

## Strategies: Structural Refinement using the Rietveld Method

Isn't the subject of this FullProf School magnetic structure determination?

Why is structure important?

1) Fundamental Reason: The magnetic structure is always on top of the nuclear structure. Even if it is incommensurate (without nuclear structure no framework to define).

2) Practical Reason: If you don't know precisely the nuclear structure you won't be able to determine the correct magnetic structure.

3) Physical Reason: The nuclear structure determines the magnetic structure (and vice-versa) and is needed for its interpretation. No conclusions possible without knowing both.

1) Has been mentioned and treated by Perez-Mato!

3) Represents the scientific work you have to do after the determination of the magnetic structure

# Strategies: Structural Refinement using the Rietveld Method

Why is structure important?

2) Practical Reason: If you don't know precisely the nuclear structure you won't be able to determine the correct magnetic structure.


Some examples:

I) K-search for the determination of the magnetic propagation vector needs to know:

- a) The presence or absence of centering conditions
- b) The exact lattice parameters at the temperature where the magnetic peaks are analysed
- c) The exact wavelength used and the exact zero-shift

```

TITLE D1A JUNE 2009
SPGR F D D 2
CELL 10.402 16.014 5.852 90.0000 90.0000 90.0000
SHORT-OUTPUT
!K_COMMENSURATE
CWTOL 2.4140 0.200
K_RANGE 0.0 1.0 0.0 1.0 0.0 1.0
K_DIV 100 100 100
!peak_position peak_intensity peak_background
2THETA_LIST 6
27.423 591.04376 0.00000
29.07 591.04376 0.00000
31.165 200.00000 0.00000
35.325 400.00000 0.00000
41.825 591.04376 0.00000
46.885 713.15057 0.00000
  
```



The number of proposed incommensurate magnetic propagation vectors decreases if you reduce the tolerance: This is extremely important in difficult cases.

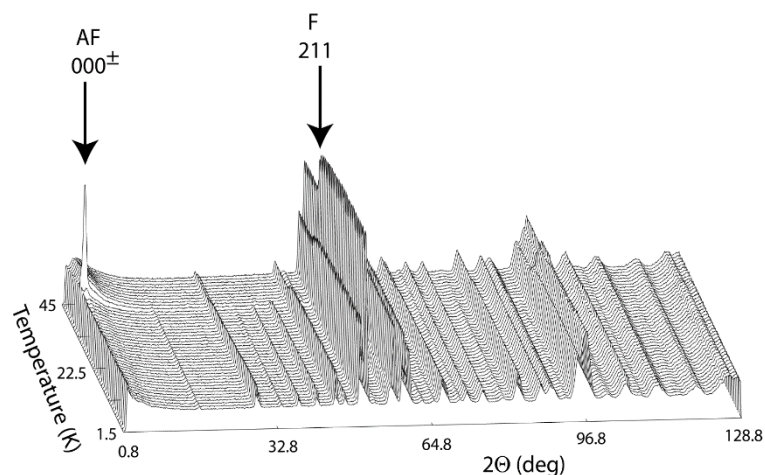
# Strategies: Structural Refinement using the Rietveld Method

Why is structure important?

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Some examples:

II)  $\text{Nd}_7\text{Pd}_3$ , transition  $P6_3mc$  to  $Cmc2_1$  as magnetic order changes from AFM to FM

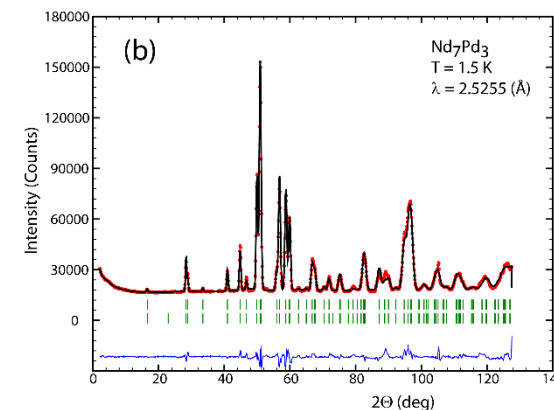
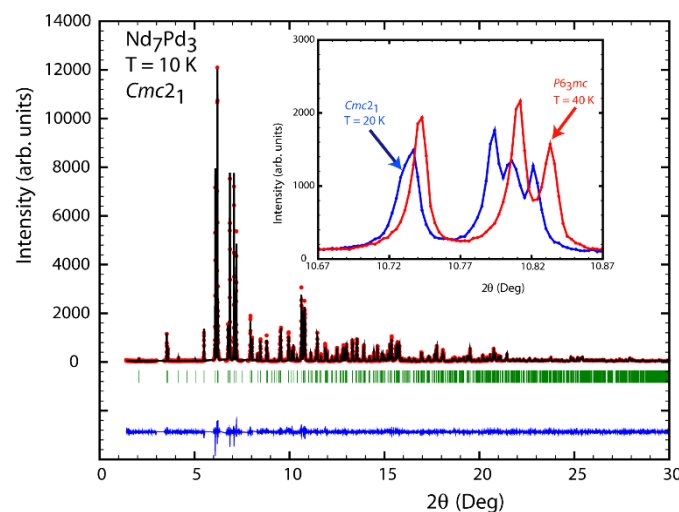


AFM,  $k = (0,0,0.12)$ , in  $P6_3mc$  2 Nd sites

Magnetic symmetry analysis with BASIREPS gives a solution which works nicely

FM,  $k = 0$ , No solution assuming  $P6_3mc$

Synchrotron data from ALBA show peak splitting not seen in neutron diffraction data



Symmetry allowed solution in  $Cmc2_1$

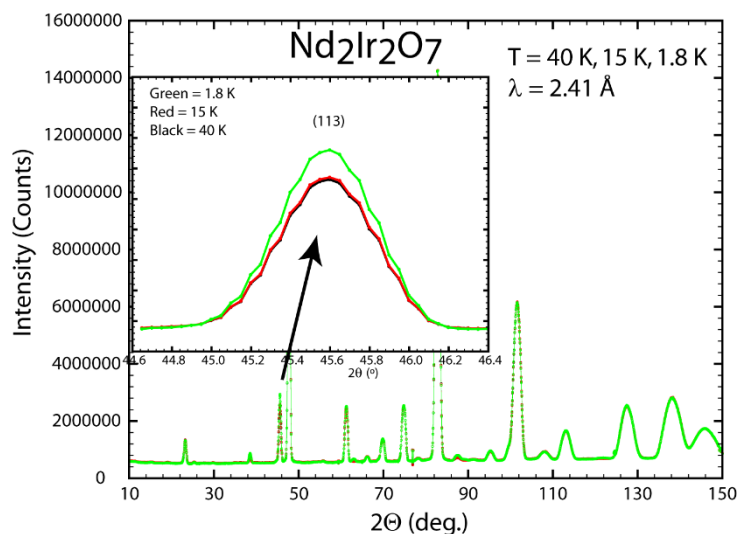
# Strategies: Structural Refinement using the Rietveld Method

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Some examples:

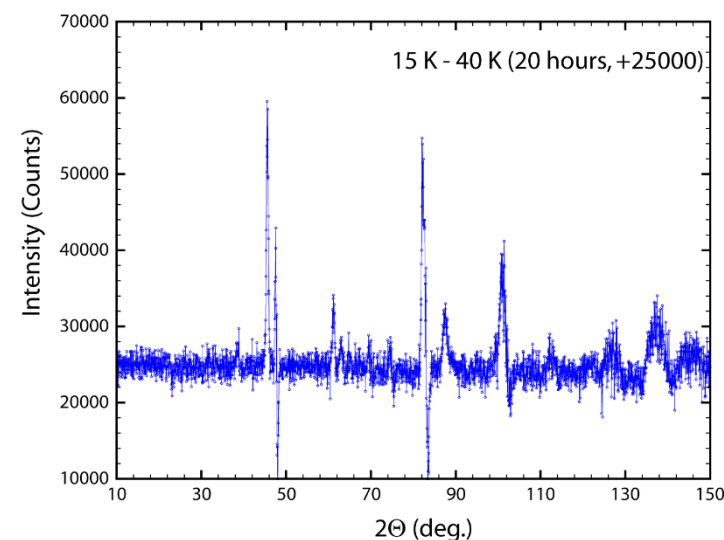
III)  $\text{Nd}_2\text{Ir}_2\text{O}_7$ , two magnetic transitions at 120 K and at 8 K, only Nd or only Ir or both magnetic?



20 Hours at 40 K, 15 K  
4 Hours at 1.8 K

Not possible to refine directly the 15 K data as magnetic intensity too small.

Only possibility: use difference data file 15 K - 40 K where the paramagnetic background has been subtracted to leave only the magnetic scattering intensity.



Difference data

# Strategies: Structural Refinement using the Rietveld Method

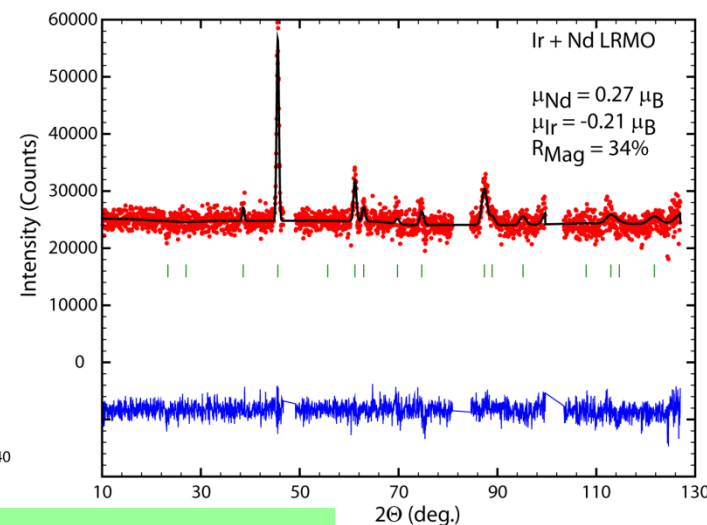
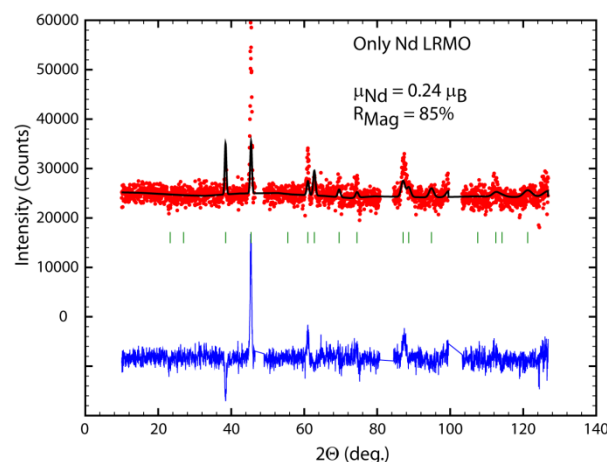
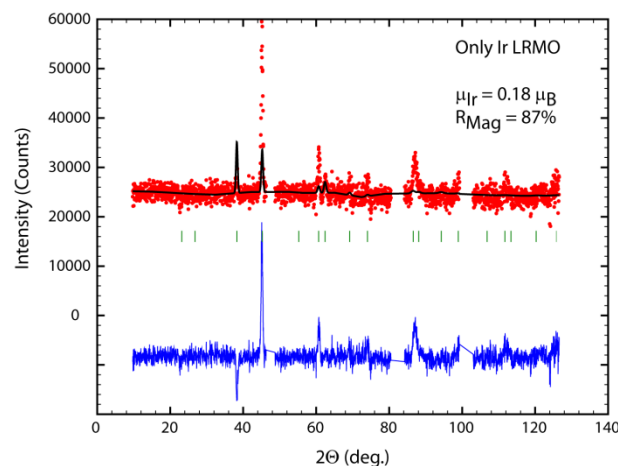
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First refine the nuclear structure using the 40 K data and determine the **scalefactor**. Then refine the **difference data file** using the determined scalefactor which stays **fixed** and allows to refine the magnetic variables.



→ Both sublattices are magnetic already below the first magnetic transition.

## Strategies: Structural Refinement using the Rietveld Method

Why is structure important?

2) Practical Reason: If you don't know precisely the nuclear structure you won't be able to determine the correct magnetic structure.

IV) Every time your nuclear refinement is not perfect you introduce possible pitfalls for the refinement of the magnetic structure:

e.g.:

Structural parameters of the nuclear phase refinement are correlated with magnetic variables.

Occupation of sites is not correctly determined inducing wrong magnetic moment values.

Non-identified Impurity peaks belong to a phase which becomes as well magnetic.

Presence of texture makes refinement impossible.

# Strategy for Rietveld refinement

## I) Experiment

- a) Sample
- b) Data Acquisition
  - 1) Choice of Instrument
  - 2) Measuring time
  - 3) Visible problems

## II) Refinement

- a) Literature Search
- b) Starting model
- c) "Strategy"
  - 1) Zeroshift, wavelength, background (by hand)
  - 2) Zeroshift, scalefactor, lattice parameters, 1st background parameter
  - 3) Atomic positions, isotropic temperature factor, background parameters
  - 4) Peak shape parameters, asymmetry parameters
  - 5) Individual B factors, atom occupancies
  - 6) Zero displacements
  - 7) Anisotropic B factors
  - 8) Preferred Orientation, microstructural parameters

## III) Some Selected Specific Problems

- 1) Peak Intensities: Fourier Difference Map
- 2) Peak Shape: Phase Separation, Microstrain, Size effects

## IV) Constraints and Restraints

- 1) Symmetry Constraints
- 2) Constraints due to direct correlation
- 3) Linear Constraints
- 4) Strategic Constraints
- 5) Restraints
- 6) Soft Distance (or Angle) Constraints

} Depends on the  
Data quality and the  
individual problem

# Strategy for Rietveld refinement

## I) Experiment:

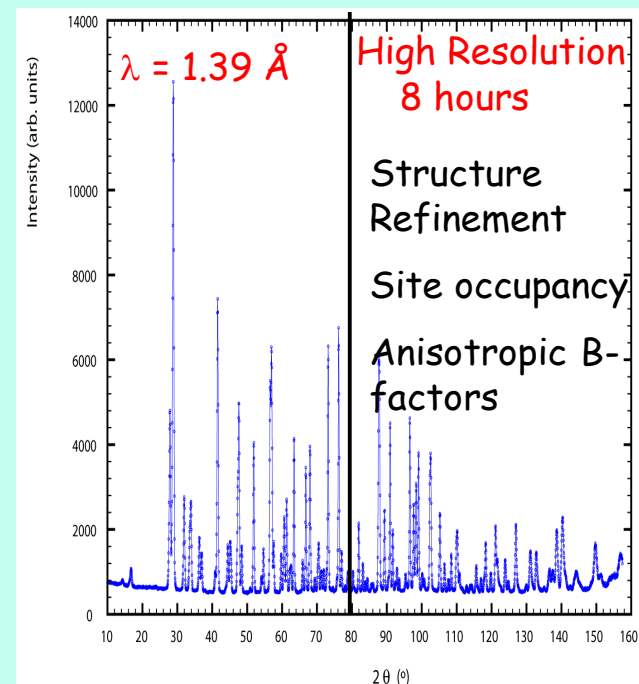
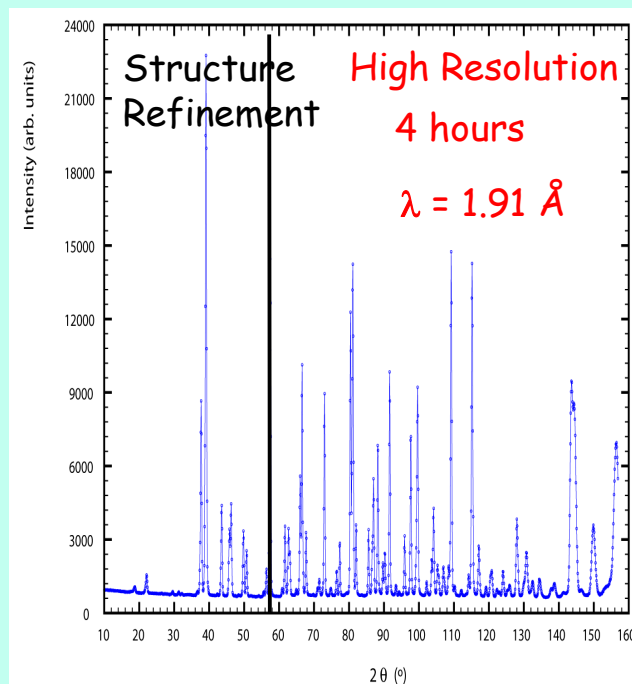
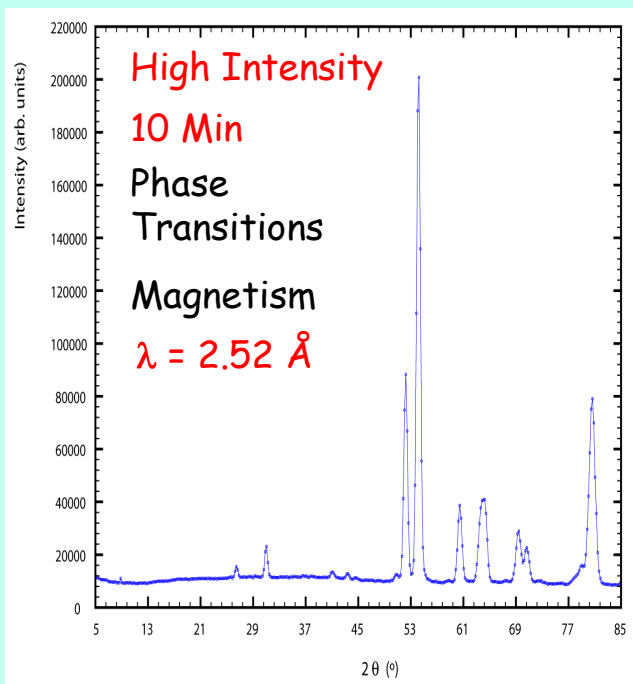
a) Sample: **should be impurity free, should be enough** (depending on Instrument and aim)

b) Data acquisition: what do I want to find out?

Crystallographic structure, phase transition, magnetic structure ...

Are the data adapted to the problem? High resolution, high intensity, q-range → **Choice of Instrument(s)**

**Run a standard on the chosen instrument:** Determine the zeroshift and the resolution function





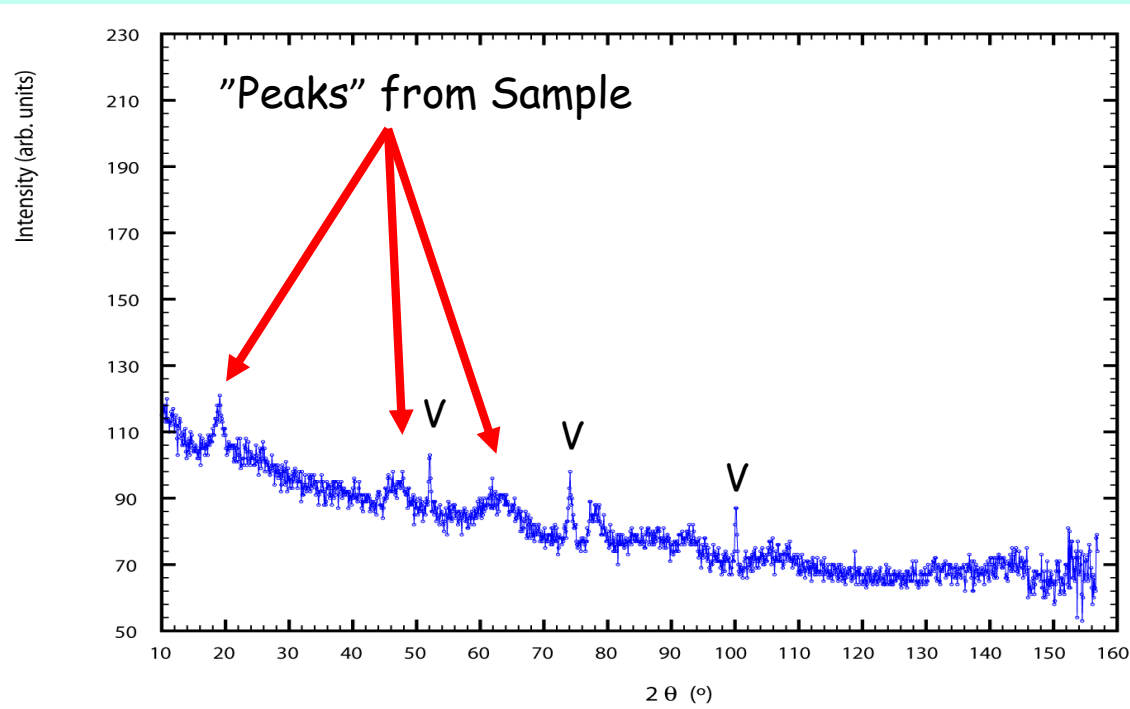
# Strategy for Rietveld refinement

## 3) Visible problems:

At the start of an experiment: **Always look at the raw data:**

Do you see peaks?, Do they have enough intensity?, How do the peaks look like? → **Measuring time**

Are the peaks only very broad? No good crystallisation, amorphous system? Go to HI machine!



# Strategy for Rietveld refinement

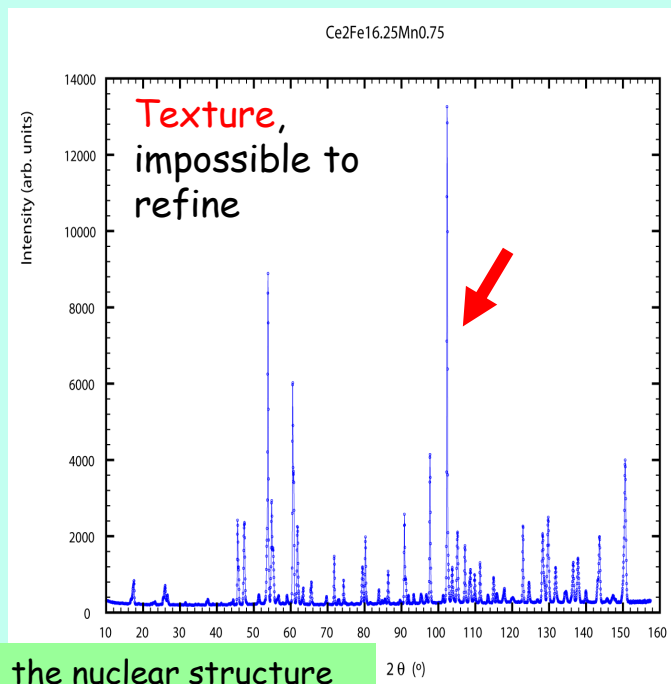
## 3) Visible problems:

Do the spectra look different between two measurements taking the powder out?

**Preferred orientation?** (crystallites with layer or needle shape) : Can be corrected for, but try to keep it constant within one measuring cycle (T-dependence).

Are there peaks which are much stronger and sharper than the rest?

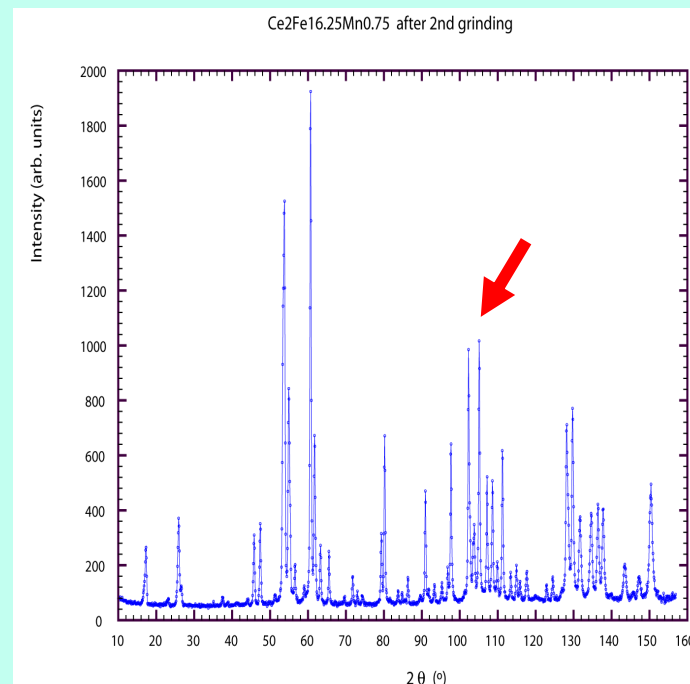
Single crystal!, no powder average = grind further. → **Try to refine as early as possible during the experiment**



If the nuclear structure is not refined correctly you can't get anything for the magnetic structure!

Same sample after grinding twice

Absolute and relative intensities have totally changed!



**Strategy is hopeless if the data are not good!**

# Strategy for Rietveld refinement

## II) Refinement

### a) Literature Search:

Recuperate all the information you can get from literature about the system studied.

X-ray results of the same compound, Results for similar compounds

### b) Starting Model:

In order to start refinement you need a model with lattice constants (**LeBail fit**), spacegroup (**CheckGroup**), and atom positions

**Recuperate old pcr file!** (one where you know that it works) and introduce your model

Peakshape parameters with starting values from instrument (Standard sample).

### c) Strategy:

Run FULLPROFF with zero parameters: Where is the background? Are the peak positions correct?

If not: Are the shifts between calculated and observed peak positions similar: zeroshift wrong

Are the shifts q-dependant: lattice constants wrong or wavelength wrong

In order to refine the lattice constants the cal/obs peak positions must at least partially overlap,

Start with small 2 Theta range at great d-spacings first.

Background can be put at suited starting value by hand.

# Strategy for Rietveld refinement

Refine the zeroshift, the scalefactor and the lattice constants.

Always keep a "reserve" pcr file in case the program diverges.

(Put the parameter Pcr = 2, this creates a \*.new file conserving the \*.pcr file)

As long as the program did not "lock in", no sense to continue!

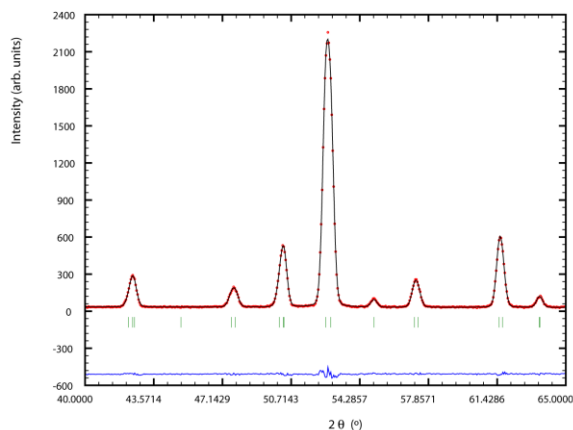
Always follow the progress of the refinement by looking at the resulting fit!

Refine the atomic positions (which are free to move), an isotropic temperature factor and the background

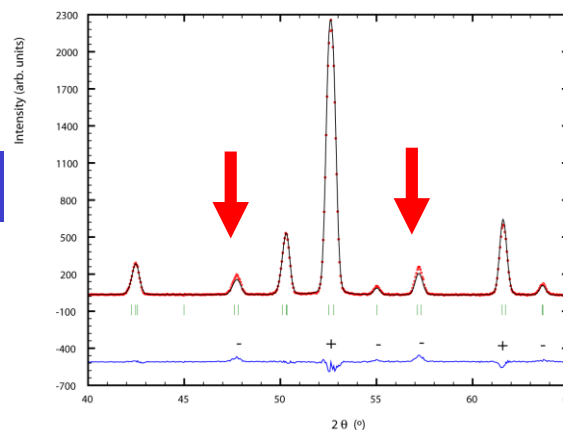
Wrong atom position: Difference curve shows "ups" and "downs",

very sensitive to Oxygen position → be careful with from x-ray data determined structures containing Oxygen

O2: x=0.7108 y=0.2887 z=0.03607



O2: x=0.7158 y=0.2837 z=0.03607



*Pnma*

Antiferromagnetic structure with  $k = 0$

Magnetic contribution to the nuclear peaks

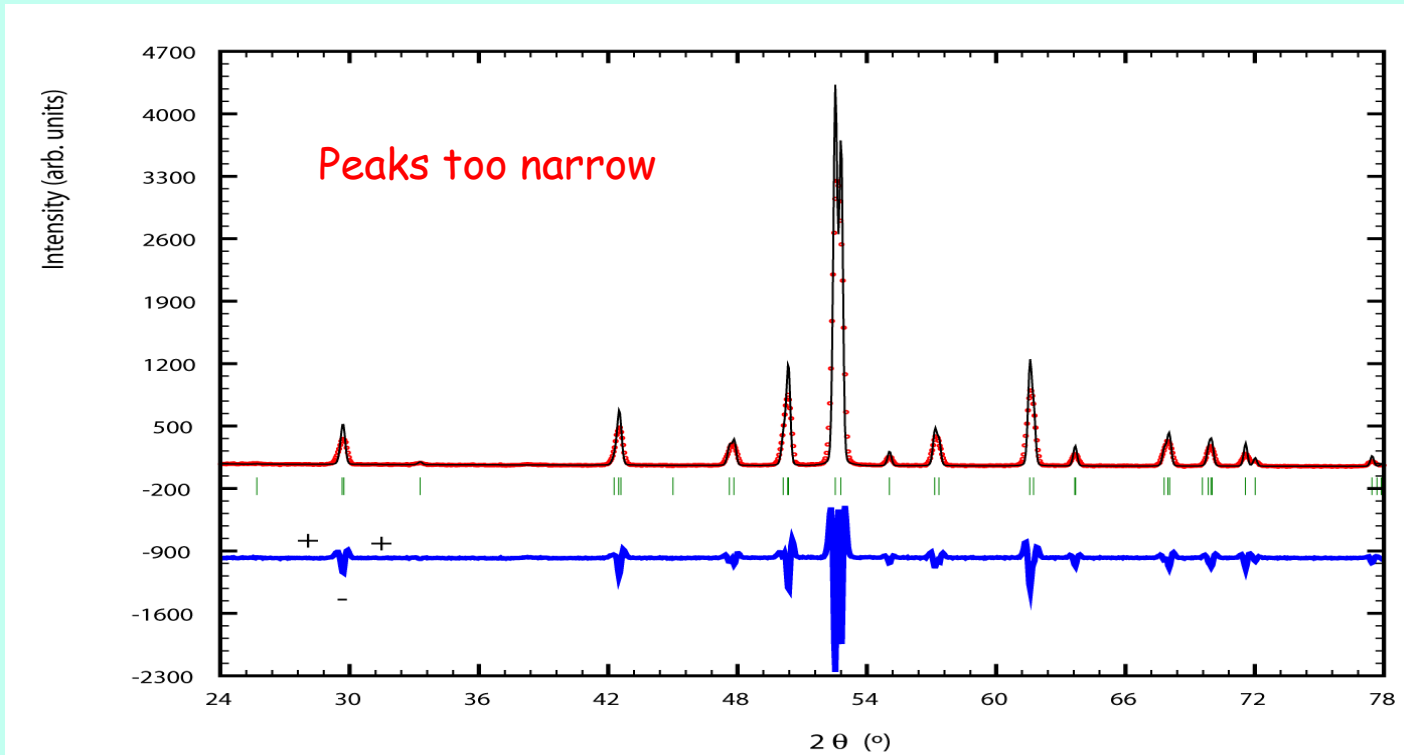
Goodness of nuclear refinement influences strongly the magnetic refinement

# Strategy for Rietveld refinement

Refine Peakshape parameters and asymmetry parameters

Wrong lineshape parameters: Calculated peakshape too narrow

**Always better to start with a too narrow peakshape!** A too broad peakshape hides the real problems!

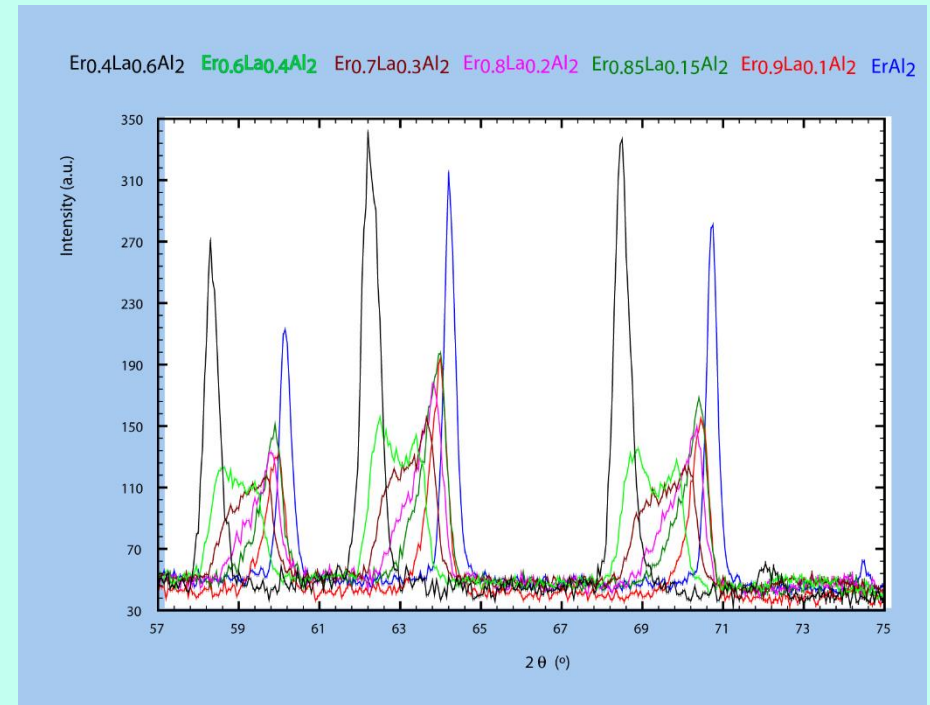
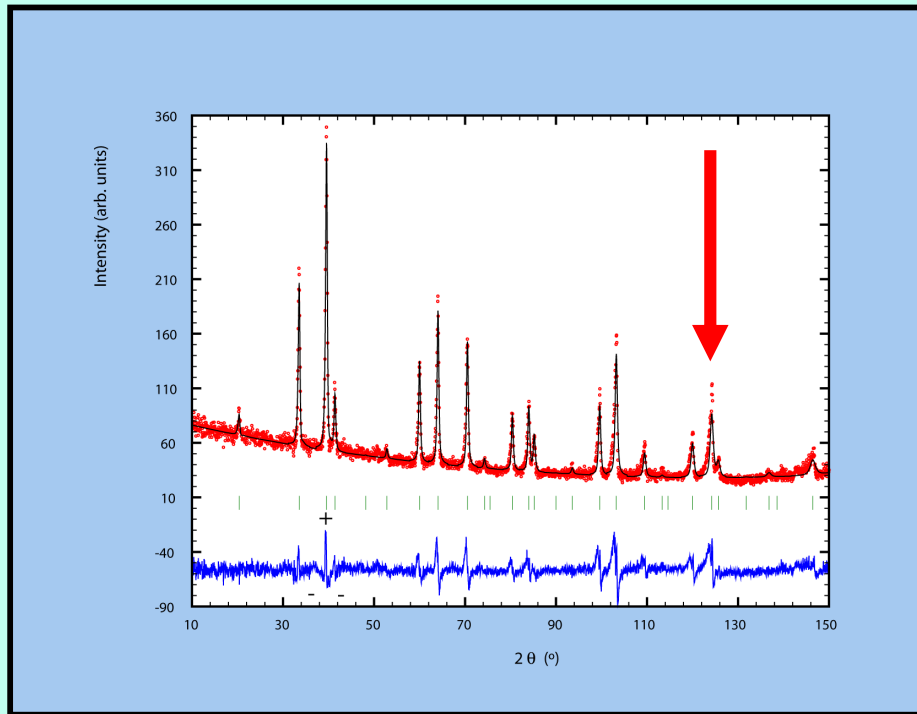


# Strategy for Rietveld refinement

Wrong lineshape parameters: Calculated peakshape too large

R-factor = 4! Look at the plot!

The broad lineshape of the calculated pattern accounts partially for the wrong model!



Inhomogeneous system:  $\text{Er}_{1-x}\text{La}_x\text{Al}_2$

No symmetry reduction but a distribution of cubic unit cell parameters

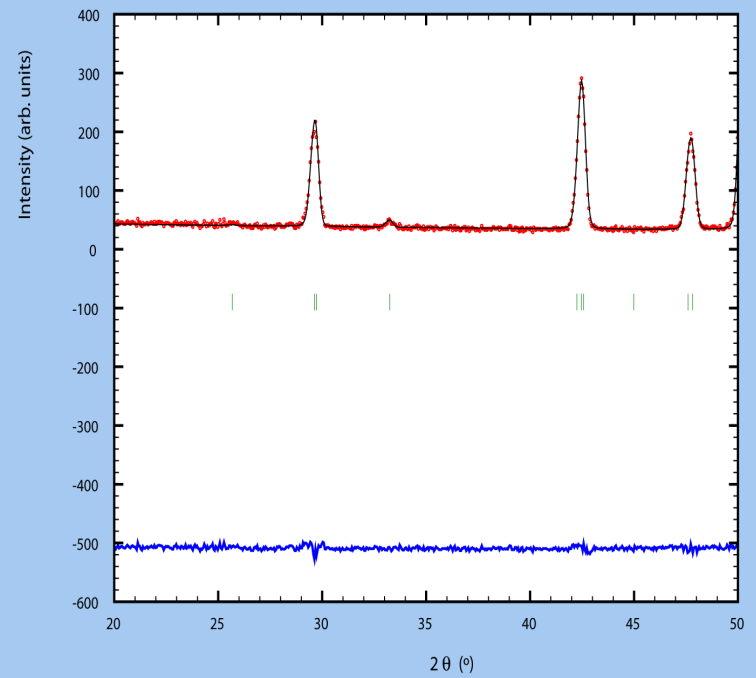
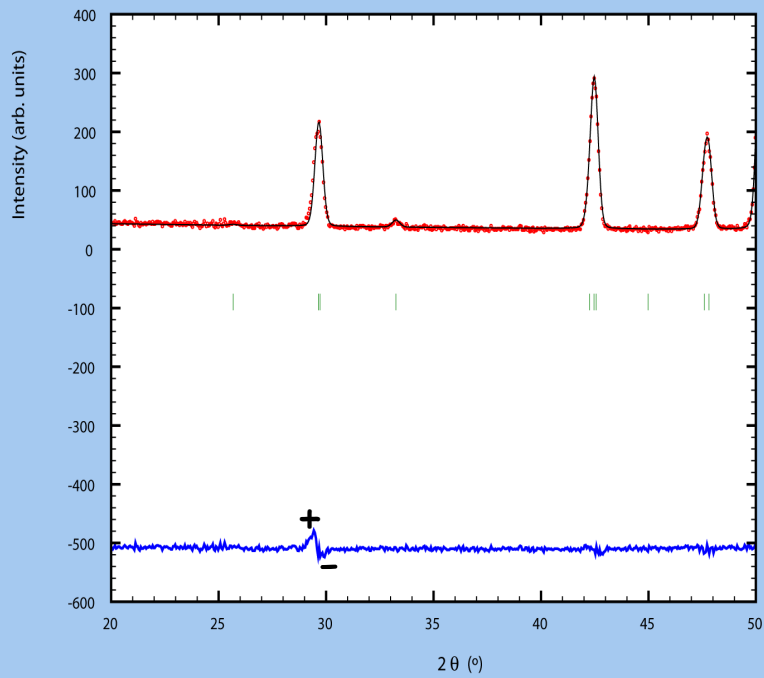
as system is not behaving as a solid solution

# Strategy for Rietveld refinement

Influence of Asymmetry parameters

Mainly important at low angles

Typical + - pattern in the difference curve



# Strategy for Rietveld refinement

- 1) Zeroshift, wavelength, background (by hand)
- 2) Zeroshift, scalefactor, lattice parameters, 1st background parameter
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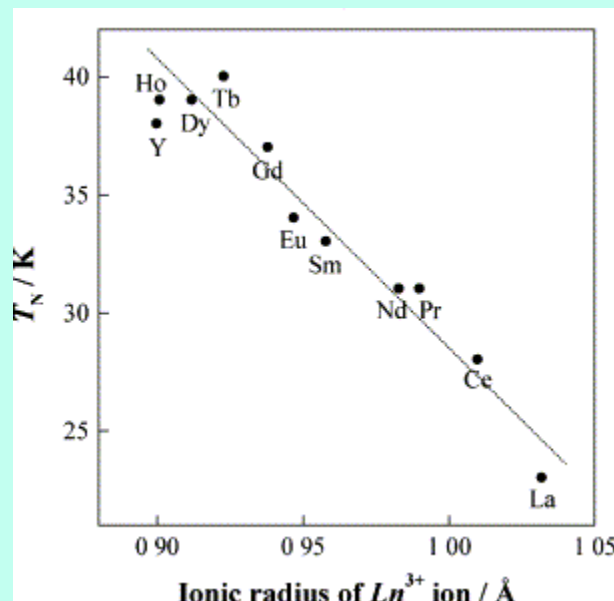
Practical Example:  $\text{YFe}_3(\text{BO}_3)_4$ , neutron data at 295 K ( $1.91\text{\AA}$ ) and 520 K ( $1.39\text{\AA}$ )

Already known:  $\text{TbFe}_3(\text{BO}_3)_4$ , recuperate the pcr file

Fp

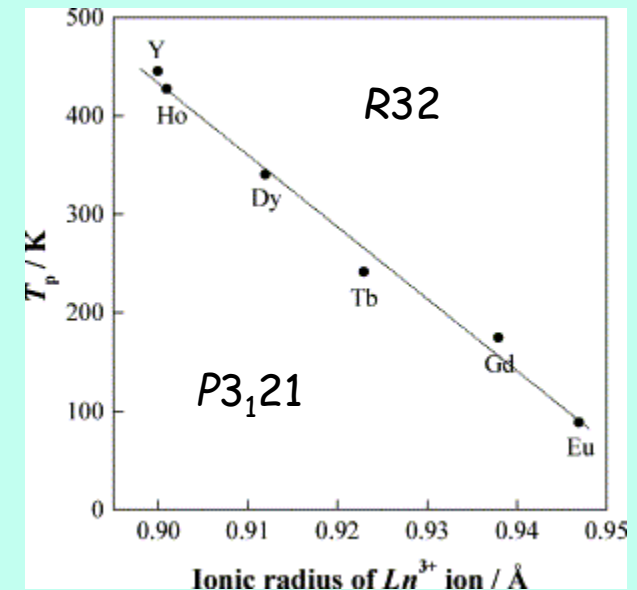
Magnetic transition temperature:

Y-compound non magnetic at RT



Crystallographic phase transition:

Y-compound at RT in same phase as Tb-compound below 240 K





# Strategy for Rietveld refinement

## III) Some Selected Specific Problems:

1) Wrong peak intensities, but all atom positions refined → Ferromagnetic? (Fe above RT!)

=> Phase No. 1 NUCLEAR

P 6<sub>3</sub>/mcm

=> No. of reflections for pattern#: 1: 70

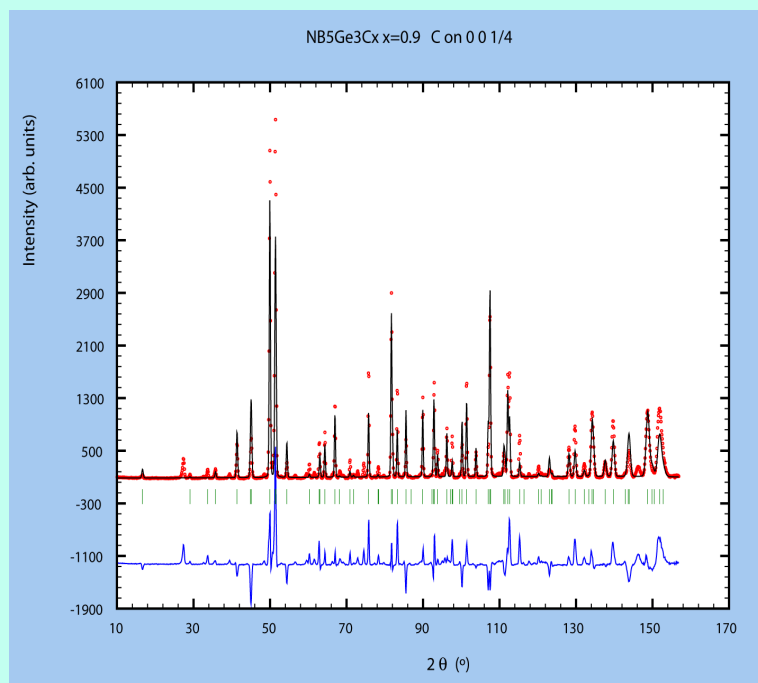
==> ATOM PARAMETERS:

Name	x	sx	y	sy	z	sz	B	sB	occ.	socc.
Nb1	0.33333 ( 0)		0.66667 ( 0)		0.00000 ( 0)		-0.164(103)	0.167 ( 0)		
Nb2	0.23783 ( 69)		0.00000 ( 0)		0.25000 ( 0)		-0.164(103)	0.250 ( 0)		
Ge1	0.59901 ( 74)		0.00000 ( 0)		0.25000 ( 0)		0.303(126)	0.250 ( 0)		
C1	0.00000 ( 0)		0.00000 ( 0)		0.25000 ( 0)		0.544 ( 0)	<b>0.006</b> ( 2)		

should be about 0.075

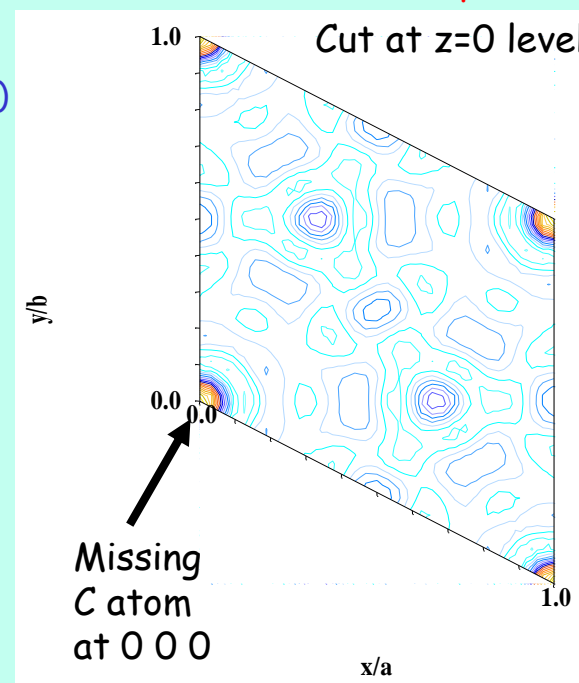
Don't refine now  
anisotropic B-  
factors!! Will always  
give better R-values ...

→ Fourier Difference Map (FOU=4 in pcr file)



Pcr file with C on (0 0 1/4)

Fp



# Strategy for Rietveld refinement

## III) Some Selected Specific Problems:

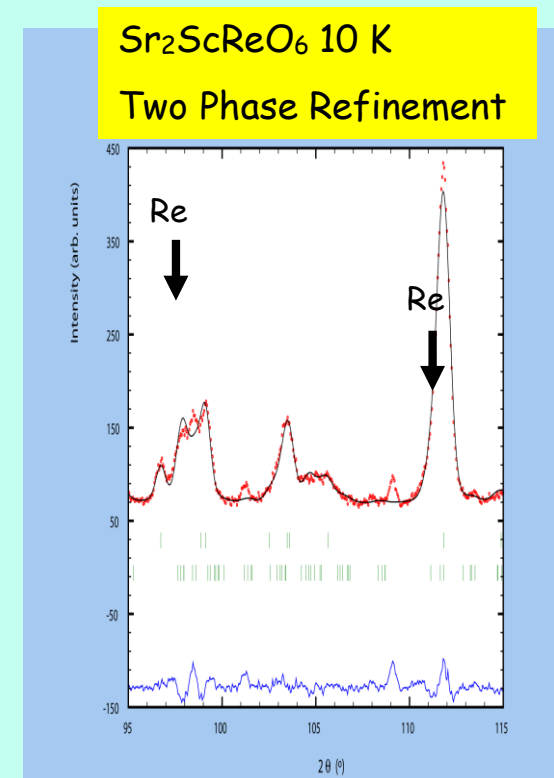
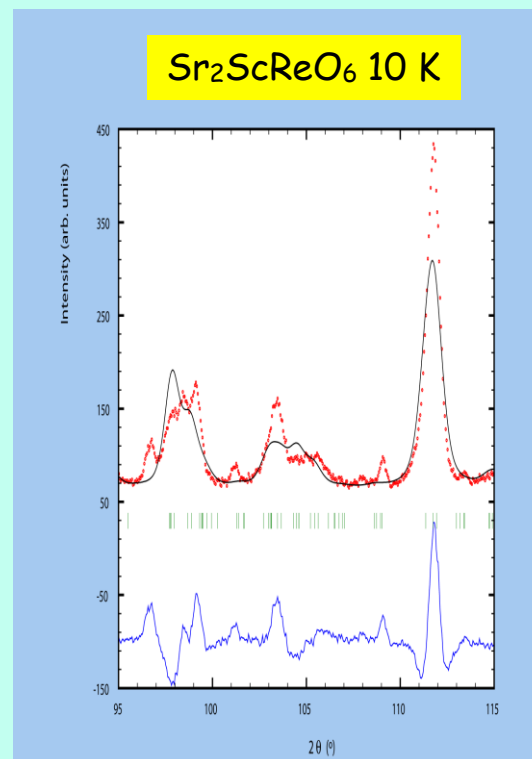
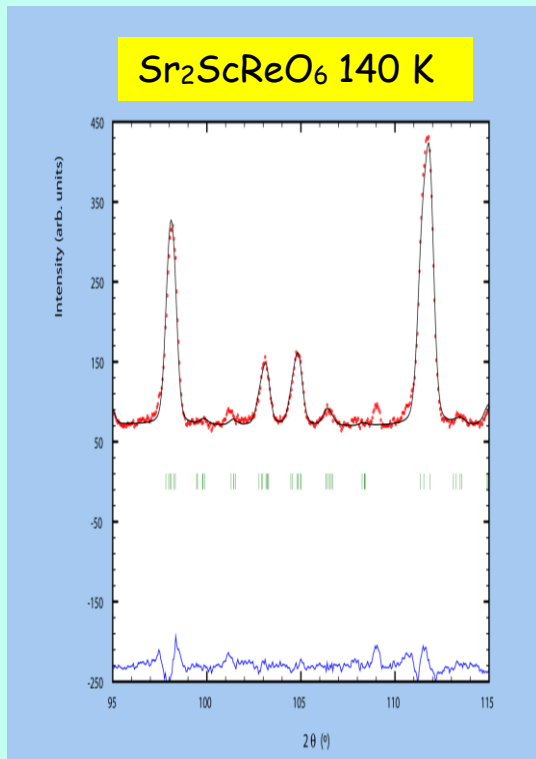
### 2) Peak Shape:

Peak Broadening, Change the model or use more parameters?

Symmetry reduction (classic), **phase separation**, microstrain, size effects

**Phase separation**: no chance of indexing, look at the evolution with temperature, peak broadening even for peaks with multiplicity 2!

Fp



# Strategy for Rietveld refinement

## III) Some Selected Specific Problems:

### 2) Peak Shape:

Peak Broadening, Change the model or use more parameters?

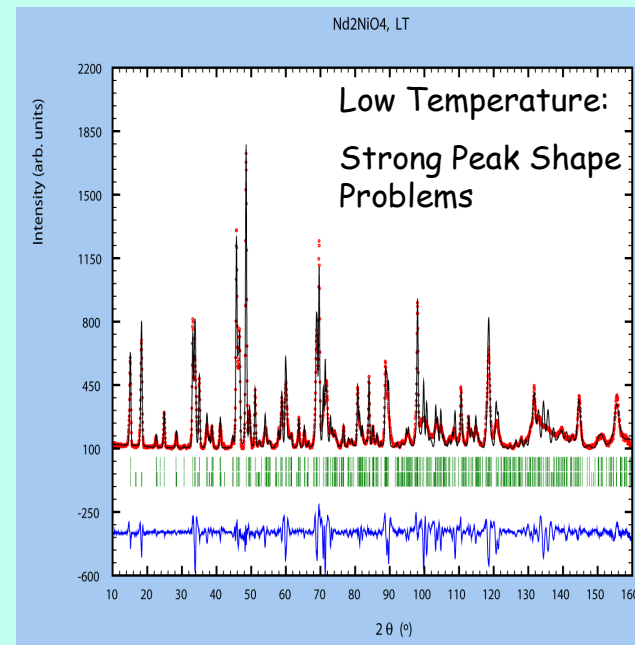
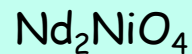
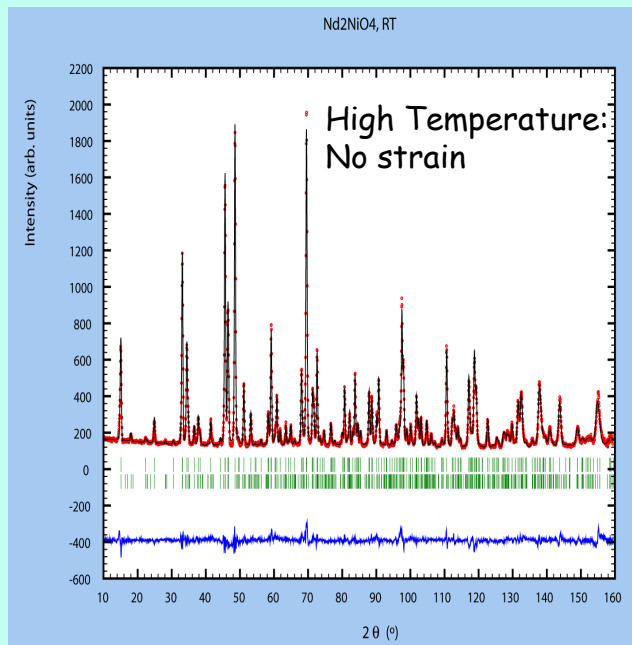
Symmetry reduction (classic), phase separation, **microstrain, size effects**

**Microstrain, size effects**, how are they visible?

Peak broadening already at low  $2\Theta$ : **size effect**, at high  $2\Theta$ : **strain**,

Refinement: Use the instrument resolution "irf" file (Res = 1 in pcr file) and

"U" and "X" for **isotropic strain** and "GauSiz" and "Y" for **isotropic size**



# Strategy for Rietveld refinement

## III) Some Selected Specific Problems:

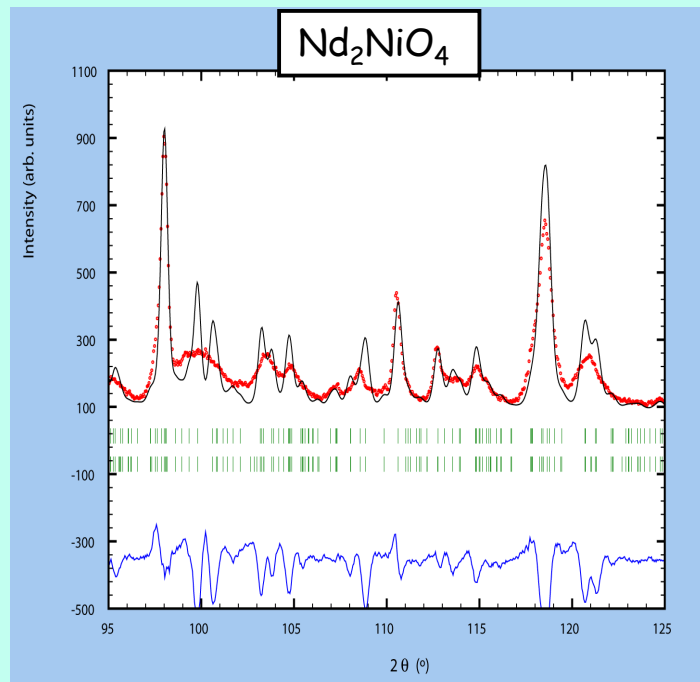
### 2) Peak Shape:

$\text{Nd}_2\text{NiO}_4$ :

Problem linked to **anisotropic Microstrain**:

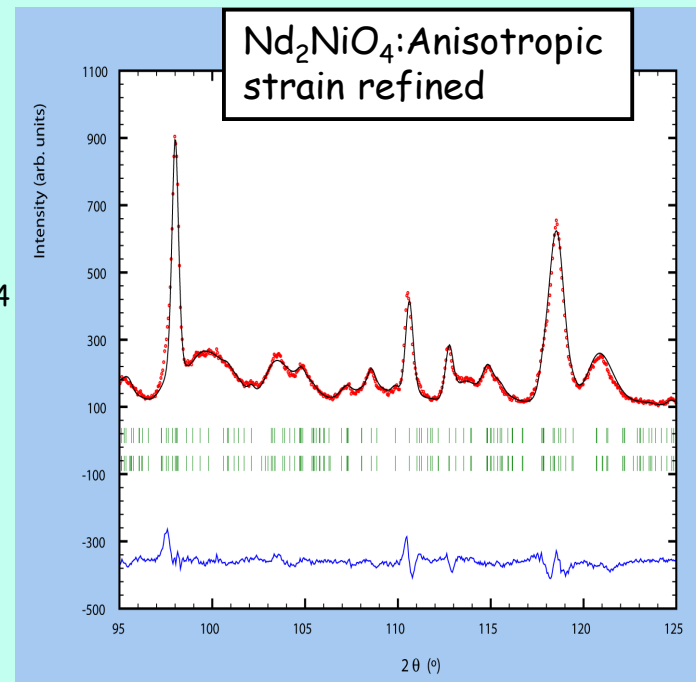
Some peaks are calculated to broad, others to narrow and some nearly perfectly well!

In order to refine **anisotropic microstrains** (or anisotropic size effects) one has to choose the correct model according to the symmetry onto which the strain is acting.



$\text{Nd}_2\text{NiO}_4$

Ins=1



# Strategy for Rietveld refinement

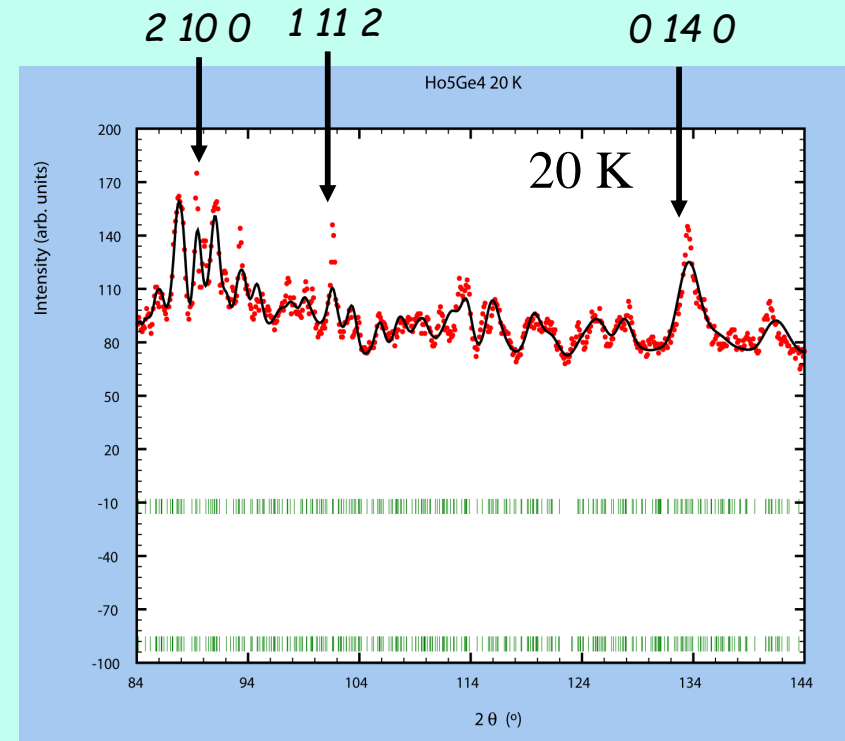
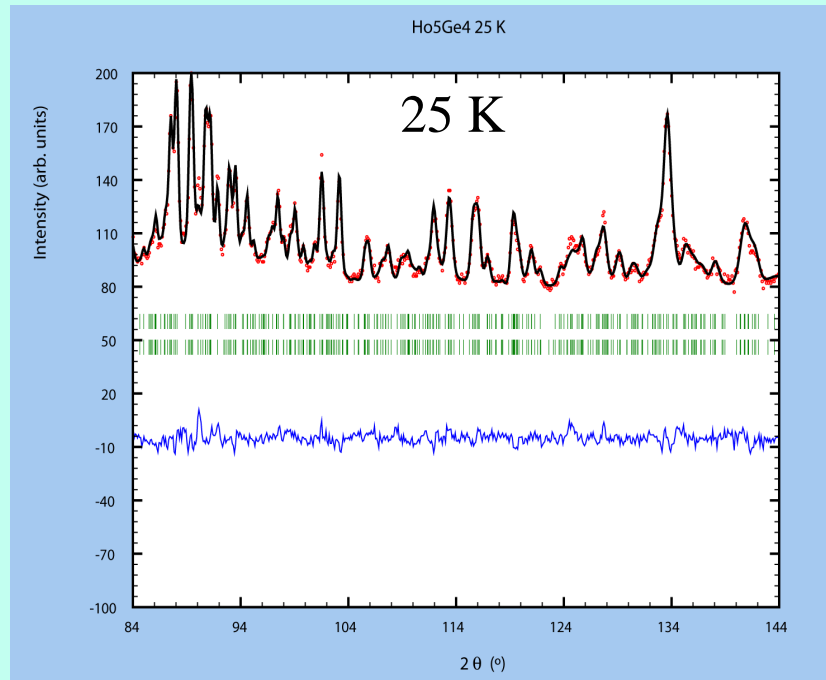
## III) Some Selected Specific Problems:

### 2) Peak Shape:

$\text{Ho}_5\text{Ge}_4$ , magnetocaloric compound showing magnetostriction, orthorhombic structure:

Strong **anisotropic microstrain** appears as the Ho becomes magnetic

hkl dependence of peakwidth: peaks with large k are narrower



# Use of the Stevens notation for the description of anisotropic strain

Needs the instrument resolution file as input!

```
!Job Npr Nph Nbg Nex Nsc Nor Dum Iwg Ilo Ios Res Ste Nre Cry Uni Cor Opt Aut
1 7 2 34 1 0 0 0 0 0 0 1 0 0 0 0 0 0 0
```

! Resolution file for Pattern# 1

New\_D1A\_191.irf

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
6 0 0 0.0 1.0 0.0 0 0 0 1 0 17501.770 0 7 0
```

Laue Class mmm

Strain-Model  
3

!-----> Profile Parameters for Pattern # 1

```
! Scale Shape1 Bov Str1 Str2 Str3
0.50723E-01 0.00000 0.00000 0.00000 0.00000 0.00000
11.00000 0.000 0.000 0.000 0.000 0.000
! U V W X Y GauSiz LorSiz Size-Model
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0
0.000 0.000 0.000 0.000 0.000 0.000 0.000
```

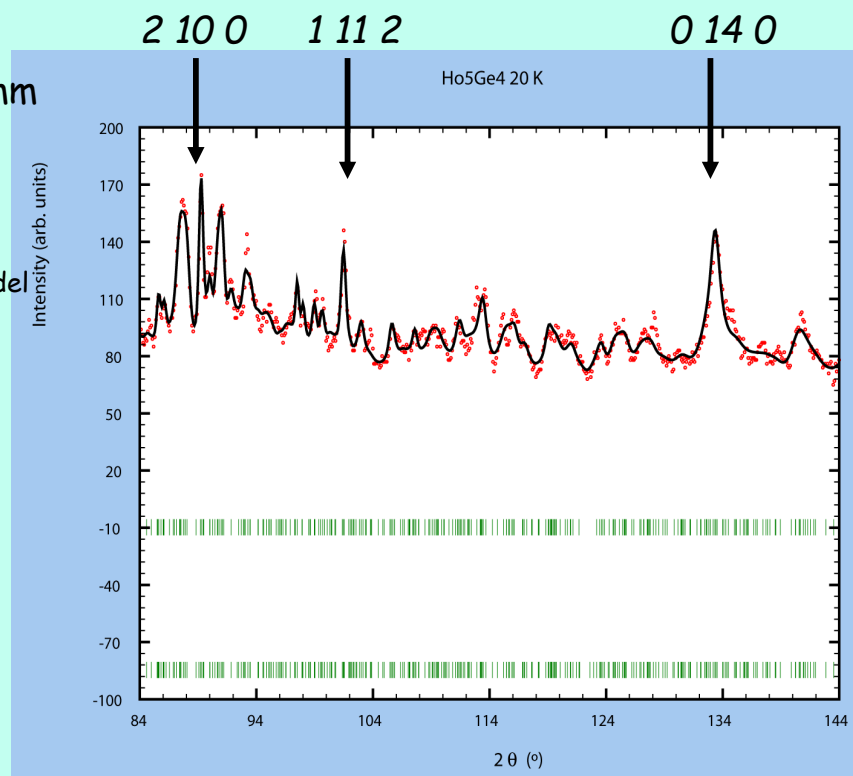
```
! a b c alpha beta gamma #Cell Info
7.565165 14.560355 7.620977 90.000000 90.000000 90.000000
21.00000 31.00000 41.00000 0.00000 0.00000 0.00000
```

```
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
```

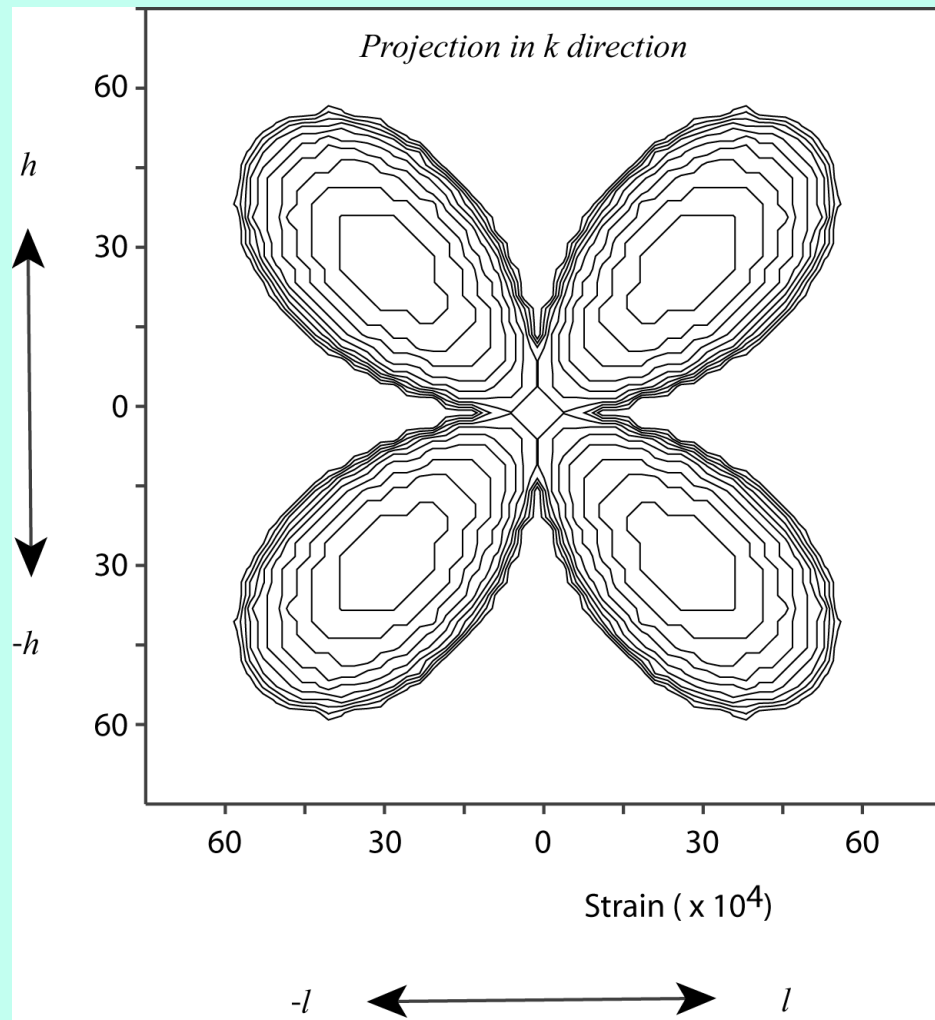
```
! S_400 S_040 S_004 S_220 S_202 S_022
0.180832 0.003863 0.043940 0.179977 20.769495 0.178759
141.00 161.00 121.00 131.00 111.00 311.00
```

```
! Lorentzian strain coeff.+ code
0.17642 151.00000
```

Refinement still not perfect



The patterns of microstrains can be visualized putting  $J_{vi}=5$  in the PCR file (More=1) and reading the binary file with GFOURIER. Use projection mode.



$S_{202}$  is very large: strong tendency of the compound to switch to a monoclinic structure

Synchrotron data revealed later the real spacegroup:  $P2_1/m$  !

Microstructural parameters (see folder "Documents"):

$$H_{hG}^2 = (U_f + (1 - \xi_f)^2 D_{fST}^2(\alpha_D)) \tan^2 \theta + \frac{I_{fG}}{\cos^2 \theta} + H_{gG}^2$$

$$H_{hL} = (X_f + \xi_f D_{fST}(\alpha_D)) \tan \theta + \frac{[Y_f + F_f(\alpha_S)]}{\cos \theta} + H_{gL}$$

PCR Notation:

$U_f$ = "U"	= Gaussian component of isotropic strain
$X_f$ = "X"	= Lorentzian component of isotropic strain
$I_{fg}$ = "GauSiz"	= Gaussian component of isotropic size
$Y_f$ = "Y"	= Lorentzian component of isotropic size

$D_{fST}$ ,  $F_f(\alpha_S)$  depend on the particular model chosen to describe anisotropic strain and size

$D_{fST}$  in the Stevens Notation of anisotropic strain, up to 15 independent variables  $S_{hkl}$  with  $(h+k+l)=4$

$\xi$  = Mixing coefficient for Lorentzian contribution to anisotropic strain  
= "Lorentzian strain coeff."

Lorentzian component to anisotropic size, depends on "Size-Model"  
= "LorSiz "



# Strategy for Rietveld refinement

## IV) Constraints and restraints:

Applied in order to couple parameters so that they undergo the same linear or proportional shifts or to restrain parameters to stay within a given range.

### 1) Symmetry Constraints:

e.g.: Lattice parameters in a tetragonal system, code e.g.: 71.00 71.00 81.00

Atomic coordinates linked by symmetry e.g.:	$x, -x, z$ , code e.g.: 101.00 -101.00 111.00
or:	$x, 2x, z$ , code e.g.: 100.50 101.00 111.00

Scale factors of nuclear and magnetic phases having different unit cells,  
with e.g.:  $a\ b\ c$  (nuc) and  $2a\ 2b\ c$  (mag): code 11.0000 (nuc) and 10.0625 (mag)

Refining a low symmetric structure with limited data (forcing e.g. part of a framework of atoms to keep a higher symmetry, e.g.: charge ordered structures with  $Mn^{3+}$  and  $Mn^{4+}$  in  $Tb_{0.5}Ca_{0.5}MnO_3$ :

$Pnma$  with  $a\ b\ c$  has 7 positional parameters,

$P2_1/m$  with  $2a\ b\ c$  has 31 positional parameters.      **Nowadays: Use Amplitudes to refine distortions**

Spin direction in highly symmetric cases, e.g.: hexagonal system: refine only  $M_x$  and  $M_z$  as powder data don't allow the determination of the moment direction within the basal plane.

# Strategy for Rietveld refinement

## IV) Constraints and restraints:

### 2) Constraints due to direct correlation, e.g.:

Wavelength or lattice parameters (refine one or the other)

Scale factor or magnetic moment value in a purely magnetic phase (using a difference data set)

Scale factor and site occupancies (has to be fixed for one site)

### General Remark 1:

Put **Ana = 1** in pcr file for analysis of Refinement:

Pay attention to message "Correlation of special kind" indicates coupling of strongly correlated = wrongly coupled parameters.

### General Remark 2:

Some correlations are very strong, e.g.: zero shift and sample displacement.

This will increase your standard deviations. If interested in relative behaviour of parameters as function of e.g. T keep some fixed.

### General Remark 3:

When you do a **sequential refinement** using data from a stationary multidetector (e.g. D20, D1B) you refine only once the **zeroshift** using one data set and then you **fix** it.

# Strategy for Rietveld refinement

## IV) Constraints and restraints:

### 3) Linear Restraints:

E.g.: Partial site occupancies (total must be fixed, not negative, with several sites ...)

		x	y	z	B	Occ				
CR	CR	0.00000	0.00000	0.00000	0.00000	0.01563	0	0	0	2
		0.00	0.00	0.00	0.00	211.00				
RE	RE	0.00000	0.00000	0.00000	0.00000	0.00190	0	0	0	3
		0.00	0.00	0.00	0.00	221.00				
FE	FE	0.00000	0.00000	0.00000	0.00000	0.00331	0	0	0	3
		0.00	0.00	0.00	0.00	271.00				
RE	RE	0.50000	0.50000	0.50000	0.00000	0.01372	0	0	0	3
		0.00	0.00	0.00	0.00	231.00				
FE	FE	0.50000	0.50000	0.50000	0.00000	0.00190	0	0	0	3
		0.00	0.00	0.00	0.00	281.00				
CR	CR	0.50000	0.50000	0.50000	0.00000	0.00520	0	0	0	2
		0.00	0.00	0.00	0.00	241.00				

Occupation of site =

Site Multiplicity/ Multiplicity of the general site  
Fm3m: 4/192 = 0.02083 if full

Site 1

$\text{Sr}_2\text{CrFe}_{0.25}\text{Re}_{0.75}\text{O}_6$  with Cr, Fe and Re distributed over 2 cation sites (4a: 0 0 0 and 4b:  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{2}$ ):

Site 2

Introduce linear restraints, NLI in pcr file, **NLI = 5** (second line of pcr-file)

! Set of 5 linear restraints:

! Identifier, number of coeff., value, sigma / List of coeff & Parameters

Site\_a 3 0.020830 0.0000001  
1.0000 21 1.0000 22 1.0000 27  
(Limits the occupation on site 0 0 0 to 0.02083 = FULL)

Site\_b 3 0.020830 0.0000001  
1.0000 23 1.0000 24 1.0000 28  
(Limits the occupation on site  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{2}$  to 0.02083 = FULL)

Chemcomp 2 0.020830 0.0000001  
1.0000 21 1.0000 24  
(Limits the total content of Cr on both sites to 0.02083 = 1)

Chemcomp 2 0.015620 0.0000001  
1.0000 22 1.0000 23  
(Limits the total content of Re on both sites to 0.01562 = 0.75)

Chemcomp 2 0.005210 0.0000001  
1.0000 27 1.0000 28  
(Limits the total content of Fe on both sites to 0.00521 = 0.25)

Constraint pcr

# Strategy for Rietveld refinement

## IV) Constraints and restraints:

- 4) 'Strategic' Constraints: Used in order to assure a successful refinement  
(can be lifted as the refinement proceeds)

In theory not needed if the data would be perfect in intensity, resolution and  $q$ -range.

In powder always limitations: Same  $q$ -value for different reflections (5 5 3, 7 1 1 in cubic system)  
Multiplicity of reflections (311, 131, 113...)

### Typical 'strategic' constraints:

- One overall temperature factor for all atoms
- The same temperature factor for all atoms of the same type
- Magnetic moment values of different magnetic sites kept alike
- Limit the possible Spin directions (basis vectors)

Refining a magnetic structure using high intensity/low resolution data:

Keep all atom coordinates fixed if the crystallographic structure had been determined before from high resolution data.

Again: Keep the zeroshift fixed in a sequential refinement!!

# Strategy for Rietveld refinement

## IV) Constraints and restraints:

- 5) Restraints: Helps the refinement program not to get trapped in false minima  
Very important for e.g. simulated annealing

P 21/n		<--Space group symbol								
!Atom Typ		X	Y	Z	Biso	Occ	In Fin	N <sub>t</sub>	Spc	/Codes
Sr	SR	0.87930	0.41798	0.73560	1.55853	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
C1	C	0.63200	0.23920	0.57800	1.48511	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
C2	C	0.58300	0.51640	0.09300	1.48511	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
C3	C	0.64800	0.27780	0.34700	1.48511	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
O1	O	0.62200	0.22870	0.15700	1.24468	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
O2	O	0.67300	0.28130	0.75600	1.24468	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
Ow3	O	0.85600	0.56610	0.57600	1.24468	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
O4	O	0.77900	0.50850	0.07000	1.24468	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
O5	O	0.57500	0.16760	0.56900	1.24468	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
O6	O	0.52400	0.55480	0.26500	1.24468	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
O7	O	0.69400	0.34880	0.32900	1.24468	1.00000	0	0	0	0
		0.00	0.00	0.00	0.00	0.00				
H1	D	0.77449	0.06512	0.01765	2.00000	1.00000	0	0	0	0
		11.00	21.00	31.00	0.00	0.00				
H2	D	0.81474	0.75317	0.49374	2.00000	1.00000	0	0	0	0
		41.00	51.00	61.00	0.00	0.00				
H3	D	0.64942	0.10371	0.81023	2.00000	1.00000	0	0	0	0
		71.00	81.00	91.00	0.00	0.00				

Strontium-Oxalate (deuterated)

Where is the Hydrogen?

Keep the known framework fixed

Coordinates of 3 H atoms free

NRE in pcr file = number of restraints

Put NRE = 9 (first line of pcr-file)

Nine Restraints to be put into the pcr-file:

*! Limits for selected parameters (+ steps & BoundCond for SA):*

1	0.0000	1.0000	0.0152	1	X_H1
2	0.0000	1.0000	0.0073	1	Y_H1
3	0.0000	1.0000	0.0264	1	Z_H1
4	0.0000	1.0000	0.0279	1	X_H2
5	0.0000	1.0000	0.0080	1	Y_H2
6	0.0000	1.0000	0.0323	1	Z_H2
7	0.0000	1.0000	0.0334	1	X_H3
8	0.0000	1.0000	0.0087	1	Y_H3
9	0.0000	1.0000	0.0346	1	Z_H3

# Strategy for Rietveld refinement

## IV) Constraints and restraints:

### 6) Soft distance (or angles) constraints

Running Fullprof with the option of calculating distances and angles (**Jdi = 3, needs More=1 in line starting with Nat**) will not only produce a file called \*.dis with all the interatomic distances and angles, but as well a file called **CFML\_Restraints.tpcr**.

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
  7  0  0  0.0 0.0 1.0  0  0  0  0  0  967.370  0  5  1
!Jvi Jdi Hel Sol Mom Ter Brind RMua RMub RMuc Jtyp Nsp_Ref Ph_Shift N_Domains
  0  3  0  0  0  0  1.0000 0.0000 0.0000 0.0000  1  0  0  0
! Max_dst(dist)(angles) Bond-Valence Calc.
  3.6000  2.6000  BVS
! N_cations N_anions Tolerance(%) / Name or cations/ and Anions
  3  1  0.00
PR+3 FE+3 B3+
O-2
```

pcr file

CFML\_Restraints.tpcr

YFe3BO34disconstraints.pcr

Fp

YFe3BO34disconstraints.dis

This file contains in the appropriate format distance or angle restraints which can be pasted into the pcr file.  
This is useful if you want to restrain a certain type of interatomic distances (or angles) to be the same

=> Help for possible angle restraints around atom FE2

FE2	O2	O2	32	33	0.0000	-1.0000	0.6667	-1.0000	-1.0000	0.3333	46.36	0.18
FE2	O2	O4	32	25	0.0000	-1.0000	0.6667	0.0000	0.0000	0.0000	5.53	0.18
FE2	O2	O5	32	26	0.0000	-1.0000	0.6667	0.0000	-1.0000	0.3333	41.58	0.24
FE2	O2	O5	32	27	0.0000	-1.0000	0.6667	0.0000	0.0000	0.6667	51.04	0.24

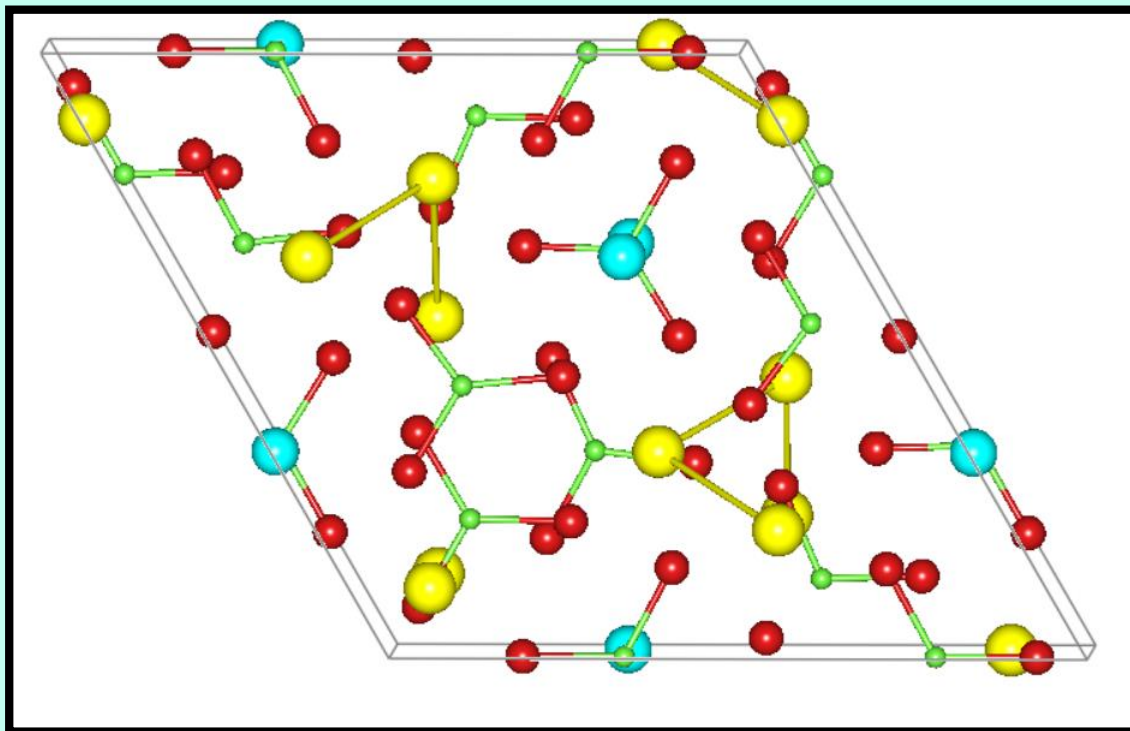
At1	At2	ITnum	T1	T2	T3	DIST	SIGMA
FE2	FE2	26	-1.00000	-1.00000	0.33333	3.1853	0.0049
FE2	FE2	27	0.00000	-1.00000	-0.33333	3.1853	0.0044
FE2	FE2	33	0.00000	0.00000	0.33333	4.4180	0.0053
FE2	Y	25	0.00000	0.00000	0.00000	3.8107	0.0073

In the pcr file you have to change as well the parameters **DIS** or **MOM** to the number of restraints you introduced.

# Strategy for Rietveld refinement

## IV) Constraints and restraints:

### 6) Soft distance (or angles) constraints



Example of  $\text{YFe}_3(\text{BO}_3)_4$ :  
Groups of  $\text{BO}_3$

$$R_{\text{Bragg}} = 3.7$$

unconstrained

$$R_{\text{Bragg}} = 3.9$$

B-O distances constrained to be equal

Thank you for your attention!