

Tb³⁺/Tb⁴⁺ Charge ordering in KTb₃F₁₂: magnetic frustration in the Tb³⁺ sublattice

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Magnetic properties of a mixed-valence (III/IV) terbium fluoride KTb₃F₁₂

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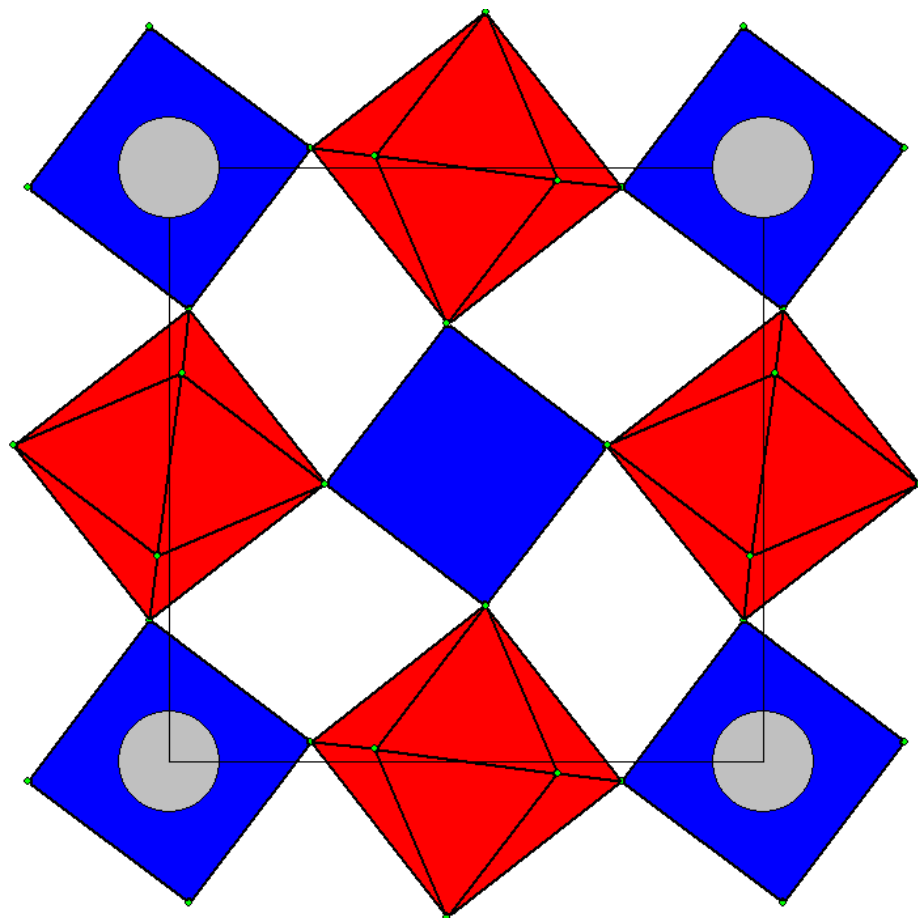
INFORMATION ABOUT THE SAMPLE

- A simple case where symmetry analysis gives a very important information to interpret the results.
- Space Group: $I4/m$, propagation vector $\mathbf{k}=(1,0,0)$ ($a=7.63\text{\AA}$, $c=7.52\text{\AA}$), 2 magnetic atoms $\{\text{Tb}_a, \text{Tb}_b\}$ in special positions (3 magnetic atoms per primitive unit cell)
Eight 1D-Irreps some of them are complex.
- The final magnetic structure is reduced to the refinement of only a single parameter.

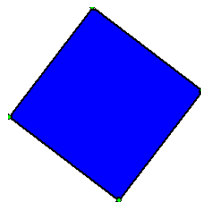
STEPS FOR USING THE SIMULATED ANNEALING OPTION IN FULLPROF FOR MAGNETIC STRUCTURE DETERMINATION

- 1- Refine the crystal structure in the paramagnetic state
- 1'- If there is a structural phase transition at T_N/T_C , then refine the crystal structure in the ordered state using high-Q reflections without magnetic contribution
- 2- Indexing: determine the propagation vector using the program **K-SEARCH**
- 3- In the ordered state fix all structural parameters and introduce the magnetic contribution as a new phase using the Le Bail fit mode and putting **More**=1, **Irf**=1 and **Jvi**=11
- 4- The above step produces an output file *.int that can be used as input data for Simulated Annealing runs

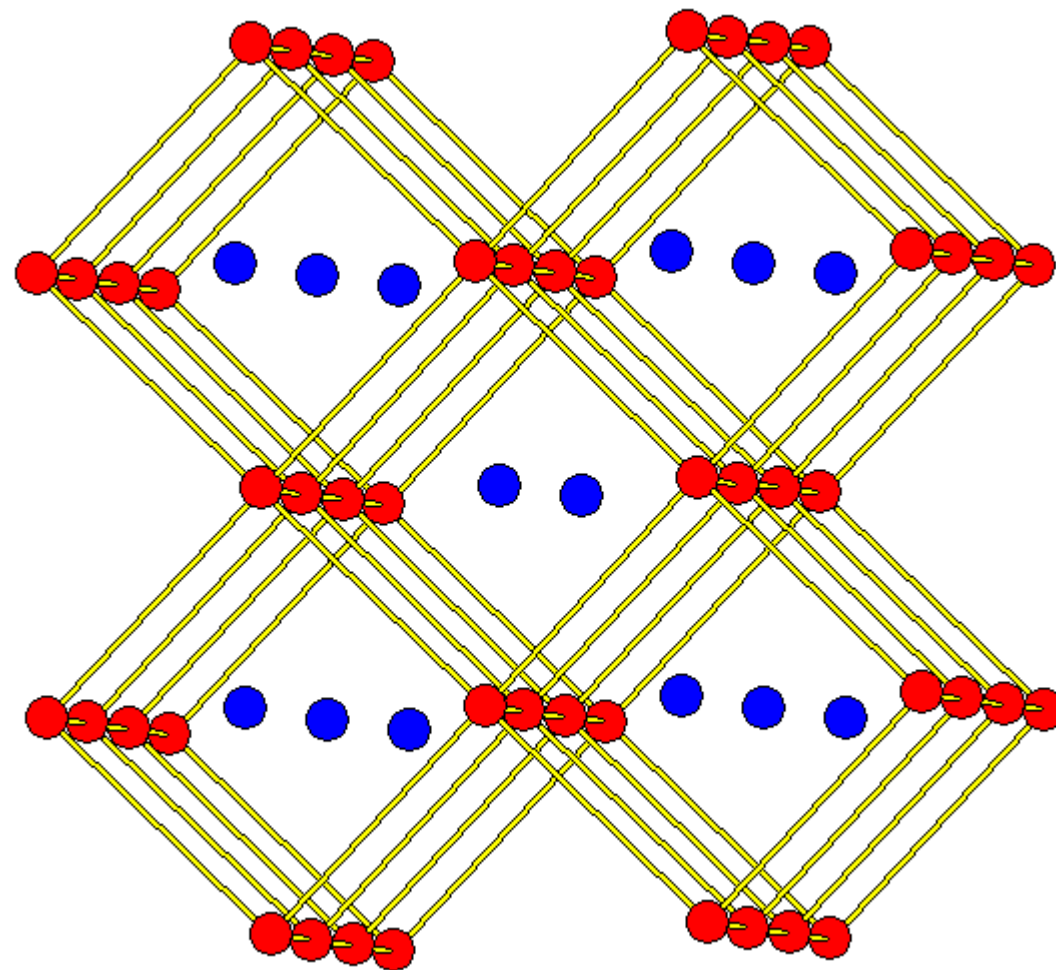
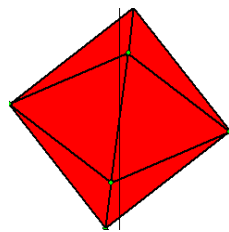
SIMULATED ANNEALING IN FULLPROF WITH A SIMPLE EXAMPLE: $\text{KTb}_3\text{F}_{12}$



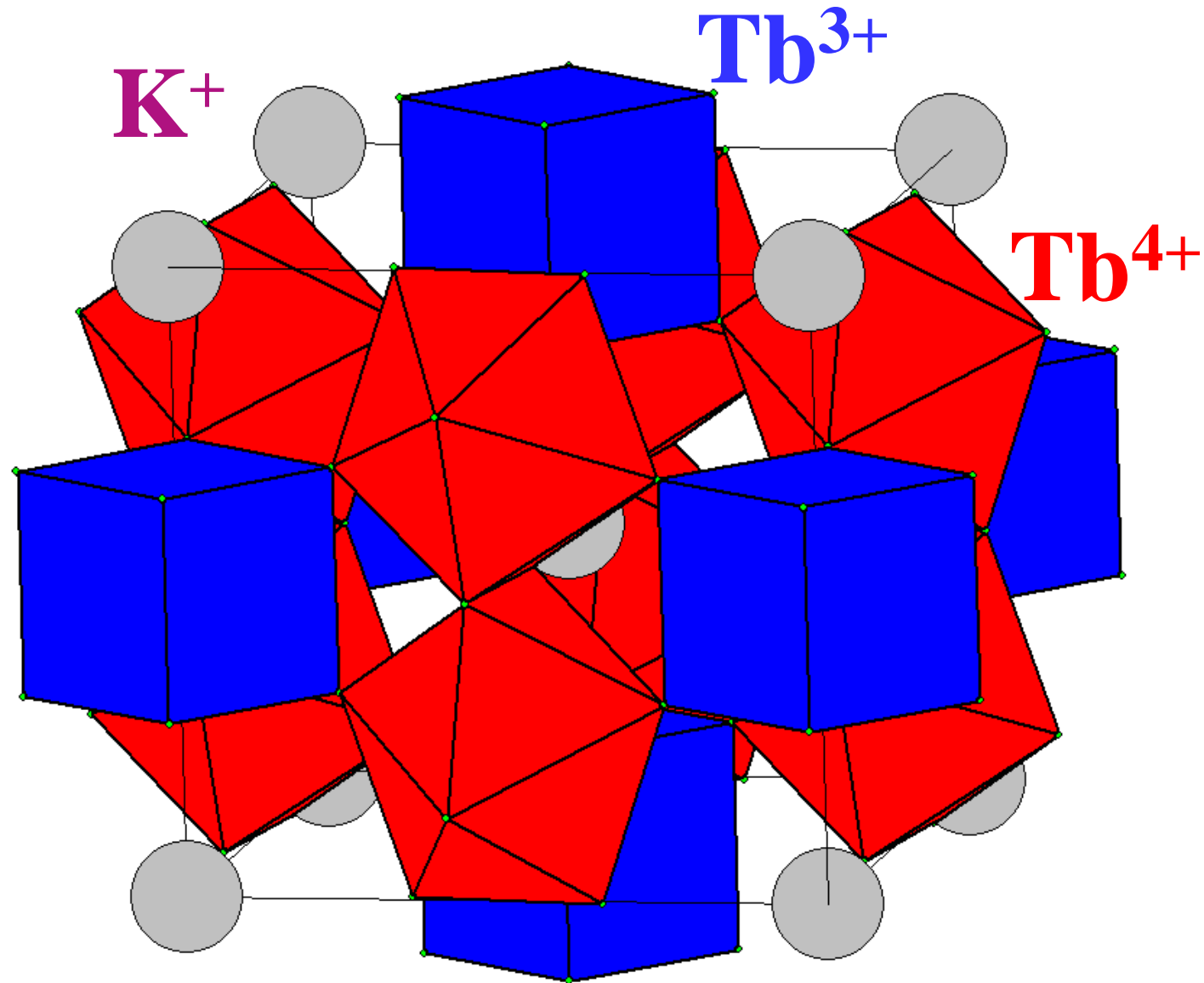
Tb^{3+}



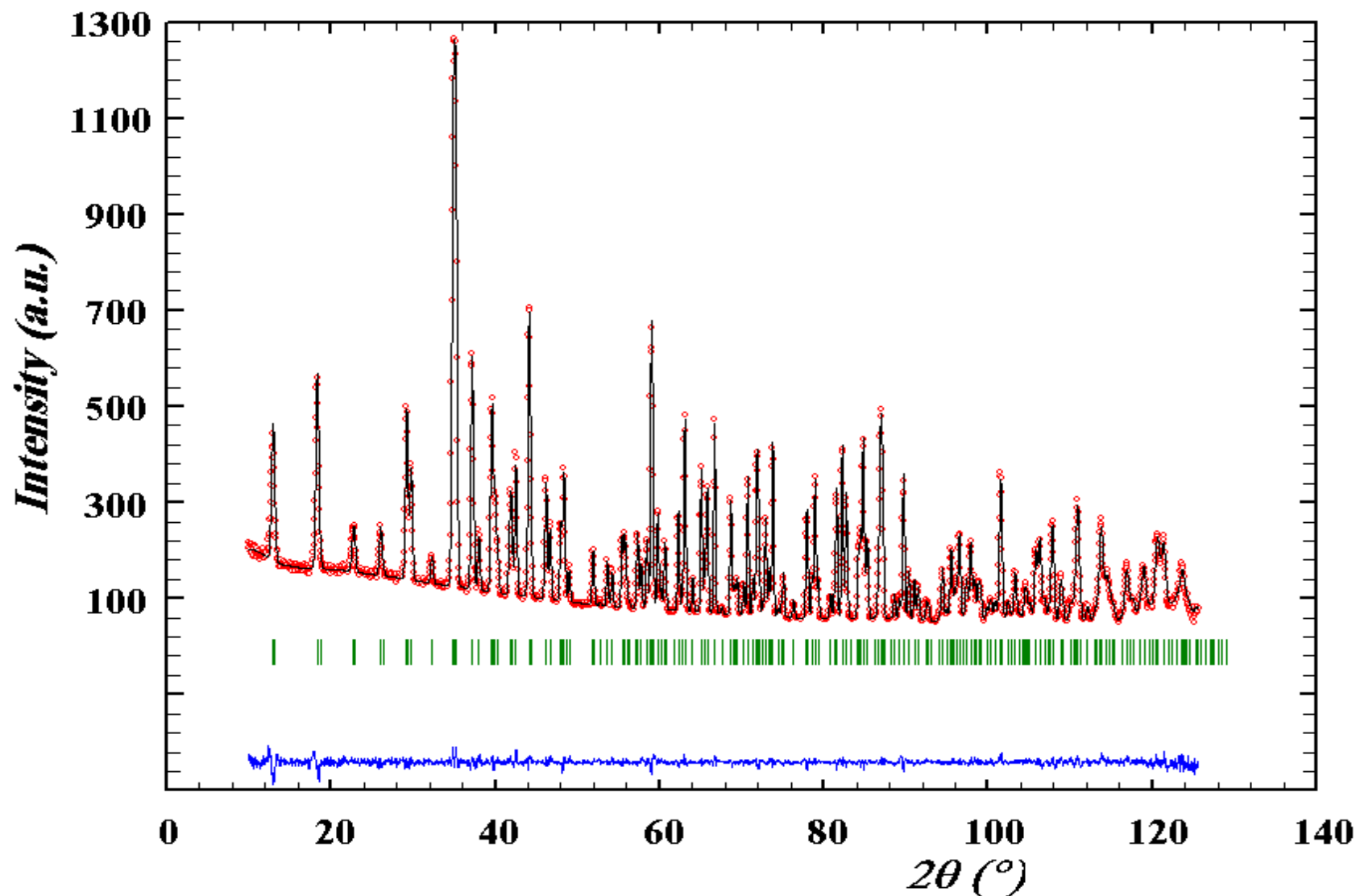
Tb^{4+}



Structure of $\text{KTb}^{3+}\text{Tb}_2^{4+}\text{F}_{12}$



REFINEMENT OF THE CRYSTAL STRUCTURE OF: $\text{KTb}_3\text{F}_{14}$ AT 5K IN THE PARAMAGNETIC STATE



This allows to know all structural parameters near the Néel temperature ($T_N=3.65\text{K}$)

How to prepare a PCR file for generating integrated intensities for SAnn?

```
!-----
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:      0.45
!-----
KTb3F12-M
!
!Nat Dis Ang Pr1 Pr2 Pr3 Ubt Irf Isy Str Furth      ATZ      Nvk Npr More
    0   0   0 0.0 0.0 1.0  2  -1  0   0   0      0.000    1   7  1
!
!Jvi Jdi Hel Sol Mom Ter Brind  RMua  RMub  RMuc  Jtyp  Nsp_Ref
  11  0   0   0   0   0 1.0000 0.0000 0.0000 0.0000  1   0
!
I -1                                <--Space group symbol
!-----> Profile Parameters for Pattern #  1
!  Scale      Shape1      Bov      Str1      Str2      Str3      Strain-Model
  4.3356      0.00000      0.00000      0.00000      0.00000      0.00000      0
    0.00000      0.000      0.000      0.000      0.000      0.000
!      U      V      W      X      Y      GauSiz      LorSiz
    0.794074  -0.280000      0.080000      0.000000      0.045159      0.000000      0.000000
    61.000      0.000      0.000      0.000      71.000      0.000      0.000
!      a      b      c      alpha      beta      gamma
    7.695388      7.695388      7.540170      90.000000      90.000000      90.000000
    31.00000      31.00000      41.00000      0.00000      0.00000      0.00000
!  Pref1      Pref2      Asy1      Asy2      Asy3      Asy4      S_L      D_L
    1.00000      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
!  Propagation vectors:
    1.0000000      0.0000000      0.0000000      Propagation Vector  1
    0.000000      0.000000      0.000000
```

How to prepare a PCR file for generating profile intensities for SAnn?

From fp2k.inf document (9 October 2019)

Simulated annealing has been extended to work with the full powder diffraction profile, for that it is necessary to make a previous run using a LeBail fit, putting `Ipr=-2` and include the name of the `*.spr` file in the next line of the PCR file. Moreover the creation of a cluster of intensities is needed but it is necessary to make `Jvi=13`, for the case of superspace description, or `Jvi=11` for other cases.

This `*.int` file is used in the simulated annealing work with the full profile only for reading the indices of reflections. The information contained in the `*.spr` file is really what is used in the process of minimizing the cost function. The PRF file for visualizing the final profile is identical to that generated using the Rietveld method.

In case of several phases, the calculated profile of the LeBail Fit corresponding to the desired phase is output to the `*.spr` file instead of the total observed profile. This is very useful in case of known impurities (treated using the Rietveld method with fixed positions) to extract an unknown phase or to extract pure magnetic reflections to solve a magnetic structure. If the user wants to use the calculated profile even in the case of a single phase in the LeBail fit the value of `Jvi` should be negative: `Jvi=-13` or `Jvi=-11`.

How to prepare a PCR file for generating profile intensities for SAnn?

Example of the relevant parts of a PCR file for preparing the simulated annealing work. We have used superspace operators to generate only incommensurate magnetic reflections (keyword "[mag_only](#)") because we are treating a difference pattern. Notice that this PCR file generates the profile information in the file [test.spr](#) and the reflection clusters in the file: [test-pm1_ctrl.int](#)

.....Start of the example

COMM My Title: LeBail fit to prepare a SAnn work with the full powder profile

! Current global Chi2 (Bragg contrib.) = 999999

! Files => DAT-file: xxxxx.dat, PCR-file: test-pm

!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut

1 0 1 25 2 0 1 1 0 0 1 0 0 0 0 0 0 1

!

!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana

[-2](#) 0 1 1 1 0 4 0 0 3 8 0 0 0 0 0 0 !

! File name (or filecode) of the *.spr file containing profile points information

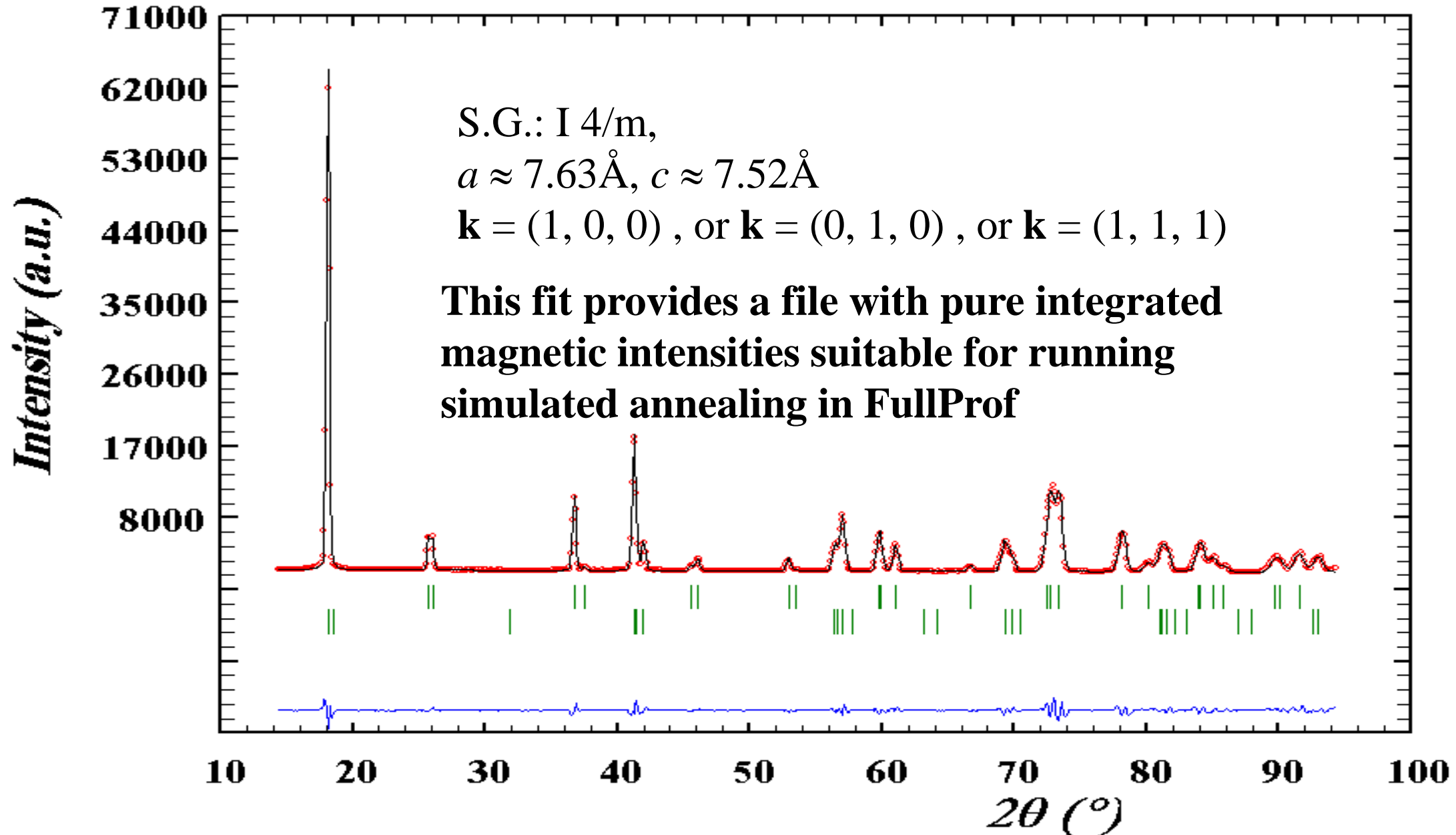
[test.spr](#)

.....

How to prepare a PCR file for generating profile intensities for SAnn?

```
!-----
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#   1:      0.08
!-----
Magnetic Structure of: mag_only
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irr Isy Str Furth      ATZ      Nvk Npr More
   0   0   0 0.0 0.0 1.0  2  -1  2   0   0      956.092    1   7   1
!
!Jvi Jdi Hel Sol Mom Ter Brind  RMua  RMub  RMuc  Jtyp  Nsp_Ref Ph_Shift N_Dom
  13   0   0   0   0   0 1.0000 0.0000 0.0000 0.0000    1      0      0      0
!
Pmn2_11' (0,0,g)s0ss 31.1.9.2.m124.2  <--Magnetic Super Space group symbol
Parent Setting: Pnm2_11' (0,0,g)ss0s (a1,a2,a3,a4;0000)
! Generators
Genr  -x1+1/2,-x2,x3+1/2,x4,1
Genr  x1,-x2+1/2,x3,x4+1/2,1
Genr  x1,x2,x3,x4+1/2,-1
N_qc  1
Q_coef
. . . . .
```

LE BAIL FIT: $\text{KTB}_3\text{F}_{14}$



Example of *.int file generated by *FullProf* using *More=1*, *Jvi=11*

Phase No: 2 Ktb3F12-M					Overlapped reflections re-grouped		
(4i4,2f12.2,i4,3f14.4)					<- Format of h,k,l,iv, Int, sigma, multip.		
2.4260 0 2					<- Wavelength, type of data, powder ind.		
1					<- Number of propagation vectors		
1	1.00000	0.00000	0.00000	<- Propagation vector			
0	0	0	1	-1.00	47.42	2	
-1	1	0	1	18893.78	67.06	2	
-1	0	1	1	0.00	1.00	2	
-2	-1	1	1	-1.00	0.00	2	
-2	1	1	1	-1.00	0.00	2	
0	-1	1	1	-1.00	0.00	2	
0	1	1	1	0.00	0.00	2	
0	2	0	1	-1.00	7.41	2	
0	-2	0	1	-1.00	1.00	2	
1	-1	0	1	-1.00	7.41	2	
1	1	0	1	-1.00	7.41	2	
-3	0	1	1	-1.00	0.42	2	
-1	-2	1	1	-1.00	0.42	2	
-1	2	1	1	-1.00	0.42	2	
1	0	1	1	6566.70	14.85	2	
-2	0	2	1	-1.00	2.24	2	
-1	-1	2	1	-1.00	2.24	2	
-1	1	2	1	-1.00	2.24	2	
0	0	2	1	1327.23	4.48	2	

.....

Negative intensity means that
the reflection contributes to the
next positive observation

How to prepare a Simulating Annealing PCR file?

Cry=3 tells the program to use the Simulated annealing mode

Nre=8 number of free parameters with box constraints

```
COMM Ktb3F12 - T=1.4K - G4.1
! Files =>
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   0   1   0   0   0   0   0   0   0   0   0   0   8   3   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   0   0   0   3   5   0   0   0   0   0   0
!
!NCY  Eps  R_at  R_an  R_pr  R_gl      Thmin      Step      Thmax      PSD      Sent0
   1  0.10  1.00  1.00  1.00  1.00      15.0000      0.100000      94.9000      0.000      0.000
!
!
      8      !Number of refined parameters
!-----
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#   1:      2.03
!-----
Ktb3F12-M
!
. . . . .
```

How to prepare a Simulating Annealing PCR file?

```

!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   4  -1   0   0      0.000    1   0   0
!
I -1                                <--Space group symbol
!Nsym Cen Laue MagMat
   1   1   1   1
!
SYMM  x,y,z
MSYM  u,v,w,0.0
!
!Atom Typ  Mag Vek   X       Y       Z       Biso   Occ       Rm       Rphi  Rtheta
!      Im    Iphi   Itheta  beta11  beta22  beta33  MagPh
T3_1  JTB3   1   0   0.00000 0.00000 0.50000 0.06775 1.00000   0.09    0.976   0.000
           0.00    0.00    0.00    0.00    0.00    0.00    0.00   11.00    31.00    41.00
           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
T4_1  JTB3   1   0   0.00000 0.50000 0.25000 0.03425 1.00000   1.909    1.927    0.00
           0.00    0.00    0.00    0.00    0.00    0.00    0.00   21.00    51.00    61.00
           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
T4_2  JTB3   1   0   0.00000 0.50000 0.75000 0.03425 1.00000   1.909    0.561    0.00
           0.00    0.00    0.00    0.00    0.00    0.00    0.00   21.00    71.00    81.00
           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

```

No symmetry constraints:
Spherical components, $m_{\text{Tb}^{4+}(1)} = m_{\text{Tb}^{4+}(2)}$

How to prepare a Simulating Annealing PCR file?

No profile parameters,
part of the file similar to single crystal format

```
! Scale Factors
! Sc1      Sc2      Sc3      Sc4      Sc5      Sc6
  4.336     0.000     0.000     0.000     0.000     0.000
    0.00     0.00     0.00     0.00     0.00     0.00
! Extinction Parameters
! Ext1      Ext2      Ext3      Ext4      Ext5      Ext6      Ext7      Ext-Model
  0.000     0.000     0.000     0.000     0.000     0.000     0.000     0
    0.00     0.00     0.00     0.00     0.00     0.00     0.00     0.00
!      a      b      c      alpha      beta      gamma
  7.695388  7.695388  7.540171  90.000000  90.000000  90.000000
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
! x-Lambda/2 +      Not yet used parameters
  0.000000  0.000000  0.000000  0.000000  0.000000
    0.00     0.00     0.00     0.00     0.00
! Propagation vectors:
  1.000000  0.000000  0.000000      Propagation Vector  1
  0.000000  0.000000  0.000000
```

How to prepare a Simulating Annealing PCR file?

Parameter number **Ranges and steps** **boundary conditions**

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

1	0.0000	9.0000	0.5831	0	Rmom_T3_1
2	0.0000	9.0000	0.0582	0	Rmom_T4_1
3	0.0000	360.0000	2.0000	1	RPhi_T3_1
4	0.0000	180.0000	2.0000	0	RThet_T3_1
5	0.0000	360.0000	2.0000	1	RPhi_T4_1
6	0.0000	180.0000	2.0000	0	RThet_T4_1
7	0.0000	360.0000	2.0000	1	RPhi_T4_2
8	0.0000	180.0000	2.0000	0	RThet_T4_2

!

T_ini	Anneal	Accept	NumTemps	NumThCyc	InitConf
5.000	0.900	0.050	45	0	0

! NCyclM Nsolu Num_Ref Nscalef NAlgor

150	1	110	0	0
-----	---	-----	---	---

Number of reflections to consider **Automatic treatment(1) or fixed(0) scale factor** **Corana algorithm Initial step = range** **Random initial configuration**



Representation analysis for magnetic structure determination of $\text{KTb}_3\text{F}_{12}$

Space group: $I4/m$

Cell parameters: $a=7.695 \text{ \AA}$, $c=7.540 \text{ \AA}$

Propagation vector $\mathbf{k} = (1, 0, 0)$

Results of *BasIreps*:

$G_{\mathbf{k}} = I4/m$ (invariant vector), $\mathbf{k} \equiv -\mathbf{k}$

8 irreducible representations of dimension 1 (some complex!)

Site Tb^{3+} : 1 sublattice \Rightarrow 1: (0,0,1/2)

$$\Gamma_m = \Gamma_1 \oplus \Gamma_5 \oplus \Gamma_7$$

Site Tb^{4+} : 2 sublattices \Rightarrow 1: (0,1/2,1/4) 2: (0,1/2,3/4)

$$\Gamma_m = \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_5 \oplus \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$$

Representation analysis for magnetic structure determination of $\text{KTb}_3\text{F}_{12}$

Basis functions of the Irreducible representations

Site Tb^{3+} :	$\Gamma_1 : \mathbf{S}_{\mathbf{k}} = (0, 0, \nu)$
1 sublattice (0,0,1/2)	$\Gamma_5 : \mathbf{S}_{\mathbf{k}} = (\nu, 0, 0) + i(0, -\nu, 0)$
	$\Gamma_7 : \mathbf{S}_{\mathbf{k}} = (\nu, 0, 0) + i(0, \nu, 0)$

Possible magnetic structures: $\Gamma_1, \Gamma_5 \oplus \Gamma_7$

Representation analysis for magnetic structure determination of $\text{KTb}_3\text{F}_{12}$

Site Tb^{4+} : 2 sublattices $(0,1/2,1/4)$, $(0,1/2,3/4)$

$$\Gamma_2 : \mathbf{S}_k(1) = (0, 0, u); \quad \mathbf{S}_k(2) = (0, 0, -u)$$

$$\Gamma_3 : \mathbf{S}_k(1) = (0, 0, u); \quad \mathbf{S}_k(2) = (0, 0, u)$$

$$\Gamma_5 : \mathbf{S}_k(1) = (u, 0, 0) + i(0, u, 0); \quad \mathbf{S}_k(2) = (u, 0, 0) + i(0, u, 0)$$

$$\Gamma_6 : \mathbf{S}_k(1) = (u, 0, 0) + i(0, -u, 0); \quad \mathbf{S}_k(2) = (-u, 0, 0) + i(0, u, 0)$$

$$\Gamma_7 : \mathbf{S}_k(1) = (u, 0, 0) + i(0, -u, 0); \quad \mathbf{S}_k(2) = (u, 0, 0) + i(0, -u, 0)$$

$$\Gamma_8 : \mathbf{S}_k(1) = (u, 0, 0) + i(0, u, 0); \quad \mathbf{S}_k(2) = (-u, 0, 0) + i(0, -u, 0)$$

Possible magnetic structures:

$$\Gamma_2, \quad \Gamma_3, \quad \Gamma_5 \oplus \Gamma_7, \quad \Gamma_6 \oplus \Gamma_8$$

Symmetry analysis for magnetic structure determination of $\text{KTb}_3\text{F}_{12}$

Site Tb^{3+} : 1 sublattice $(0,0,1/2)$

Site Tb^{4+} : 2 sublattices $(0,1/2,1/4)$, $(0,1/2,3/4)$,

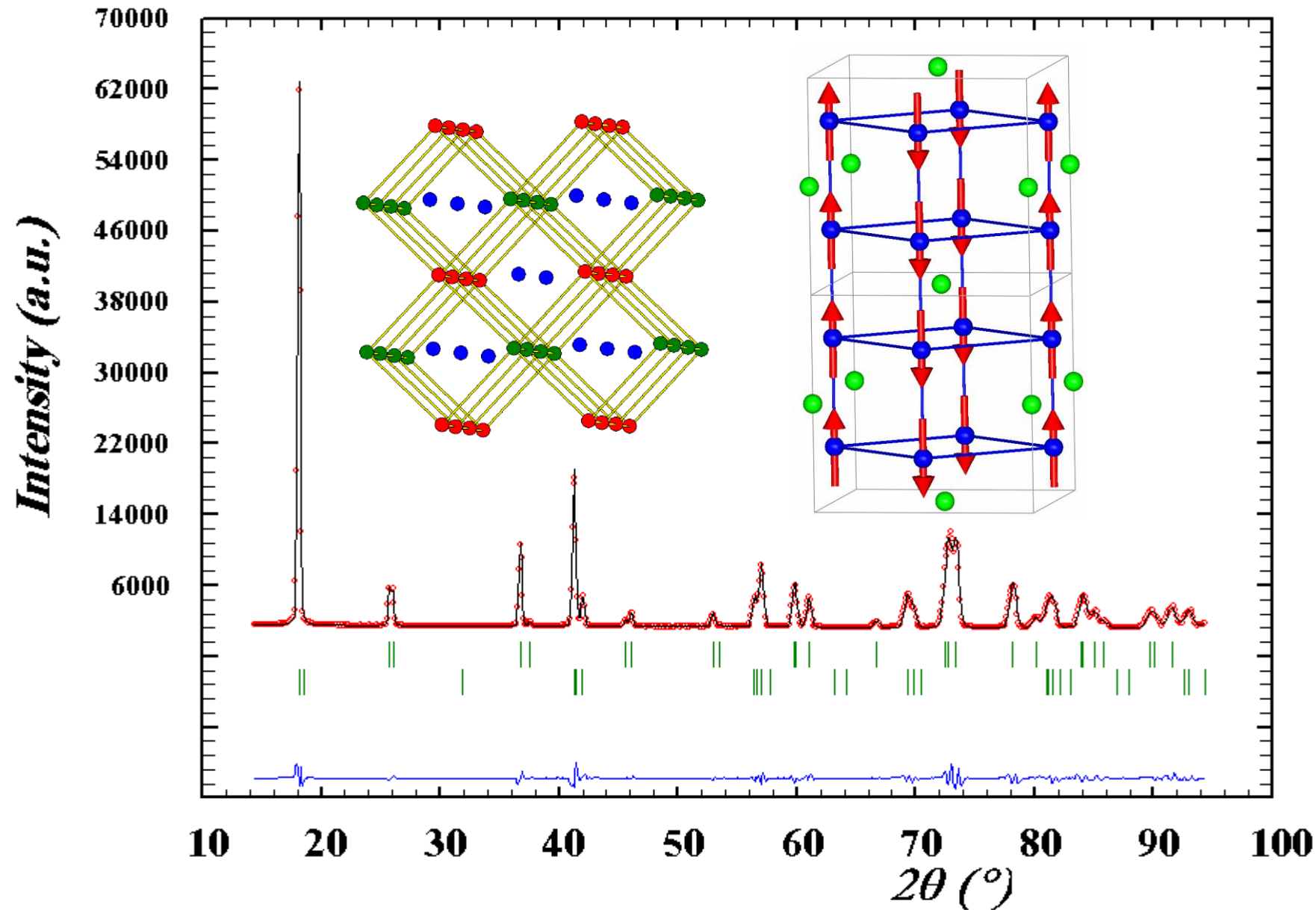
Possible magnetic structures:

Only the mixed representation $\Gamma_5 \oplus \Gamma_7$ is possible for having magnetic moments in both sites. We have found experimentally that the Tb^{4+} orders according to the representation Γ_3 that is not allowed for the Tb^{3+} site, so this ion should not have a magnetic moment.

The representation Γ_3 is one dimensional, so there exist a magnetic Shubnikov group that is easily found realizing that for this representation the four-fold axis is primed (negative character) contrary to the mirror plane.

The Shubnikov group is: $I_p 4' / m$

Rietveld refinement of the magnetic structure of $\text{KTb}_3\text{F}_{12}$ on G4.1 (LLB)



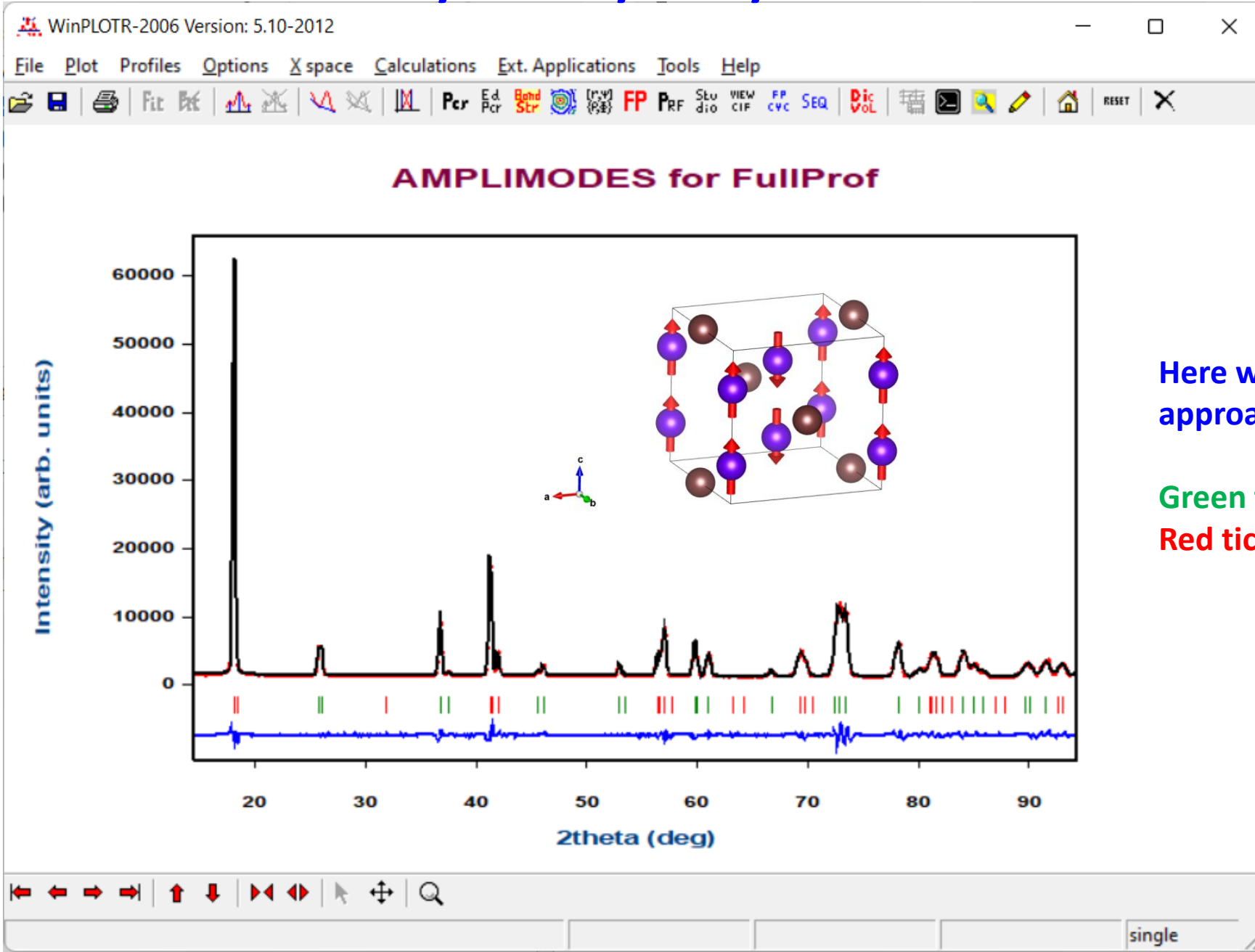
$\text{KTb}_3\text{F}_{12}$
T=1.5K, SG: $I4/m$
a=7.63Å, c=7.52Å
 $\mathbf{k}=(1,0,0)$

Symmetry analysis with ISODISTORT

The results obtained with Simulated Annealing can be straightforwardly corroborated by symmetry analysis using Baslreps or ISODISTORT

ISODISTORT generates a PCR file with the proper magnetic group and the basis vectors of the irreducible representations involved in the magnetic phase transition.

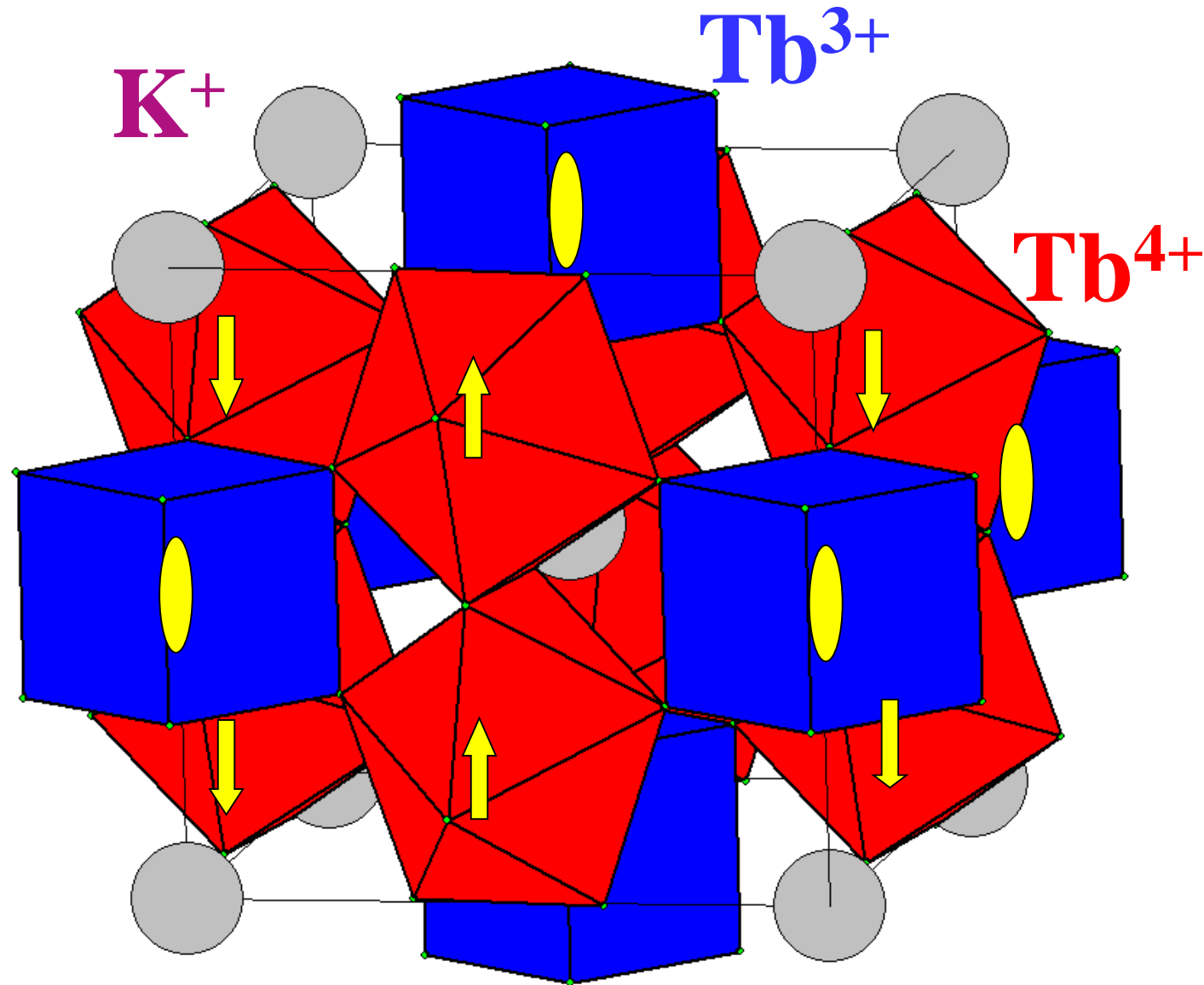
Symmetry analysis with ISODISTORT



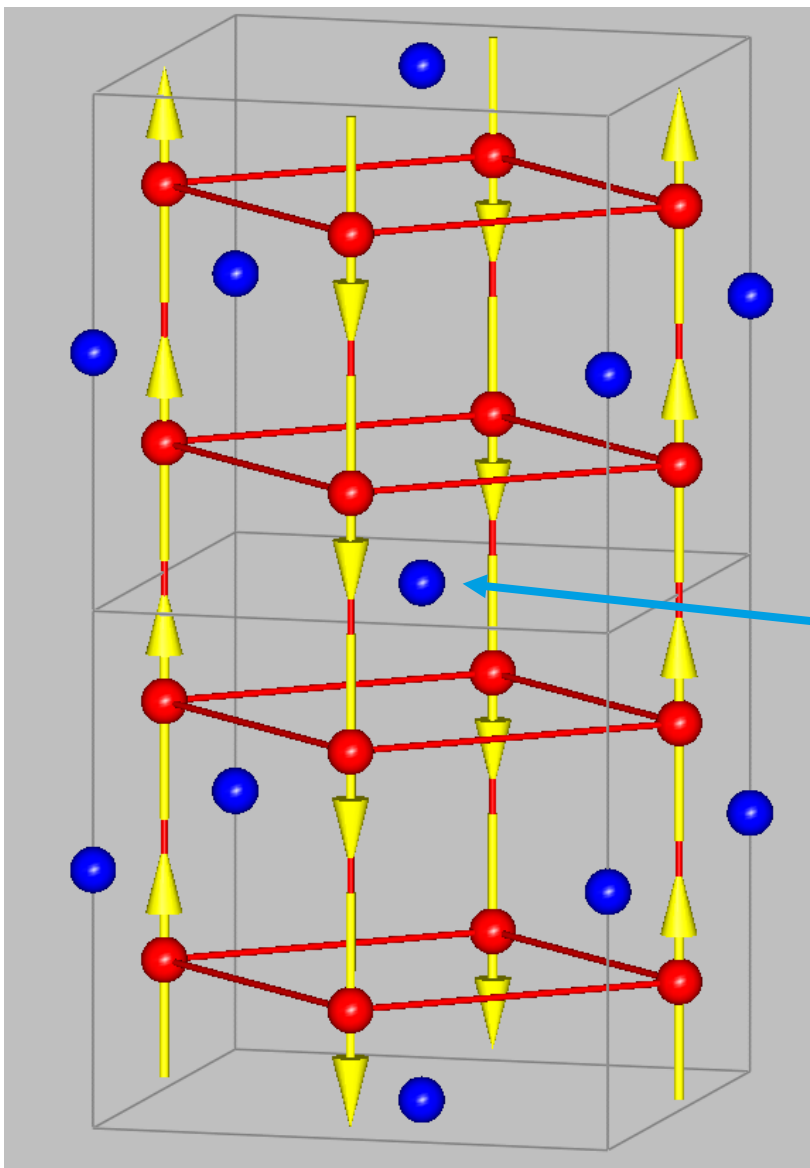
Here we have used the symmetry modes approach using a single phases

Green ticks: Nuclear contribution
Red ticks: Magnetic contribution

Magnetic Structure of $\text{KTb}^{3+}\text{Tb}_2^{4+}\text{F}_{12}$



Magnetic Structure of $\text{KTb}^{3+}\text{Tb}_2^{4+}\text{F}_{12}$



Only Tb^{4+} is ordered as F chains along c that are AF coupled in the basal plane

Tb^{3+} does not have static magnetic moment because the molecular field due to Tb^{4+} is exactly zero at its site. Tb^{3+} remains paramagnetic

Conclusions about the determination of the magnetic structure of $\text{KTb}_3\text{F}_{12}$

Simulated Annealing:

In this case, the information contained in the powder diffraction pattern is enough to obtain the magnetic structure without symmetry constraints.

Representation Analysis:

The irreducible representation involved in the magnetic phase transition, Γ_3 , is not allowed for the site of Tb^{3+} , so that this ion remains disordered (idle spin, “spin fou”). One can verify that in the Shubnikov group I_p4'/m (OG notation) the magnetic point group of the site $2b(\text{Tb}^{3+})$, $4'/m$, is not admissible.

Full Symmetry Analysis with ISODISTORT

This combines magnetic space groups together with basis functions of irreducible representations. The obtained magnetic group in BNS setting is PA_2/m .