



SPring-8  
IWMC 2024

# **Z-Rietveld and its cooperation with other magnetic crystallography tools**

M. Hagihala

Materials and Sciences Research Center(MSRC)  
Japan Atomic Energy Agency (JAEA)

# Outline

## Z-Rietveld

- background of development
- project and package
- user friendly interface
- problems on magnetic structure analysis

## Demonstration of magnetic structure analysis

- simple case
- commensurate structure using irreducible representation
- commensurate and incommensurate structure using magnetic (super)space group

future and summary

# Background

Since neutron powder diffraction at MLF, J-PARC was expected to

- 1) cover  $S(Q)$  and SANS as well as Powder Diffraction:  
 $Q$  ( $< 0.01 \text{ \AA}^{-1}$  &  $> 50 \text{ \AA}^{-1}$ )  
→ nano structure, crystal structure, and local structure
  - 2) have the highest intensity or the highest resolution  
→ operando studies/ real time/ *in situ* studies,  
tiny distortion, peak broadening, complicated structures, etc...
  - 3) adopt event data recording  
→ each  $\sim 10^4$  detector pixels have  $\sim 10^4$  time channel
- long-term development of various hard & software developments were considered

# Development of Z-Code project

## **Z-Code Project (from credits)**

### **member**

Takashi Kamiyama (CSNS), Toru Ishigaki (CROSS), Yoshihisa Ishikawa (CROSS)  
Masato Hagihara (JAEA),

### **Development of GUI**

Innoface Inc.

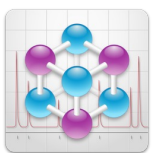
### **algorithm and program**

Ryoko Oishi-Tomiyasu (Kyushu Univ.), Satoshi Tamura(VIC)

### **former member**

Masao Yonemura, Ryoko Oishi-Tomiyasu, Miao Ping, Junrong Zhang  
Shanghyun Lee, Akinori Hoshikawa, Takashi Saito, Shuki Torii, Ryoji Kiyanagi,  
Takahiro Morishima





# Z-Rietveld software

## Rietveld analysis for

- NPD for both **TOF** and angle-dispersive
- XRD data for both laboratory and synchrotron radiation
- Analysis of multiple histogram data
- Multi-points analyses

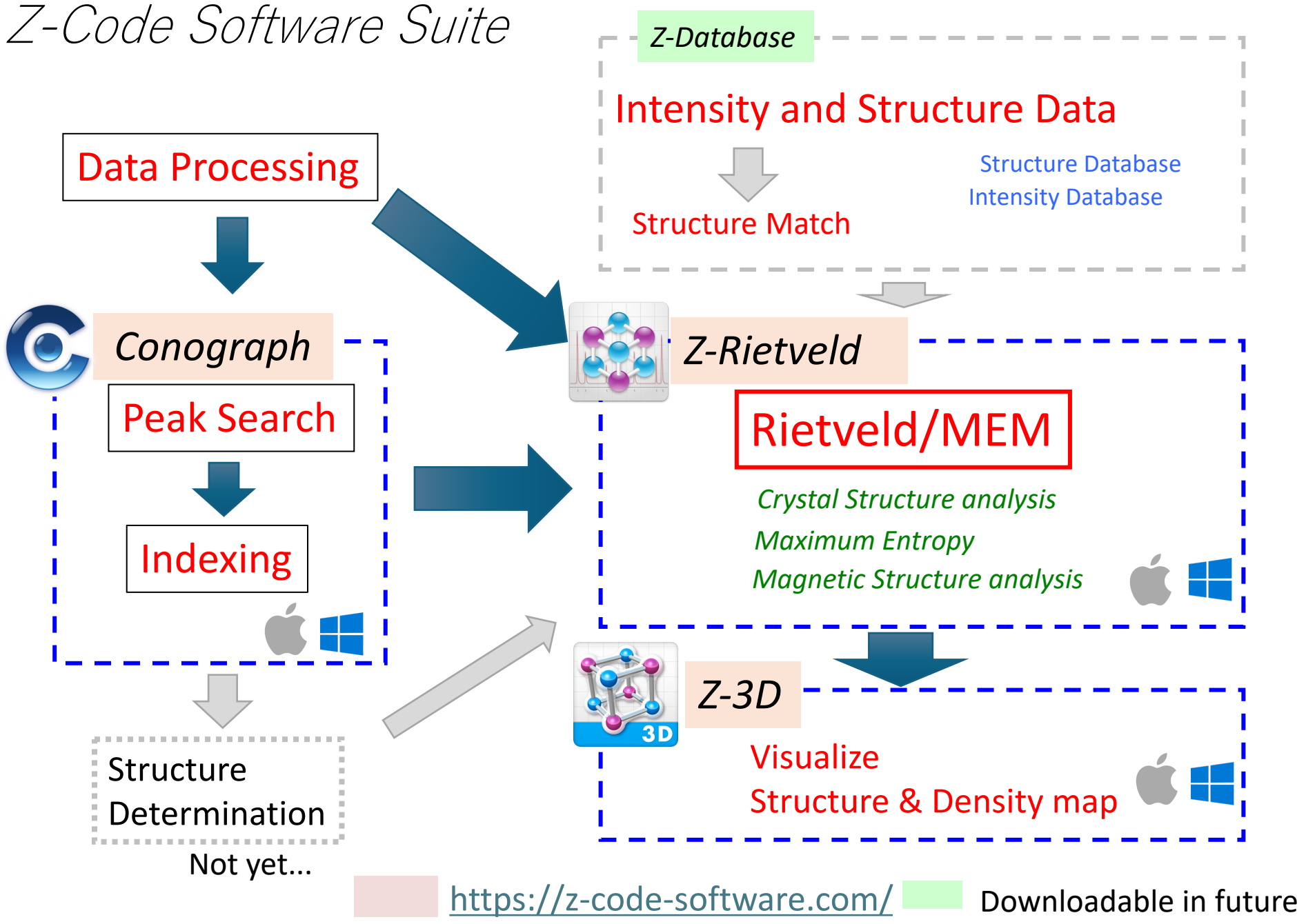
## User friendly functions

- **GUI** based program
- Japanese/Korean/Chinese OS as well as English OS

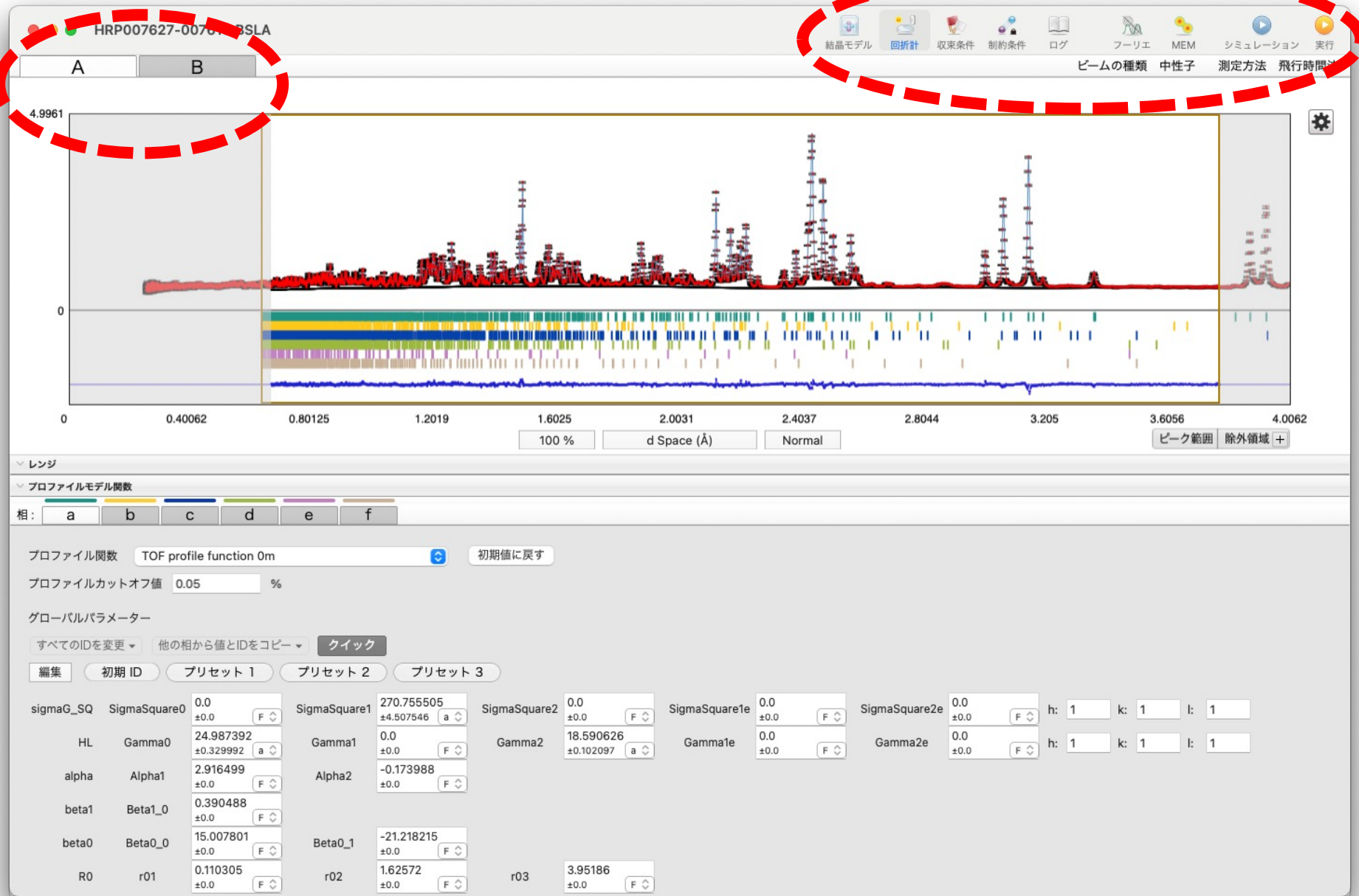
## Advanced functions

- Inequality constraints available
- New global optimization using Sequential Quadratic Programming (conventional Levenberg-Marquardt Algorithm is also available)
- Pawley method, and joint Pawley and Rietveld analysis
- MEM and Fourier analysis

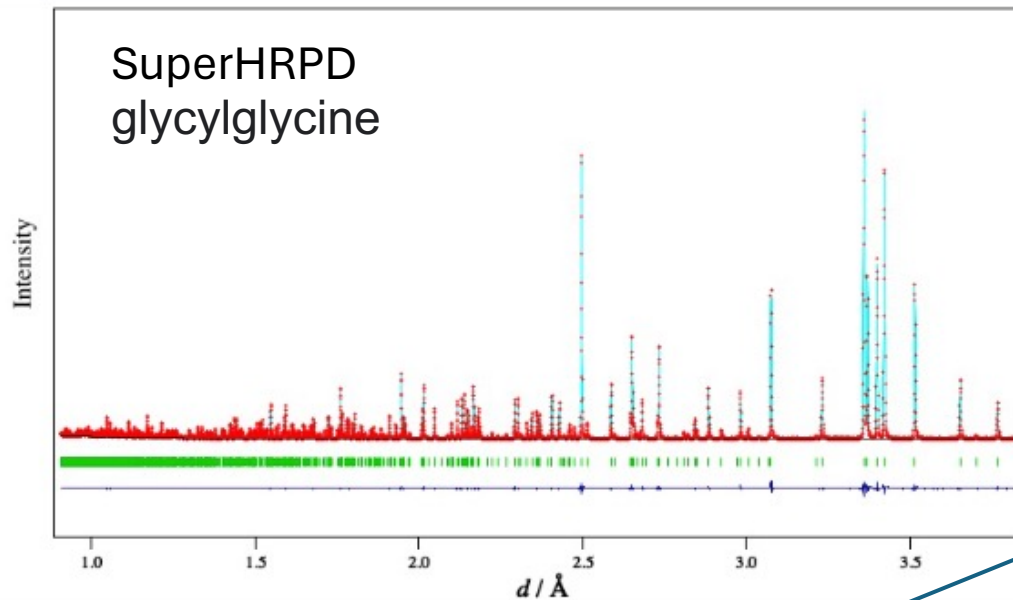
# Z-Code Software Suite



# Z-Rietveld user friendly interface



# Z-Rietveld Advanced functions 1



Pawley method

high degree of freedom

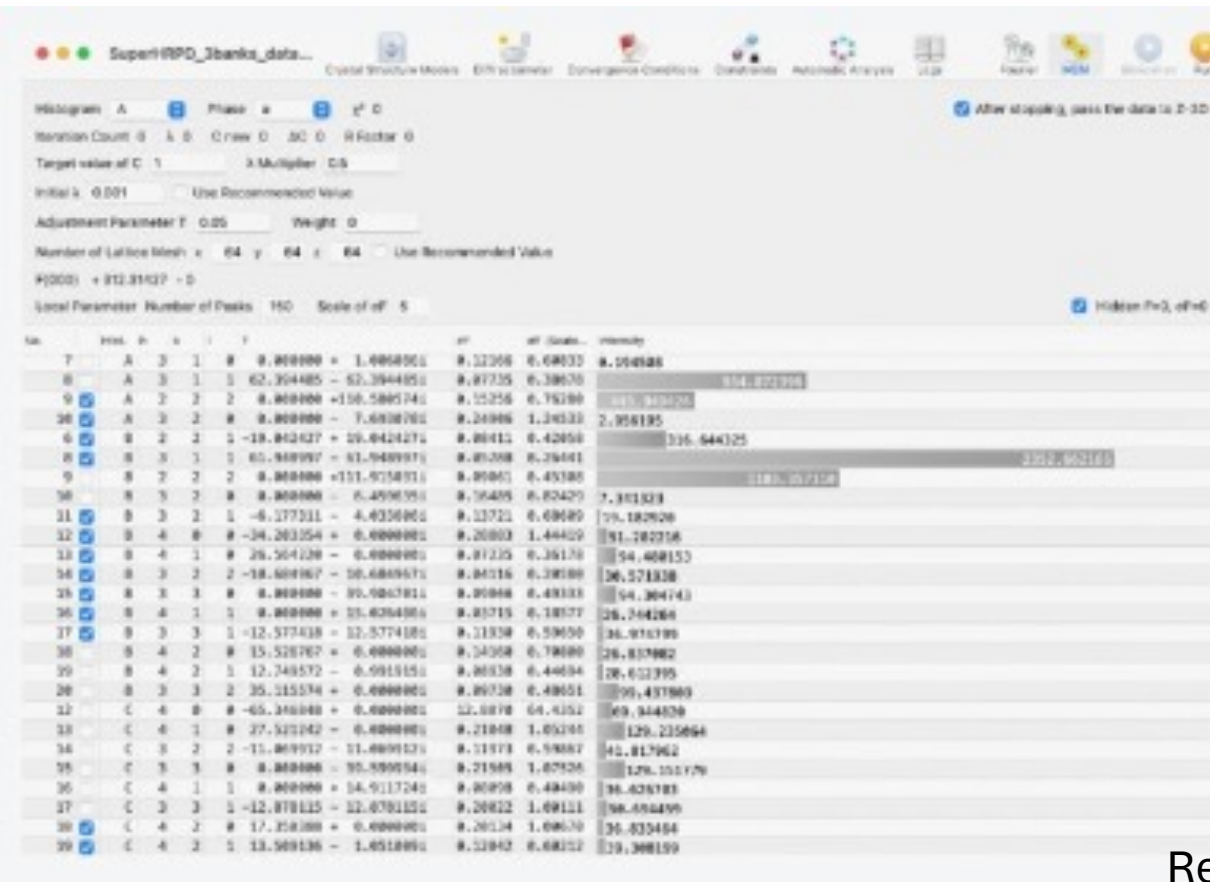
combination of  
sort and limited range function  
is very useful

ローカルパラメーター Line  ~

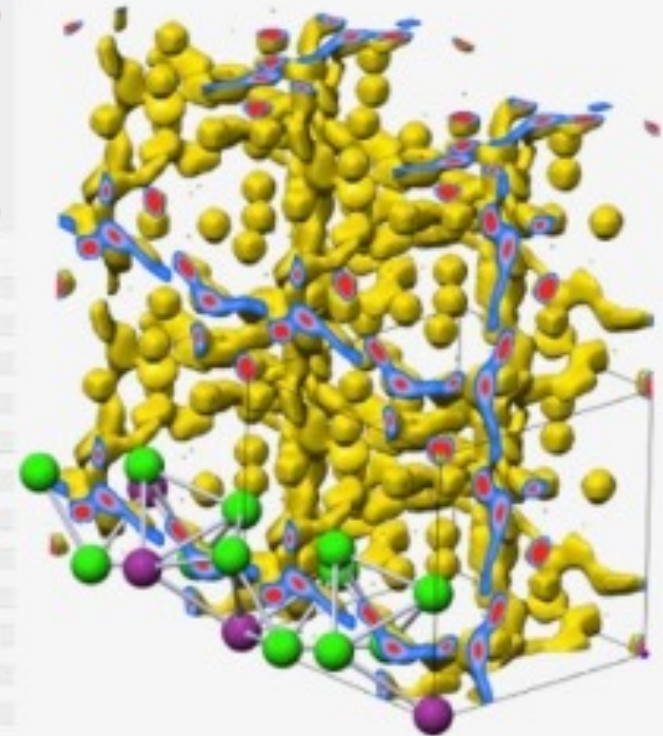
Line	No.	$h$	$k$	$l$	Peak Position	$d$	Intensity	sigmaG_SQ	HL	alpha	beta1	beta0	R0	
1	1	2	1	0	186486.1452... $\pm 0.087073$ <input type="button" value="D"/>	3.913753	27.15 $\pm 0$ <input type="button" value="V"/>	2147.4 $\pm 19.5$ <input type="button" value="D"/>	5.0963 $\pm 0.4864$ <input type="button" value="D"/>	0.4767 $\pm 0$ <input type="button" value="D"/>	0.4557 $\pm 0$ <input type="button" value="D"/>	2.3561 $\pm 0$ <input type="button" value="D"/>	0.104 $\pm 0$ <input type="button" value="D"/>	1
2	2	1	0	2	179587.0852... $\pm 0.104423$ <input type="button" value="D"/>	3.768958	440.47 $\pm 3.23$ <input type="button" value="V"/>	1979.1 $\pm 15.8$ <input type="button" value="D"/>	5.5648 $\pm 0.4171$ <input type="button" value="D"/>	0.4671 $\pm 0$ <input type="button" value="D"/>	0.4557 $\pm 0$ <input type="button" value="D"/>	2.4128 $\pm 0$ <input type="button" value="D"/>	0.104 $\pm 0$ <input type="button" value="D"/>	1
3	3	1	2	1	176416.5725... $\pm 0.059156$ <input type="button" value="D"/>	3.702417	104.17 $\pm 2.2$ <input type="button" value="V"/>	1904.5 $\pm 14.3$ <input type="button" value="D"/>	5.7608 $\pm 0.3874$ <input type="button" value="D"/>	0.4629 $\pm 0$ <input type="button" value="D"/>	0.4557 $\pm 0$ <input type="button" value="D"/>	2.4403 $\pm 0$ <input type="button" value="D"/>	0.1039 $\pm 0$ <input type="button" value="D"/>	1
4	4	2	0	-2	174100.618781 $\pm 0.087197$ <input type="button" value="D"/>	3.653811	852.64 $\pm 3.79$ <input type="button" value="V"/>	1851.1 $\pm 13.3$ <input type="button" value="D"/>	5.8963 $\pm 0.3665$ <input type="button" value="D"/>	0.4598 $\pm 0$ <input type="button" value="D"/>	0.4557 $\pm 0$ <input type="button" value="D"/>	2.4611 $\pm 0$ <input type="button" value="D"/>	0.1039 $\pm 0$ <input type="button" value="D"/>	1
5	5	1	1	2	167519.4696... $\pm 0.080933$ <input type="button" value="D"/>	3.515689	1935.4 $\pm 5$ <input type="button" value="V"/>	1704.2 $\pm 10.7$ <input type="button" value="D"/>	6.2457 $\pm 0.3115$ <input type="button" value="D"/>	0.4514 $\pm 0$ <input type="button" value="D"/>	0.4557 $\pm 0$ <input type="button" value="D"/>	2.5231 $\pm 0$ <input type="button" value="D"/>	0.1038 $\pm 0$ <input type="button" value="D"/>	1
6	6	2	1	-2	163039.95206 $\pm 0.087197$ <input type="button" value="D"/>	3.421676	3626.2 $\pm 5$ <input type="button" value="V"/>	1608.3 $\pm 10.7$ <input type="button" value="D"/>	6.4536 $\pm 0.3115$ <input type="button" value="D"/>	0.4458 $\pm 0$ <input type="button" value="D"/>	0.4557 $\pm 0$ <input type="button" value="D"/>	2.5683 $\pm 0$ <input type="button" value="D"/>	0.1037 $\pm 0$ <input type="button" value="D"/>	1

# Z-Rietveld Advanced functions 2

## MEM analysis



visualized by Z-3D



Represents the positive and negative density of the scattering length

support to multi-histograms  
with sorting function of Bragg reflection based on standard deviation



# Z-Rietveld Advanced functions 3

Extensive automatic successive histogram analysis function



The bottom screenshot shows the 'Automatic Analysis' settings window. The 'Automatic Analysis' checkbox is checked (Yes). The 'Preset' dropdown is set to 'Multiphase'. The 'Single-point data analysis with multiple phases. ex. one-temperature point data with multiple-banks can be analyzed with multiple phases.' text is visible. The 'Parameter to be Varied' section lists various parameters, with 'Scale factor Full' and 'Background Full' highlighted. The 'Full-automatic (Fixed priority Ignore)' section lists parameters, with 'Scale factor Full', 'Lattice constant Full', 'Mass ratio Full', 'Occupancy Full', 'Atomic coordinates Full', and 'ADP's Full' highlighted. A table at the bottom shows the sequence of steps for the analysis, with 'Token' highlighted in a blue box.

Step	Numbe...	Parameter to be Varied
1	5	Scale factor Full Background Full
2	20	Scale factor Full Mass ratio Full Background Full Peak shift Semi
3	20	Scale factor Full Lattice constant Full Background Full Peak shift Semi
4	20	Scale factor Full Lattice constant Full Mass ratio Full Common Global parameters Preset Full Background Full Peak shift Semi
5	20	Scale factor Full Lattice constant Full Mass ratio Full Occupancy Semi Atomic coordinates Full ADP's Full Background Full Peak shift Semi
6	20	Scale factor Full Lattice constant Full Common Global parameters Preset Full Background Full Peak shift Semi

Please check if you're interested in these advanced functions.

<https://z-code-software.com/new-features-of-z-rietveld-2-0-0/>



# Z-Rietveld for magnetic structure analysis

In this time, magnetic structure analysis can be carried out by Z-Rietveld,

BUT it is not user friendly at all

# Under construction

- i/o of .mcif files



- magnetic (super)space group

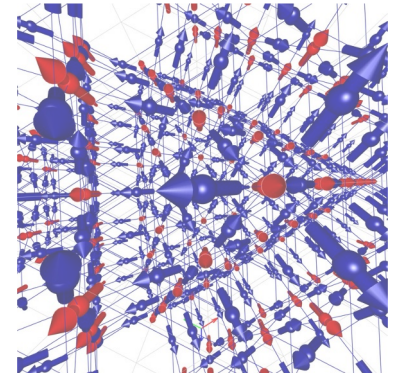
- irreducible representation

## input basis vectors manually💧💧

BV2				0 s0	F	0 s0	F			
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	x	y	z	0	0	0		0.160537	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	x+1/2	-y+1/2	-z	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	-x	y+1/2	-z+1/2	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	-x+1/2	-y	z+1/2	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	z	x	y	0	0	0		0	0.160537	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	z+1/2	-x+1/2	-y	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	-z	x+1/2	-y+1/2	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	-z+1/2	-x	y+1/2	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	y	z	x	0	0	0		0	0	0.160537
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	y+1/2	-z+1/2	-x	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	-y	z+1/2	-x+1/2	0	0	0		0	0	0
磁気サイト				スピンの方向 実部 x	y	z		虚部 x	y	z
Mn	x+1/2			0	0	0		0	0	0

implement in the future

- visualization of magnetic structure using Z-mag program temporary

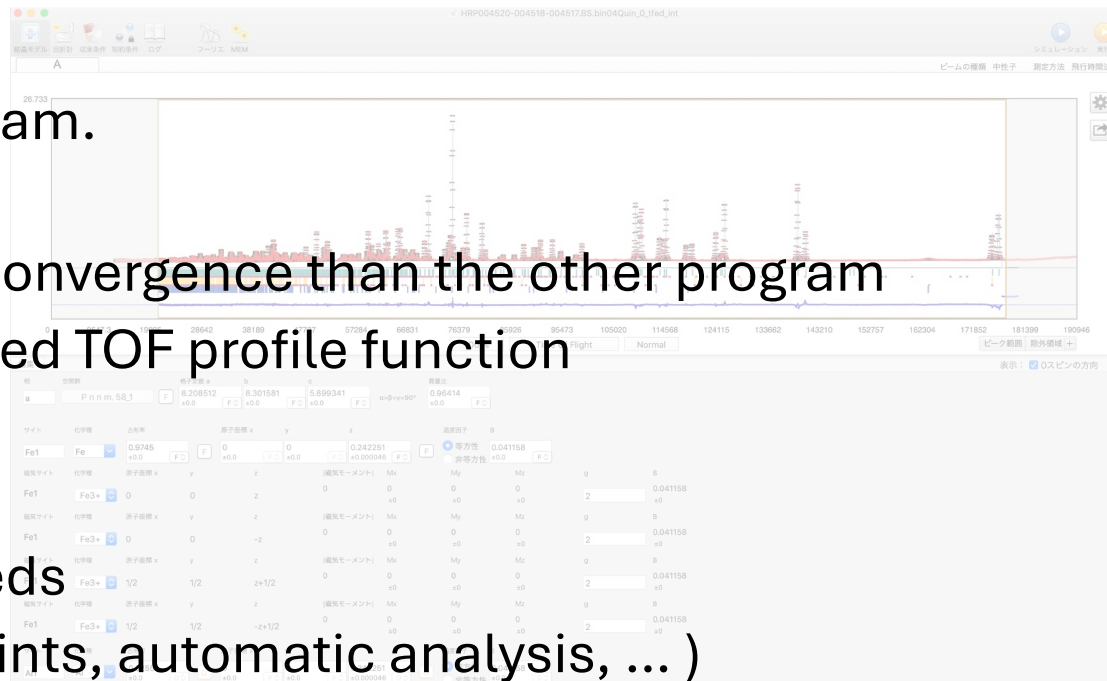


# Motivation

We hope to make easier for any user  
to do magnetic structure analysis.

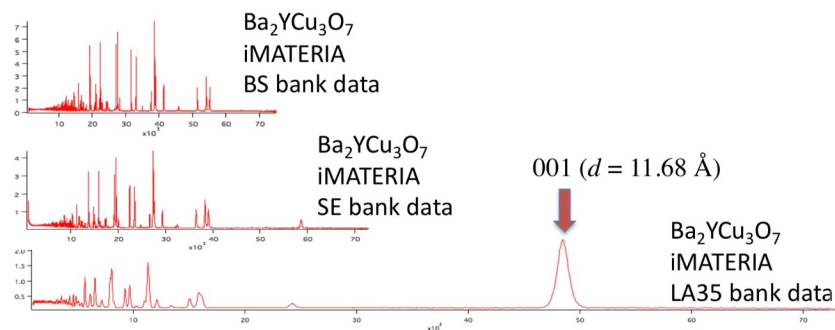
Z-Rietveld is

- User friendly GUI program.
- rarely divergence  
probably better convergence than the other program
- use of specially designed TOF profile function



moreover...

- aim to satisfy user needs  
(e.g. special constraints, automatic analysis, ... )

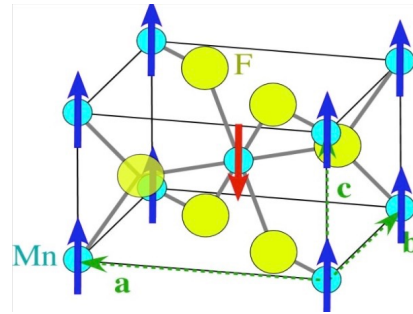


The screenshot shows the "Histogram and Refinement File Selection" dialog box. It contains a table with columns for "Histogram File (File Name)", "Refinement File (File Name)", "Beam Type", and "Measurement Method". The table lists several files and their corresponding refinement files. Below the table, there are buttons for "Add Histogram File", "Delete Histogram File", and "Load New Data".

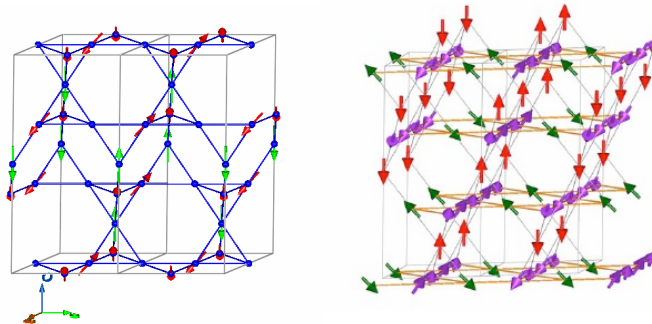
ヒストグラムファイル(ファイル名)	回折計ファイル(ファイル名)	ビームの種類	測定方法	
WAT002344 BS bin02d_0.c	imateria_0_BS_type2_120516	中性子線	Time Of Flight 時間飛行法	回折計ファイルを選択
WAT002344 SE bin02d_0.c	imateria_0_SE_type2_120515	中性子線	Time Of Flight 時間飛行法	回折計ファイルを選択
WAT002344 LA35 bin02d_0.c	imateria_0_LA35_type0_1205	中性子線	Time Of Flight 時間飛行法	回折計ファイルを選択
WAT002344 LA25 bin02d_0.c	imateria_0_LA25_type0_1205	中性子線	Time Of Flight 時間飛行法	回折計ファイルを選択
WAT002344 LA15 bin02d_0.c	imateria_0_LA15_type0_1205	中性子線	Time Of Flight 時間飛行法	回折計ファイルを選択

# Example of magnetic structure analysis using current version

- $\text{MnF}_2$  antiferromagnetic

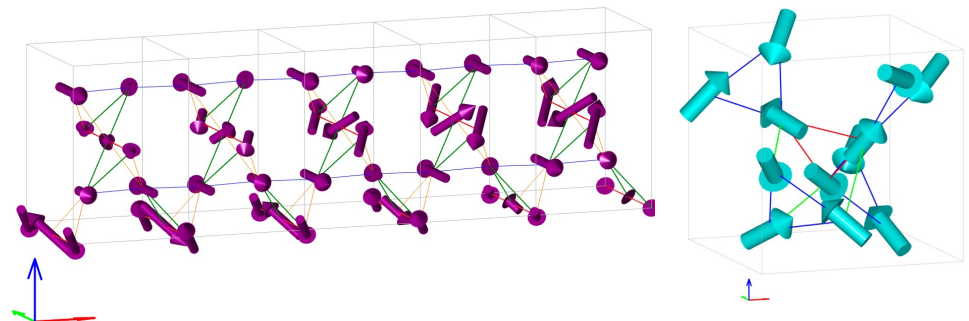


- $\text{Co}_2(\text{OD})_3\text{Br}$  commensurate structure with multi- $q$

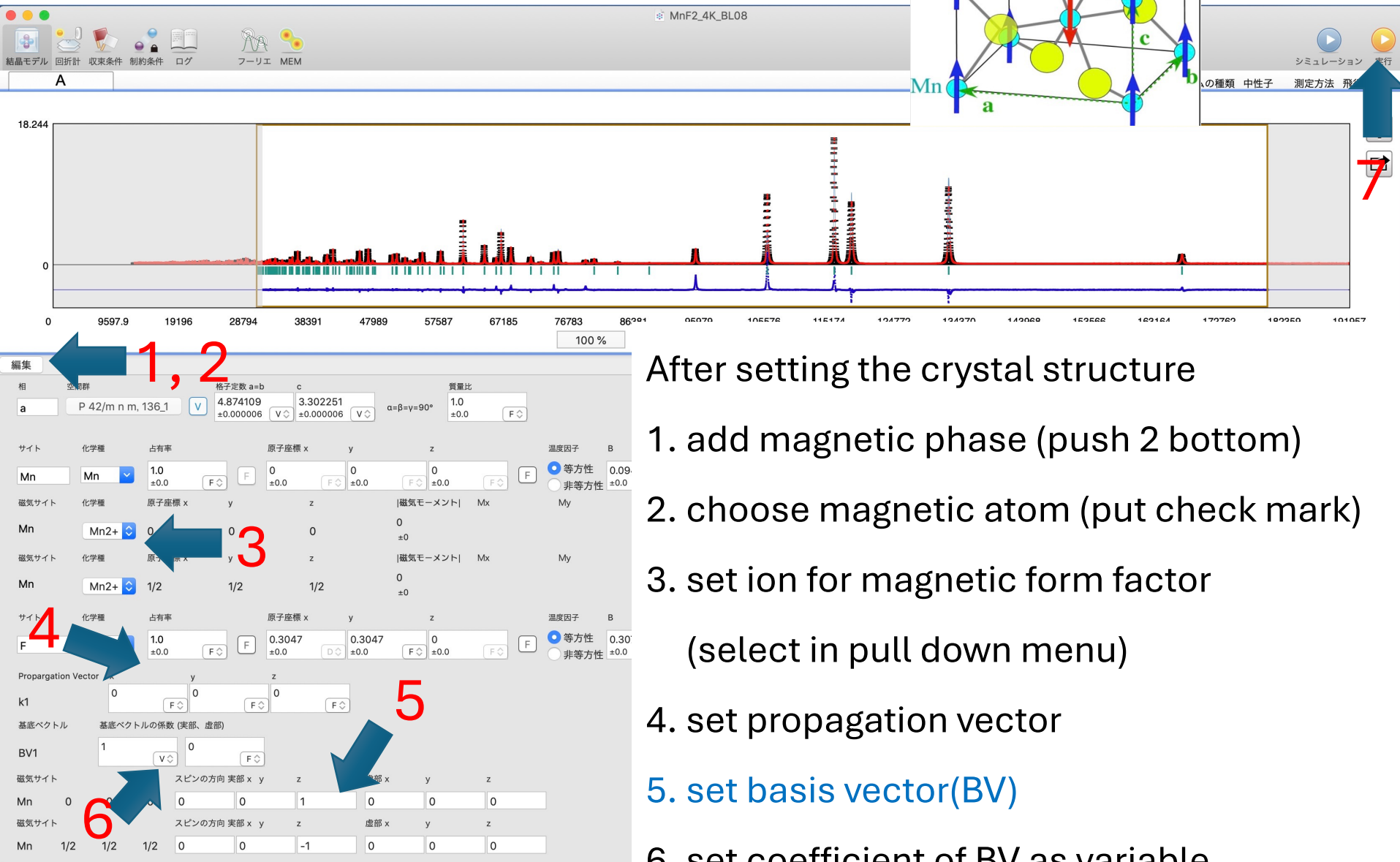


- incommensurate structure (multi- $q$ )

Not shown in this slide. Sorry...



# MnF<sub>2</sub>

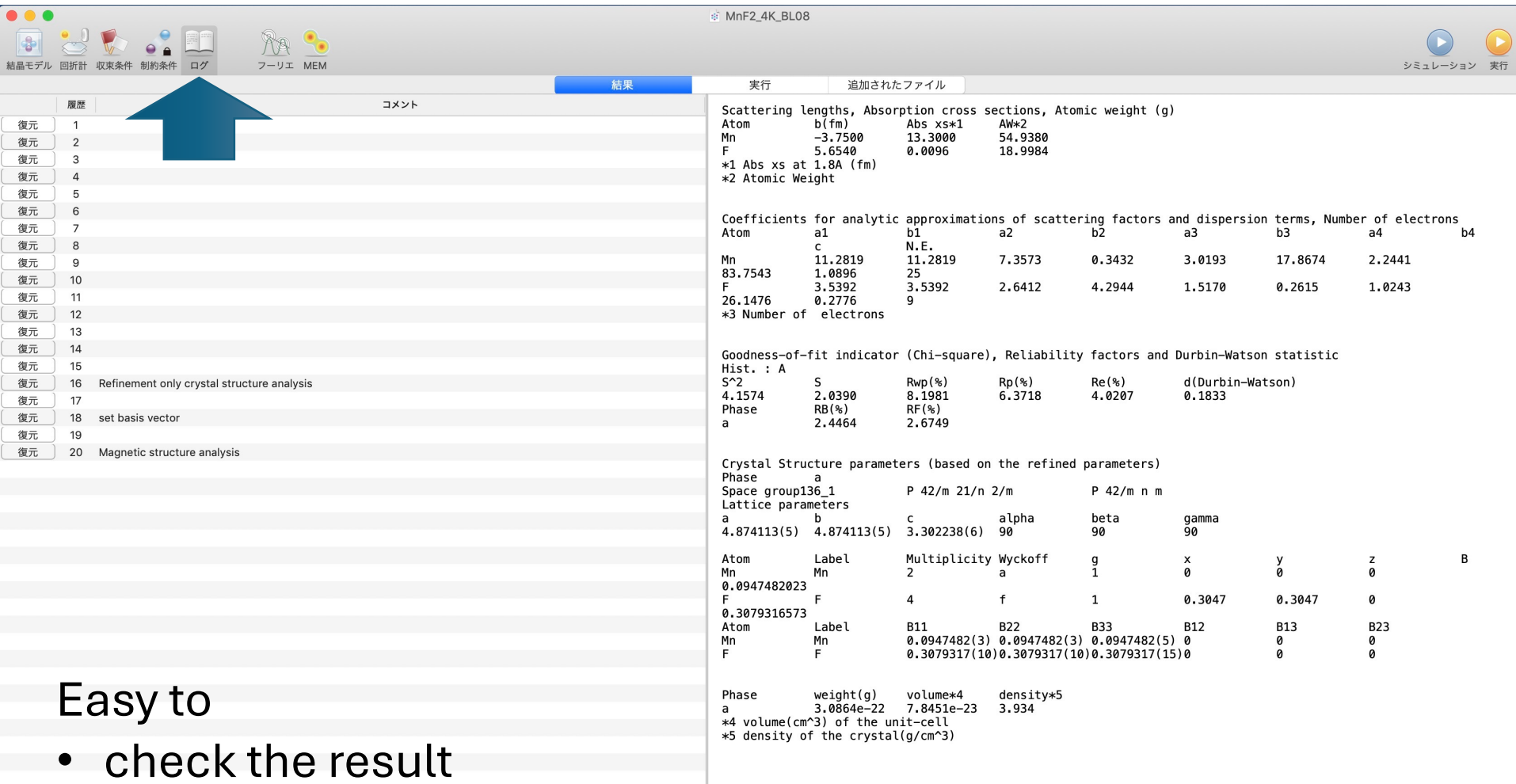


After setting the crystal structure

1. add magnetic phase (push 2 bottom)
2. choose magnetic atom (put check mark)
3. set ion for magnetic form factor  
(select in pull down menu)
4. set propagation vector
5. set basis vector(BV)
6. set coefficient of BV as variable
7. push refinement bottom



# Load and save function



**結果**

Scattering lengths, Absorption cross sections, Atomic weight (g)

Atom	b(fm)	Abs xs*1	AW*2
Mn	-3.7500	13.3000	54.9380
F	5.6540	0.0096	18.9984

\*1 Abs xs at 1.8Å (fm)  
\*2 Atomic Weight

Coefficients for analytic approximations of scattering factors and dispersion terms, Number of electrons

Atom	a1	b1	a2	b2	a3	b3	a4	b4
Mn	11.2819	11.2819	7.3573	0.3432	3.0193	17.8674	2.2441	
F	3.5392	3.5392	2.6412	4.2944	1.5170	0.2615	1.0243	

\*3 Number of electrons

Goodness-of-fit indicator (Chi-square), Reliability factors and Durbin-Watson statistic

Hist. : A	S <sup>2</sup>	Rwp(%)	Re(%)	Re(%)	d(Durbin-Watson)
4.1574	2.0390	8.1981	6.3718	4.0207	0.1833

Crystal Structure parameters (based on the refined parameters)

Phase a  
Space group 136\_1 P 42/m 21/n 2/m P 42/m n m  
Lattice parameters  
a b c alpha beta gamma  
4.874113(5) 4.874113(5) 3.302238(6) 90 90 90

Atom	Label	Multiplicity	Wyckoff	g	x	y	z	B
Mn	Mn	2	a	1	0	0	0	
F	F	4	f	1	0.3047	0.3047	0	

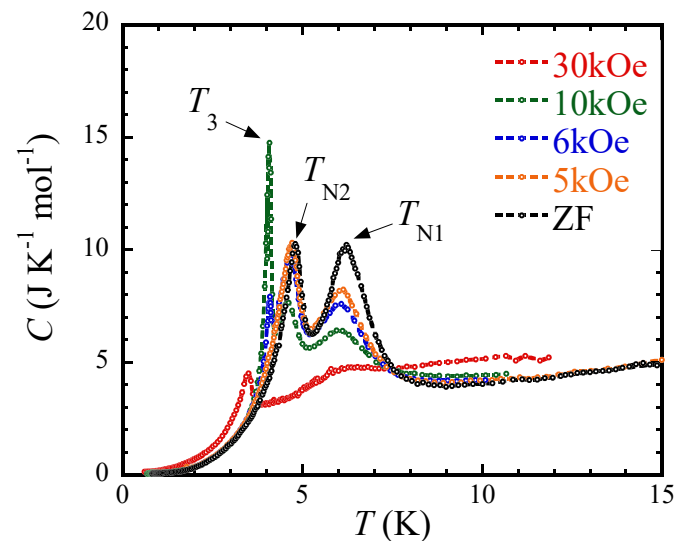
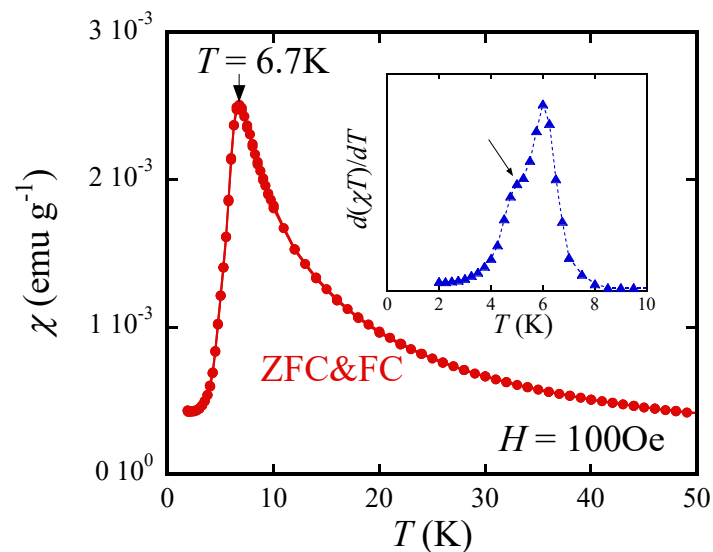
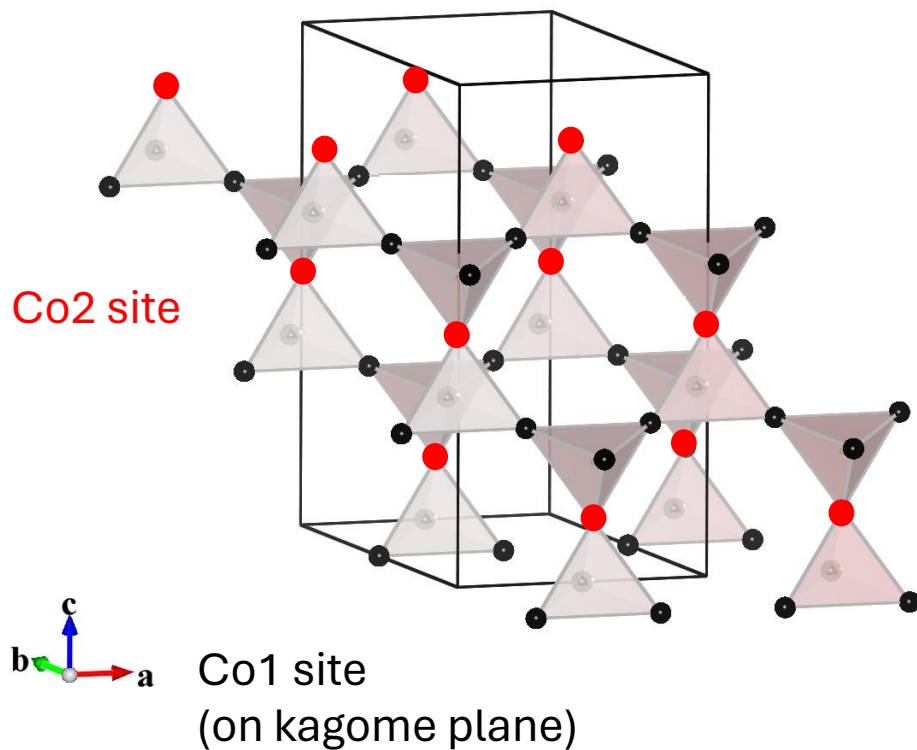
Atom Label Multiplicity Wyckoff g x y z B  
Mn Mn 2 a 1 0 0 0  
F F 4 f 1 0.3047 0.3047 0

Atom Label B11 B22 B33 B12 B13 B23  
Mn Mn 0.0947482(3) 0.0947482(3) 0.0947482(5) 0 0 0  
F F 0.3079317(10) 0.3079317(10) 0.3079317(15) 0 0 0

Phase weight(g) volume\*4 density\*5  
a 3.0864e-22 7.8451e-23 3.934  
\*4 volume(cm<sup>3</sup>) of the unit-cell  
\*5 density of the crystal(g/cm<sup>3</sup>)

Easy to

- check the result
- go back previous result
- compare the results



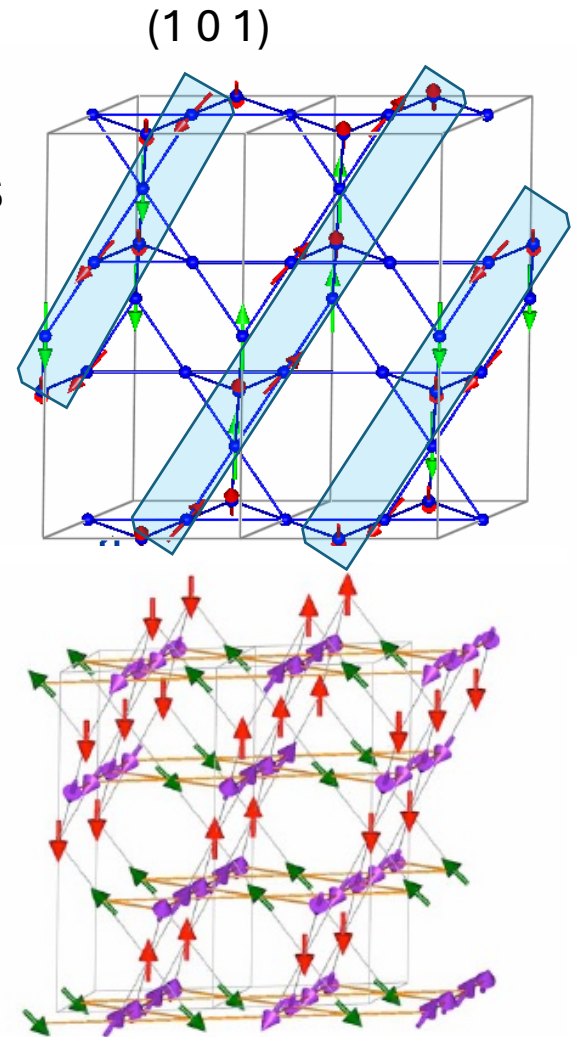
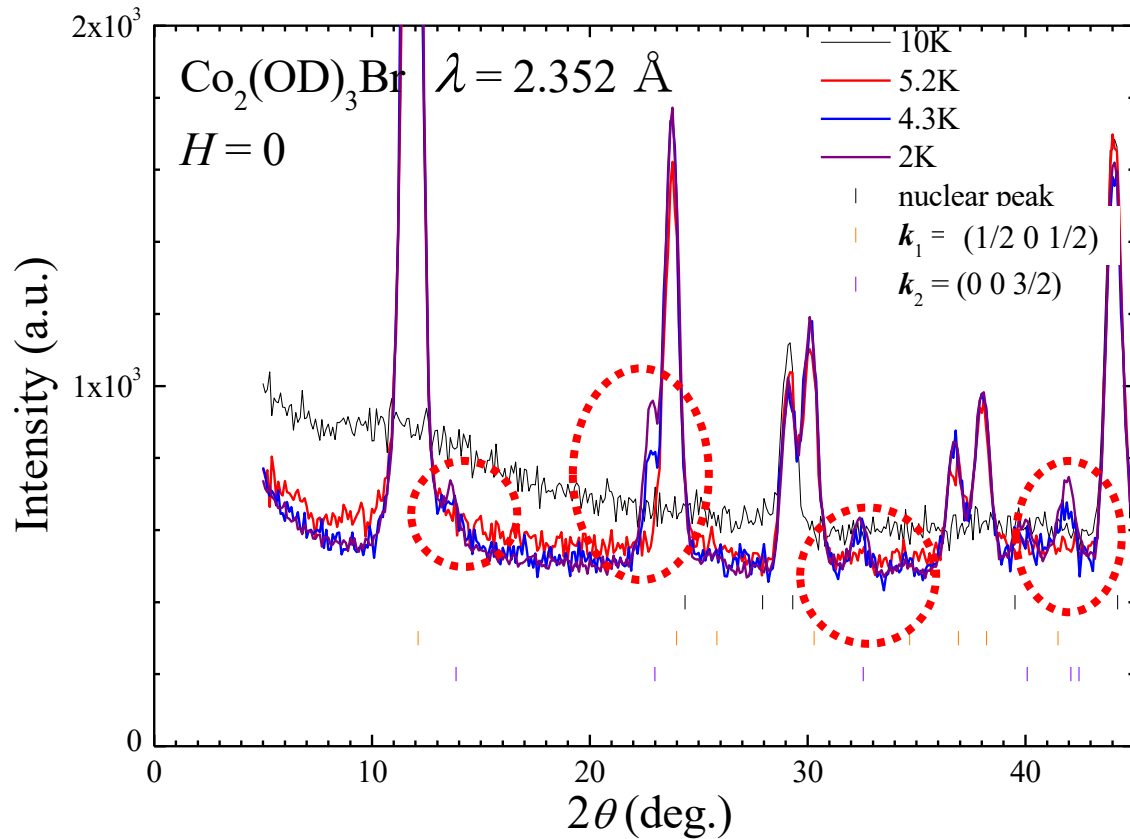
M. Hagihala, et. al., Phys. Rev. B **82**, 214424 (2010).

$\text{Co}_2(\text{OH})_3\text{Br}$  is antiferromagnetic while  $\text{Co}_2(\text{OH})_3\text{Cl}$  is ferromagnetic ( $\mathbf{k} = \mathbf{0}$ )

Two successive transitions  $T_{N1} = 6.2\text{K}$ ,  $T_{N2} = 4.8\text{K}$

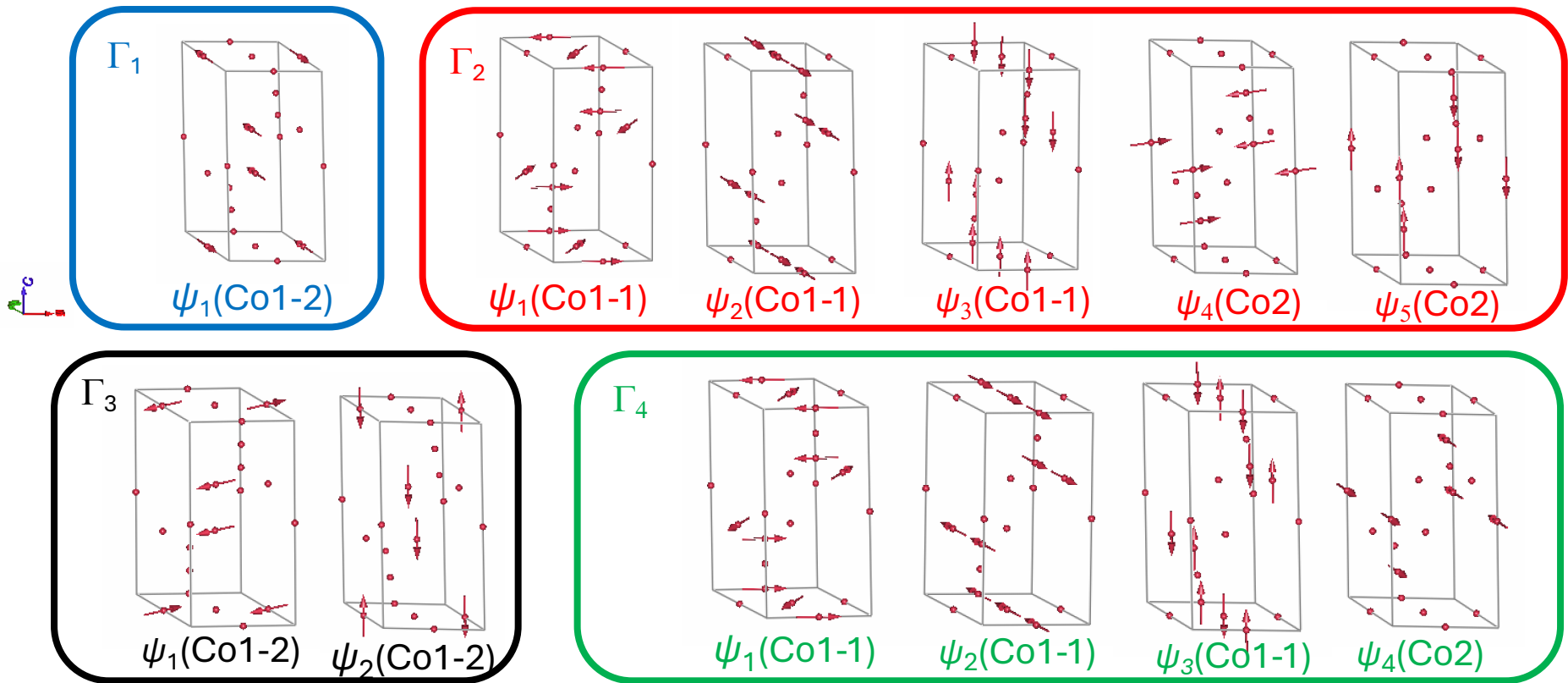


4G:GPTAS  
(JRR-3)

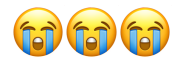


- Partial order phase with  $\mathbf{k}_1 = (1/2 \ 0 \ 1/2)$  at  $T_{N2} < T < T_{N1}$
- All the spin order with  $\mathbf{k}_1$  and  $\mathbf{k}_2 = (0 \ 0 \ 3/2)$  below  $T_{N2}$

# Irreducible Representation Analysis $R\text{-}3m$ $k=(1/2\ 0\ 1/2)$ , Co1(1/2,0,0), Co2(0,0,1/2)



Unfortunately,  
Basis vectors are input manually...

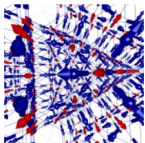


Note that Z-Rietveld's BVs are defined as on the origin point.

Propagation Vector		x	y	z
k1		0.5 ±0	0 ±0	0.5 ±0
基底ベクトル		基底ベクトルの係数 (実部、虚部)		
BV1		-0.926249 ±0.091275	0 ±0	
磁気サイト	スピンの方向	実部 x	y	z
Co1	1/2	0	0	0
Co1	1/6	1/3	1/3	0
Co1	5/6	2/3	2/3	0



# Z-mag

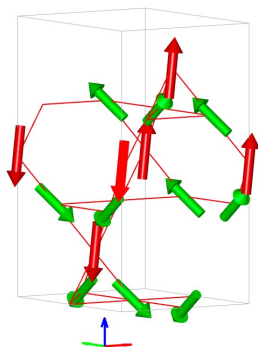


復元	49	
復元	50	log
復元	51	
復元	52	Gamma2 fitting $x^2=2.6255$
復元	53	
復元	54	Gamma3 fitting $x^2=3.4310$
復元	55	
復元	56	Gamma2 fitting without BV4 $x^2=2.6978$

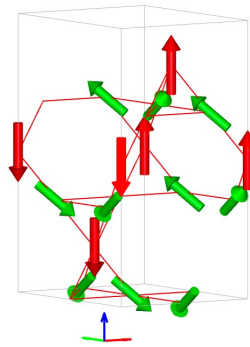
Finder ファイル 編集 表示 移動 ウィンドウ ヘルプ

Figure 1

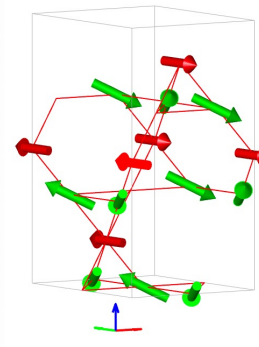
52



56



54



ファイルパス:

/Users/masato/Downloads/14-23/

ファイル名:

Co2OD3Br\_5p5K

相:

1

logの番号(0は最新のもの):

56

描画範囲:

0,1,2;0,1,2;0,1

磁気モーメントの長さ、太さの倍率、ヘッドの割合:

1,1,0.25

原子の倍率(0は表示しない):

0

図の番号:

3

磁気モーメント、原子の色(option):

Co1,[0,1,0];Co2,[1,0,0]

bondの描画(option):

Co1,Co1,0,4,[1,0,0],1;Co1,Co2,0,4,[1,0,0],1

Draw

Co2 (0, 1, 0.5)

$$m = 3.17(6) \mu_B$$

$$\mathbf{m} = (-5.4(6) \times 10^{-1}, -2.7(3) \times 10^{-1}, -3.13(6))$$

OK

Co2 (0, 0, 0.5)

$$m = 3.12(7) \mu_B$$

$$\mathbf{m} = (0, 0, -3.12(7))$$

OK

スクリーンショット  
2024-11...15.32.13

スクリーンショット  
2024-11...16.00.06



# treatment of multi-q structure



multi-q structure can be represented by additional propagation vector and basis vector.

# In the future

## Magnetic structure analysis

- Modification of input format
- i/o .mcif file
- Developed Semidefinite Relaxation of quadratic optimization

K. Tomiyasu et al., Scientific Report 8, 16228 (2018).

Z-Rietveld have a potential to be a powerful tool  
for magnetic structure analysis!

## Z-Rietveld

- Rigid body analysis
- Automatic analysis system
- Simulation annealing

# Summary

- Z-Code project and Z-Rietveld program
- Current state of magnetic structure analysis on Z-Rietveld
- Future plan of Z-Rietveld

We believe to enlarge user community of Z-Rietveld by continuous developments and modifications!

Download software

<https://z-code-software.com/>

Support mail

[pjzcode@gmail.com](mailto:pjzcode@gmail.com)