FullProf
for magnetic structure determination and refinement
example: KTb_3F_{12}

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Steps for magnetic structure determination using powder diffraction

Step	Input
Propagation vector(s) ***SuperCell***	***Peak positions of magnetic reflections*** ⇐ ***Cell parameters***
Symmetry Analysis ***BasIreps***	***Propagation vector*** ⇐ ***Space Group*** ***Atom positions***
Magnetic structure solution (Sim. Ann.) ***FullProf***	***Integrated intensities*** ⇐ ***Atomic components of basis functions***

Problems of magnetic structure refinement using powder diffraction

Input

Magnetic structure Refinement
FullProf

⇐ ***Complete structural model should be provided***

Different runs of SAnn jobs may give you an idea of the degeneracy of solutions for your particular problem.

In many cases the number of free parameters is too much high to be refined by LSQ: try to reduce the number of parameters or make soft constraints.

Use spherical components of Fourier coefficients in order to have better control of the amplitude of the magnetic moment

Tutorial
Magnetic Structure of KTb_3F_{12}

- A simple case where symmetry analysis gives a very important information to interpret the results.
- Space Group: *I4/m*, prop. vector **k**=(1,0,0) (a=7.63Å, c=7.52Å), 2 magnetic atoms {Tb_a,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 within *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

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 and **`Jvi`**=11

4- The above step produces an output file *.int that can be used as input data for Simulated Annealing runs

Tb^{3+}/Tb^{4+} Charge ordering in KTb_3F_{12}: magnetic frustration in the Tb^{3+} sublattice

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Magnetic properties of a mixed-valence (III/IV) terbium fluoride KTb_3F_{12}

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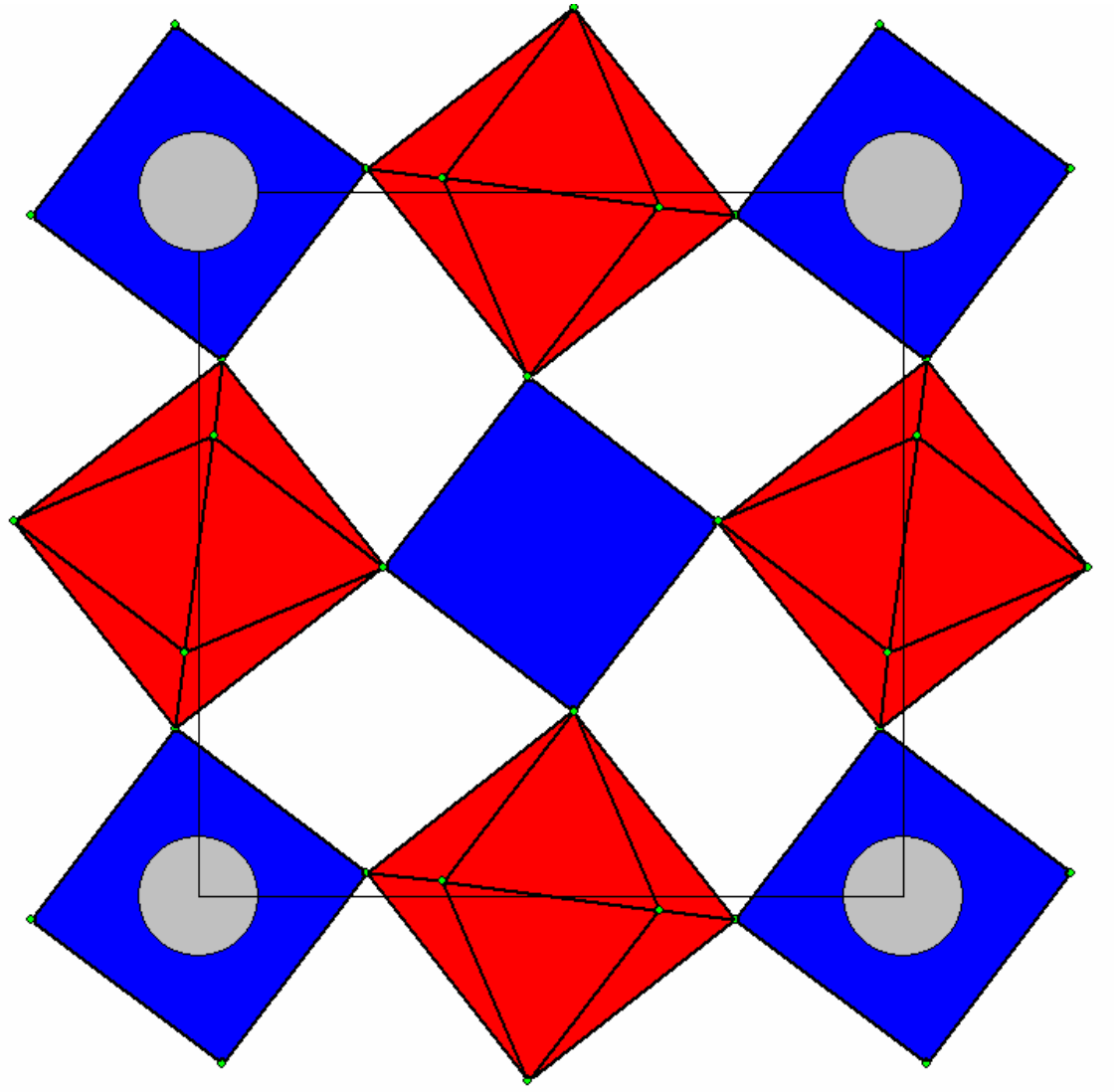
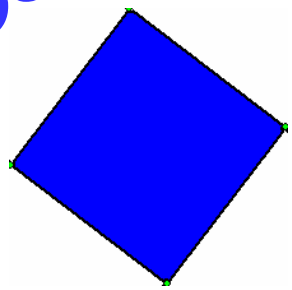
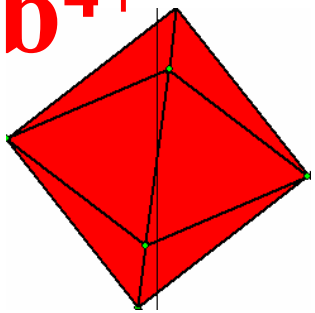
Structure of $KTb^{3+}Tb_2^{4+}F_{12}$



Tb^{3+}



Tb^{4+}



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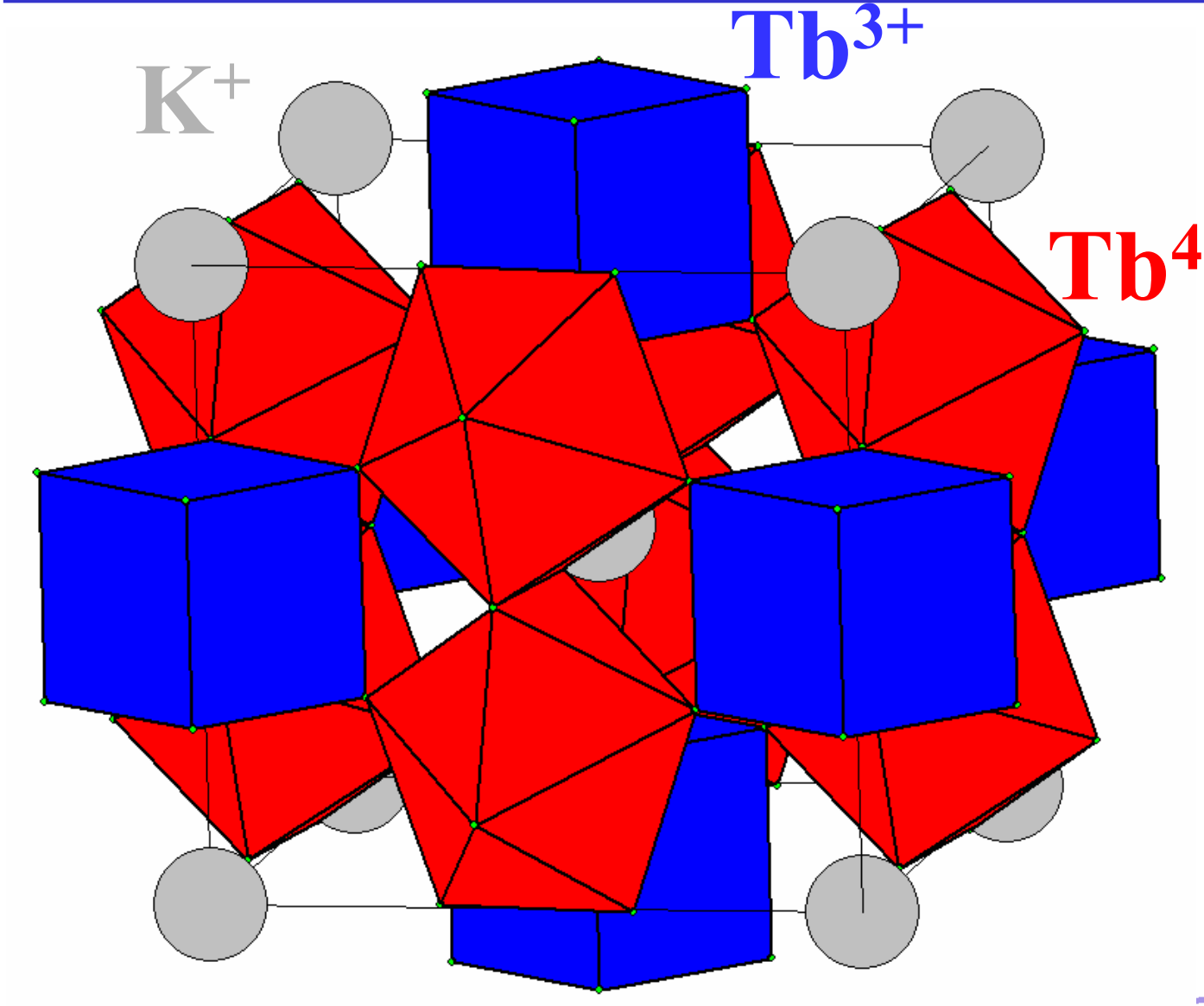
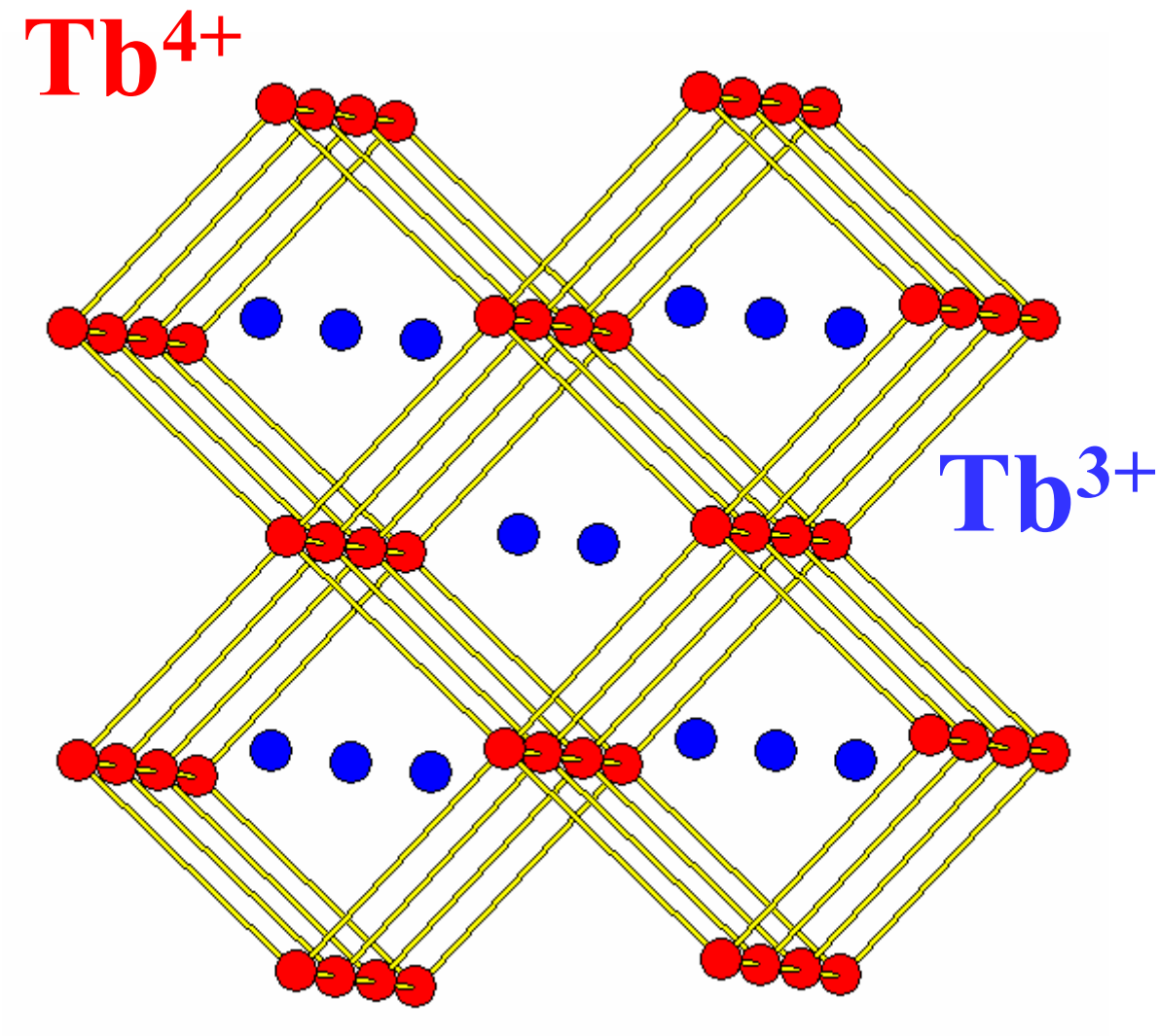
Structure of $KTb^{3+}Tb_2^{4+}F_{12}$



Topology of Magnetic ions in $KTb^{3+}Tb_2^{4+}F_{12}$



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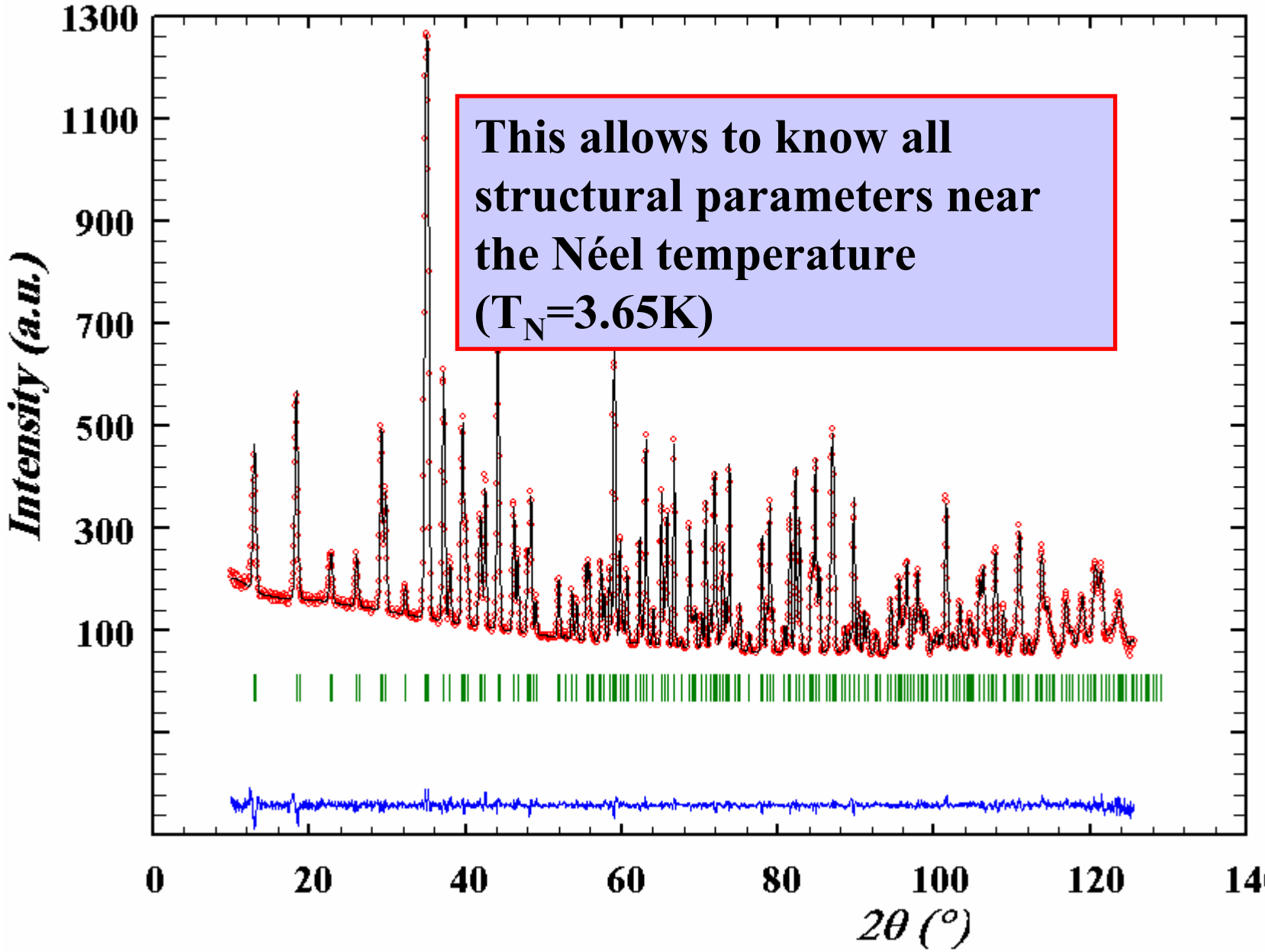
Refinement of the crystal structure of: KTb_3F_{14} at 5K



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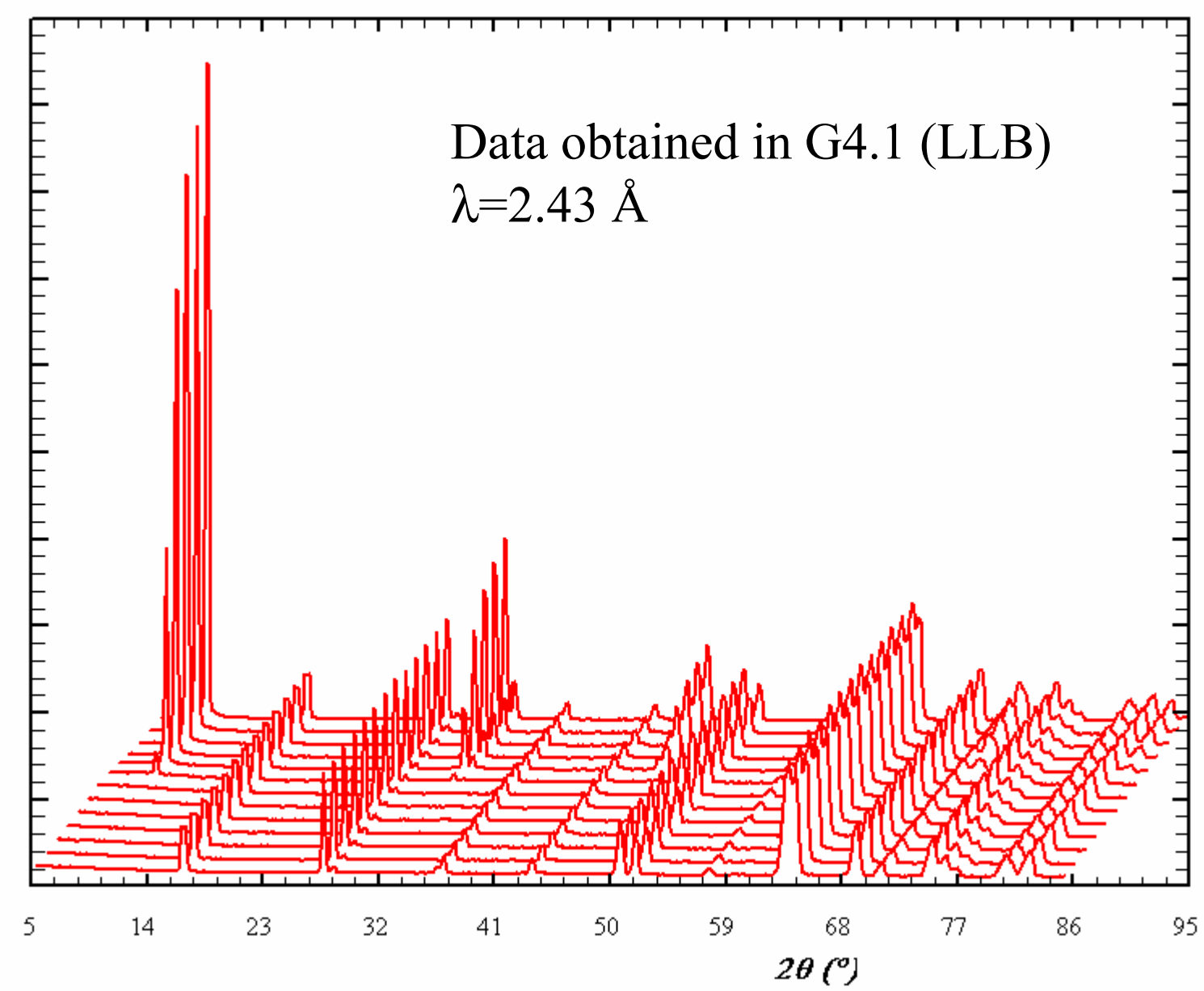
Powder diffraction patterns of KTb_3F_{14}



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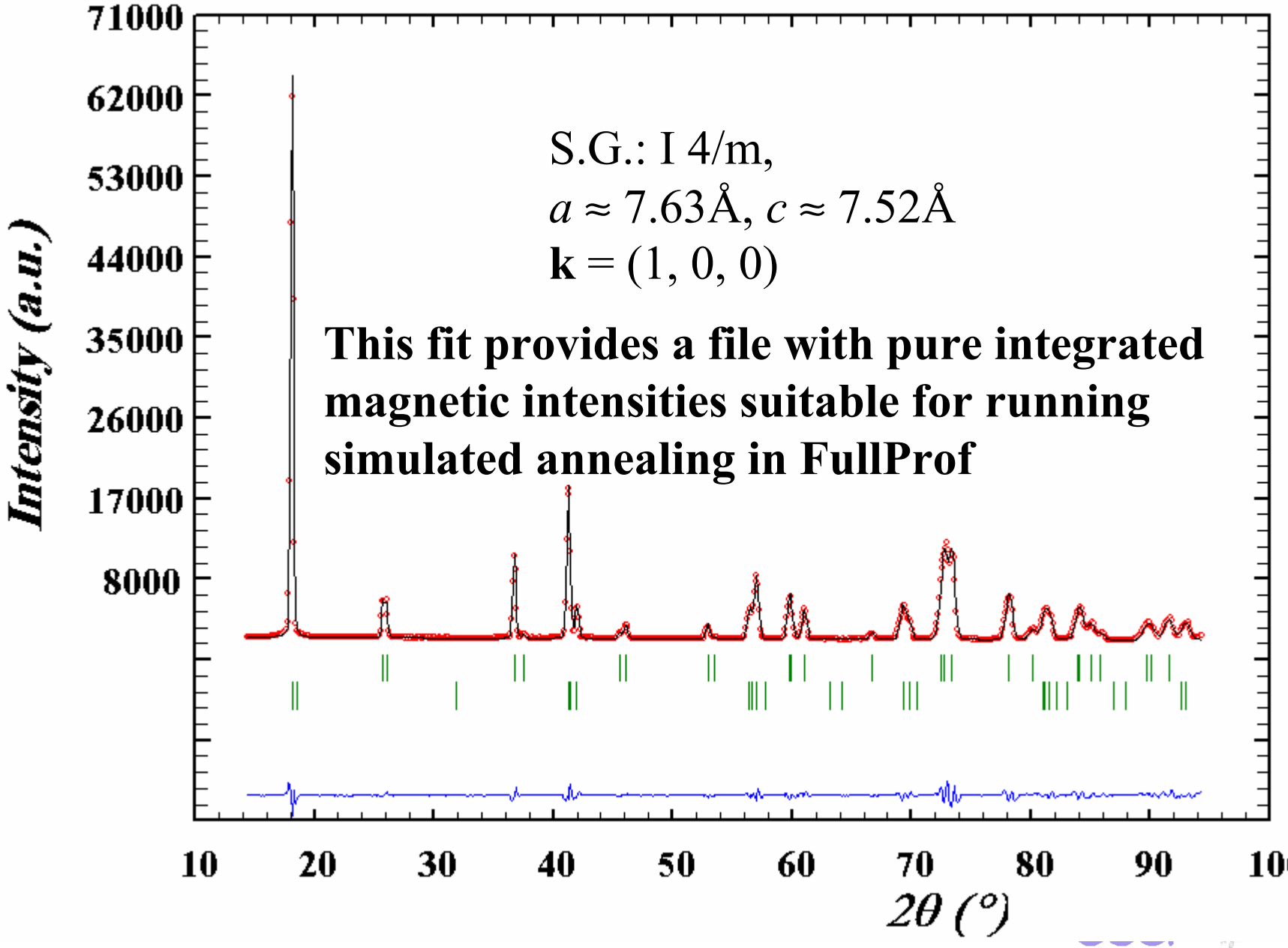
```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:     0.45
!-------------------------------------------------------------------------------
KTb3F12-M
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       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
```

Profile matching (Le Bail) fit: KTb_3F_{14}



S.G.: I 4/m,
$a \approx 7.63$Å, $c \approx 7.52$Å
$\mathbf{k} = (1, 0, 0)$

This fit provides a file with pure integrated magnetic intensities suitable for running simulated annealing in FullProf

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   Negative intensity means that
 -2  -1   1   1        -1.00        0.00   2   the reflection contributes to the
 -2   1   1   1        -1.00        0.00   2   next positive observation
  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
. . . . . . . . . . . . . . . . . . . . . . . .
```

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   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   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   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   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_Tb^{4+}(1)= m_Tb^{4+}(2)

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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
!     a            b            c          alpha        beta         gamma
    7.695388    7.695388    7.540171   90.000000   90.000000   90.000000
     0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
! x-Lambda/2  +           Not yet used parameters
      0.00000      0.00000      0.00000      0.00000      0.00000
         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 Simulating Annealing PCR file?

Parameter number

Ranges and steps

boundary conditions

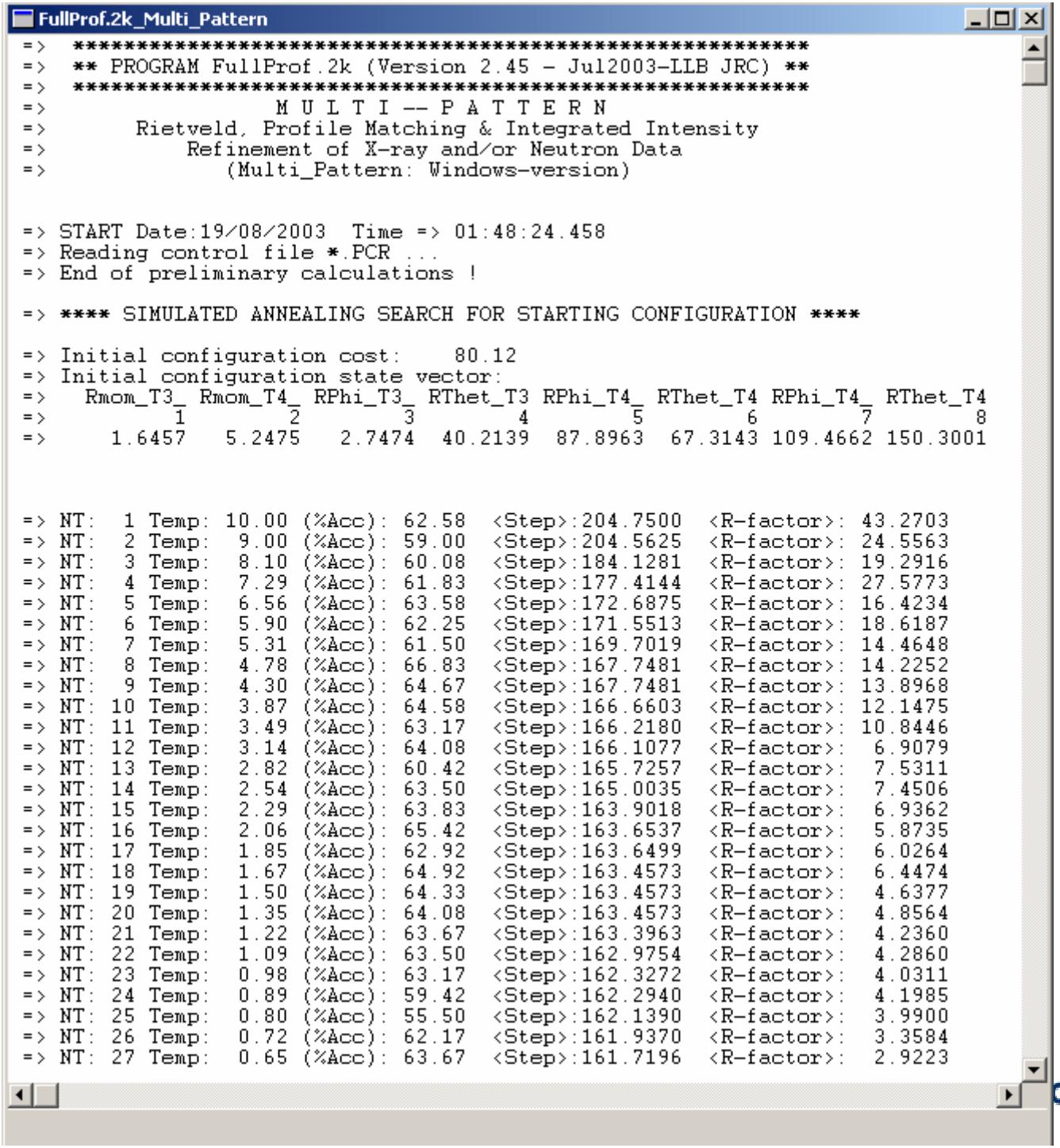
```
! Limits for selected parameters (+ steps & BoundCond for SA):
    1        0.0000       9.0000       0.5831    0   Rmom_T3_1
    2        0.0000       9.0000       0.0582    0   Rmom_T4_1
    3        0.0000     360.0000       2.0000    1   RPhi_T3_1
    4        0.0000     180.0000       2.0000    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
```

Random initial configuration

Corana algorithm
Initial step = range

Number of reflections to consider

Automatic treatment(1) or fixed(0) scale factor


FullProf.2k_Multi_Pattern
=> **
=> ** PROGRAM FullProf.2k (Version 2.45 - Jul2003-LLB JRC) **
=> **
=>   M U L T I -- P A T T E R N
=>   Rietveld, Profile Matching & Integrated Intensity
=>   Refinement of X-ray and/or Neutron Data
=>   (Multi_Pattern: Windows-version)
=> START Date:19/08/2003 Time => 01:48:24.458
=> Reading control file *.PCR ...
=> End of preliminary calculations !
=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****
=> Initial configuration cost: 80.12
=> Initial configuration state vector:
=>   Rmom_T3_ Rmom_T4_ RPhi_T3_ RThet_T3 RPhi_T4_ RThet_T4 RPhi_T4_ RThet_T4
=>   1   2   3   4   5   6   7   8
=>   1.6457   5.2475   2.7474 40.2139 87.8963 67.3143 109.4662 150.3001
=> NT: 1 Temp: 10.00 (%Acc): 62.58 <Step>:204.7500 <R-factor>: 43.2703
=> NT: 2 Temp: 9.00 (%Acc): 59.00 <Step>:204.5625 <R-factor>: 24.5563
=> NT: 3 Temp: 8.10 (%Acc): 60.08 <Step>:184.1281 <R-factor>: 19.2916
=> NT: 4 Temp: 7.29 (%Acc): 61.83 <Step>:177.4144 <R-factor>: 27.5773
=> NT: 5 Temp: 6.56 (%Acc): 63.58 <Step>:172.6875 <R-factor>: 16.4234
=> NT: 6 Temp: 5.90 (%Acc): 62.25 <Step>:171.5513 <R-factor>: 18.6187
=> NT: 7 Temp: 5.31 (%Acc): 61.50 <Step>:169.7019 <R-factor>: 14.4648
=> NT: 8 Temp: 4.78 (%Acc): 66.83 <Step>:167.7481 <R-factor>: 14.2252
=> NT: 9 Temp: 4.30 (%Acc): 64.67 <Step>:167.7481 <R-factor>: 13.8968
=> NT: 10 Temp: 3.87 (%Acc): 64.58 <Step>:166.6603 <R-factor>: 12.1475
=> NT: 11 Temp: 3.49 (%Acc): 63.17 <Step>:166.2180 <R-factor>: 10.8446
=> NT: 12 Temp: 3.14 (%Acc): 64.08 <Step>:166.1077 <R-factor>: 6.9079
=> NT: 13 Temp: 2.82 (%Acc): 60.42 <Step>:165.7257 <R-factor>: 7.5311
=> NT: 14 Temp: 2.54 (%Acc): 63.50 <Step>:165.0035 <R-factor>: 7.4506
=> NT: 15 Temp: 2.29 (%Acc): 63.83 <Step>:163.9018 <R-factor>: 6.9362
=> NT: 16 Temp: 2.06 (%Acc): 65.42 <Step>:163.6537 <R-factor>: 5.8735
=> NT: 17 Temp: 1.85 (%Acc): 62.92 <Step>:163.6499 <R-factor>: 6.0264
=> NT: 18 Temp: 1.67 (%Acc): 64.92 <Step>:163.4573 <R-factor>: 6.4474
=> NT: 19 Temp: 1.50 (%Acc): 64.33 <Step>:163.4573 <R-factor>: 4.6377
=> NT: 20 Temp: 1.35 (%Acc): 64.08 <Step>:163.4573 <R-factor>: 4.8564
=> NT: 21 Temp: 1.22 (%Acc): 63.67 <Step>:163.3963 <R-factor>: 4.2360
=> NT: 22 Temp: 1.09 (%Acc): 63.50 <Step>:162.9754 <R-factor>: 4.2860
=> NT: 23 Temp: 0.98 (%Acc): 63.17 <Step>:162.3272 <R-factor>: 4.0311
=> NT: 24 Temp: 0.89 (%Acc): 59.42 <Step>:162.2940 <R-factor>: 4.1985
=> NT: 25 Temp: 0.80 (%Acc): 55.50 <Step>:162.1390 <R-factor>: 3.9900
=> NT: 26 Temp: 0.72 (%Acc): 62.17 <Step>:161.9370 <R-factor>: 3.3584
=> NT: 27 Temp: 0.65 (%Acc): 63.67 <Step>:161.7196 <R-factor>: 2.9223

Simulated Annealing run of *FullProf*

FullProf.2k_Multi_Pattern

```
=> NT:  73 Temp:   0.01 (%Acc): 41.42  <Step>: 14.1507  <R-factor>:  1.7957
=> NT:  74 Temp:   0.00 (%Acc): 38.75  <Step>: 13.1795  <R-factor>:  1.7943
=> NT:  75 Temp:   0.00 (%Acc): 41.92  <Step>: 11.1802  <R-factor>:  1.7894
=> NT:  76 Temp:   0.00 (%Acc): 40.67  <Step>: 10.9559  <R-factor>:  1.7851
=> NT:  77 Temp:   0.00 (%Acc): 43.25  <Step>: 10.5303  <R-factor>:  1.7886
=> NT:  78 Temp:   0.00 (%Acc): 39.67  <Step>:  9.9443  <R-factor>:  1.7834
=> NT:  79 Temp:   0.00 (%Acc): 40.50  <Step>:  9.4706  <R-factor>:  1.7828
=> NT:  80 Temp:   0.00 (%Acc): 42.33  <Step>:  9.1180  <R-factor>:  1.7809
=> NT:  81 Temp:   0.00 (%Acc): 43.25  <Step>:  8.7911  <R-factor>:  1.7829
=> NT:  82 Temp:   0.00 (%Acc): 41.42  <Step>:  8.7285  <R-factor>:  1.7799
=> NT:  83 Temp:   0.00 (%Acc): 38.58  <Step>:  8.5013  <R-factor>:  1.7779
=> NT:  84 Temp:   0.00 (%Acc): 39.75  <Step>:  7.7504  <R-factor>:  1.7774
=> NT:  85 Temp:   0.00 (%Acc): 45.50  <Step>:  6.3718  <R-factor>:  1.7776

=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   110 reflections):

=> Sol#: 1 RF2=   1.772 ::
=>   Rmom_T3_ Rmom_T4_ RPhi_T3_ RThet_T3 RPhi_T4_ RThet_T4 RPhi_T4_ RThet_T4
=>         1        2         3        4        5        6        7        8
=>     0.6694   6.8896 133.9639  89.7299  47.1463   7.8380  46.9585   7.8030




=>              CPU Time:    89.018 seconds
=>                           1.484 minutes

=> END   Date:19/08/2003  Time => 01:49:53.476

=> Data Files :
=>             - 1p4-pm2
=> PCR  File   : simann
```

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Symmetry analysis for magnetic structure determination of KTb_3F_{12}

Space group: *I4/m*
Cell parameters: a=7.695 Å, c=7.540 Å
Propagation vector **k** = (1, 0, 0)
Results of ***BasIreps***:
$G_{\mathbf{k}}$= *I4/m* (invariant vector), **k ≡ -k**
8 irreducible representations of dimension 1 (some complex!)

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

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

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

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

Symmetry analysis for magnetic structure determination of KTb_3F_{12}

Basis functions of the Irreducible representations

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

$$\Gamma_1 : \mathbf{S_k} = (0,0,v)$$

$$\Gamma_5 : \mathbf{S_k} = (v,0,0) + i(0,-v,0)$$

$$\Gamma_7 : \mathbf{S_k} = (v,0,0) + i(0,\ \ v,0)$$

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

Symmetry analysis for magnetic structure determination of KTb_3F_{12}

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

$$\Gamma_2 : \mathbf{S_k}(1) = (0,0,u); \qquad \mathbf{S_k}(2) = (0,0,-u)$$

$$\Gamma_3 : \mathbf{S_k}(1) = (0,0,u); \qquad \mathbf{S_k}(2) = (0,0,u)$$

$$\Gamma_5 : \mathbf{S_k}(1) = (u,0,0) + i(0,u,0); \qquad \mathbf{S_k}(2) = (u,0,0) + i(0,u,0)$$

$$\Gamma_6 : \mathbf{S_k}(1) = (u,0,0) + i(0,-u,0); \qquad \mathbf{S_k}(2) = (-u,0,0) + i(0,u,0)$$

$$\Gamma_7 : \mathbf{S_k}(1) = (u,0,0) + i(0,-u,0); \qquad \mathbf{S_k}(2) = (u,0,0) + i(0,-u,0)$$

$$\Gamma_8 : \mathbf{S_k}(1) = (u,0,0) + i(0,u,0); \qquad \mathbf{S_k}(2) = (-u,0,0) + i(0,-u,0)$$

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 KTb_3F_{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),

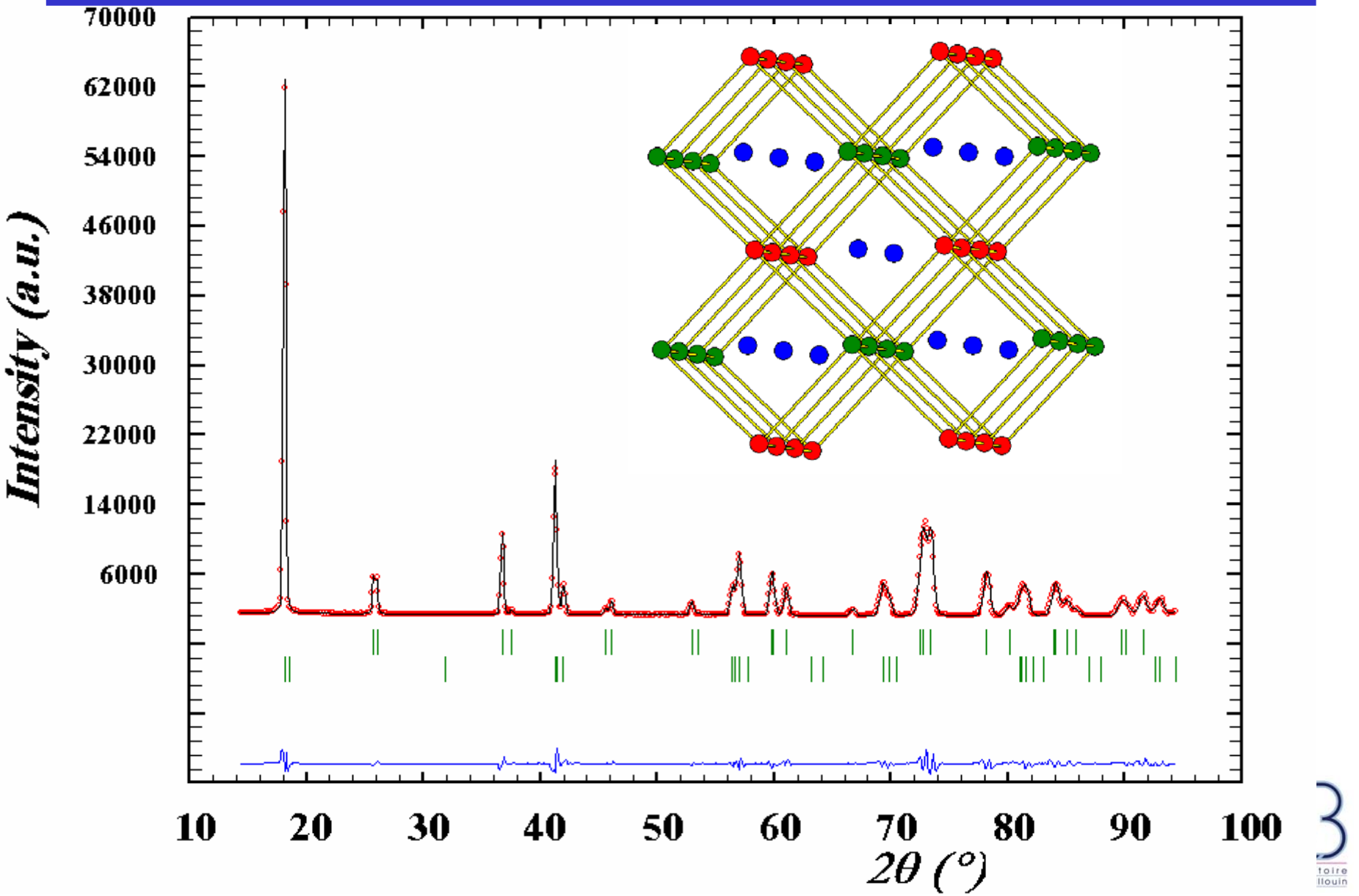
Possible magnetic structures:

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.

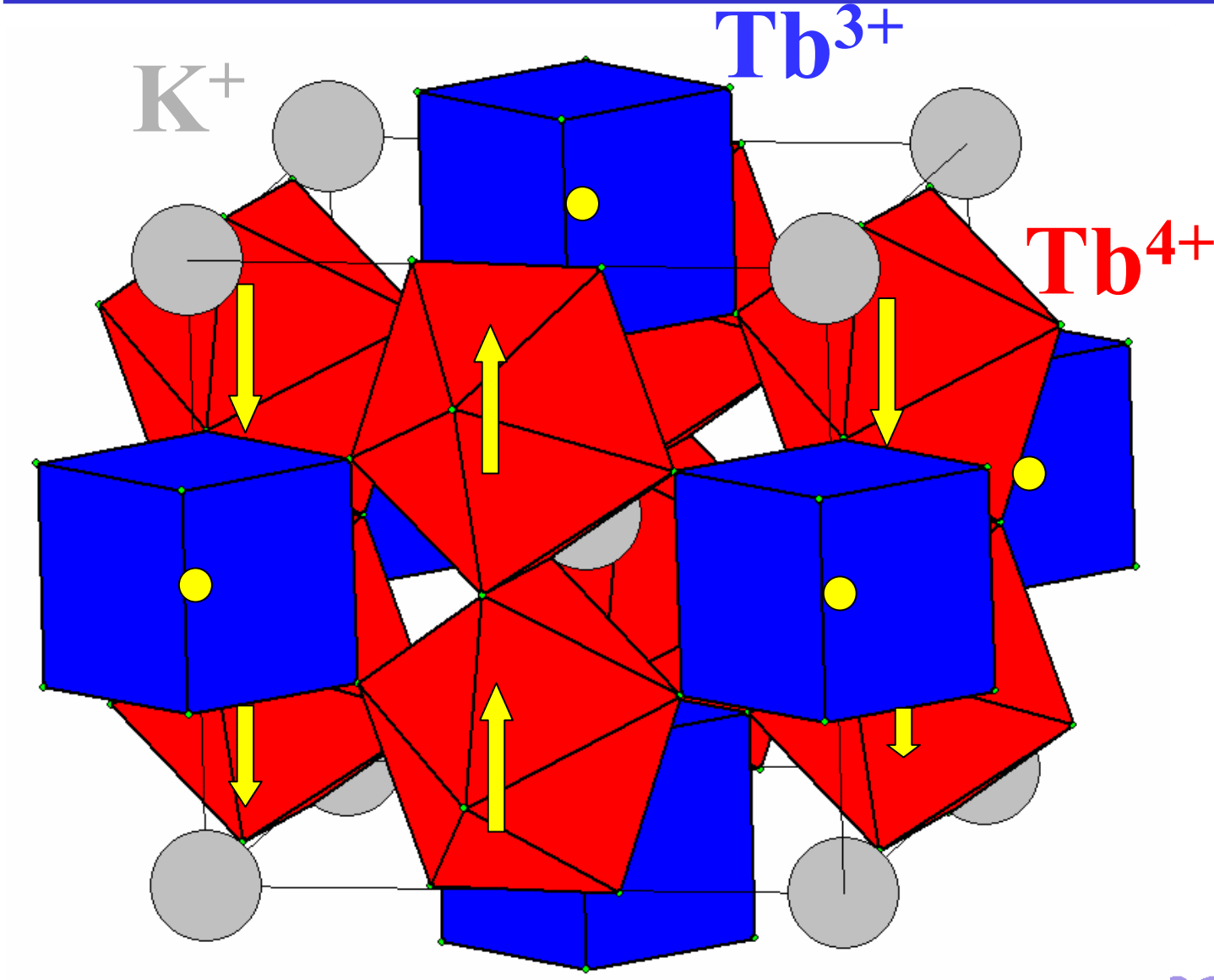
The representation Γ_3 is one dimensional, so there exist a magnetic Shubnikov group that is easily found realizing that for this representation the four-fold axis is primed (negative character) contrary to the mirror plane.

The Shubnikov group is: I_P4'/m

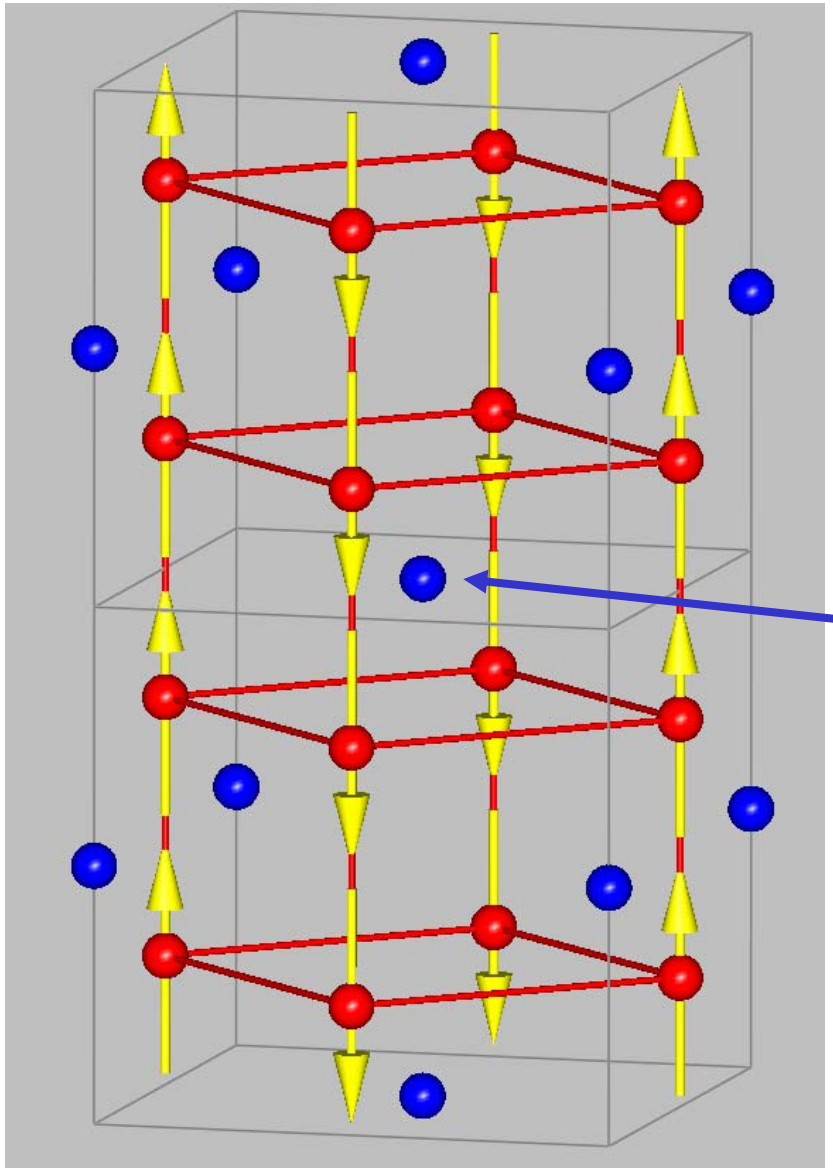
Rietveld refinement of the magnetic structure of KTb_3F_{12} on G4.1 (LLB)



Magnetic Structure of $KTb^{3+}Tb_2^{4+}F_{12}$



Magnetic Structure of $KTb^{3+}Tb_2^{4+}F_{12}$



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

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Conclusions about the determination of the magnetic structure of KTb_3F_{12}

Simulated Annealing:

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

Symmetry 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 the magnetic point group of the site *2b*(Tb^{3+}), *4'/m,* is not admissible.

The end

Downloading of Software **http://www.ccp14.ac.uk**

Graphical tutorial run-through of most of this software is located via (**"look before you try"**):

http://www.ccp14.ac.uk/tutorial/

FullProf Suite and related programs:

ftp://ftp.cea.fr/pub/llb/divers/

Set of directories with different programs, documents, tutorials and examples of powder diffraction data analysis