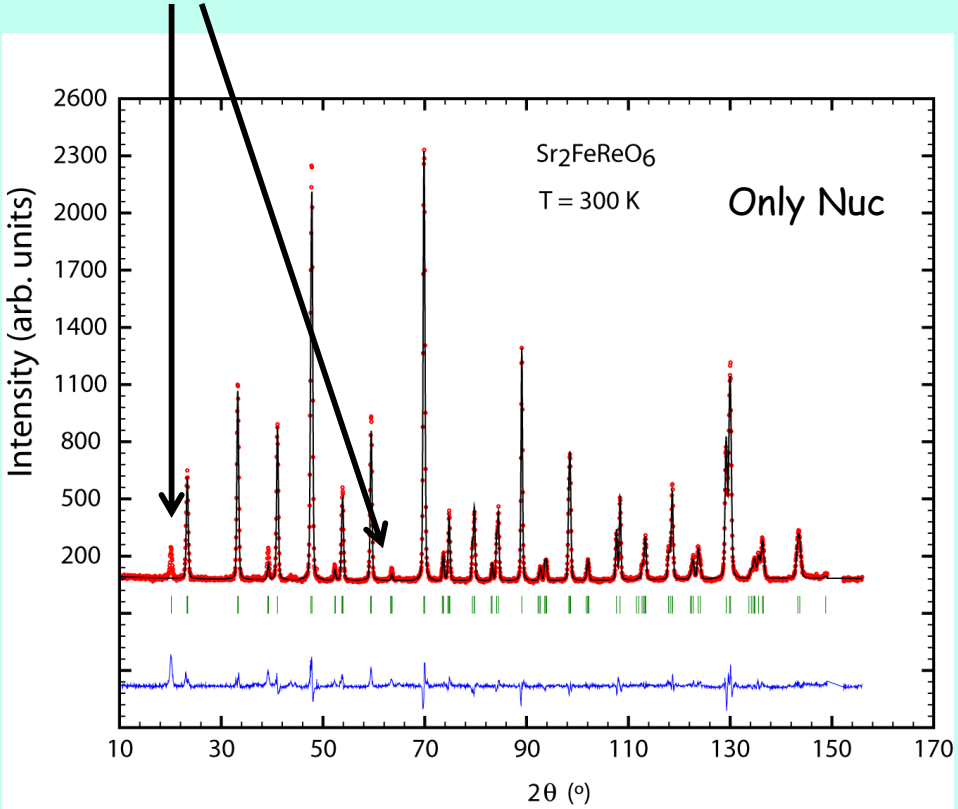
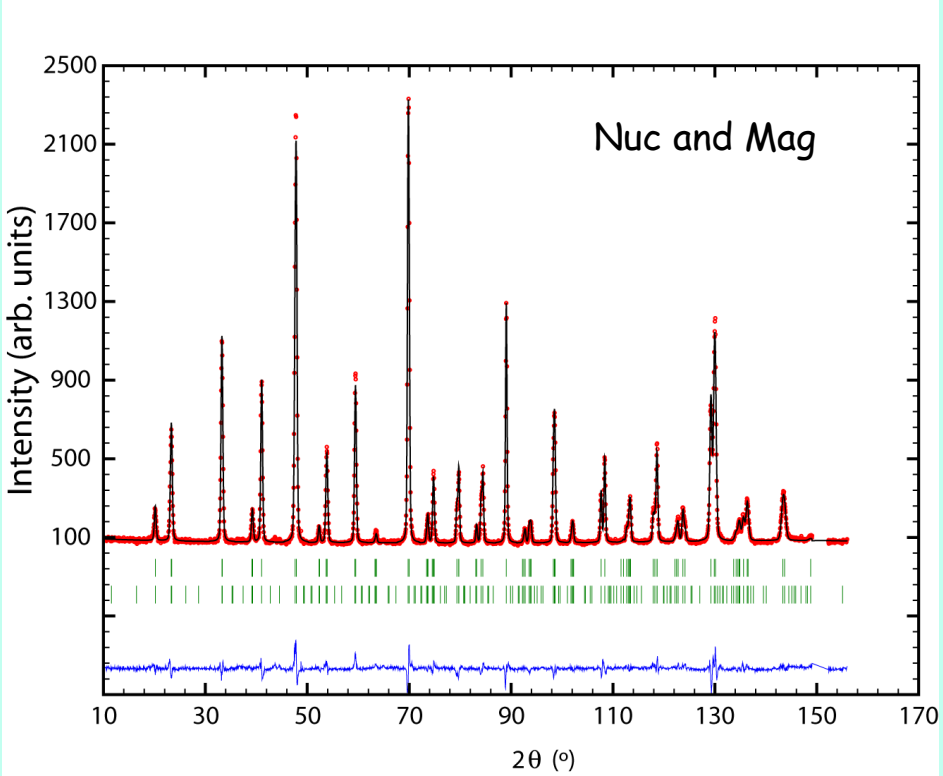
Magnetic Scattering, how can we detect it's existence? (1)

E.g.: Refining a neutron diffraction data set using a model for the crystallographic structure which is known from x-ray data

Strong intensity not accounted for by the model on allowed Bragg peaks or in additional Bragg peaks.





Missing intensity stronger at lower scattering angles ---> magnetic scattering

For room temperature data only if transition metals (Fe, Co) are present in the compound.

Magnetic Scattering, how can we detect it's existence? (2)

Measuring the temperature dependence (thermodiffractogram) of the neutron spectrum and look for changes.

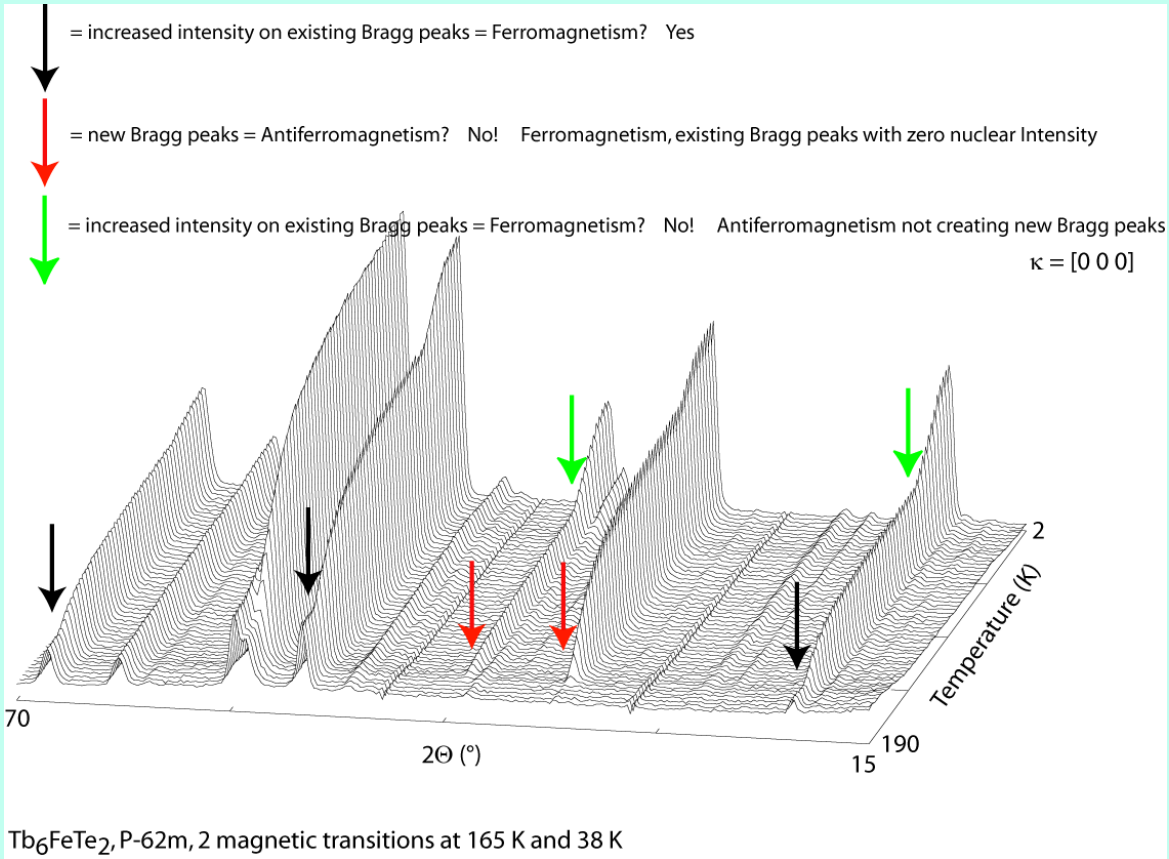
I) Ferromagnetism, Ferrimagnetism: Intensity is added to existing Bragg peaks

II) Antiferromagnetism:

1) Magnetic unit cell = Crystallographic unit cell, magnetic propagation vector κ = [0 0 0], new Bragg peaks can be created

2) a) Magnetic unit cell ≠ Crystallographic unit cell, commensurate magnetic propagation vector, e.g. $\kappa = [\frac{1}{2}\ \frac{1}{2}\ 0]$, new Bragg peaks

b) Magnetic unit cell ≠ Crystallographic unit cell, incommensurate magnetic propagation vector, e.g. $\kappa = [0\ \frac{1}{2}\ 0.21]$, new Bragg peaks



Exclude structural transitions as reasons for changes:

Peak splittings point to structural transitions through distortions.

Appearence of new peaks is accompanied by an intensity reduction of old peaks.

But:

Magnetostructural transitions where the magnetic phase transition triggers a structural transition or vice versa.

When does antiferromagnetism **not create** new reflections with κ = [0 0 0] ?

e.g.: *P2/m*, *Pmmm*, *P-62m*, *P432*

When does antiferromagnetism **create** new reflections with κ = [0 0 0] ?

e.g.: $P2_1/m$, *Pnma*

In general:

Symmetry elements which create systematic extinctions within the crystallographic unit cell:

Lattice centering: A, B, C, F, I, R	(e.g.: I ---> $+\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$)
Screw axes: 2_1, 3_1, 4_1, 4_2, 6_1, 6_2, 63	(Rotation + Translation)
Glide planes: *a*, *b*, *c*, *n*, *d*	(Reflection + Translation)

In structures where the crystallographic unit cell contains screw axes or glide planes a magnetic propagation vector κ = [0 0 0] creates new magnetic Bragg reflections for antiferromagnetic structures.

Structures having lattice centering like *I4/m*, *R-3* create no new reflections for κ = [0 0 0], spins are parallel.

If the centering condition is lost, propagation vectors like κ = [1 0 0] or κ = [0 0 1.5] result and new reflections are formed, spins are anti-parallel.

Introduction to the use of the program BASIREPS

NEUTRONS FOR SOCIETY

Aim: Efficient use of neutron diffraction data to solve magnetic structures

Ideal diffraction data for the determination of magnetic structures:

1) High resolution neutron data of the compound in the paramagnetic phase: Initial structure

2) High intensity neutron thermodiffractogram from $T > T_C$ or T_N down to lowest possible T:

   Appearence of magnetic scattering and its T-dependence
   Existence of different transitions?
   Different magnetic propagation vectors?

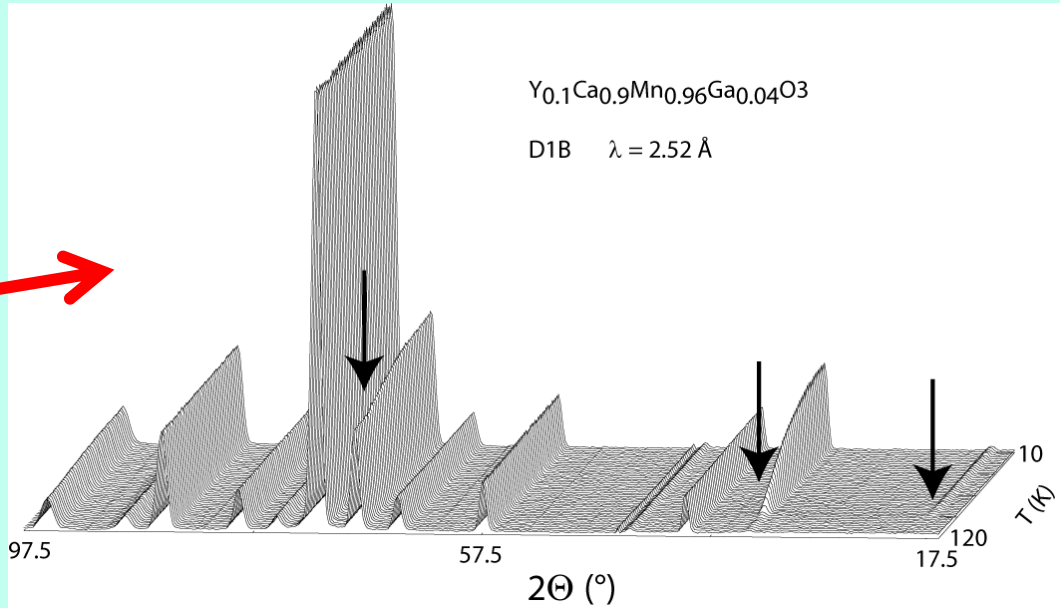
3) High resolution neutron data (and synchrotron data) at lowest T:
   Final structure, Existence of a structural phase transition?

Example 1: $Y_{0.1}Ca_{0.9}Mn_{0.96}Ga_{0.04}O_3$

Temperature dependence of the neutron diffraction data:

Thermodiffractogram

Conclusion: 1 magnetic transition at about 95 K



Introduction to the use of the program BASIREPS

NEUTRONS FOR SOCIETY

1) Determination of the structure in the paramagnetic phase

Fit at 130 K > T_N → *Pnma*, Mn on 0 0 $\frac{1}{2}$

Paramagnetic.pcr

Paramagnetic.prf

2) Determination of the magnetic propagation vector

Fit at 10 K < T_N Structure10K.pcr Structure10K.prf

Difference pattern

Insert Peaks, K-Search Ksearch1.sat Ksearch.kub → κ = (⅓, ⅓, 0)

κ = (0, 0, 0)

Introduction to the use of the program BASIREPS

Finding a magnetic structure by trial and error:

κ = [0 0 0] → magnetic unit cell = nuclear unit cell

Refine the magnetic contribution using a second phase in the FULLPROF pcr file

Give all the magnetic atoms separately and imagine the magnetic coupling between the magnetic moments in the cell: Mn on (0,0,½), (½,0,0), (0, ½, ½), (½, ½,0)

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:     4.50
!-------------------------------------------------------------------------------
LAYCA magnetic
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   4   0   0 0.0 0.0 1.0   1   0   1   0   0         0.000   0   5   0
!
P -1                      <--Space group symbol for hkl generation
!Nsym Cen Laue MagMat
   1   1   1   1
!S11 S12 S13     T1        S21 S22 S23     T2     S31 S32 S33       T3
!M11 M12 M13  M21 M22 M23  M31 M32 M33     Ph
   1   0   0    0.000000   0   1   0    0.000000   0   0   1    0.000000
   1   0   0   0   1   0   0   0   1    0.000000
!Atom   Typ  Mag Vek    X       Y       Z       Biso    Occ      Rx      Ry      Rz
!     Ix     Iy     Iz    beta11  beta22  beta33    MagPh
MN1    MMN3  1  0  0.00000 0.00000 0.50000 0.20484  0.96000   2.000   2.000   2.000
                     0.00    0.00    0.00  241.00     0.00  311.00  291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
MN1    MMN3  1  0  0.50000 0.00000 0.00000 0.20484  0.96000   2.000   2.000   2.000
                     0.00    0.00    0.00  241.00     0.00  311.00  291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
MN1    MMN3  1  0  0.00000 0.50000 0.50000 0.20484  0.96000   2.000   2.000   2.000
                     0.00    0.00    0.00  241.00     0.00  311.00  291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
MN1    MMN3  1  0  0.50000 0.50000 0.00000 0.20484  0.96000   2.000   2.000   2.000
                     0.00    0.00    0.00  241.00     0.00  311.00  291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
!-------> Profile Parameters for Pattern #  1
```

Site

1

2

3

4

Here we assume e.g. a ferromagnetic coupling in all three directions:

F_x F_y F_z

Trial_and_Error1.pcr

Trial_and_Error.prf

Trial_and_Error1.new

Couplings within a 4-fold site:

Site	Coupling			
1	+	+	+	+
2	+	+	-	-
3	+	-	-	+
4	+	-	+	-
	F	A	G	C

Resulting fit is very bad!!

Introduction to the use of the program BASIREPS

Trial and error 2 (or 41 or 99 or …)

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:     4.50
!-------------------------------------------------------------------------------
LAYCA magnetic
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   4   0   0 0.0 0.0 1.0   1   0   1   0   0         0.000   0   5   0
!
P -1                      <--Space group symbol for hkl generation
!Nsym Cen Laue MagMat
   1   1   1   1
!S11 S12 S13     T1        S21 S22 S23     T2    S31 S32 S33       T3
!M11 M12 M13  M21 M22 M23  M31 M32 M33     Ph
   1   0   0    0.000000   0   1   0    0.000000   0   0   1    0.000000
   1   0   0   0   1   0   0   0   1    0.000000
!Atom   Typ  Mag Vek    X      Y      Z      Biso    Occ      Rx      Ry      Rz
!     Ix     Iy     Iz    beta11  beta22  beta33    MagPh
MN1    MMN3  1  0  0.00000 0.00000 0.50000 0.20484  0.96000   2.000   2.000   2.000
                      0.00    0.00    0.00  241.00     0.00  311.00  291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
MN1    MMN3  1  0  0.50000 0.00000 0.00000 0.20484  0.96000   2.000  -2.000   2.000
                      0.00    0.00    0.00  241.00     0.00  311.00 -291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
MN1    MMN3  1  0  0.00000 0.50000 0.50000 0.20484  0.96000  -2.000  -2.000   2.000
                      0.00    0.00    0.00  241.00     0.00 -311.00 -291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
MN1    MMN3  1  0  0.50000 0.50000 0.00000 0.20484  0.96000  -2.000   2.000   2.000
                      0.00    0.00    0.00  241.00     0.00 -311.00  291.00  321.00
     0.000   0.000   0.000   0.000   0.000   0.000  0.00000
      0.00    0.00    0.00    0.00    0.00    0.00     0.00
!-------> Profile Parameters for Pattern #  1
```

A_x G_y F_z

More than 100 possibilities to put F, A, C, G in the three directions. They can appear twice or three times.

→ Trial and error ???

Couplings within a 4-fold site:

Site	Coupling			
1	+	+	+	+
2	+	+	-	-
3	+	-	-	+
4	+	-	+	-
	F	A	G	C

Introduction to the use of the program BASIREPS

Refine Trial_and_error2.pcr → Trial_and_error2.prf

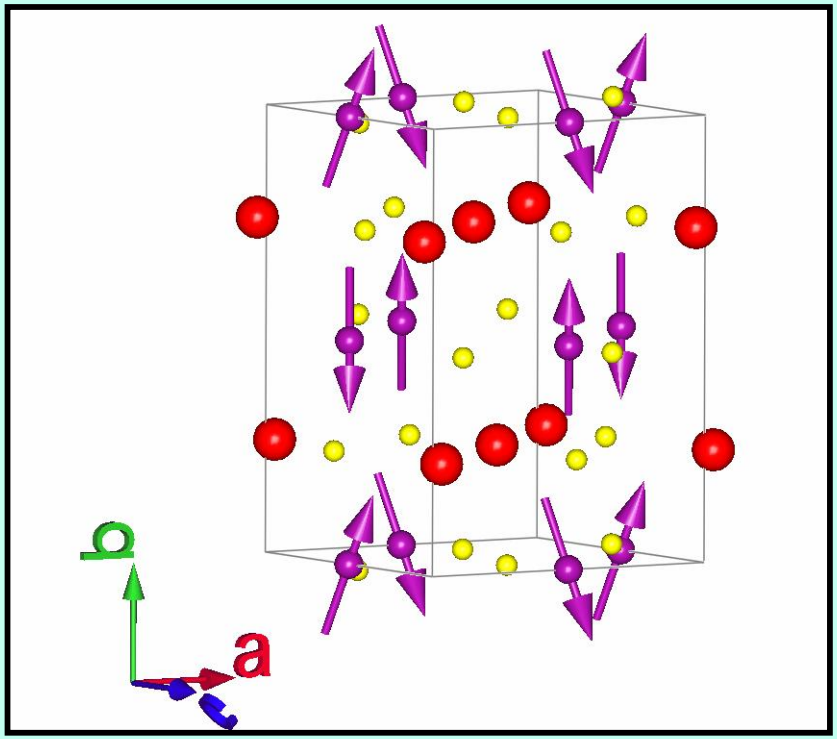
Results looks really good!

Difference plot shows all magnetic peaks to be refined

Trial_and_error2.new

R_{mag} is low

$A_xG_yF_z$ seems to be the solution, let's publish!



Introduction to the use of the program BASIREPS

Short reminder on the way a magnetic moment is defined:

$$m_j = \sum_{\kappa} S_{\kappa j}\, e^{-2\pi i \kappa t}$$

$\mathbf{S}_{\kappa j}$ are the Fourier components of atom j in the zeroth unit cell, t is the translation (e.g. t = (1 0 0) to neighbouring unit cell in x-direction)

If only one propagation vector κ:

$$m_j = S_{\kappa j}\, e^{-2\pi i \kappa t}$$

$$\downarrow$$

$$S_{\kappa j} = \sum_{n} C_{\kappa j n}\, S_{\kappa n}$$

Linear combination of n Basis vectors gives the magnetic moment value and its direction

n Coefficients (variables) to be determined for n Basis vectors for spin on atom j

Examples of Basis vectors:

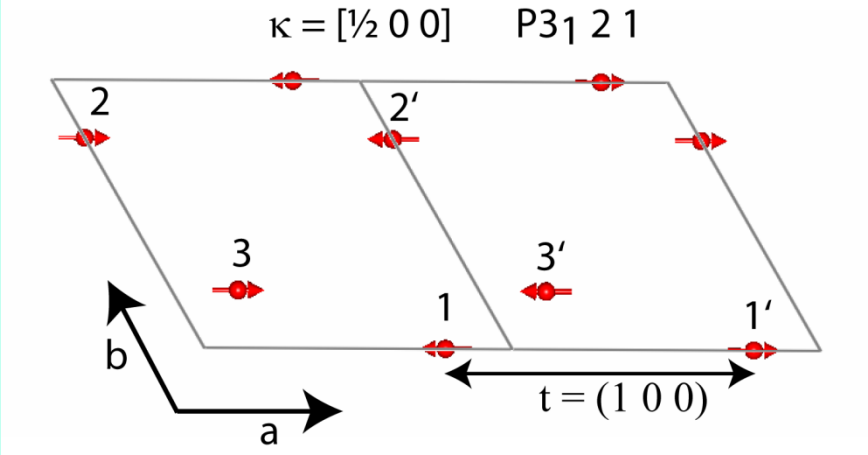
(1 0 0) (0 1 0) (0 0 1) corresponds to the x, y and z directions of an orthogonal lattice

But can be as well e.g. in a hexagonal unit cell:
(1 1 0) or (1 2 0)

They can be real or complex

Short reminder of the meaning of the term: " magnetic propagation vector"

The magnetic propagation vector describes how the magnetic structure within the nuclear unit cell is periodically repeated in space. It is equivalent to the translations used to describe the periodicity of crystal structures.



With the use of the propagation vector one can describe the relation between the magnetic moments (size and direction) on equivalent atom sites in different unit cells.

If e.g. there is only one Basis vector $S_\kappa = (1\ 0\ 0)$ and $\kappa = [\frac{1}{2}\ 0\ 0]$ then the magnetic moment in the zeroth unit cell ($t = (0\ 0\ 0)$) is:

$$m_j = S_{\kappa j}\, e^{-2\pi i \kappa t} = C_{\kappa j}\, S_\kappa (\cos 2\pi\kappa t + i \sin 2\pi\kappa t) = C_{\kappa j} (1\ 0\ 0) \cos \underbrace{2\pi (\tfrac{1}{2}\ 0\ 0)(0\ 0\ 0)}_{1} = C_{\kappa j} (1\ 0\ 0)$$

In the neighbouring unit cell in x-direction one has with $t = (1\ 0\ 0)$:

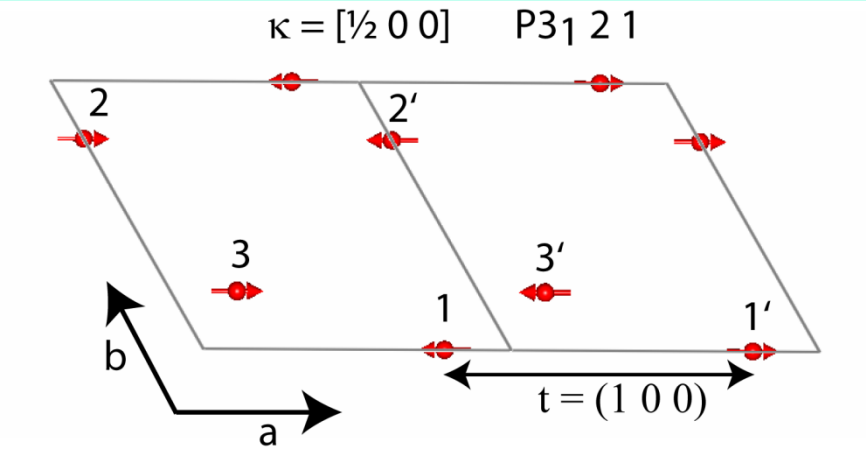
$$m_j = S_{\kappa j}\, e^{-2\pi i \kappa t} = C_{\kappa j}\, S_\kappa (\cos 2\pi\kappa t + i \sin 2\pi\kappa t) = C_{\kappa j} (1\ 0\ 0) \cos \underbrace{2\pi (\tfrac{1}{2}\ 0\ 0)(1\ 0\ 0)}_{-1} = C_{\kappa j} (-1\ 0\ 0)$$

➔ Antiferromagnetic alignment of magnetic moments in neighbouring unit cells along the *x*-direction

We know now that a magnetic moment on an atom site is described by a linear combination of Basis vectors (multiplied by their coefficients) and that the periodicity within the crystal lattice is described by the propagation vector.

If one has a crystallographic unit cell where the magnetic atom occupies a site with multiplicity 1 (e.g. Wykoff site $1d$ ($\frac{1}{2}$ 0 $\frac{1}{2}$) in *Pmmm*) this is all the information we need.

If, however, the magnetic site(s) has(ve) higher multiplicities we have to determine the relation the different sites which are created through the symmetry elements of the spacegroup have to each other.



One has to determine the relation between the moment size and direction of the magnetic moment on site 1 to those on the symmetry related sites 2 and 3 within the crystallographic unit cell

We have seen that it is possible to do this using a trial and error method, however, in most of the cases this will be very tedious or nearly impossible and furthermore lead to often non-physical results. This is the reason why the method of Magnetic symmetry analysis has been developed by E.F. Bertaut in the sixties. Only, however, in the last 20 years the method has been applied routinely due to the availability of easy to use programs like BASIREPS or SARAH.

Introduction to the use of the program BASIREPS

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Magnetic symmetry analysis (a simple glimps):

The symmetry of the crystallographic structure is described by its spacegroup and the corresponding symmetry elements.

As the periodicity of the magnetic unit cell is not necessarily the same as the periodicity of the nuclear unit cell its symmetry can be lower.

The symmetry elements of the original crystallographic spacegroup which leave the magnetic propagation vector invariant form a subgroup called the « little group ».

The operators (matrixes) of these symmetry elements (permutation matrixes) multiplied by the operators which describe how the magnetic moment components are transformed as axial vectors by the symmetry elements of the little group form the magnetic representation.

This means that the magnetic representation describes the effect of the symmetry operators of the little group on the position of the atoms and on the magnetic moments.

This magnetic representation can be simplified by applying an appropiate rotation bringing the representation in the block-diagonal form where one is only left with square blocks of matrixes on the diagonal and zeros everywhere else.

Each square block forms a smaller representation and if they cannot be reduced further into a block-diagonal form; they are called irreducibel.

The different irreducible representations contain the information on the possible magnetic structures which fulfill the symmetry restrictions of the crystal structure. This limits dramatically the number of magnetic structures which have to be taken into account for the refinement.

The basis vectors of these irreducible representations can be calculated using existing programs (BASIREPS, SARAH) and will serve for the refinement of the magnetic structures.

Introduction to the use of the program BASIREPS

Landau theorie of second order phase transitions:

The free energy of a system which sees a magnetic ordering with wave vector κ must be invariant under the action of the symmetry elements of the little group of κ.

Or simpler: If a magnetic ordering is of second order only a single irreducible representation should be involved.

This reduces strongly the possible magnetic structures: Group theory has determined a limited number of possible irreducible representations (IREP), Landau theory tells us now that only one IREP should be involved as a magnetic structure is formed.

So we are happy!! But:

I) This is not always valid (higher order terms in the free energy)

II) What happens if we have the Presence of several magnetic sublattices, e.g. A and B:

1) If the intrasite interactions I_{AA} and I_{BB} are large compared to the intersite interaction I_{AB} then one can expect two different transitions and different IREPS for each site.

2) If the intersite I_{AB} is dominant then both sites A and B should order at the same temperature and follow the same IREP

3) If only one intrasite interaction I_{AA} is large and the intersite interaction I_{AB} as well strong then the second site B gets polarized and adopts a magnetic structure similar to site A. At lower temperatures a second magnetic transition will appear for the ordering of site B. Due to the strong I_{AB} its symmetry should still follow the same IREP as A.

III) The long range magnetic order induces a strong magnetostructural effect: first order transition.

E.g.:Strong single-ion anisotropy of the magnetic ion. Especially for rare earth ions which have a strong unquenched orbital angular moment. Interaction with the crystal field leads to easy axis or easy plane anisotropy which can determine the moment orientation in contradiction to the group theory. Does not necessarely lead to a visible structural transition.

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Intermediate summary:

Magnetic structures are defined by the moment size and direction of a first magnetic site, its relation to the other magnetic atoms on the symmetry related sites within the nuclear unit cell and finally by the magnetic propagation vector.

Thanks to magnetic symmetry analysis and the Landau theory one can normally strongly reduce the number of parameters to be determined for the description of a magnetic structure from 3 x n, where n is the number of magnetic atoms in the unit cell.

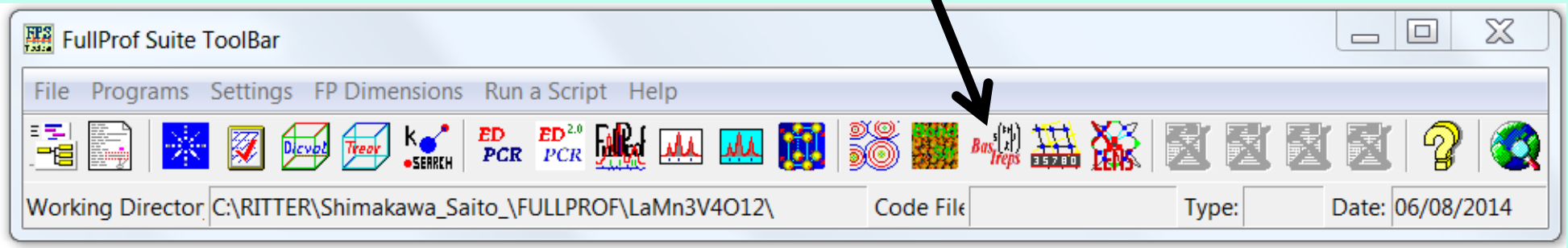
The solutions will be physically reasonable.

The complicated mathematics and the tedious calculations involved in the magnetic symmetry analysis are nowadays done by easy to use programs.

In the second part of the talk we will learn how to use the program BASIREPS which calculates IREPS and their Basis vectors (BV) using very limited input information.

Introduction to the use of the program BASIREPS

BASIREPS: Included in the Fullprof_Suite of programs



BASIREPS:

calculates through magnetic symmetry analysis the allowed irreducible representations and their basis vectors

needs as input the crystallographic spacegroup, the position of the magnetic atoms and the magnetic propagation vector

creates a file called *.fp which contains the results of the calculations in a form which can be copied directly to the *.pcr file for the refinement and a file called *.bsr which contains details of the calculations.

Introduction to the use of the program BASIREPS

2 Examples:

1) $Y_{0.1}Ca_{0.9}Mn_{0.96}Ga_{0.04}O_3$ *P n m a*

Mn on 0 0 $\frac{1}{2}$ (Wykoff site $4b$)

κ = [0 0 0] T_N = 100 K

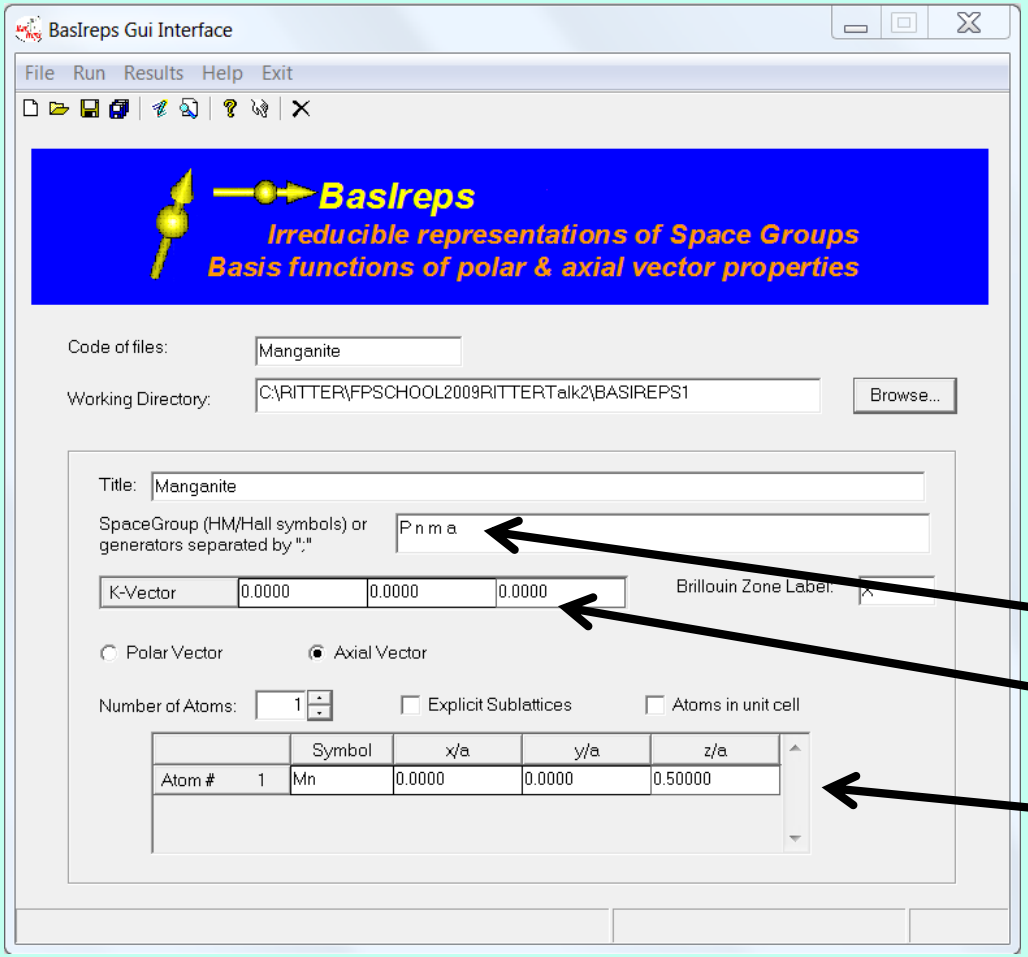
2) $TbFe_3(BO_3)_4$ *P* 3_1 *2 1*

Fe1 on 0.12 0.12 0 (Wykoff site $3a$)
Fe2 on 0.79 0.45 0.34 (Wykoff site $6c$)
Tb on 0.66 0.66 0 (Wykoff site $3a$)

κ = [0 0 $\frac{1}{2}$] T_N = 40 K

Introduction to the use of the program BASIREPS

1) $Y_{0.1}Ca_{0.9}Mn_{0.96}Ga_{0.04}O_3$



Fullprof Toolbar

Manganite_fp

Details of Manganite_fp

File « *.fp » contains the results of the BASIREPS calculations and the lines to be introduced into the *.pcr file for the refinement of the magnetic phase

Specific Input:

Spacegroup

Propagation vector

Atom positions

Introduction to the use of the program BASIREPS

One of the possible 4 solutions:

This has to be copied to the FULLPROF pcr file in order to try a refinement

Nsym = Number of symmetry elements

N_Bas = Number of Basisvectors

```
P -1

! Nsym   Cen  Laue Ireps N_Bas
   4      1     1    -1     3

! Real(0)-Imaginary(1) indicator for Ci
0  0  0

SYMM x,y,z
BASR | 1  0  0 | | 0  1  0 | | 0  0  1 |
BASI | 0  0  0 | | 0  0  0 | | 0  0  0 |

SYMM -x+1/2,-y,z+1/2
BASR |-1  0  0 | | 0 -1  0 | | 0  0  1 |
BASI | 0  0  0 | | 0  0  0 | | 0  0  0 |

SYMM -x,y+1/2,-z
BASR |-1  0  0 | | 0  1  0 | | 0  0 -1 |
BASI | 0  0  0 | | 0  0  0 | | 0  0  0 |

SYMM x+1/2,-y+1/2,-z+1/2
BASR | 1  0  0 | | 0 -1  0 | | 0  0 -1 |
BASI | 0  0  0 | | 0  0  0 | | 0  0  0 |
```

3 Basisvectors = 3 free Coefficients

| C1 | | C2 | | C3 |

In FULLPROF you will refine these 3 Coefficients

Model of Basireps
Input pcr file

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:     5.29
!-------------------------------------------------------------------------------!
!
!   Jbt=1 : Phase is treated as pure magnetic phase
!
!              Irf=-1 : Satellite reflections generated from space group symbol
!
!                     Isy=-2 : The basis functions of the irreducible representation are read in the form:    SYMM ...
!                                                                                                            BASR ...
!                                                                                                            BASI ...
!                                                  Nvk = Number of propagation vectors
!
Magnetic phase
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
  1    0    0   0.0  0.0 1.0   1   -1   -2   0    0      17501.770  1    5    0
!
P -1                  <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
    4       1     3     -1      3                        Laue Class: mmm = 3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0                                                 Ireps: Number of irreducible representations, often equal to the number of
!                                                                 magnetically independant atoms, here therefore = 1
SYMM x,y,z
BASR   1  0  0   0  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x+1/2,-y,z+1/2
BASR  -1  0  0   0 -1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x,y+1/2,-z
BASR  -1  0  0   0  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
SYMM x+1/2,-y+1/2,-z+1/2
BASR   1  0  0   0 -1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
```

```
!   Typ = Magnetic formfactor MMN3 = Mn 3+
!
!           Mag = Irreducible representation used for this Atom
!
!                   Vek = Magnetic propagation vector used for this Atom
!
!Atom  Typ   Mag Vek   X         Y         Z      Biso      Occ       C1       C2      C3
!                              C4      C5      C6      C7      C8       C9      MagPh
MN1  MMN3  1    1  0.00000 0.00000 0.50000 0.22051 0.96000  -0.373   0.290  -4.112
                     0.00      0.00      0.00     241.00      0.00     11.00    21.00   31.00
                            0.000   0.000   0.000   0.000   0.000   0.000  0.00000
                             0.00     0.00     0.00     0.00     0.00     0.00      0.00
!-------> Profile Parameters for Pattern #  1
!  Scale      Shape1     Bov     Str1     Str2     Str3   Strain-Model
  2.8989      0.28936   0.00000   0.00000   0.00000   0.00000      0
   311.00000   121.000     0.000     0.000     0.000     0.000
!      U        V        W        X        Y      GauSiz   LorSiz Size-Model
   0.122186  -0.184594   0.205900   0.000000   0.000000   0.000000   0.000000    0
    131.000    141.000    151.000      0.000      0.000      0.000      0.000
!       a           b           c          alpha         beta         gamma     #Cell Info
   5.300002   7.451008   5.261796  90.000000  90.000000  90.000000
   91.00000  101.00000  111.00000      0.00000      0.00000      0.00000
!  Pref1      Pref2      Asy1      Asy2      Asy3      Asy4
  0.00000  0.00000  0.03350  0.01794  0.00000  0.00000
    0.00       0.00    271.00     281.00       0.00       0.00
! Propagation vectors:
   0.0000000   0.0000000   0.0000000        Propagation Vector  1
    0.000000     0.000000     0.000000
```

Introduction to the use of the program BASIREPS

Trying out the 4 different solutions proposed by BASIREPS

Copy the corresponding lines of the manganite.fr file created by BASIREPS into the *.pcr file

Manganite_pcr Model1

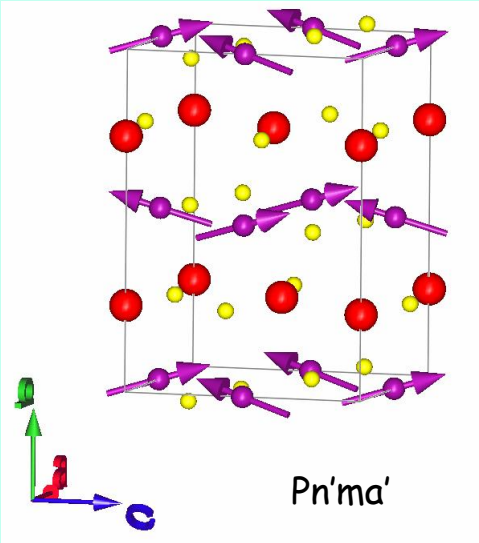
Refine and decide from the R-factors and from the visual inspection of the fit whether the solution is correct

WinplotR

As this model does not work return to the fp file and copy a different IREP into the pcr file

Best Fit with couplings:

x	y	z	
+	+	+	
+	+	-	$= A_x F_y G_z$
-	+	-	
-	+	+	



Manganite_fp

Manganite_pcr Model2

Manganite_pcr Model3

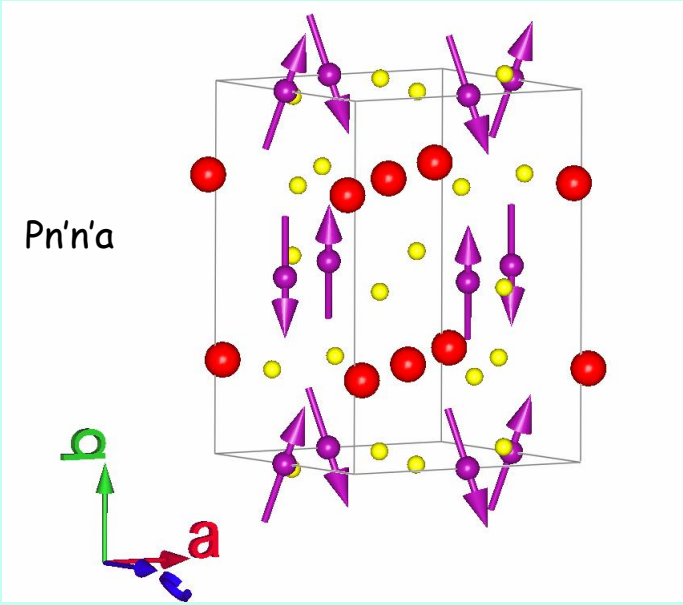
Introduction to the use of the program BASIREPS

Compare with the intuitively (trial and error) found solution: $A_xG_yF_z$

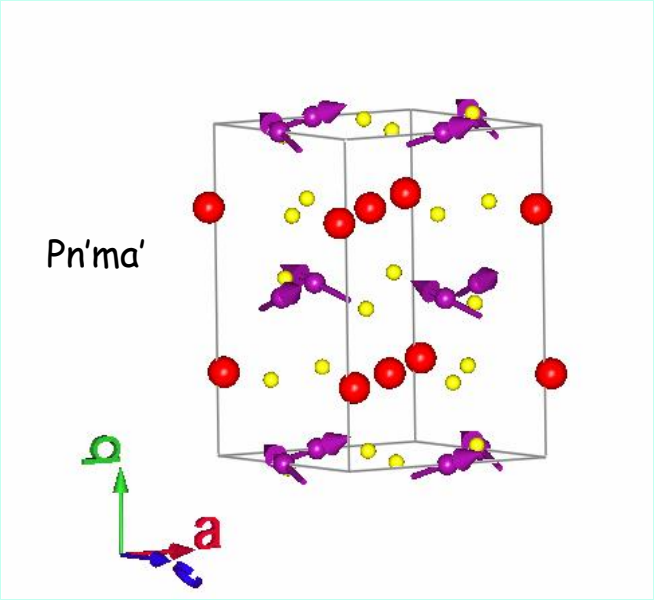
Pseudosymmetry and not sufficient resolution are causing this situation

Only BASIREPS gives you the correct spin direction,

Trial and error: $A_xG_yF_z$



Symmetry analysis: $A_xF_yG_z$



Pseudosymmetry and not sufficient resolution are causing this situation:

a = 5.2998 b = 7.4507 c = 5.2616

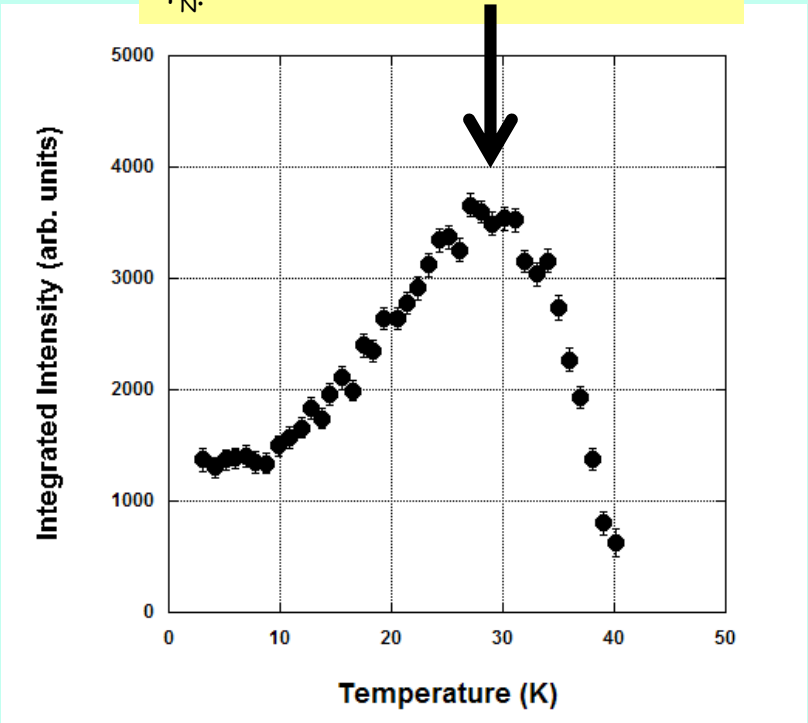
b/√2 = 5.2685

Manganite_prf

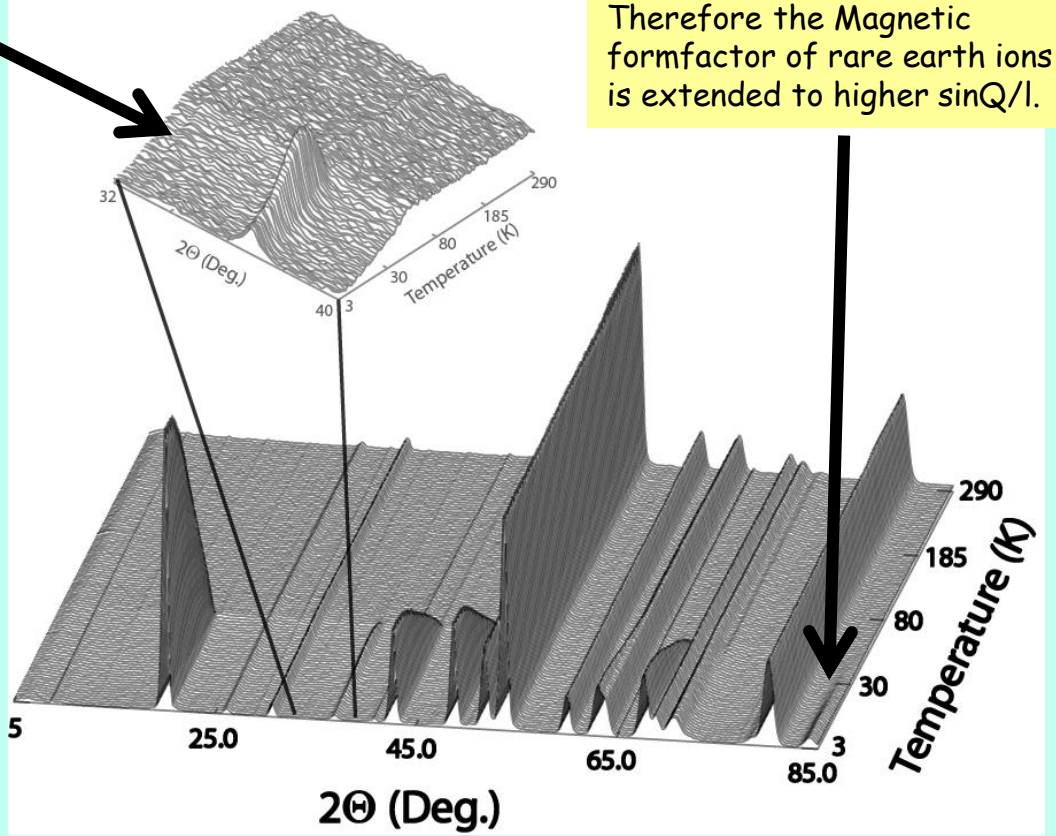
Introduction to the use of the program BASIREPS

2) $TbFe_3(BO_3)_4$

Integrated intensity of one magnetic Bragg peak:
2 sublattices having different T-dependence: Tb and Fe, but only one T_N.



Thermodiffractogram of $TbFe_3(BO_3)_4$



Magnetic intensity at high 2Q values points to Tb being magnetic.
The unpaired electrons of the rare earth ions are found in the 4f shell which is closer to the nucleus than e.g. the 3*d* shell. Therefore the Magnetic formfactor of rare earth ions is extended to higher sinQ/l.

Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$

1) Fit at 50 K > T_N

Nuclear Structure pcr

Nuclear Structure prf

2) Compare data at 50 K and 2 K and fit the peak positions of the magnetic peaks

WinplotR

3) Create a *.sat file for K-search, apply the zeroshift of the 50 K refinement to the determined peak positions

TbFe3(BO3)4_sat

```
! Input file for K_SEARCH (created by WinPLOTR)
! created by WinPLOTR-2006:25/ 1/2009 at 11:30:56
! Data file : C:\Documents and Settings\ritter\Bureau\FPSCHOOL2009_2\
TITLE       TbFe3(BO3)4     2 K  Only Nuclear
SPGR      P 31 2 1
CELL         9.53779    9.53779    7.56713    90.0000    90.0000   120.0000
SHORT-OUTPUT
K_COMMENSURATE
CWTOL          1.91000     0.300
K_RANGE     0.0  0.5     0.0  0.5     0.0  0.5
K_DIV          100         100         100
! peak_position  peak_intensity  peak_background
2THETA_LIST      5
       15.07276     2521.21362      109.30181
       31.95011     1205.86206      109.30181
       36.36218     1308.35693      109.30181
       46.60749      736.09369      109.30181
       49.85853     1120.44958      109.30181
```

4) Run K-search from the green version of WINPLOTR

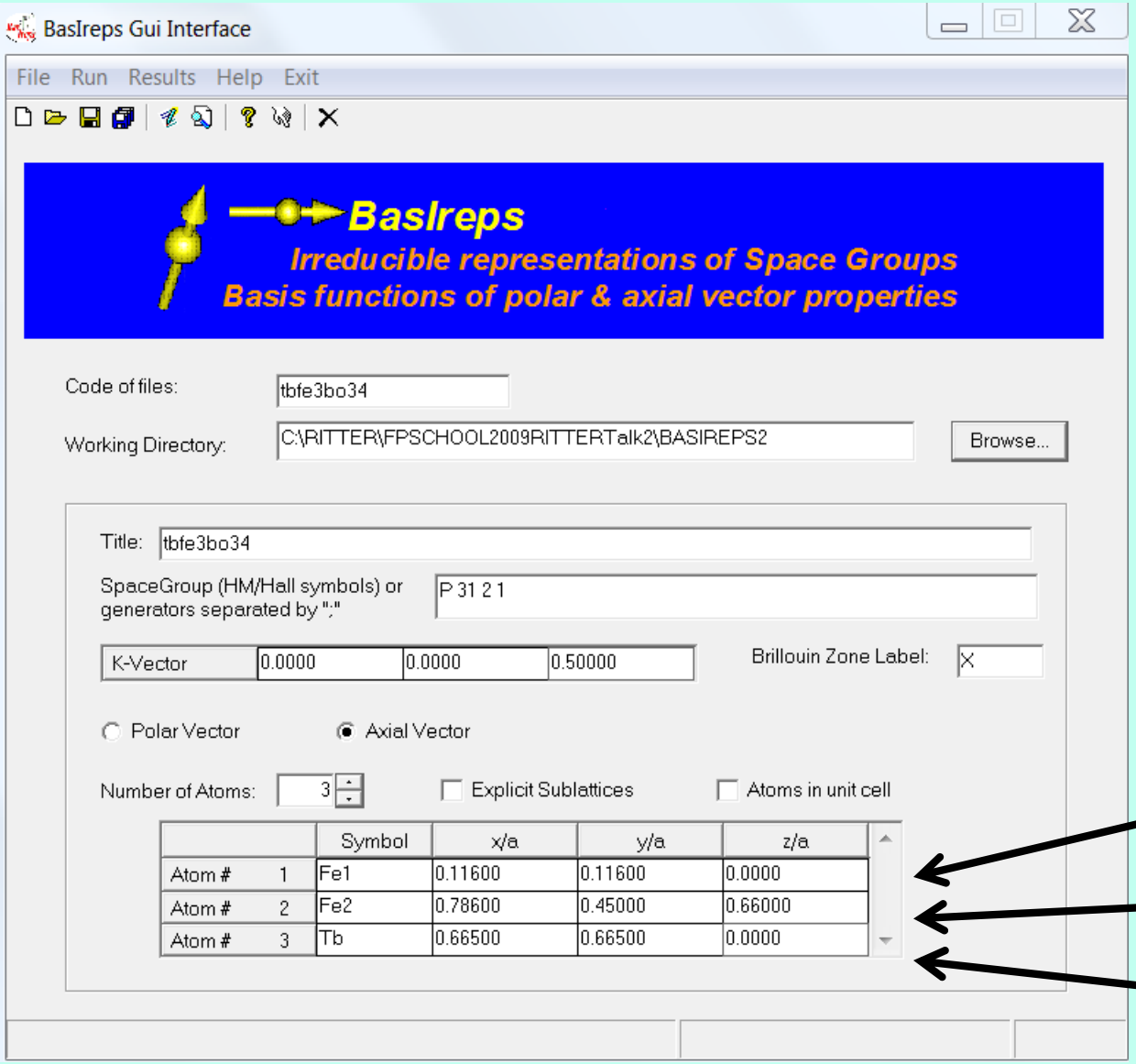
5) Look at the result file TbFe3(BO3)4_kub

(Notice that there are a lot of solutions of type "($\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{4}$)" or "($\frac{1}{8}$, $\frac{1}{4}$, 0)" or "($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) ",
→ Ignore these in 99% of cases!!)

→ $\kappa = [0\ 0\ \frac{1}{2}]$

Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$



Fullprof Toolbar

TbFe3BO34_fp

3 IREPS with 6, 1, 2 BVs

3 IREPS with 12, 3, 3 BVs

3 IREPS with 6, 1, 2 BVs

Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$

IREP3: TbFe3BO34_fp

Nsym = Number of symmetry operators

N_Bas = Number of Basis Vectors → 2 Basis Vectors = 2 free Coefficients C

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     3    1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
1 SYMM x,y,z
  BASR  1 -1  0   0  0  1
  BASI  0  0  0   0  0  0
2 SYMM -y,x-y,z+1/3
  BASR -1 -2  0   0  0 -1
  BASI  0  0  0   0  0  0
3 SYMM -x+y,-x,z+2/3
  BASR -2 -1  0   0  0  1
  BASI  0  0  0   0  0  0
```

IREP 3 ofFe1

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     3    1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
SYMM x,y,z
BASR  1 -1  0   0  0  1
BASI  0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR -1 -2  0   0  0 -1
BASI  0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR -2 -1  0   0  0  1
BASI  0  0  0   0  0  0
```

IREP 3 of Tb

Both IREPS are identical! This is normal as both atoms are sitting on the same Wykoff site $3a\ (x\ x\ 0)$

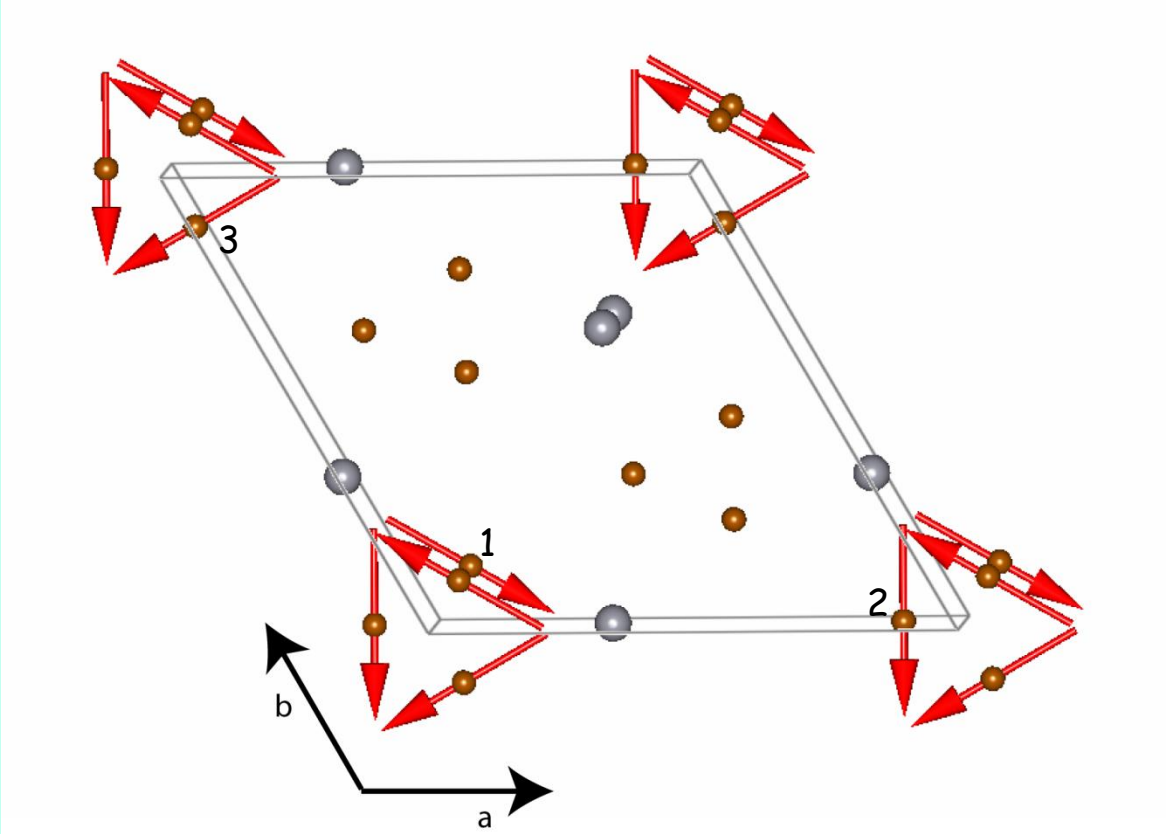
Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     3     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
SYMM x,y,z
BASR   1 -1  0   0  0  1
BASI   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR  -1 -2  0   0  0 -1
BASI   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -2 -1  0   0  0  1
BASI   0  0  0   0  0  0
```

IREP3 of Fe1

Magnetic structure with only BV1



Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$

IREP 3 of Fe2 has 6 symmetry operators
and 3 BVs → 3 C_i

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     6     1     1    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
SYMM x,y,z
BASR   1  0  0   0  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR   0 -1  0   1  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -1 -1  0   1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM y,x,-z
BASR   0 -1  0  -1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM x-y,-y,-z+2/3
BASR  -1  0  0   1  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x,-x+y,-z+1/3
BASR  -1 -1  0   0  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
```

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     3     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
SYMM x,y,z
BASR   1 -1  0   0  0  1
BASI   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR  -1 -2  0   0  0 -1
BASI   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -2 -1  0   0  0  1
BASI   0  0  0   0  0  0
```

The BVs of the Wykoff site $6c$ (Fe2) are different than those of site $3a$ (Fe1, Tb)

$TbFe_3(BO_3)_4$ Construction of the pcr file for IREP3

I)

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     3     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
SYMM x,y,z
BASR   1 -1  0   0  0  1
BASI   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR  -1 -2  0   0  0 -1
BASI   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -2 -1  0   0  0  1
BASI   0  0  0   0  0  0
```

Fe1

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     6     1     1    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
SYMM x,y,z
BASR   1  0  0   0  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR   0 -1  0   1  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -1 -1  0   1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM y,x,-z
BASR   0 -1  0  -1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM x-y,-y,-z+2/3
BASR  -1  0  0   1  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x,-x+y,-z+1/3
BASR  -1 -1  0   0  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
```

Fe2

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     3     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
SYMM x,y,z
BASR   1 -1  0   0  0  1
BASI   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR  -1 -2  0   0  0 -1
BASI   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -2 -1  0   0  0  1
BASI   0  0  0   0  0  0
```

Tb

II)

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     6     1     9    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0
SYMM x,y,z
BASR   1 -1  0   0  0  1
BASI   0  0  0   0  0  0
BASR   1  0  0   0  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
BASR   1 -1  0   0  0  1
BASI   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR  -1 -2  0   0  0 -1
BASI   0  0  0   0  0  0
BASR   0 -1  0   1  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
BASR  -1 -2  0   0  0 -1
BASI   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -2 -1  0   0  0  1
BASI   0  0  0   0  0  0
BASR  -1 -1  0   1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
BASR  -2 -1  0   0  0  1
BASI   0  0  0   0  0  0
SYMM y,x,-z
BASR   0 -1  0  -1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM x-y,-y,-z+2/3
BASR  -1  0  0   1  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x,-x+y,-z+1/3
BASR  -1 -1  0   0  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
```

Group together under the same symmetry operators

III)

```
P -1
! Nsym   Cen  Laue Ireps N_Bas
     6     1     9    -3     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
SYMM x,y,z
BASR   1 -1  0   0  0  1   0  0  0
BASI   0  0  0   0  0  0   0  0  0
BASR   1  0  0   0  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -y,x-y,z+1/3
BASR  -1 -2  0   0  0 -1   0  0  0
BASI   0  0  0   0  0  0   0  0  0
BASR   0 -1  0   1  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x+y,-x,z+2/3
BASR  -2 -1  0   0  0  1   0  0  0
BASI   0  0  0   0  0  0   0  0  0
BASR  -1 -1  0   1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM y,x,-z
BASR   0  0  0   0  0  0   0  0  0
BASI   0  0  0   0  0  0   0  0  0
BASR   0 -1  0  -1  0  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM x-y,-y,-z+2/3
BASR   0  0  0   0  0  0   0  0  0
BASI   0  0  0   0  0  0   0  0  0
BASR  -1  0  0   1  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x,-x+y,-z+1/3
BASR   0  0  0   0  0  0   0  0  0
BASI   0  0  0   0  0  0   0  0  0
BASR  -1 -1  0   0  1  0   0  0 -1
BASR   0  0  0   0  0  0   0  0  0
```

Add zeros to get the same number of BVs

Add zeros under the symmetry operators which do not concern Fe1 and Tb

Remove the identical lines as IREP3 of Fe1 and Tb are the same

$TbFe_3(BO_3)_4$

NEUTRONS FOR SCIENCE®

```
Magnetic Phase
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
   3   0   0 0.0 0.0 1.0   1  -1  -2   0   0       0.000   1   5   0
!
P -1                    <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
    6     1     9    -2     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
!
SYMM X, Y, Z
BASR      1   -1    0       0    0    1       0    0    0
BASI      0    0    0       0    0    0       0    0    0
BASR      1    0    0       0    1    0       0    0    1
BASI      0    0    0       0    0    0       0    0    0
SYMM -Y+1, X-Y, Z+1/3
BASR     -1   -2    0       0    0   -1       0    0    0
BASI      0    0    0       0    0    0       0    0    0
BASR      0   -1    0       1    1    0       0    0   -1
BASI      0    0    0       0    0    0       0    0    0
SYMM -X+Y, -X+1, Z+2/
BASR     -2   -1    0       0    0    1       0    0    0
BASI      0    0    0       0    0    0       0    0    0
BASR     -1   -1    0       1    0    0       0    0    1
BASI      0    0    0       0    0    0       0    0    0
SYMM Y, X, -Z+1
BASR      0    0    0       0    0    0       0    0    0
BASI      0    0    0       0    0    0       0    0    0
BASR      0    1    0       1    0    0       0    0   -1
BASI      0    0    0       0    0    0       0    0    0
SYMM X-Y, -Y+1, -Z+2/3
BASR      0    0    0       0    0    0       0    0    0
BASI      0    0    0       0    0    0       0    0    0
BASR     -1    0    0       1    1    0       0    0    1
BASI      0    0    0       0    0    0       0    0    0
SYMM -X+1, -X+Y+1, -Z+4/3
BASR      0    0    0       0    0    0       0    0    0
BASI      0    0    0       0    0    0       0    0    0
BASR      1    1    0       0   -1    0       0    0    1
BASR      0    0    0       0    0    0       0    0    0
!
!Atom Typ  Mag Vek    X       Y       Z       Biso   Occ      C1      C2      C3
!    C4     C5     C6      C7      C8      C9     MagPh
FE1  MFE3  1  1  0.11692 0.11692 0.00000-0.08487 1.00000   0.444  -4.108   0.000
                 181.00   181.00    0.00     451.00    0.00  511.00  481.00    0.00
   0.000   0.000   0.000   0.000   0.000   0.000 0.00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
FE2  MFE3  2  1  0.78623 0.44960 0.34164-0.08487 1.00000   0.957   0.053   4.431
                 191.00   201.00  211.00     451.00    0.00  531.00  541.00  501.00
   0.000   0.000   0.000   0.000   0.000   0.000 0.00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
TB1  MTB3  1  1  0.66508 0.66508 0.00000-0.49219 1.00000  -0.939   8.714   0.000
                 171.00   171.00    0.00     441.00    0.00  521.00  491.00    0.00
   0.000   0.000   0.000   0.000   0.000   0.000 0.00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
```

3 BVs

2 IREPS

TbFe3BO34_free_pcr

Magnetic part of pcr-file for IREP3

This "2" means that the programme uses for Fe2 IREP2

All coefficients are refined: 2 C for Fe1 and Tb, 3 C for Fe2

Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$ Refinement

WinplotR

1) Refinement with all 7 coefficients free

TbFe3BO34_free_pcr

TbFe3BO34_free_sum

Fit not stable, large error bars, peak at low angles?

2) Refinement with only 2 coefficients

TbFe3BO34_fixed_pcr

TbFe3BO34_fixed.sum

Fit stable, small error bars if C2(Fe1) = -C2(Fe2), low angle peak not longer there.

3) Refinement with single crystal data

TbFe3BO34_SingleCrystal_free_pcr

TbFe3BO34_SingleCrystal_free_prf

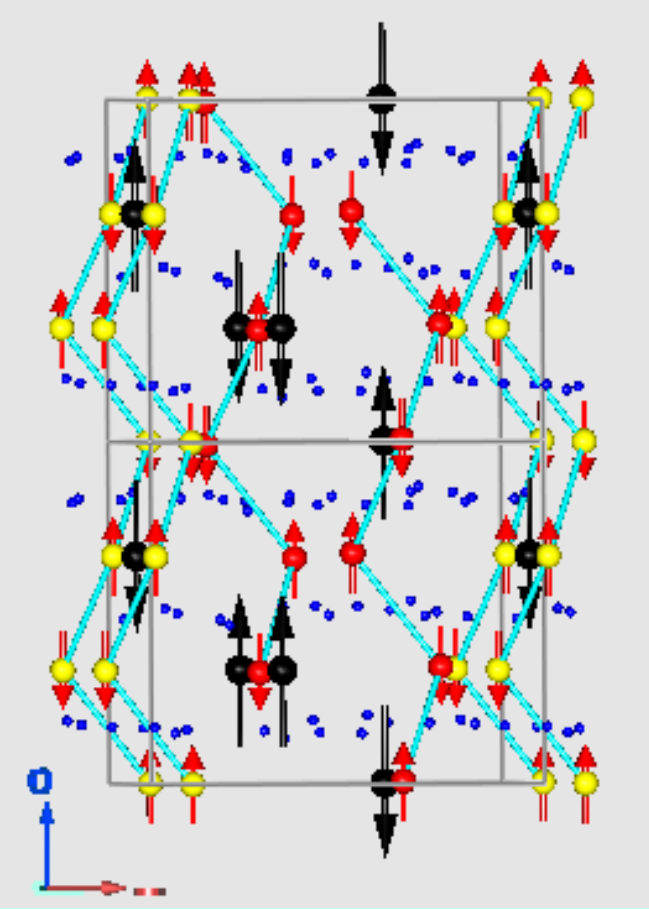
TbFe3BO34_PowderRefinement_using SingleCrystal_results_prf

Fe1	C1=-0.21(17) C2=-3.46(72) C3=0.00	C1=0.00 C2=4.34(4) C3=0.00	C1=0.39(5) C2=3.95(5) C3=0.00
Fe2	C1=-0.45(26) C2=-0.04(11) C3=4.81(37)	C1=0.00 C2=0.00 C3=-4.34(4)	C1=-0.09(6) C2=-0.07(6) C3=-3.92(4)
Tb1	C1=-0.52(11) C2=8.66(7) C3=0.00	C1=0.00 C2=-8.56(6) C3=0.00	C1=0.16(4) C2=-8.09(3) C3=0.00

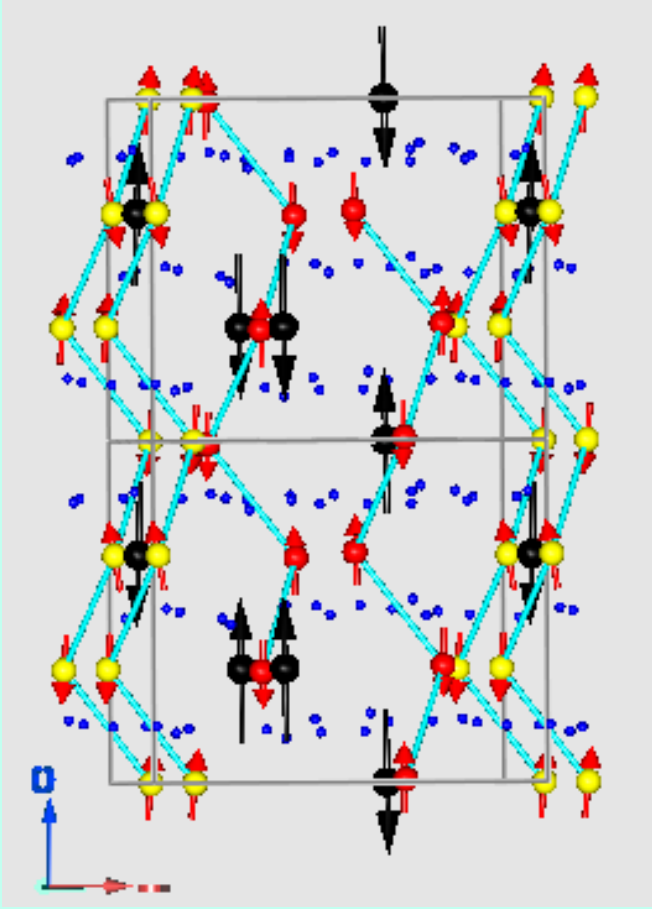
Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$ Results of magnetic refinements

Powder, 2 Coefficients



Single Crystal, 7 Coefficients



Bilbao Crystallographic Server: MAXMAGN

https://www.cryst.ehu.es/

Magnetic super spacegroup: 2- P_c3_221 (#154.44)

Introduction to the use of the program BASIREPS

$TbFe_3(BO_3)_4$ Test of IREP2 WinplotR

TbFe3BO34_IREP2_pcr TbFe3BO34_IREP2_sum TbFe3BO34_IREP2_prf

```
SYMM X, Y, Z
BASR     1     1     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     1     0     0     0     1     0     0     0     1
BASI     0     0     0     0     0     0     0     0     0
SYMM -Y+1, X-Y, Z+1/3
BASR     1     0     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     0    -1     0     1     1     0     0     0    -1
BASI     0     0     0     0     0     0     0     0     0
SYMM -X+Y, -X+1, Z+2/3
BASR     0    -1     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR    -1    -1     0     1     0     0     0     0     1
BASI     0     0     0     0     0     0     0     0     0
SYMM Y, X, -Z+1
BASR     0     0     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     0     1     0     1     0     0     0     0    -1
BASI     0     0     0     0     0     0     0     0     0
SYMM X-Y, -Y+1, -Z+2/3
BASR     0     0     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     1     0     0    -1    -1     0     0     0    -1
BASI     0     0     0     0     0     0     0     0     0
SYMM -X+1, -X+Y+1, -Z+4/3
BASR     0     0     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     1     1     0     0    -1     0     0     0     1
BASR     0     0     0     0     0     0     0     0     0
```

IREP 2, e.g. no z-component for Fe1 and Tb

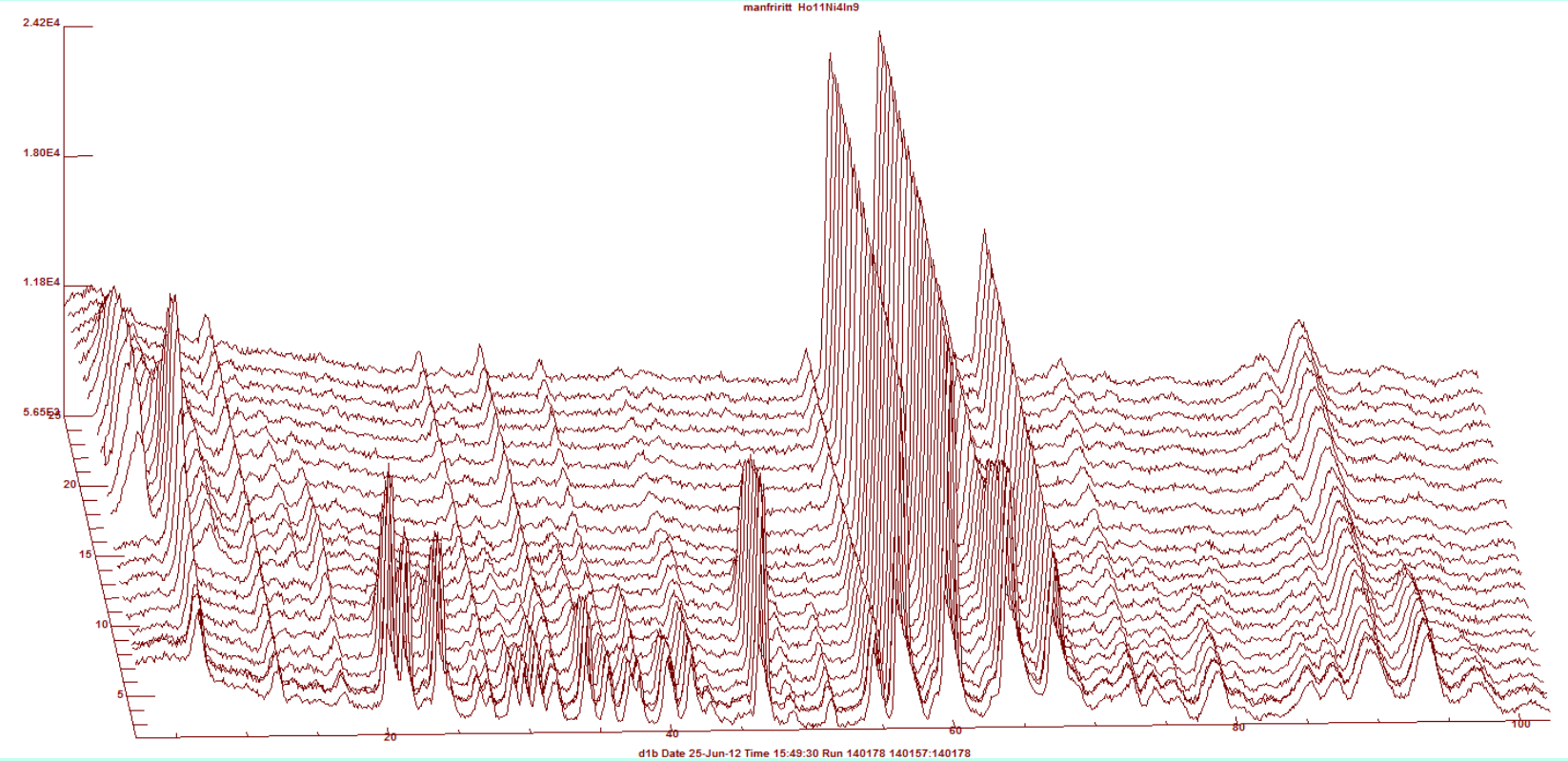
```
SYMM X, Y, Z
BASR     1    -1     0     0     0     1     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     1     0     0     0     1     0     0     0     1
BASI     0     0     0     0     0     0     0     0     0
SYMM -Y+1, X-Y, Z+1/3
BASR    -1    -2     0     0     0    -1     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     0    -1     0     1     1     0     0     0    -1
BASI     0     0     0     0     0     0     0     0     0
SYMM -X+Y, -X+1, Z+2/3
BASR    -2    -1     0     0     0     1     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR    -1    -1     0     1     0     0     0     0     1
BASI     0     0     0     0     0     0     0     0     0
SYMM Y, X, -Z+1
BASR     0     0     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR     0    -1     0    -1     0     0     0     0     1
BASI     0     0     0     0     0     0     0     0     0
SYMM X-Y, -Y+1, -Z+2/3
BASR     0     0     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR    -1     0     0     1     1     0     0     0     1
BASI     0     0     0     0     0     0     0     0     0
SYMM -X+1, -X+Y+1, -Z+4/3
BASR     0     0     0     0     0     0     0     0     0
BASI     0     0     0     0     0     0     0     0     0
BASR    -1    -1     0     0     1     0     0     0    -1
BASR     0     0     0     0     0     0     0     0     0
```

IREP 3

Introduction to the use of the program BASIREPS

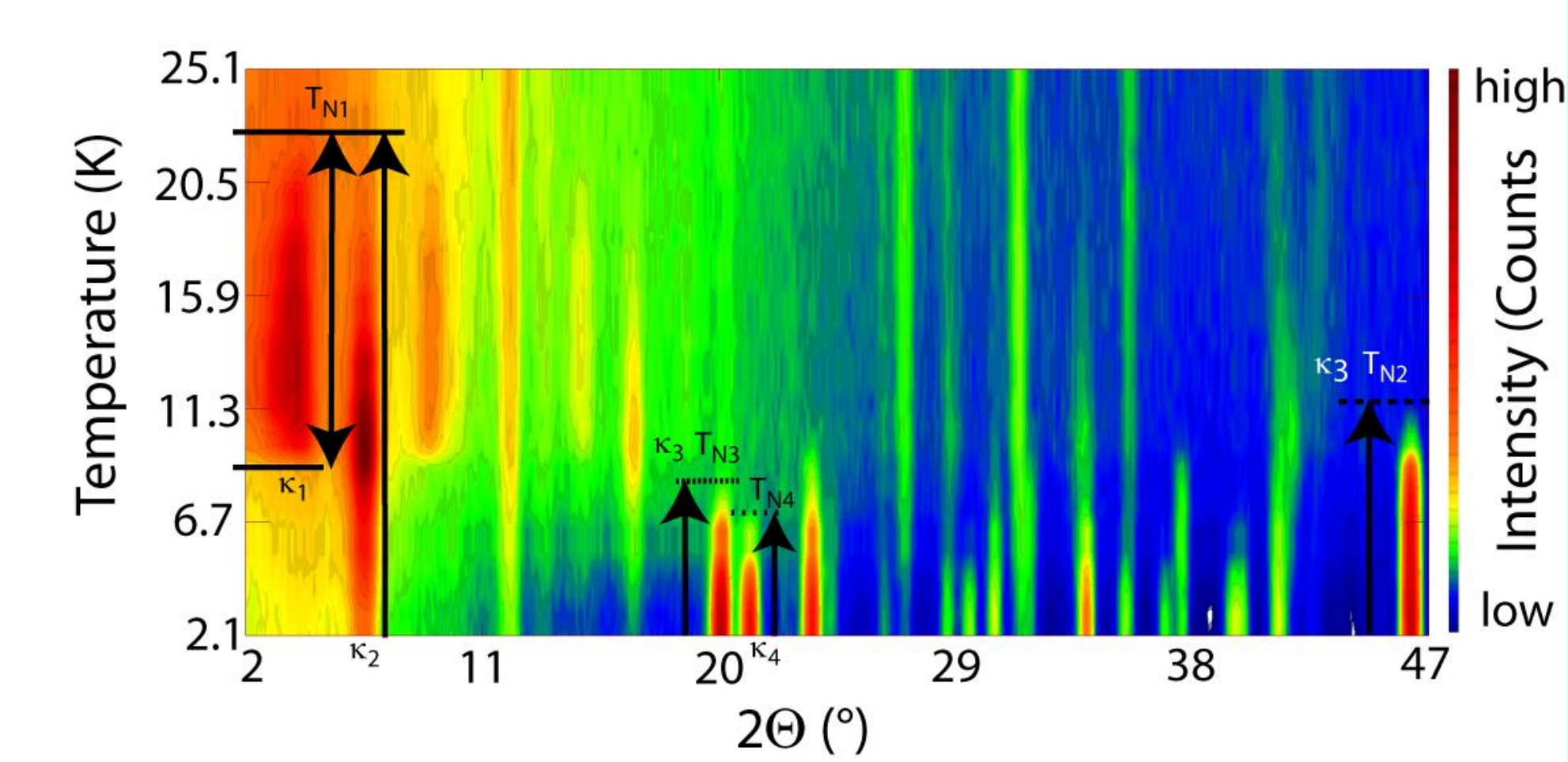
More difficult case:

$Ho_{11}Ni_4In_9$: several k-vectors
several magnetic sites
different T-dependencies



Introduction to the use of the program BASIREPS

$Ho_{11}Ni_4In_9$: *Cmmm*, 5 Ho in crystallographic unit cell
Ho1 on $8p$, Ho2 and Ho3 on $4i$ Ho4 on $4g$ and Ho5 on $2a$



κ_1 = [0 0.62 0], κ_2 = [0 1 0], κ_3 = [0 0 $\frac{1}{2}$], κ_4 = [0 1 $\frac{1}{2}$]

16K_pcr 16K_prf

At 16 K: κ_1 only Ho2 κ_2 only Ho5 κ_4 only Ho3 and only below T_{N4}

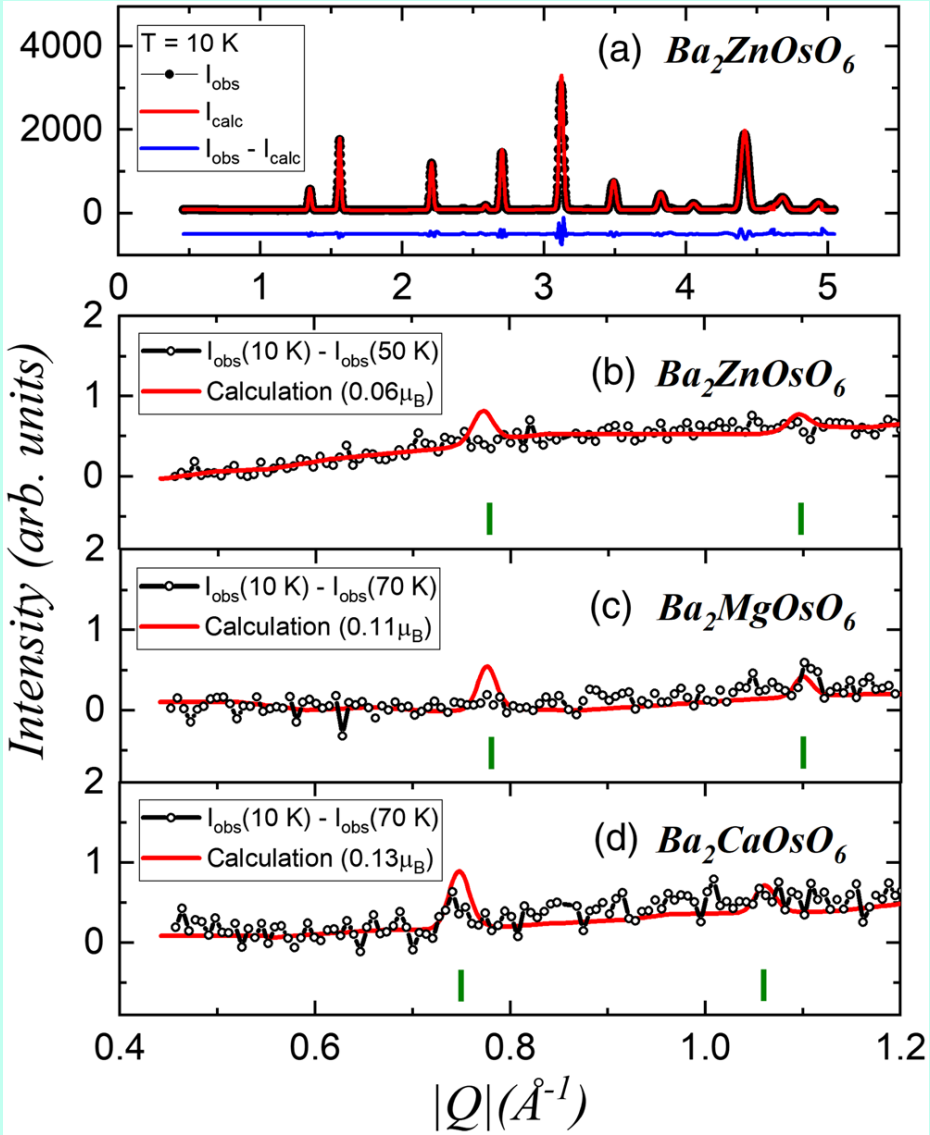
Introduction to the use of the program BASIREPS

Simulation:

If you determine the symmetry allowed magnetic structures for a given magnetic propagation vector you can simulate the magnetic diffraction pattern and determine the upper limit of the magnetic moment.

Absence of dipolar magnetic order in cubic $5d^2$ Double Perovskites → Strong indication for Octupolar order

Sarah



10 h (10 K) – 10 h (50 K):
$\mu_{Os} < 0.06\ \mu_B$

Introduction to the use of the program BASIREPS

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A short sumamary:

The different irreducible representations contain the information on the possible magnetic structures, which fulfill the symmetry restrictions of the crystal structure.

The basis vectors of these irreducible representations can be calculated using existing programs (BASIREPS, SARAH) and serve for the refinement of the magnetic structures.

Magnetic symmetry analysis limits dramatically the number of magnetic structures, which have to be taken into account for the refinement.

Magnetic symmetry analysis helps to avoid "wrong" solutions.

Magnetic symmetry analysis indicates the possible existence of a structural phase transition.

Magnetic symmetry analysis allows to simulate magnetic diffraction patterns to determine lower limits for magnetic moments.

Apart from BASIREPS there is as well the Program SARAh which does the same thing

SARAh: http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/