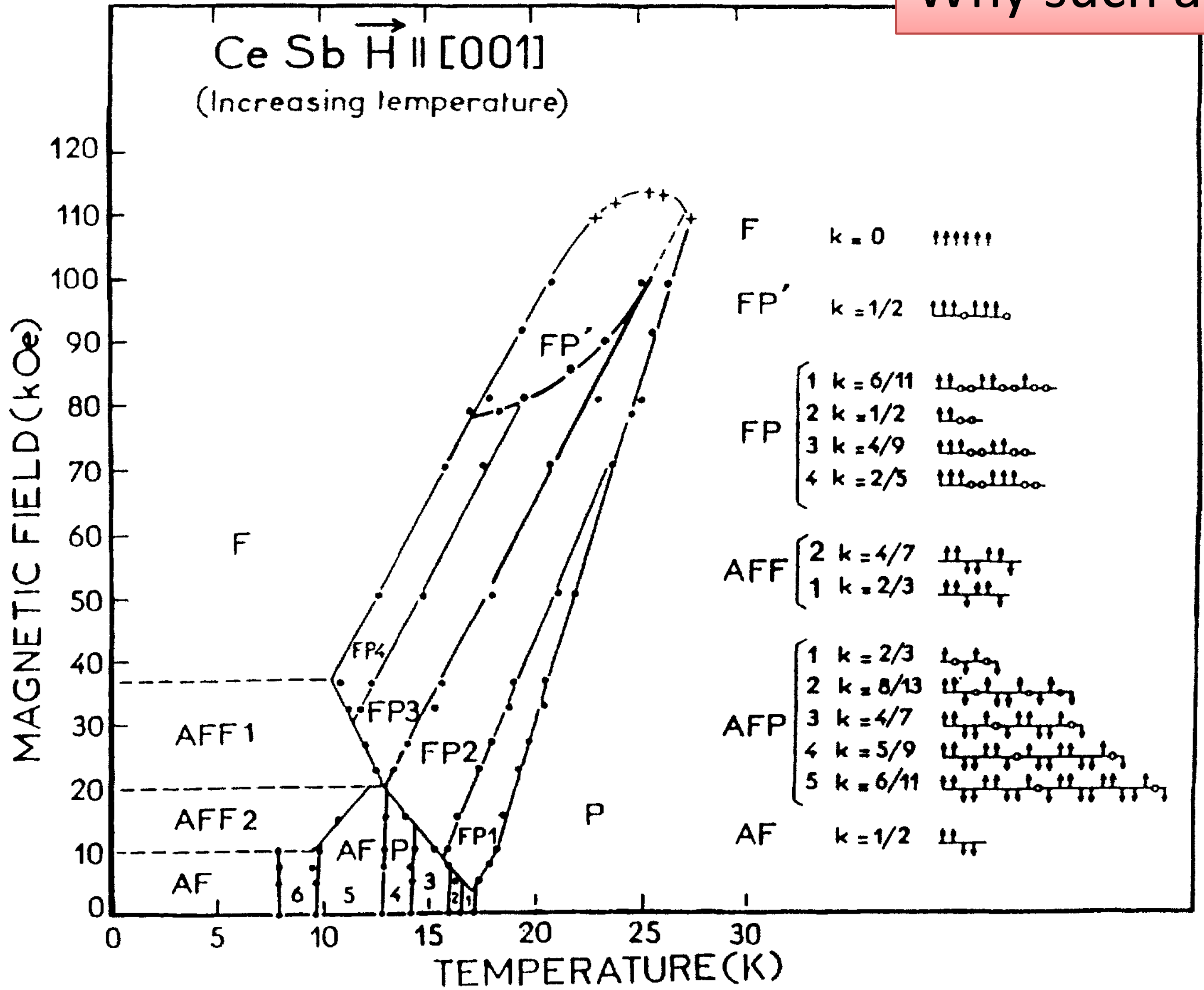
The most drastic change in magnets
Magnetic Ordering

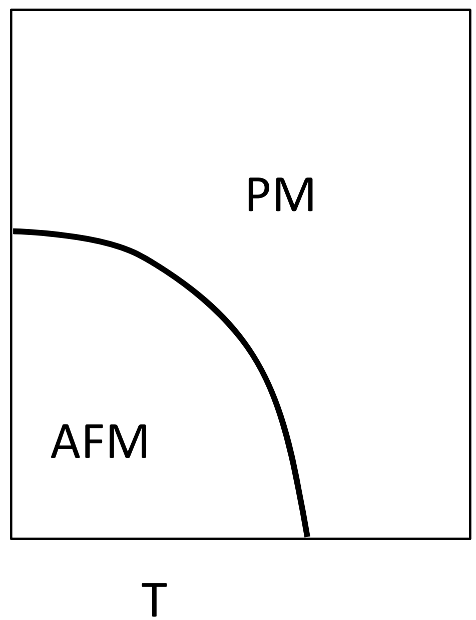
Purpose of Magnetic Physics is understanding of interactions.

Information on magnetic structures is indispensable.

H-T phase diagram: Develis Stairs :CeSb

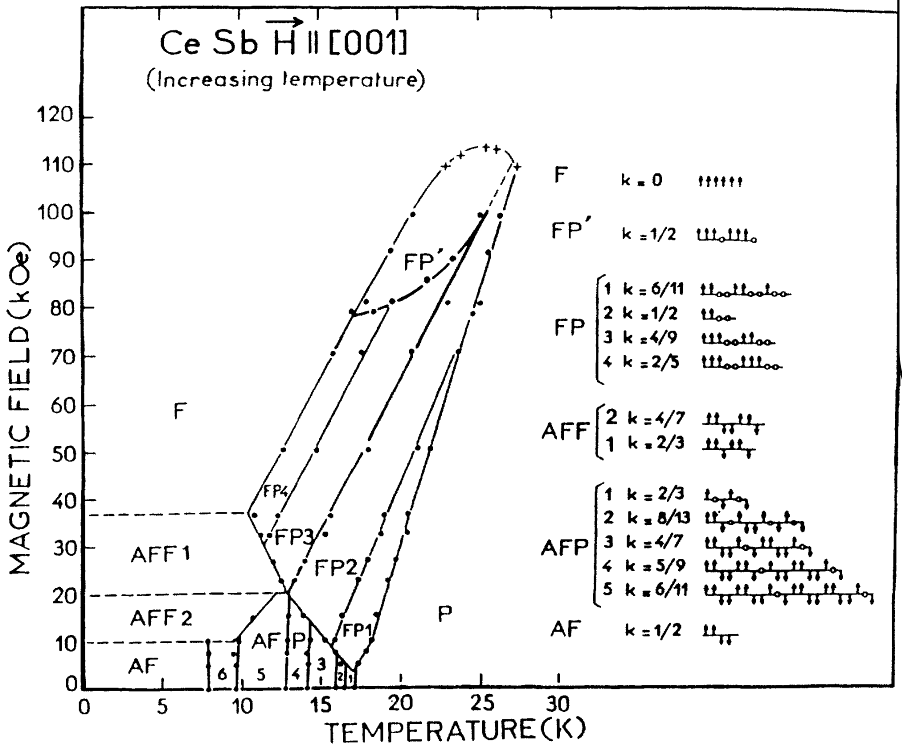
Why such a complicated one?





T. Chattopadhyay et al. Phys Rev. B 49, 15096 - 15104 (1994)

Why you have to know magnetic structures?



T. Chattopadhyay et al. Phys Rev. B 49, 15096 (1994)

It is not a purpose.

But, to understand the phase diagrams, magnetic structures (spin alignments) are indispensable.

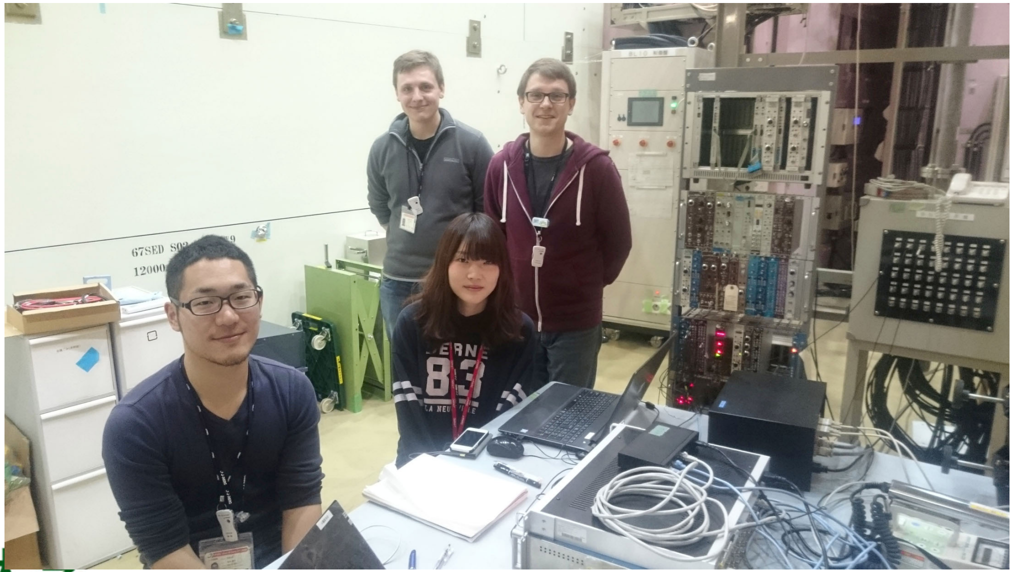
What is the origin which stabilize the spin in magnets?

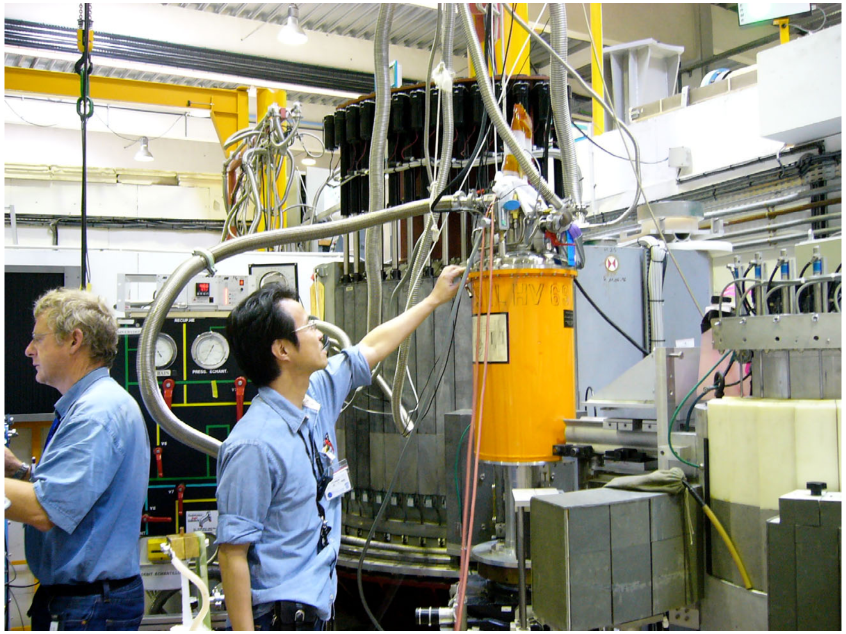
Magnetic Structure

Why you have to understand magnetic structures?

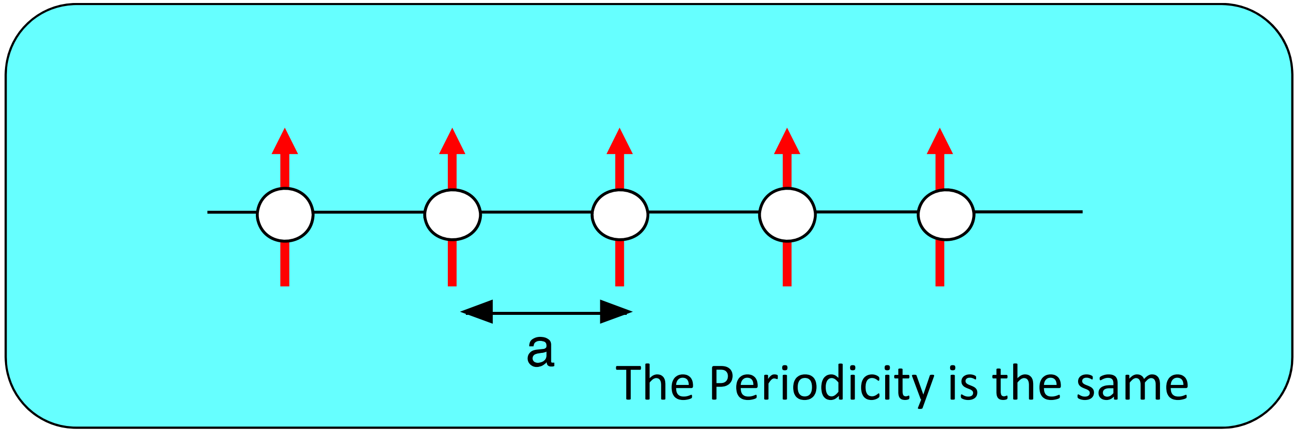
How you can observe it by Neutron

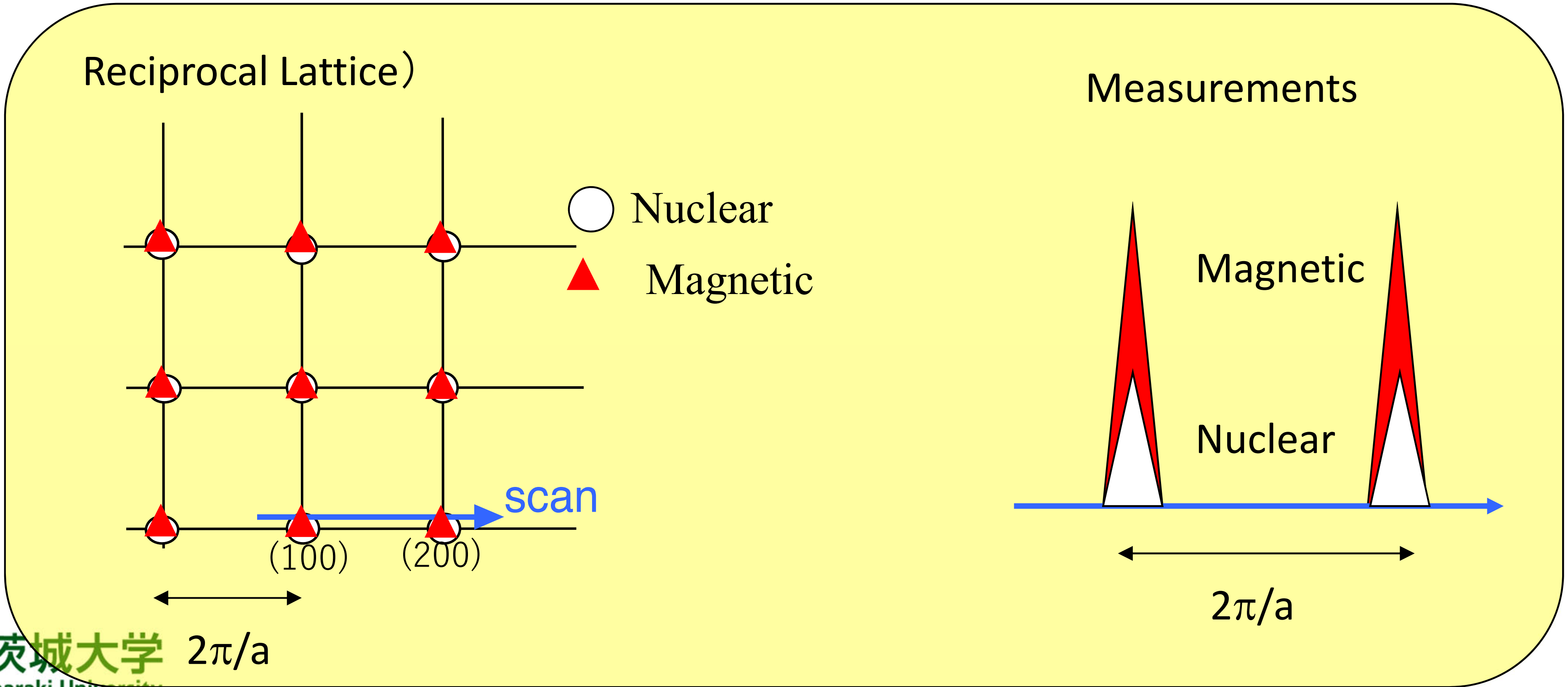
Magnetic structure refinement



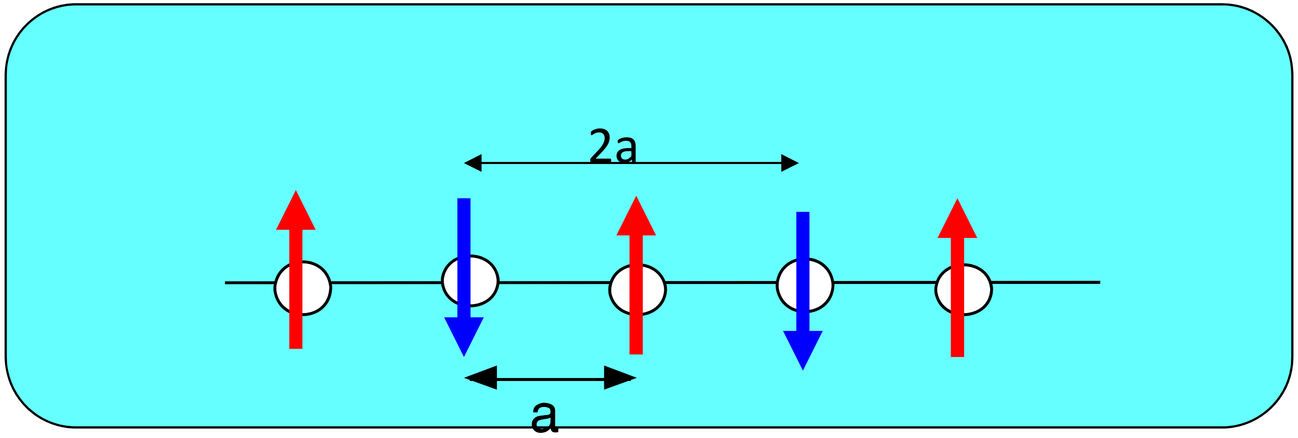


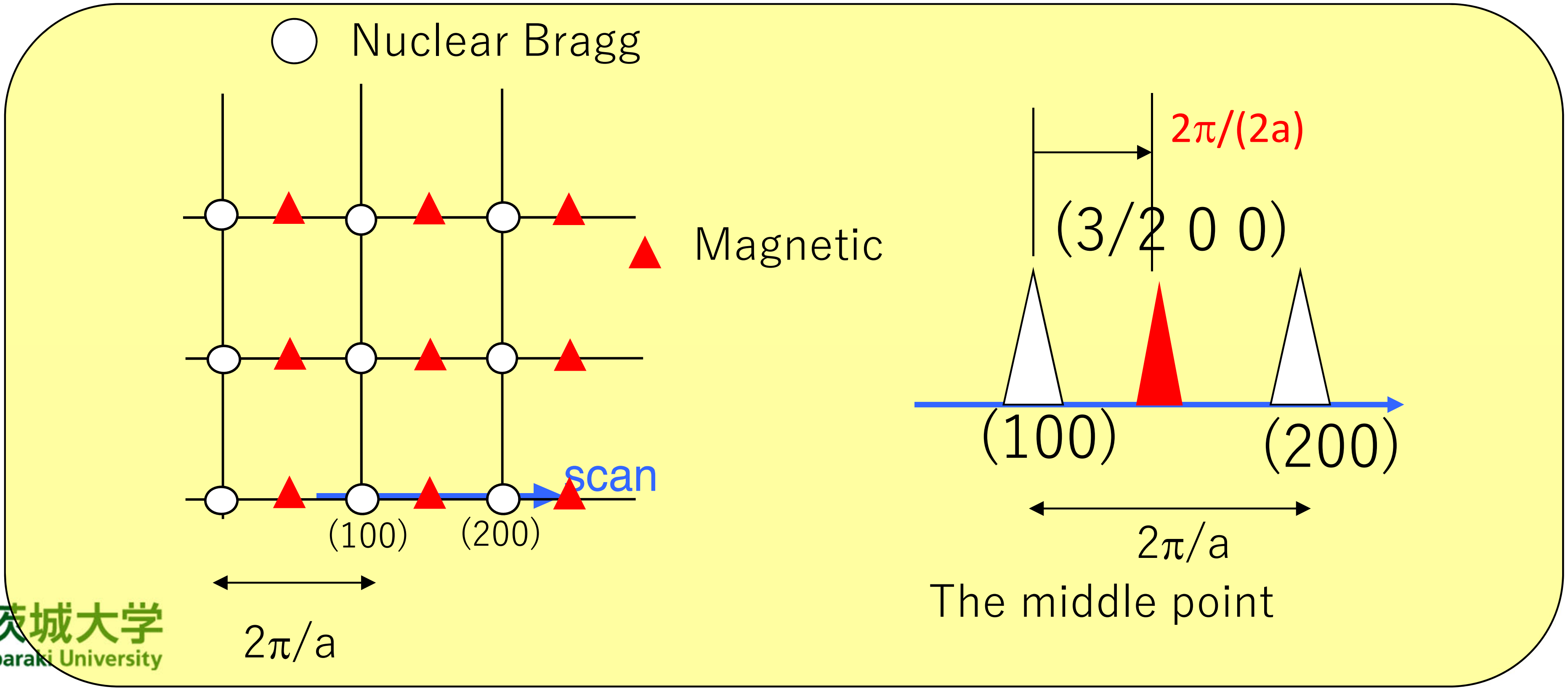
Observation by ND：Ferromagnet





Observation by ND：Antierromagnet



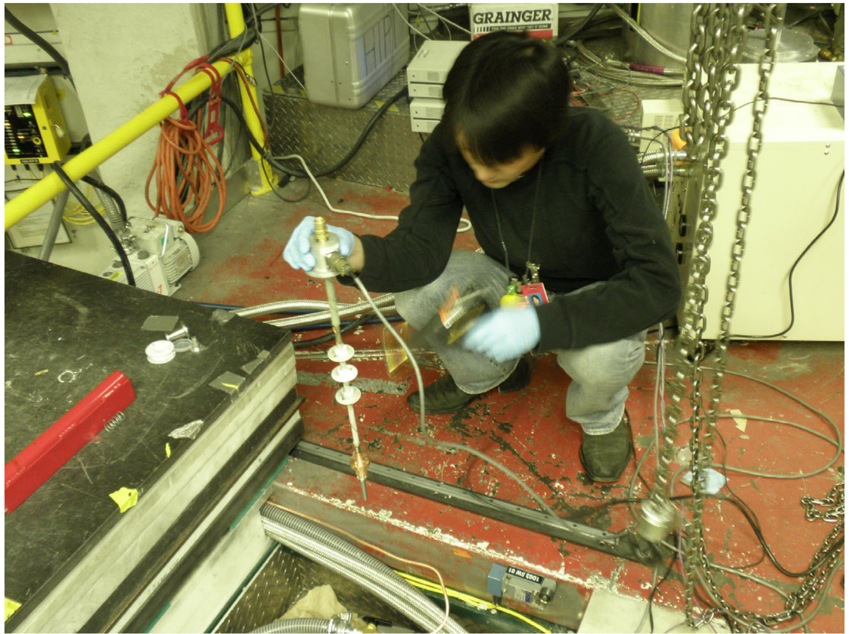


Magnetic Structure

Why you have to understand magnetic structures?

How you can observe it by Neutron

Magnetic Structure Refinement for Rare earth Compounds



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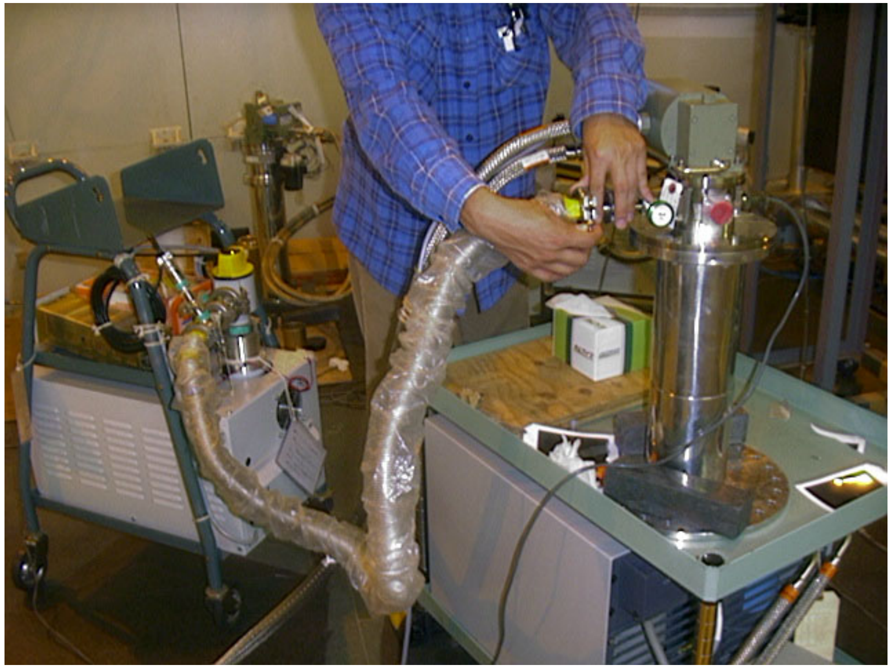
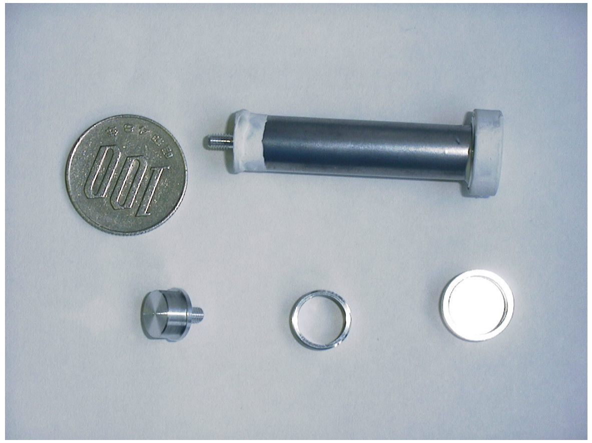
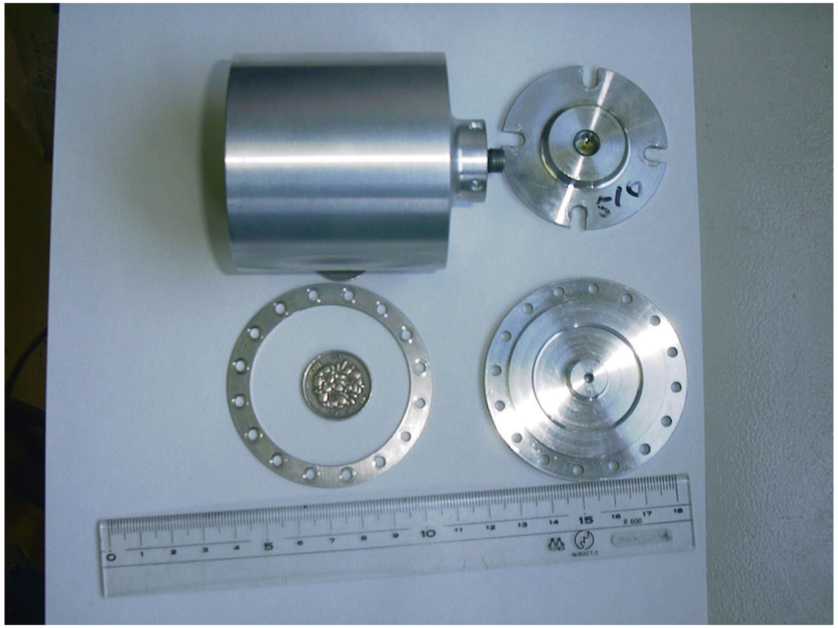
Experimemts



Cryostat（10K~300K)

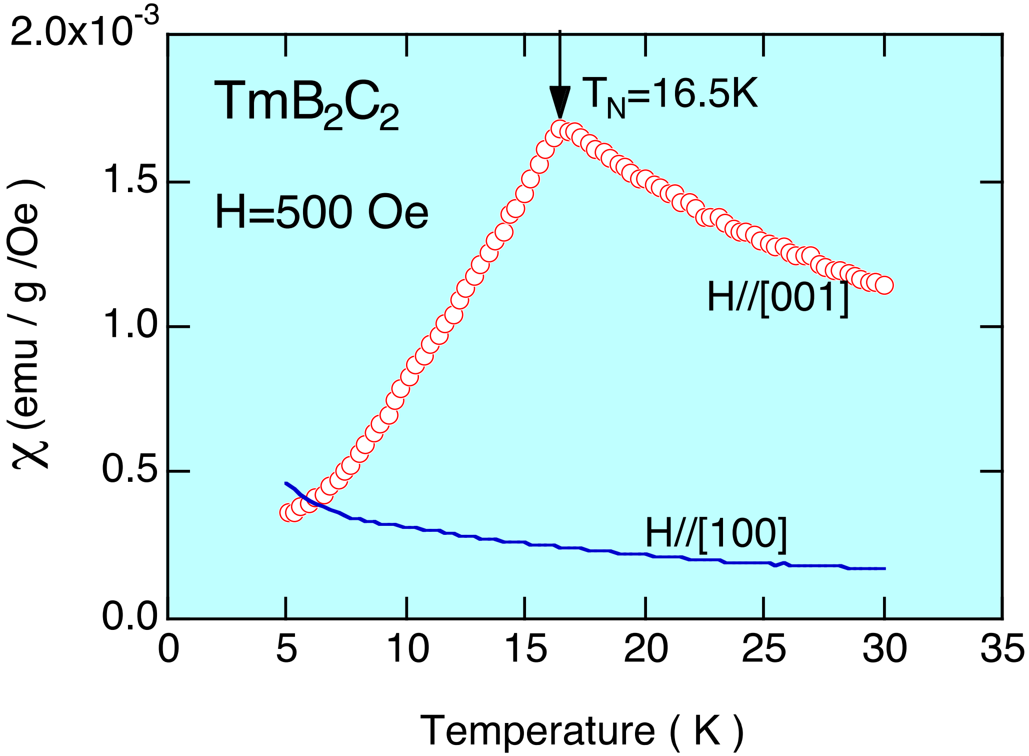


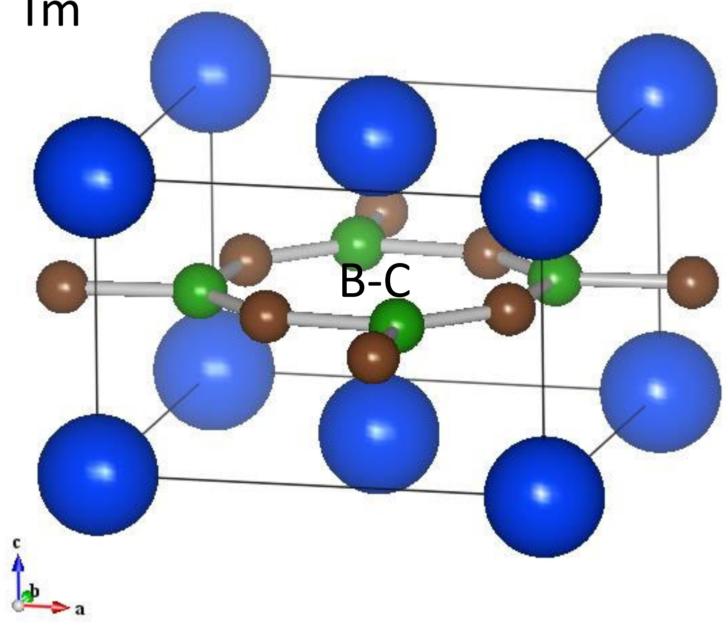
Vanadium Cell



Al Cell

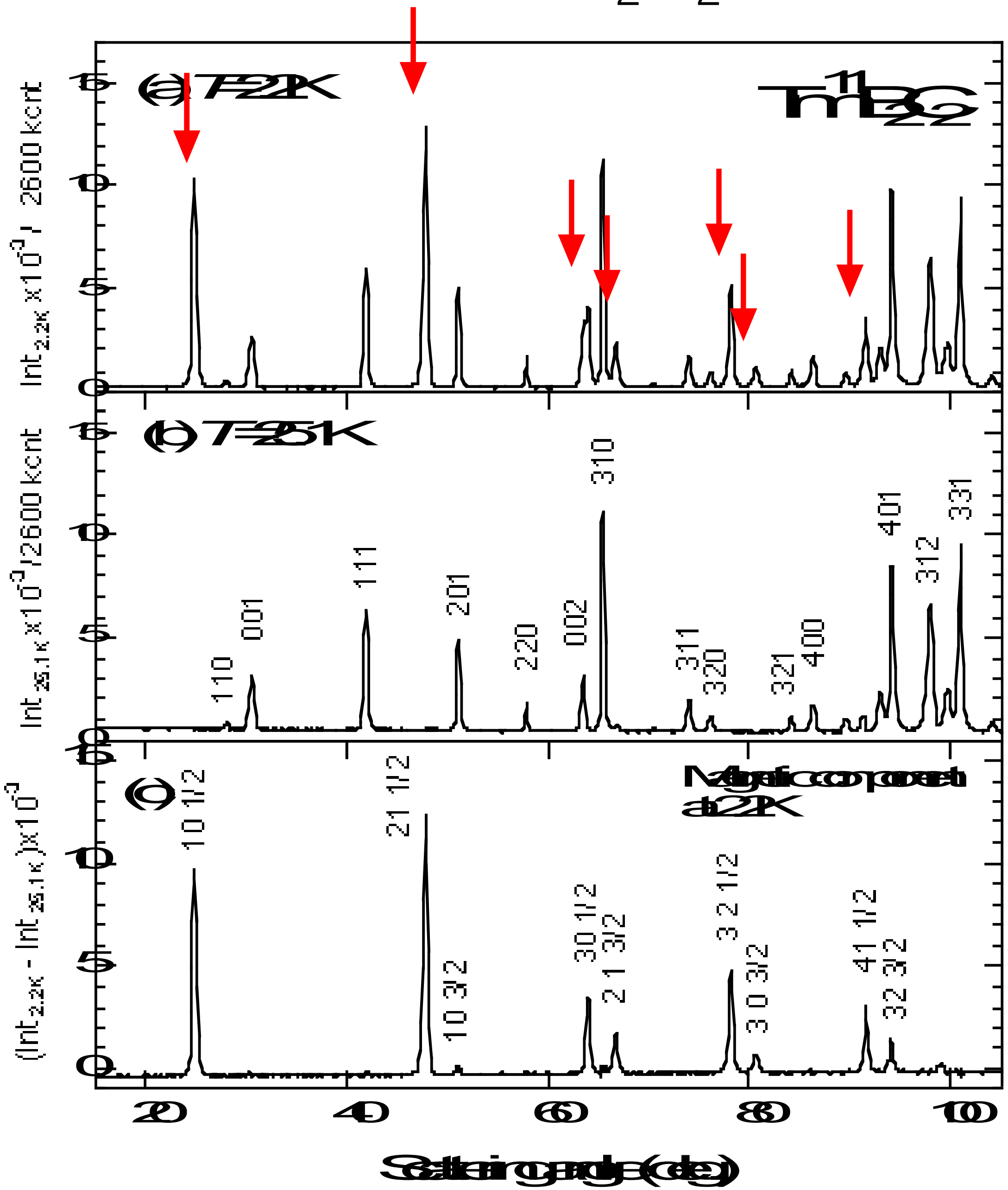
TmB_2C_2





P4/mbm

ND of TmB_2C_2



Nuclear	Magnetic
000	1 0 1/2
110	2 1 1/2
001	1 0 3/2
200	3 0 1/2
111	2 1 3/2

k=(1,0,1/2)

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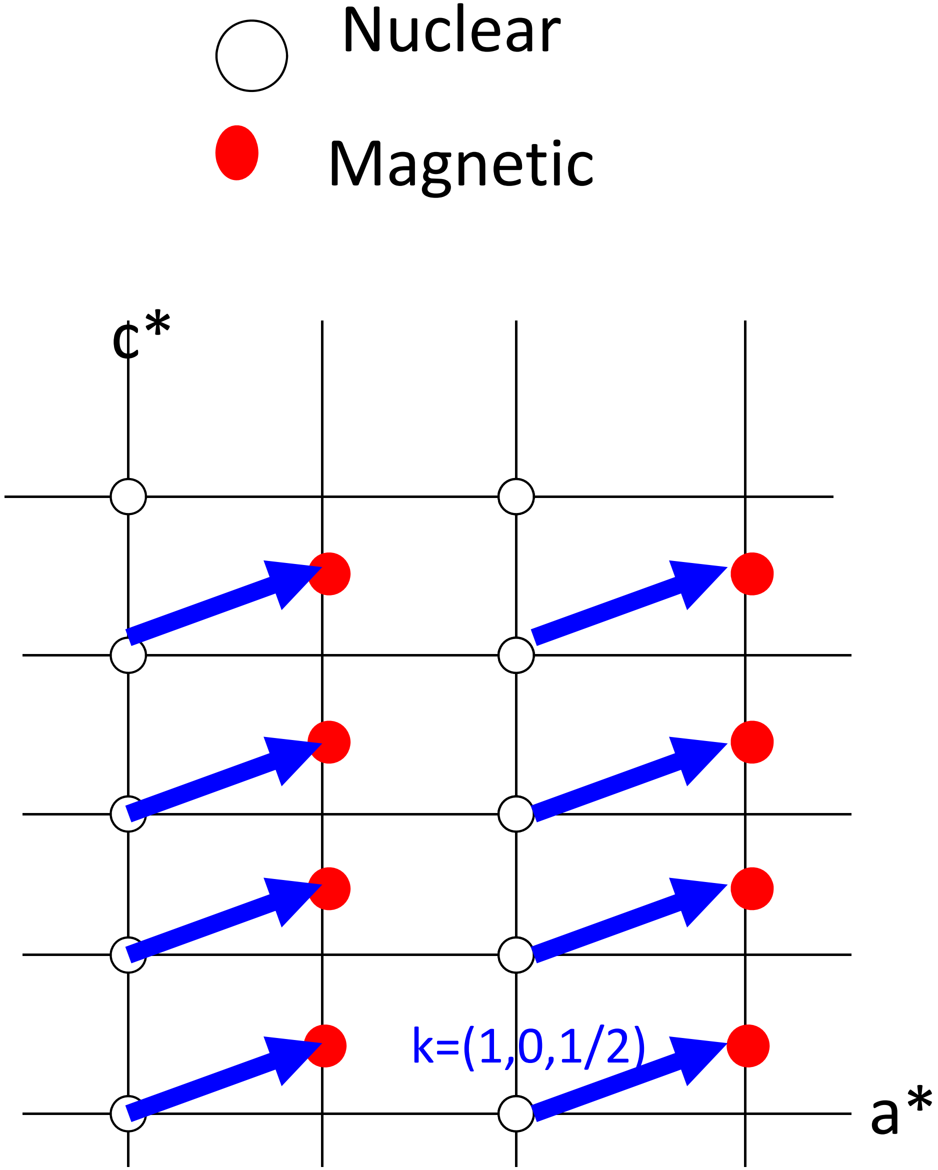
In the Reciprocal Lattice

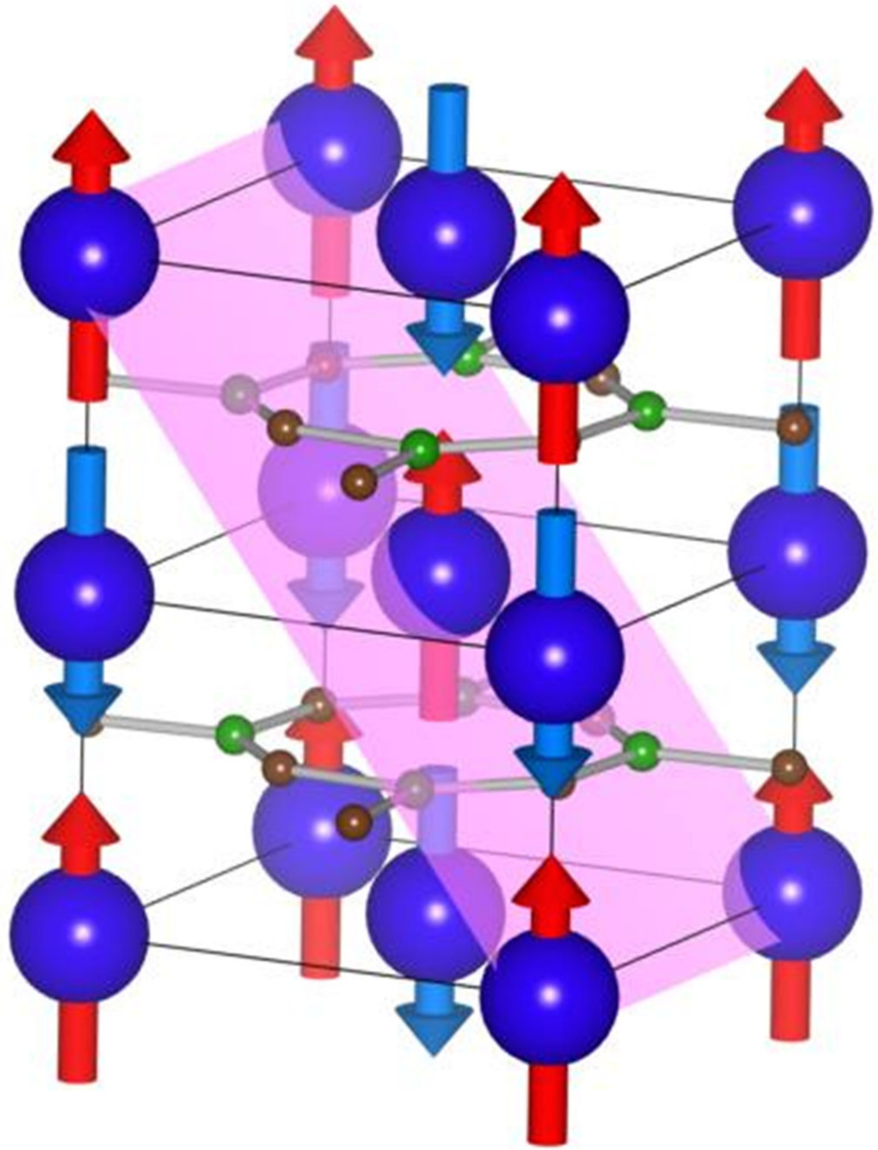
k=(1,0,1/2)



a*-c* plane

a-axis 1unit-> 1 Rotation

C-axis 2unit-> 1 Rotation



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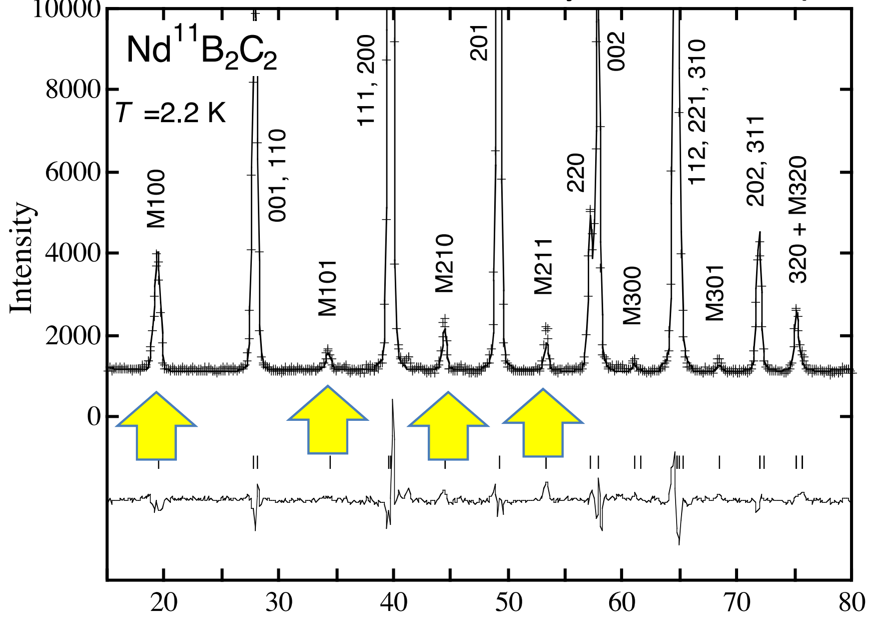
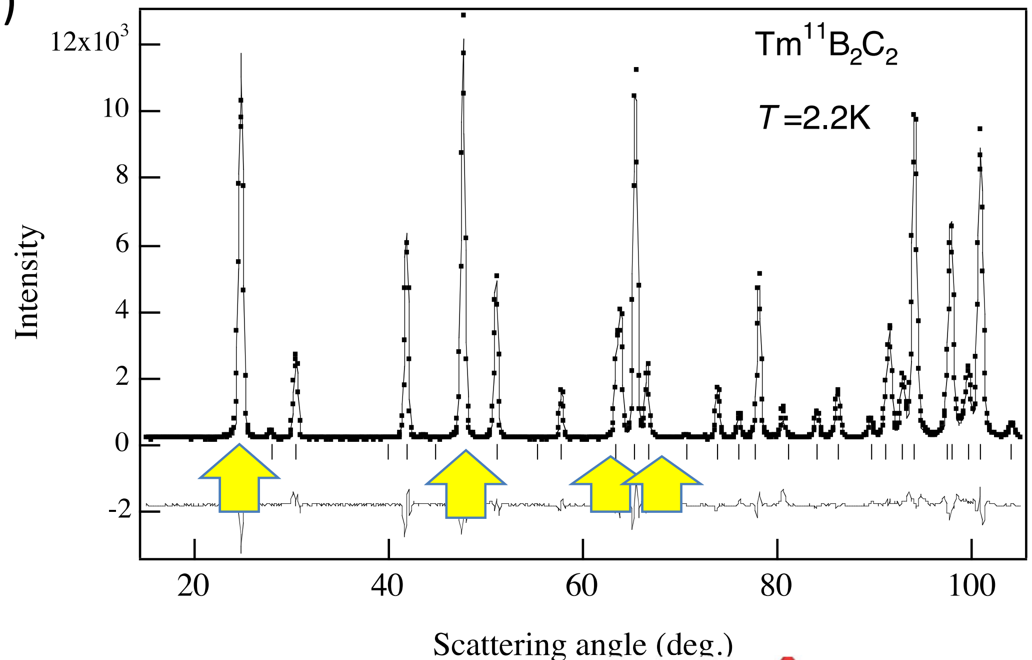
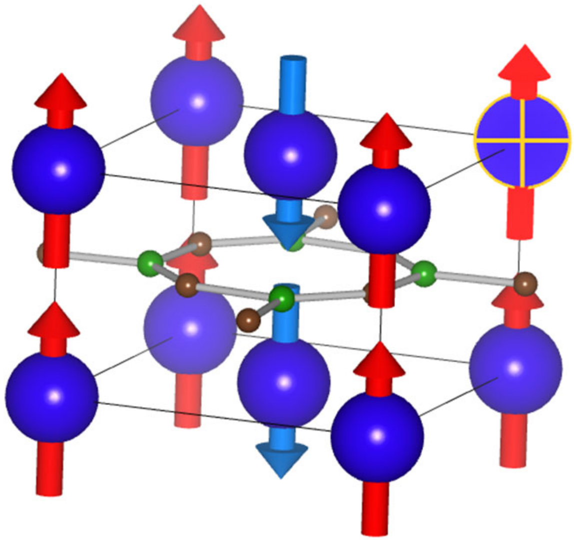
Rietveld Analysis

NdB_2C_2 Ohoyama et al (2000)

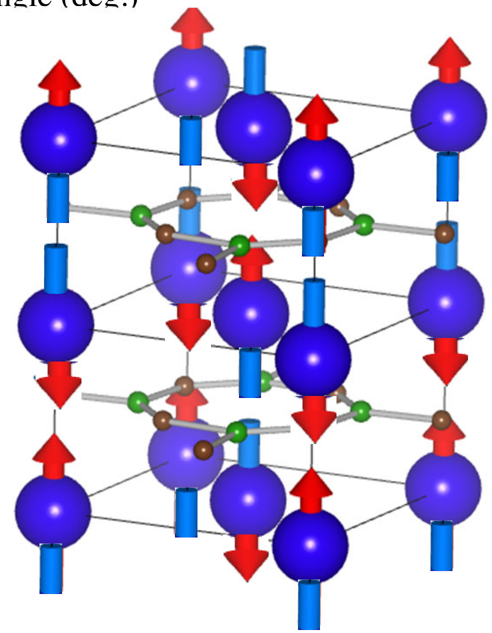


TmB_2C_2 Ohoyama et al (2002)





By simultaneous analysis of nuclear and magnetic Bragg peaks, one can obtain direction and amplitude of magnetic moments.



Summary

○ Neutron Diffraction experiments provide information on detailed structures of materials with light elements such as Hydrogen, Oxygen.

○ Neutron also can determine magnetic structures in magnets.

Diffraction is the method to observe the reciprocal lattice:
For structure refinement , information on the reciprocal lattice is quite rich and useful.