

FullProf School

Simulated Annealing on
powder and single crystal
data for determining
magnetic structures



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OUTLINE

- 1: LE BAIL FITS FOR EXTRACTING INTEGRATED INTENSITIES**
 - 2: SOLVING (MAGNETIC) STRUCTURES IN DIRECT SPACE**
 - 3: WHAT IS SIMULATED ANNEALING?**
 - 4: HOW TO USE SIMULATED ANNEALING IN FULLPROF.**
- A VERY SIMPLE EXAMPLE $\text{KTb}_3\text{F}_{12}$.**

LE BAIL FITS FOR EXTRACTING INTEGRATED INTENSITIES

$$y_{ci} = \sum_{\{h\}} I_h \Omega(T_i - T_h) + b_i$$

When the resolution function of the diffractometer and the cell parameters are known approximately, one can try to get the value of the integrated intensities from the powder diffraction pattern.

Problem: If one uses least squares to refine the values of I_h (Pawley) one has to introduce strong constraints because the problem is not well defined, sometimes negative intensities can be obtained due to overlap.

LE BAIL FITS FOR EXTRACTING INTEGRATED INTENSITIES

$$y_{ci} = \sum_{\{h\}} I_h \Omega(T_i - T_h) + b_i$$

$$'I_h(obs)' = I_h \sum_i \left\{ \frac{\Omega(T_i - T_h)(y_{obs,i} - B_i)}{(y_{calc,i} - B_i)} \right\}$$

Provides 'observed' integrates intensities for calculating Bragg R-factor

Starting from an arbitrary set of values for I_h and using the Rietveld formula for calculating the Bragg R-factor, it is possible to obtain the so called ' $I_h(obs)$ '.

These intensities can be taken as new values for I_h and repeat iteratively the procedure up to no net improvement of the whole profile is reached.

LE BAIL FITS FOR EXTRACTING INTEGRATED INTENSITIES

$$'I_h(obs)' = I_h \sum_i \left\{ \frac{\Omega(T_i - T_h)(y_{obs,i} - B_i)}{(y_{calc,i} - B_i)} \right\}$$

The values of I_h are of low quality when the overlap of reflections is important. This is the reason one cannot use these integrated intensities directly for solving the structure.

Many methods of solving the structure from powders (direct methods) use a special strategy for changing the partitioning of overlapped reflections

SOLVING STRUCTURES

Classically, crystal structure determination is considered as a process to determine the “phases” of the structure factors

$$\rho(\mathbf{r}) = \sum_{\{\mathbf{h}\}} F_{\mathbf{h}} \exp\{-2\pi i \mathbf{h} \mathbf{r}\}$$

$$\rho(\mathbf{r}) = \sum_{\{\mathbf{h}\}} |F_{\mathbf{h}}| \exp\{-2\pi i (\mathbf{h} \mathbf{r} + \Phi_{\mathbf{h}})\}$$

For a centrosymmetric structure $\Phi_{\mathbf{h}}$ is 0 or 1/2

The knowledge of all phases for the measured structure factors provides a density map from which the structure is derived (chemically recognised).

SOLVING STRUCTURES

The resolution of the “phase problem” is the goal of the crystal structure determination methods

Direct Methods tackle the problem looking for phase relations (tangent formula) between structure factors of different reflections
Direct methods need a high number of reflections and good resolution (powders)

Direct methods are generally very efficient

But ...

sometimes direct methods fail in solving particular structures
or
cannot be applied because poor data quality (low resolution)

SOLVING STRUCTURES

$$F(\mathbf{h}) = \sum_{j=1}^n O_j f_j(\mathbf{h}) T_j \sum_s \exp \left\{ 2\pi i [\mathbf{h} \{S|\mathbf{t}\}_s \mathbf{r}_j] \right\}$$

If the chemical composition and the space group are known we have to determine just the $3n$ variables

$$F_{obs}(\mathbf{h})_r \approx \left| \sum_{j=1}^n O_j f_j T_j \sum_s \exp \left\{ 2\pi i [\mathbf{h} \{S|\mathbf{t}\}_s \mathbf{r}_j] \right\} \right|_r$$

$$\mathbf{h}_r = (h, k, l)_r \quad (r = 1, 2, \dots, N)$$

$$\mathbf{r}_j = (x_j, y_j, z_j) \quad (j = 1, 2, \dots, n)$$

SOLVING STRUCTURES BY DIRECT SPACE METHODS

Look directly for atom positions explaining the experimental data

Minimize a reliability factor with respect to the “configuration vector”

$$\boldsymbol{\omega} = \left| x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_n, y_n, z_n \right\rangle$$

$$R(\boldsymbol{\omega}) = c \sum_{r=1}^N \left| F_{obs}^2(\mathbf{h}_r) - F_{calc}^2(\mathbf{h}_r, \boldsymbol{\omega}) \right|$$

MAGNETIC STRUCTURES

Look directly for magnetic moments of atoms explaining the experimental data

Minimize a reliability factor with respect to the “configuration vector”

$$\omega = \left| m_{x1}, m_{y1}, m_{z1}, m_{x2}, m_{y2}, m_{z2}, \dots, m_{xn}, m_{yn}, m_{zn} \right\rangle$$

$$\omega = \left| S_{kx1}, S_{ky1}, S_{kz1}, S_{kx2}, S_{ky2}, S_{kz2}, \dots, S_{kxn}, S_{kyn}, S_{kzn} \right\rangle$$

$$\omega = \left| C_1, C_2, \dots, C_n \right\rangle$$

$$R(\omega) = c \sum_{r=1}^N \left| \mathbf{M}_{\perp obs}^2(\mathbf{h}_r) - \mathbf{M}_{\perp calc}^2(\mathbf{h}_r, \omega) \right|$$

SOLVING STRUCTURES BY SIMULATED ANNEALING

The SA method is a general purpose optimisation technique for large combinatorial problems introduced by:

Kirpatrick, Gelatt and Vecchi, *Science* **220**, 671-680 (1983).

Minimize a cost function, energy $E(\omega)$, with respect to the configuration vector ω .

Origin: Monte Carlo methods for simulating properties of liquids (Metropolis algorithm)

Algorithm trying to mimic the process of annealing a sample to obtain a good crystalline state (ground state):

A temperature schedule (starting high temperature + cooling rate) is needed.

Procedure to generate new configurations (Markov chains) and a Boltzmann probability to explore the phase space (importance sampling)

THE SIMULATED ANNEALING ALGORITHM

```
begin
  Initialise (set to zero useful quantities, do preliminary calculations )
   $\tau = 1$ 
  do
    do
      Perturb the system:
       $\omega_{\text{old}} \rightarrow \omega_{\text{new}}, \Delta = E(\omega_{\text{new}}) - E(\omega_{\text{old}})$ 
      if  $\Delta \leq 0$  then accept, else
        if  $\exp(-\Delta/T_\tau) > \text{random}[0,1]$  then accept
        if accept then Update (replace  $\omega_{\text{old}}$  by  $\omega_{\text{new}}$ )
      until equilibrium is approached closely enough (Ncyc)
       $T_{\tau+1} = f(T_\tau)$  (decrease temperature, usually  $T_{\tau+1} = q T_\tau, q \approx 0.9$ )
       $\tau = \tau + 1$ 
    until stop criterion is true (maximum  $\tau$ , convergence, low % accepted...)
  end
```

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

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

M. Guillot^{a)}

High Magnetic Field Laboratory, MPI/CNRS, 38042 Grenoble, France

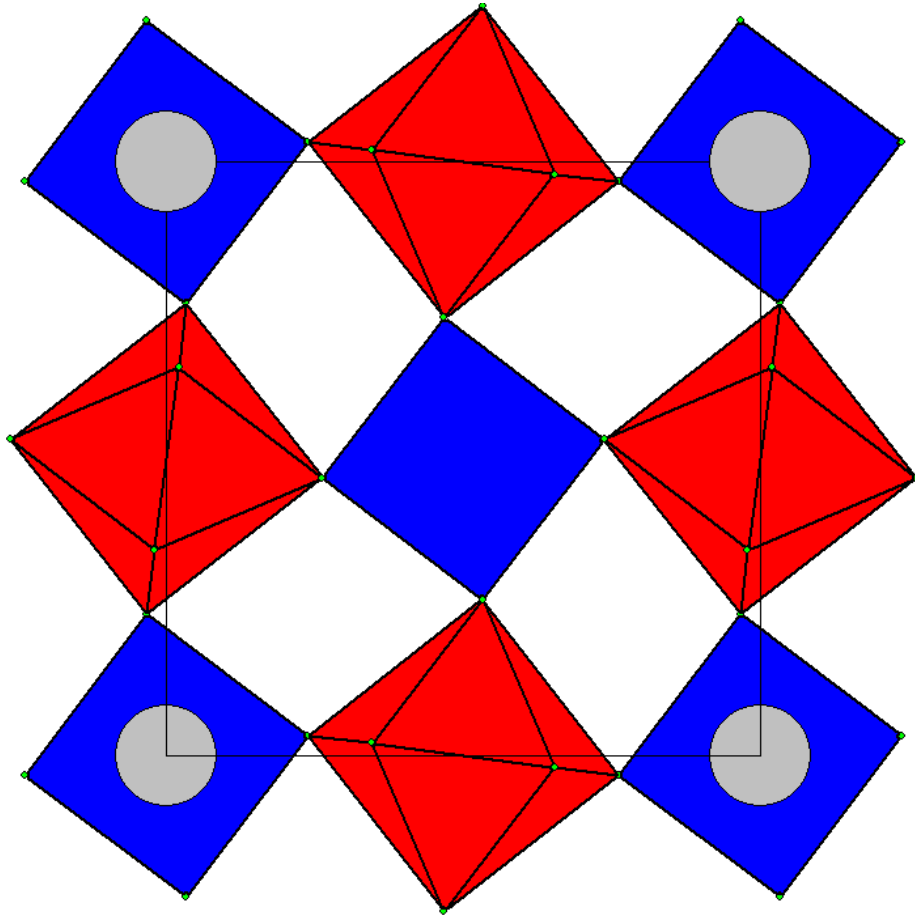
M. El-Ghozzi and D. Avignant

*Laboratoire des Matériaux Inorganiques, UMR 6002 CNRS, Université Blaise Pascal,
63177 Aubière, France*

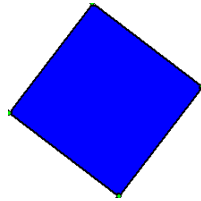
G. Andre, F. Bouree, and A. Cousson

Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif sur Yvette, France

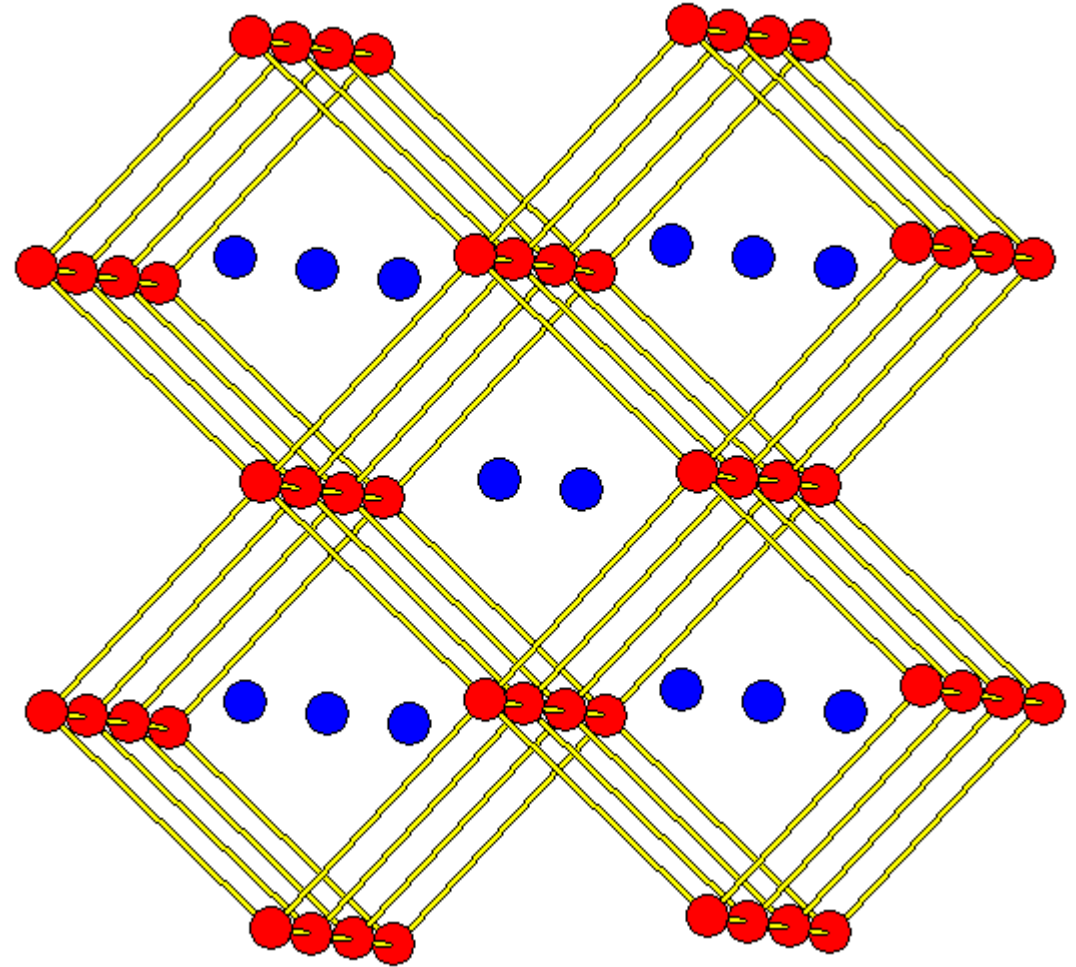
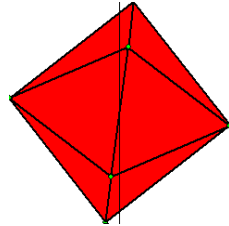
SIMULATED ANNEALING IN FULLPROF WITH A SIMPLE EXAMPLE: $\text{KTb}_3\text{F}_{12}$



Tb^{3+}



Tb^{4+}



SIMULATED ANNEALING IN FULLPROF WITH A SIMPLE

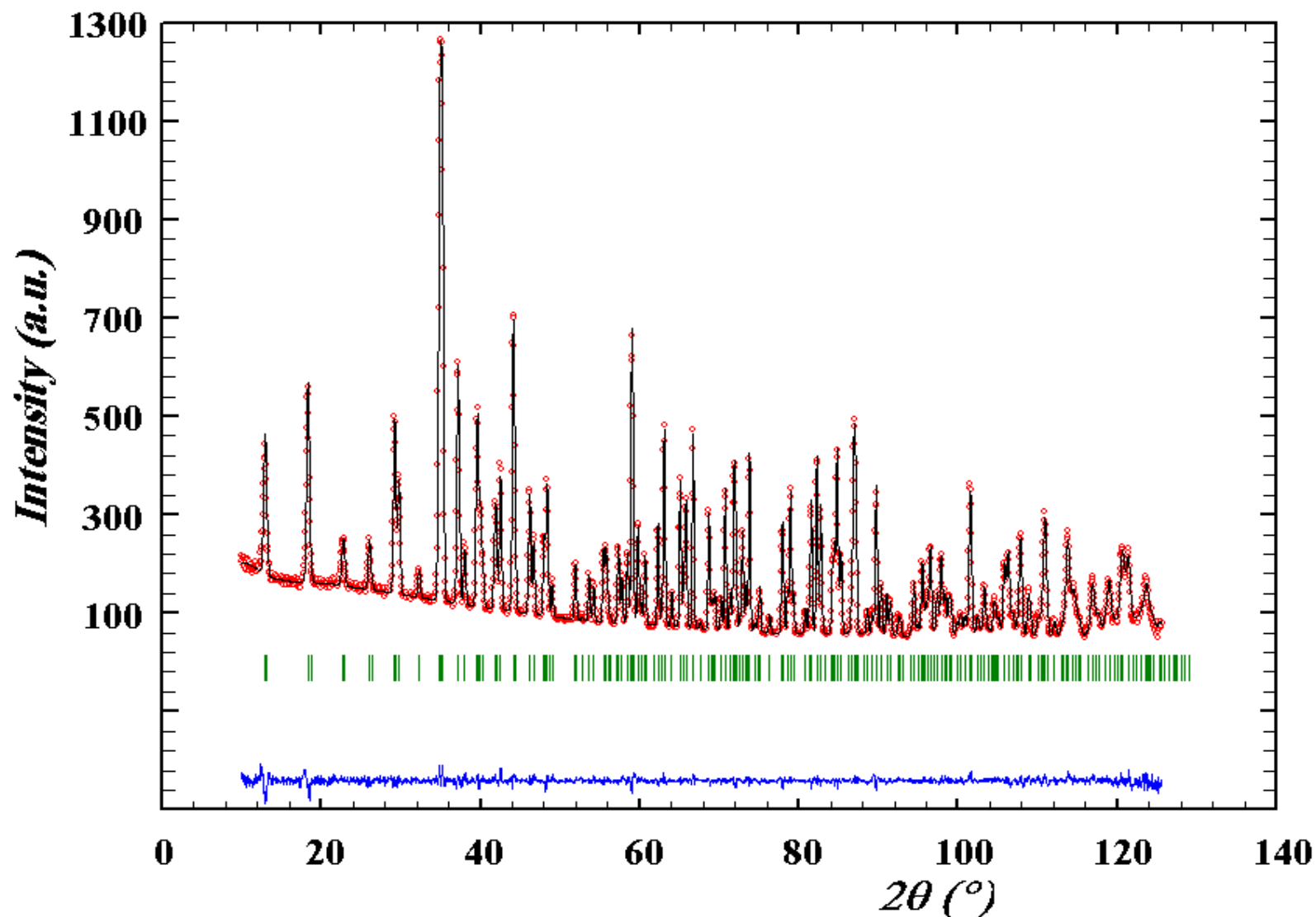
EXAMPLE: $\text{KTb}_3\text{F}_{12}$

```

I 4/m                                <--Space group symbol
!Atom Typ      X      Y      Z      Biso      Occ      In Fin N_t Spc /Codes
!      beta11    beta22    beta33    beta12    beta13    beta23    /Codes
K      K      0.00000  0.00000  0.00000  0.00000  0.12500    0    0    2    0    # color green
           0.00      0.00      0.00      0.00      0.00      0.00
           0.00264  0.00264 -0.00038  0.00000  0.00000  0.00000
           0.00      0.00      0.00      0.00      0.00      0.00
Tb3+ TB      0.00000  0.00000  0.50000  0.04652  0.12500    0    0    0    0    # color blue
           0.00      0.00      0.00      0.00      0.00      0.00
Tb4+ TB      0.00000  0.50000  0.25000  0.01556  0.25000    0    0    0    0    # color red
           0.00      0.00      0.00      0.00      0.00      0.00
F1      F      0.34606  0.02658  0.00000  0.00000  0.50000    0    0    2    0    # color brown  conn
           0.00      0.00      0.00      0.00      0.00      0.00
           0.00149  0.00259  0.00036  0.00039  0.00000  0.00000
           0.00      0.00      0.00      0.00      0.00      0.00
F2      F      0.23820  0.04363  0.67942  0.00000  1.00000    0    0    2    0    # color brown
           0.00      0.00      0.00      0.00      0.00      0.00
           0.00167  0.00227  0.00082 -0.00006 -0.00032  -0.00012
           0.00      0.00      0.00      0.00      0.00      0.00

```

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 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
```

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.pcr](#) 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 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

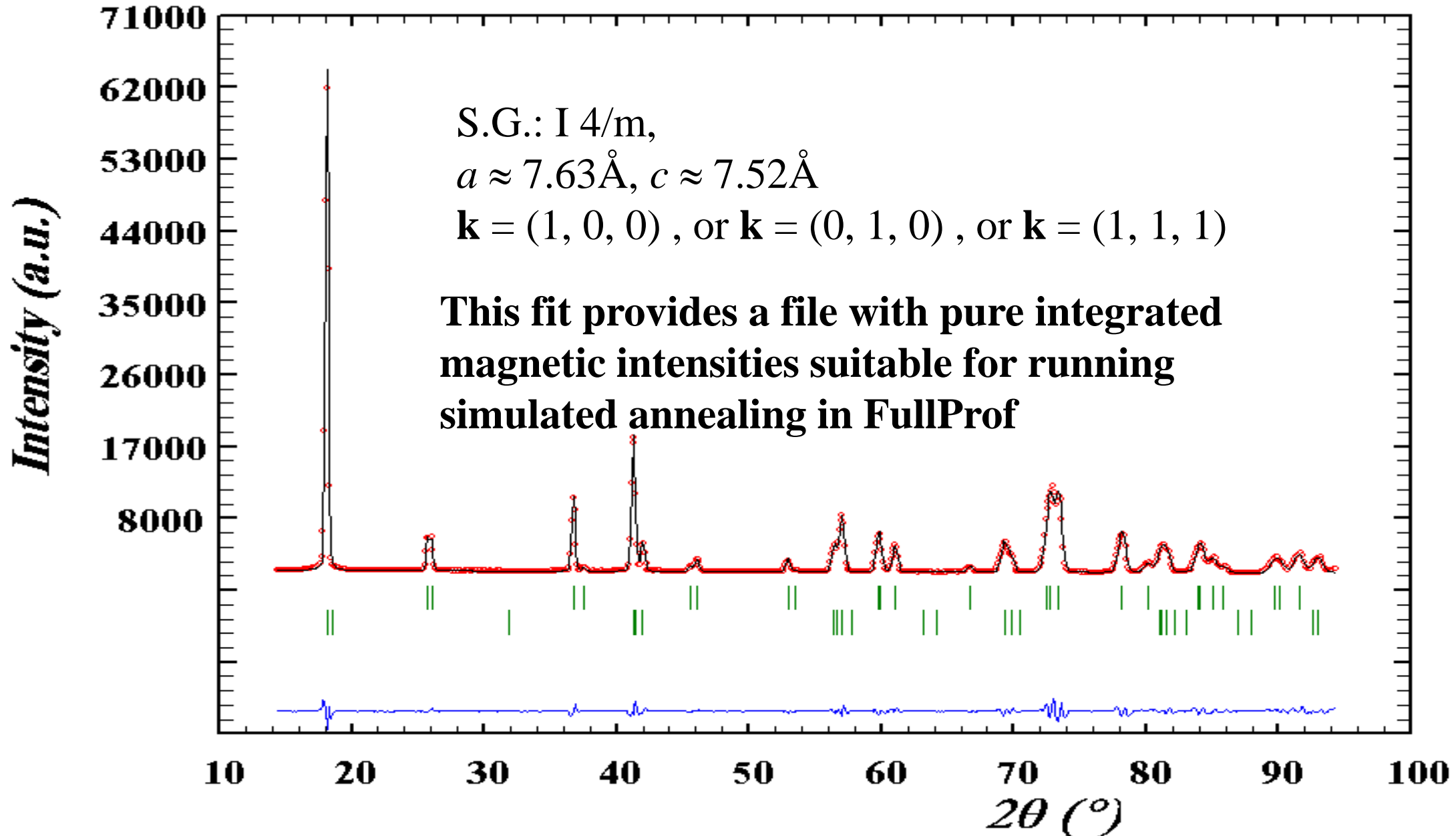
[test.spr](#)

.....

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
. . . . .
```

PROFILE MATCHING (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	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 PCR file for Simulated Annealing?

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 PCR file for Simulated Annealing?

```

!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 PCR file for Simulated Annealing?

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
  0.000000  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:
  1.0000000  0.0000000  0.0000000      Propagation Vector 1
    0.000000  0.000000  0.000000
```

How to prepare a PCR file for Simulated Annealing?

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

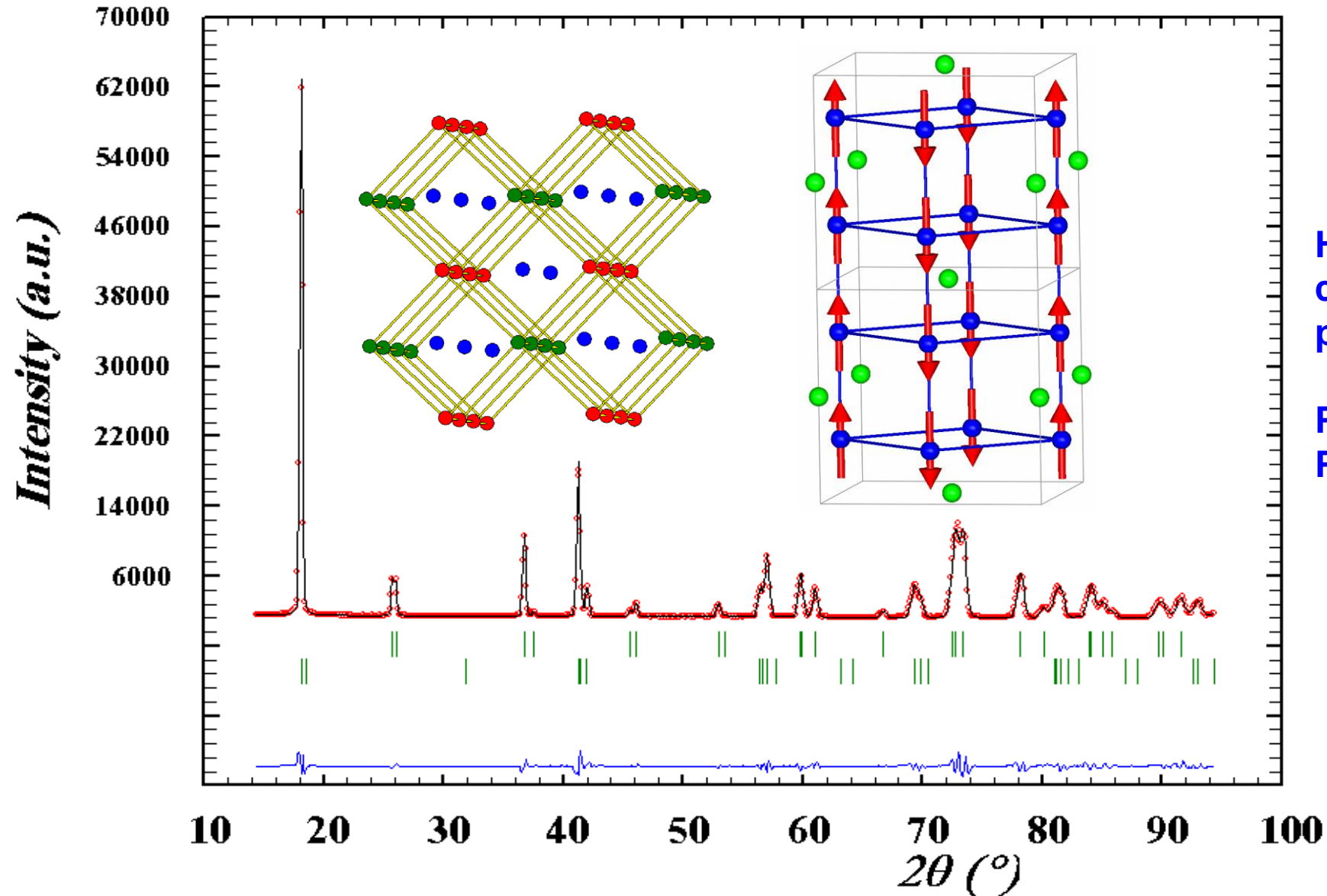
Automatic treatment(1) or
fixed(0) scale factor

Corana algorithm
Initial step = range

Random initial
configuration



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



Here we have used the conventional way of working putting two phases:

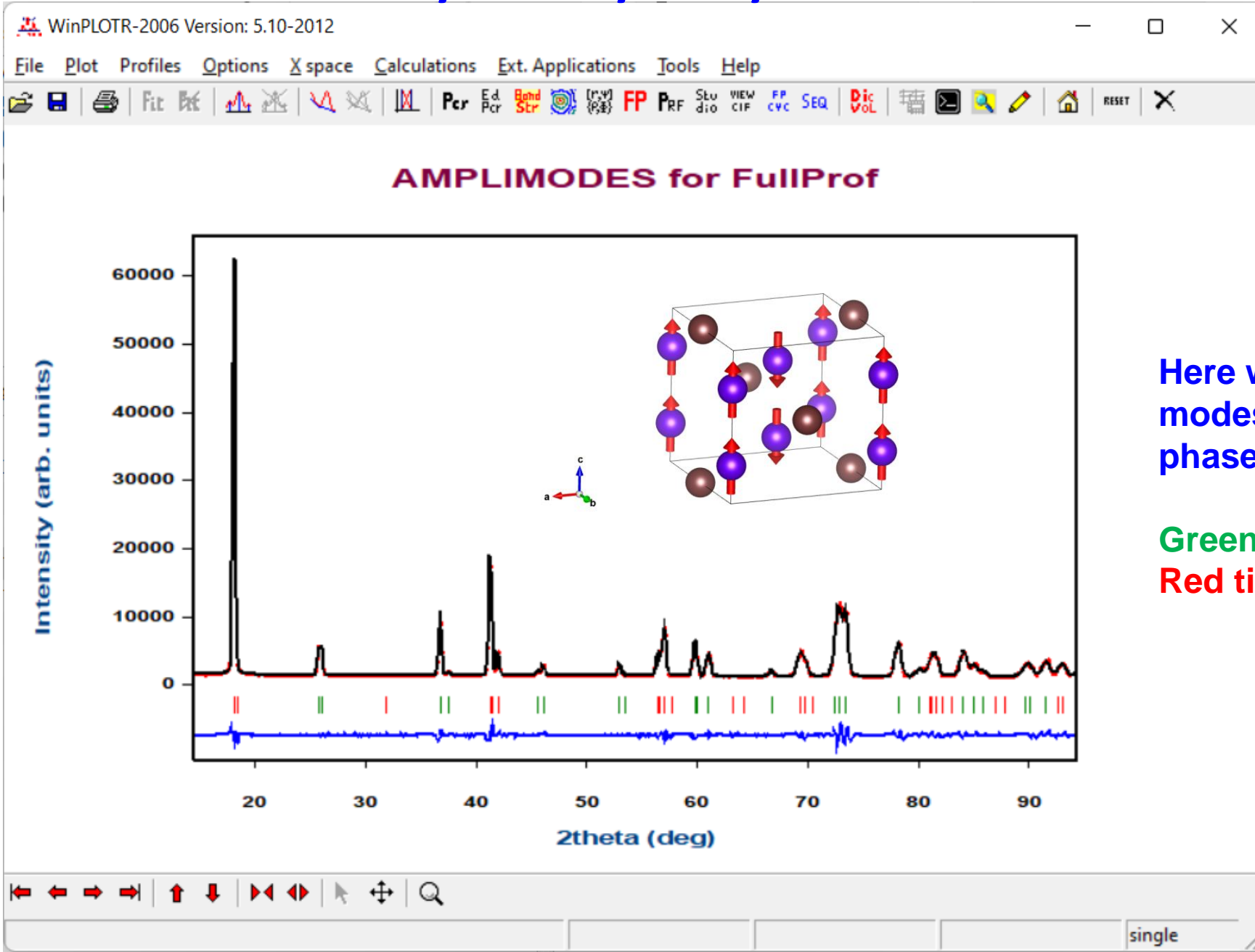
Phase 1: Nuclear contribution
Phase 2: Magnetic contribution

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.

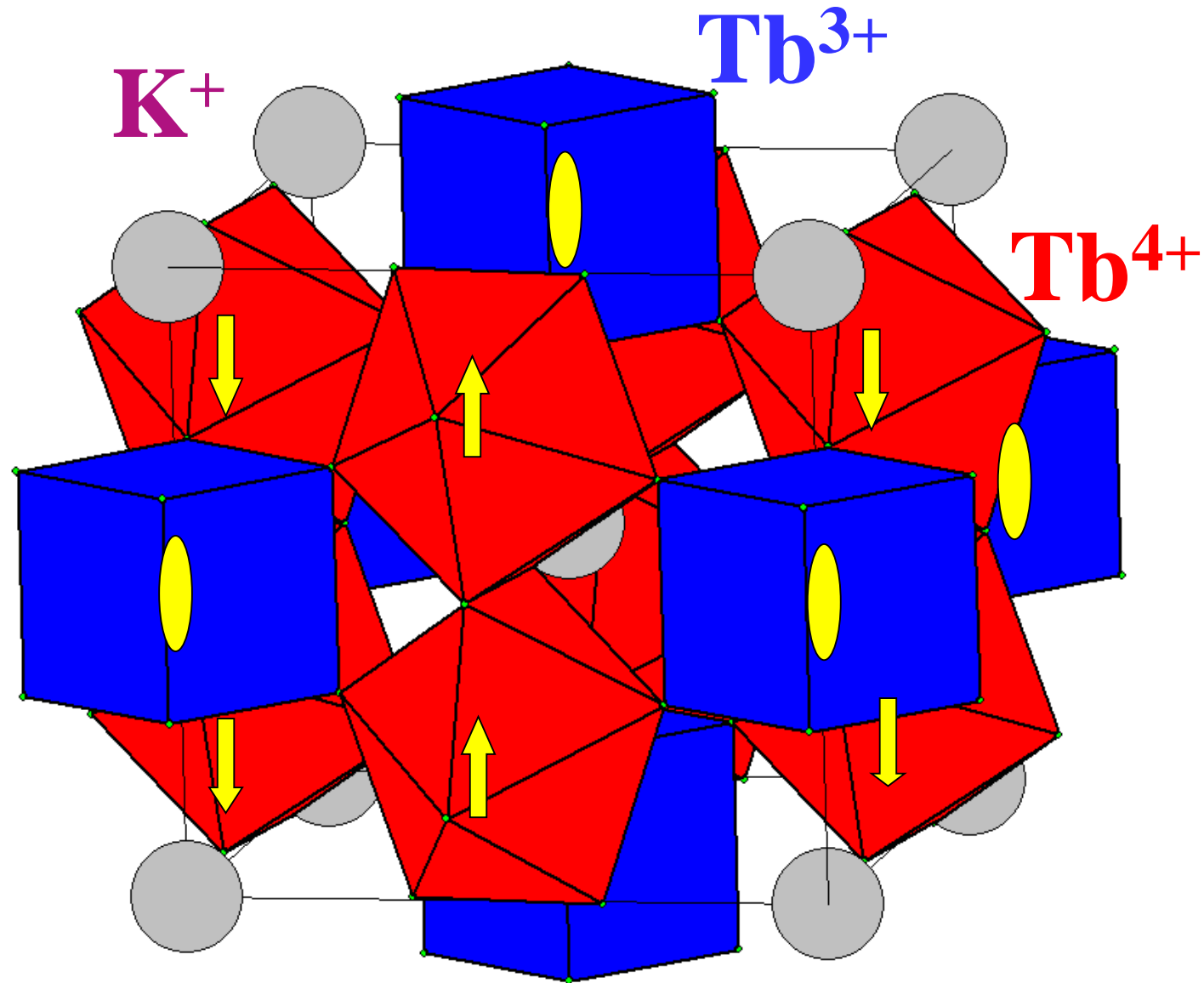
Symmetry analysis with ISODISTORT



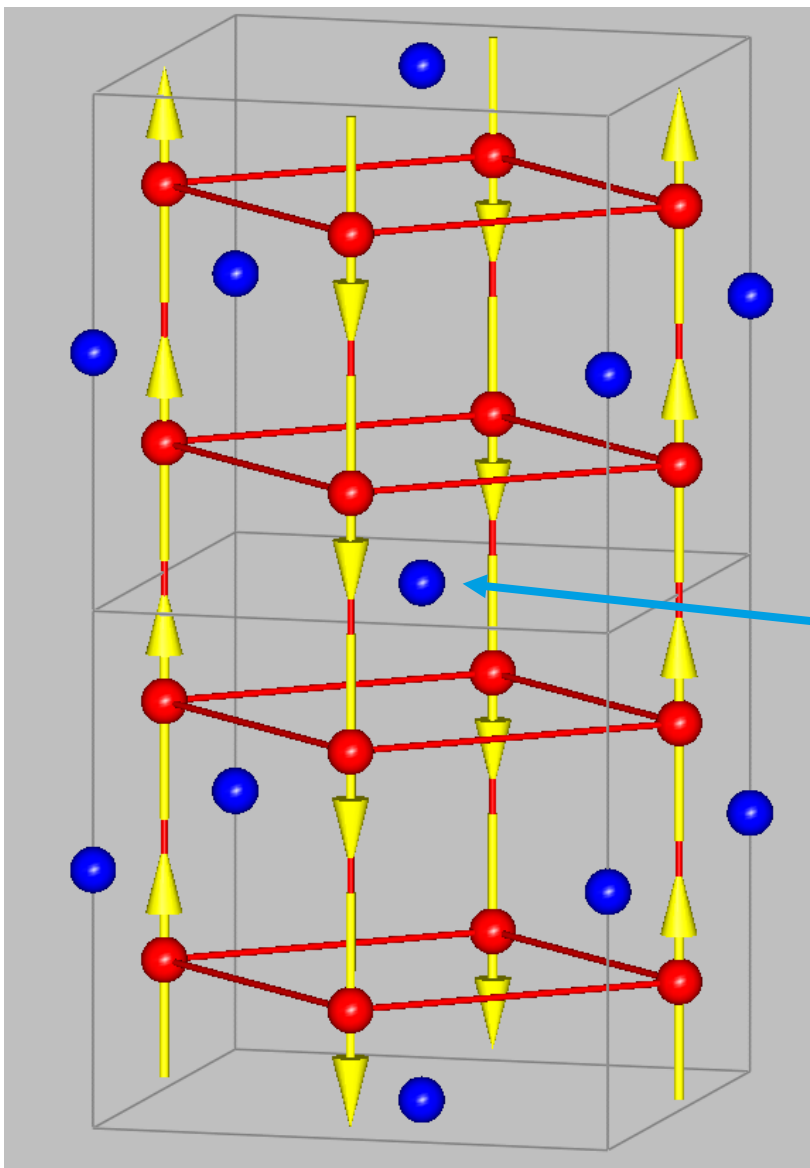
Here we have used the symmetry modes approach using a single phases

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 .



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