晶体学结构的解析

X-ray粉末衍射法

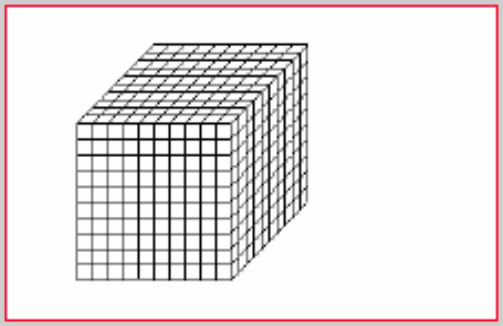
Topas软件

晶体学结构

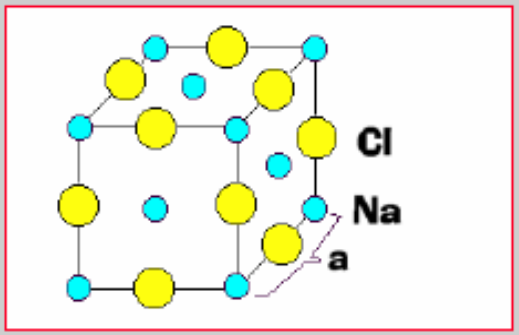
BRUKER ANALYTICAL X-RAY SYSTEMS

a. 晶体结构与空间点阵

- 晶体基本特点：质点（结构单元）沿三维空间周期性排列（晶体定义），并有对称性。
- 空间点阵：实际晶体中的几何点，其所处几何环境和物质环境均同，这些"点集"称空间点阵。
- 晶体结构=空间点阵+结构单元。



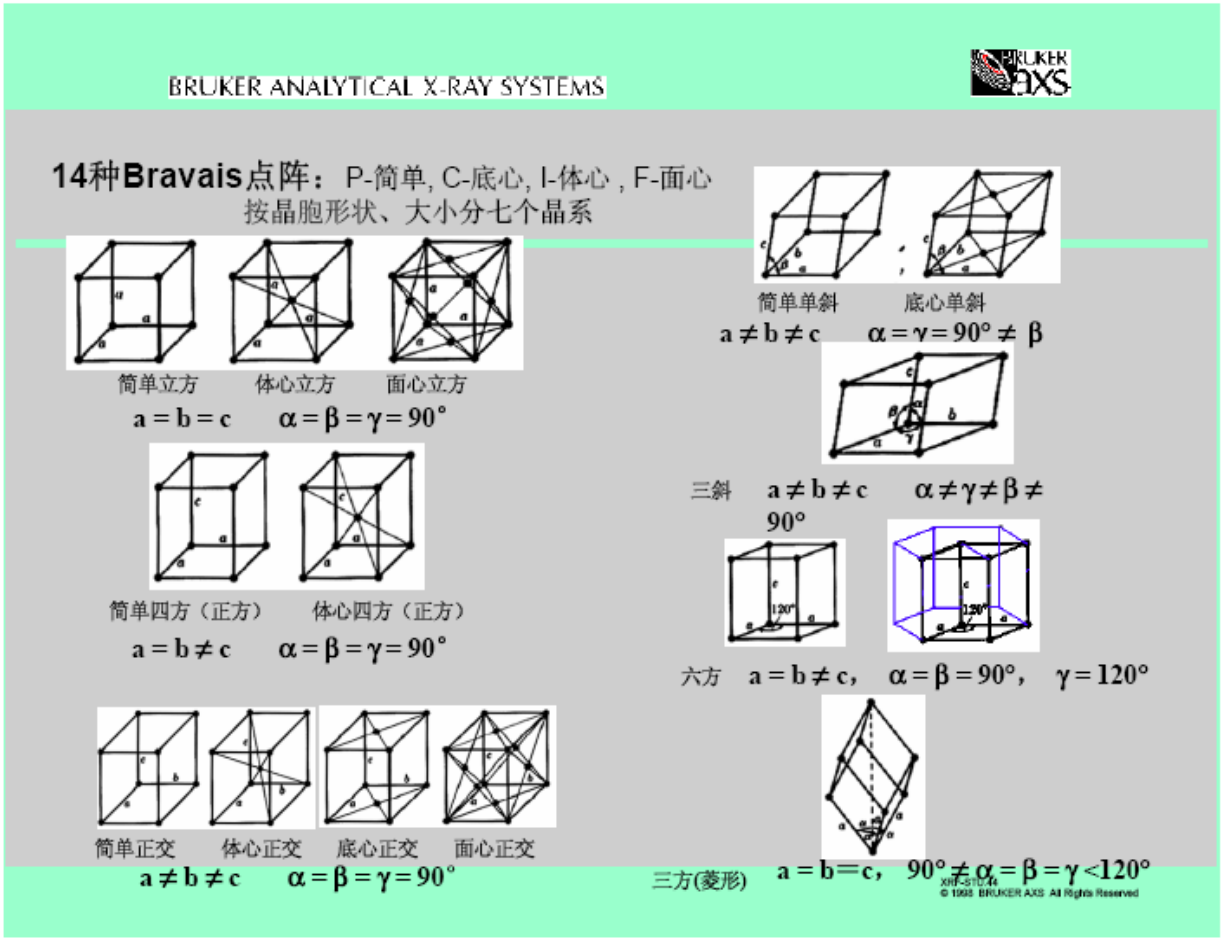
Space Lattice and Unit Cell



- Every unit cell has identical size and is formed in the same manner by atoms.
- It contains Na^+-cations (o) and Cl^--anions (O).
- Each edge is of the length a.

晶体学结构

- 一种描述
- 简单原则
  三斜
- 合理原则

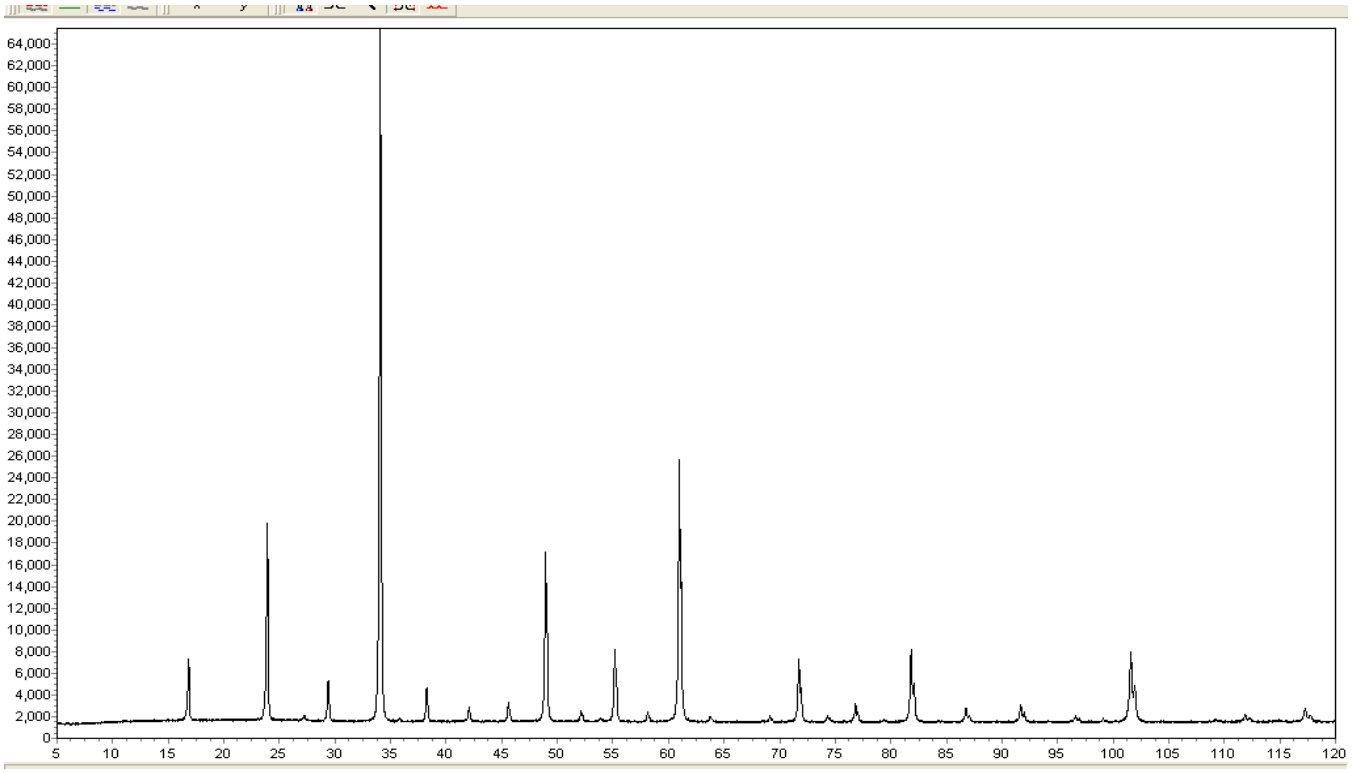


讨论内容

- 基本处理(结构解析(一))
- 结构解析(二)
- 结构精修
- 一般性问题

结构解析(一):基本处理

- 样品的准备和数据的采集
- 数据的处理(衍射图)



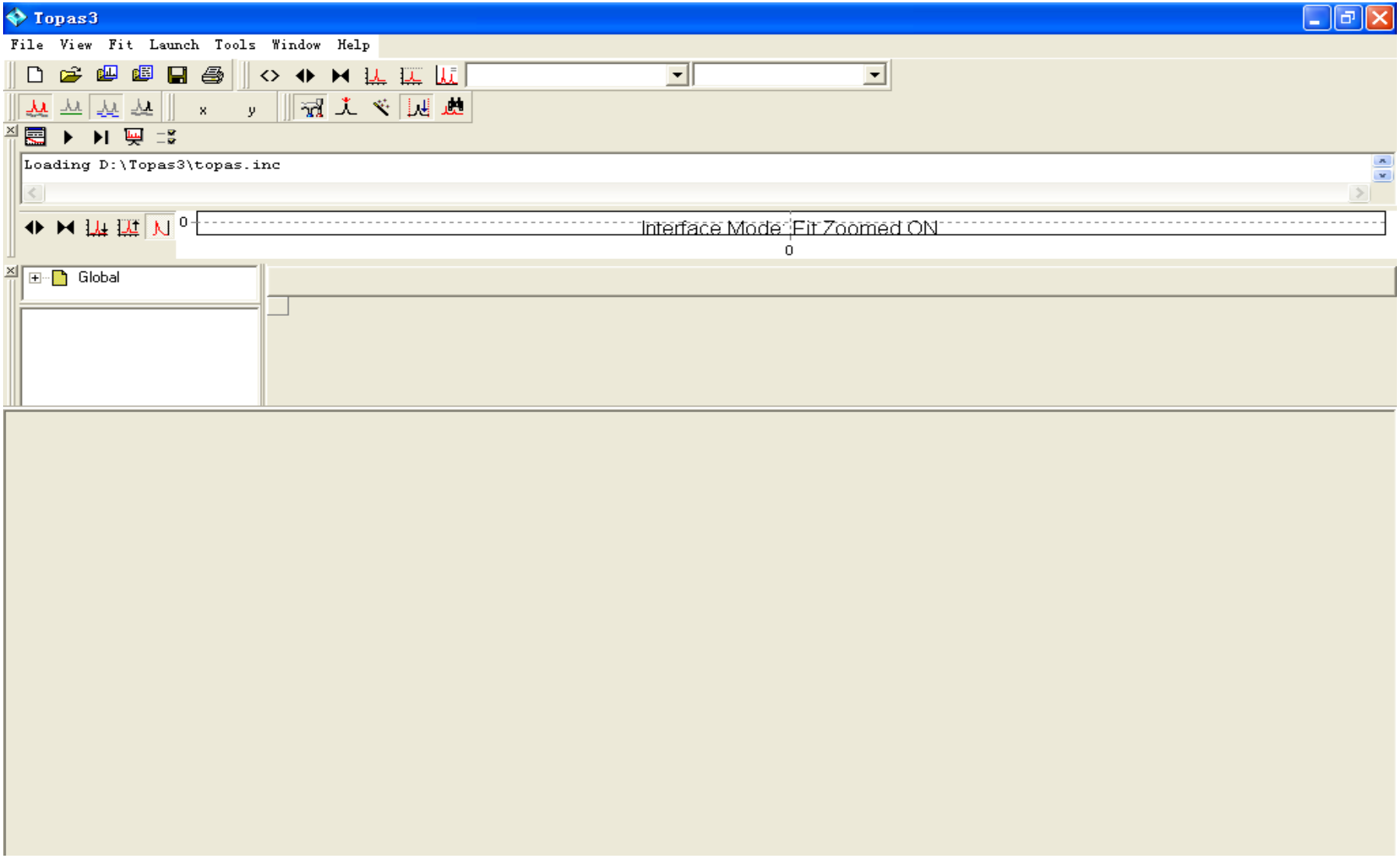
一般步骤

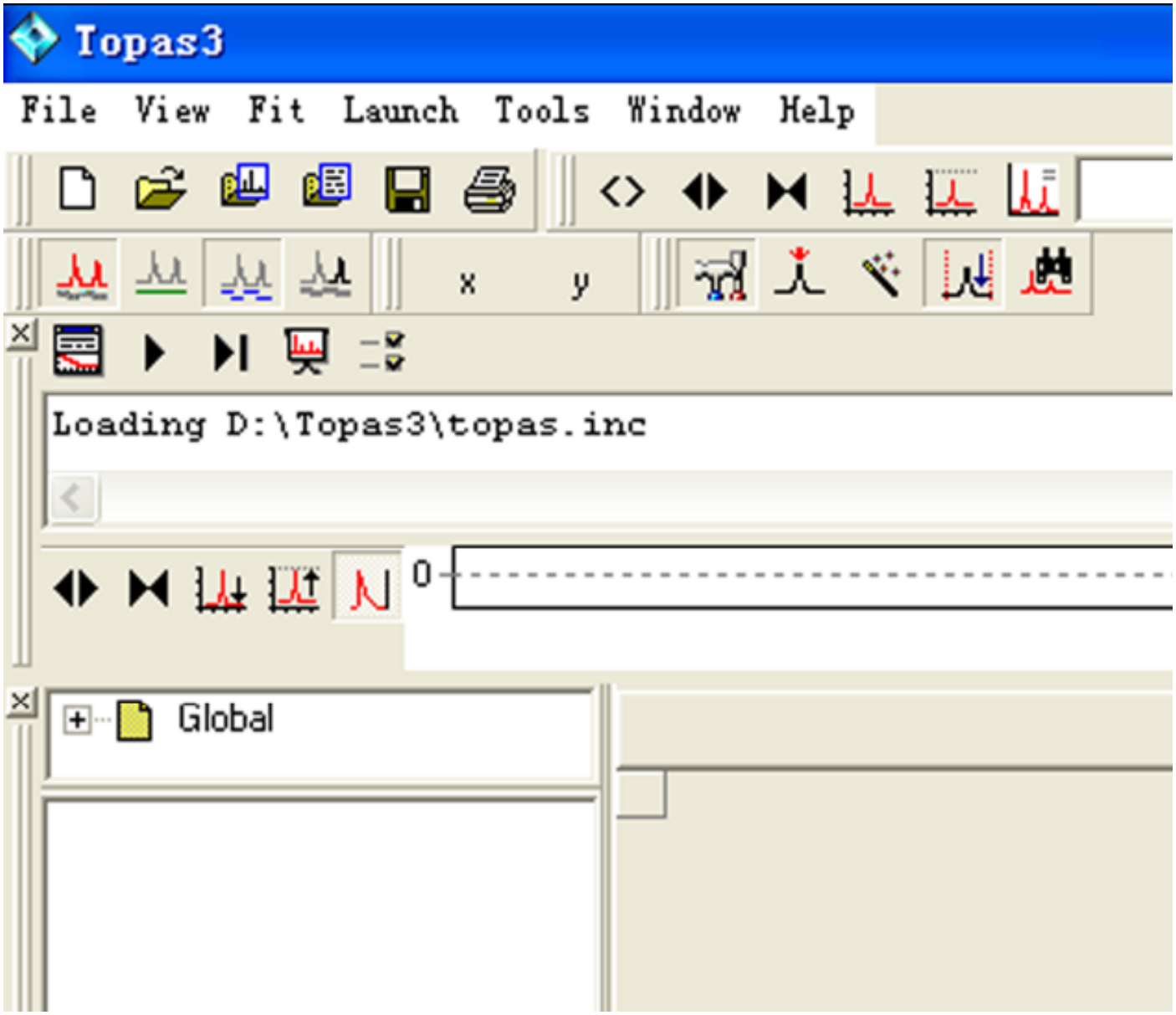
- 数据的读入
- 寻峰(峰形拟合)
- 指标化
- 空间群的判断
- 结构解析

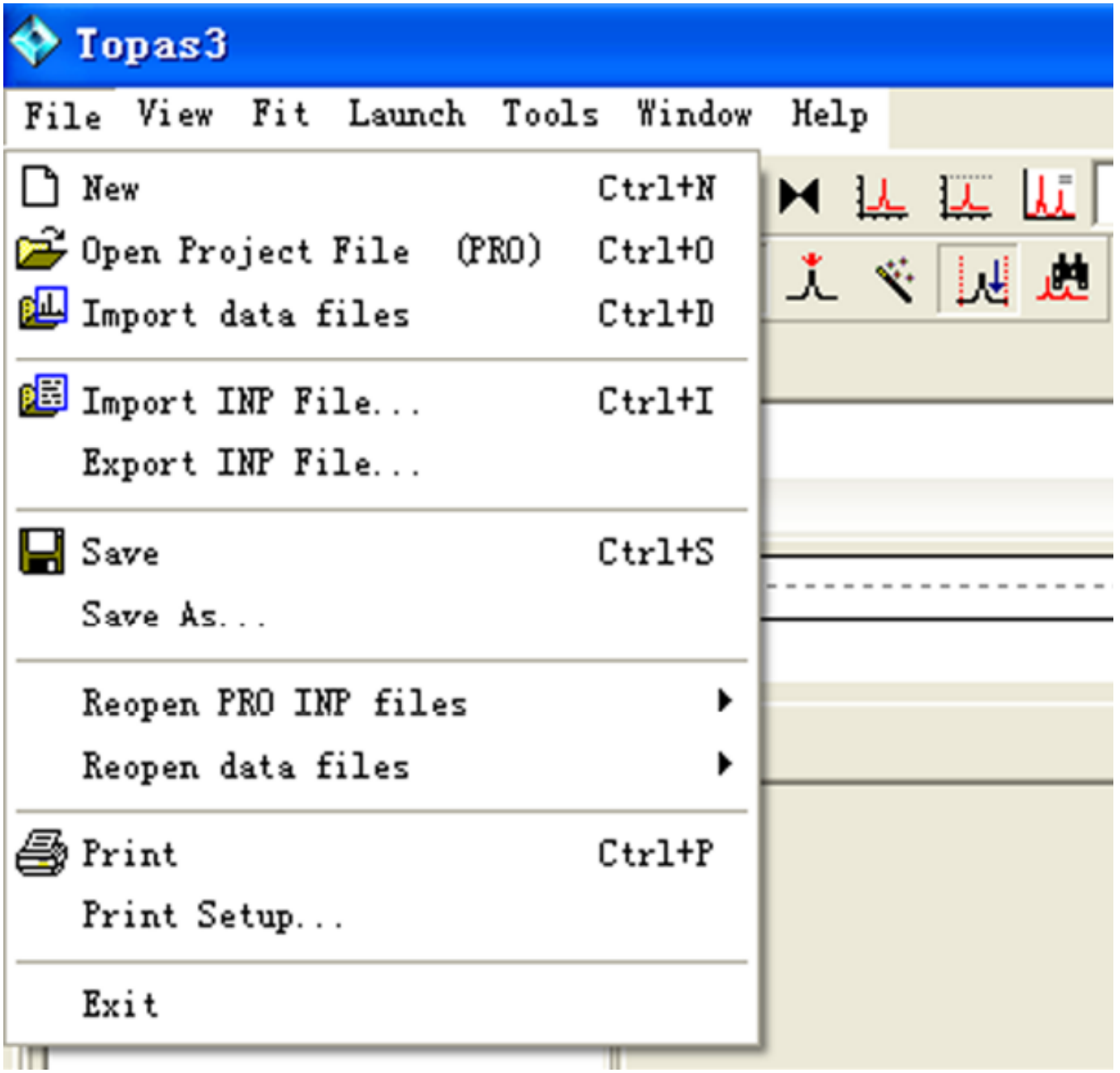
数据的读入

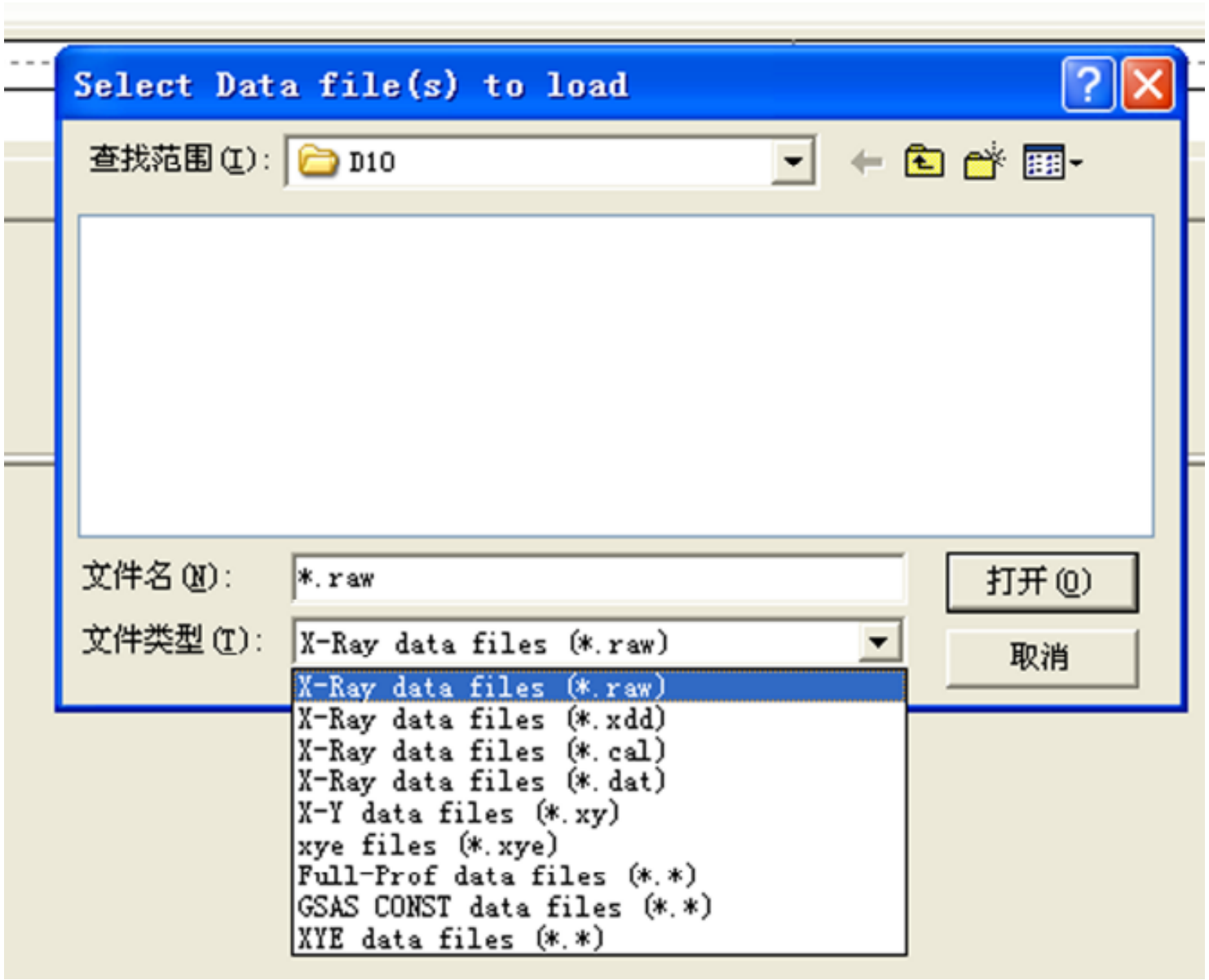
- 布鲁克衍射仪的数据(*.raw)
- 理学衍射仪的数据
- 中子衍射的数据

程序的启用


Topas3
File View Fit Launch Tools Window Help
x y
Loading D:\Topas3\topas.inc
0
Interface Mode Fit Zoomed ON
0
Global


Topas3
File View Fit Launch Tools Window Help
x y
Loading D:\Topas3\topas.inc
0
Global


Topas3
File View Fit Launch Tools Window Help
New Ctrl+N
Open Project File (PRO) Ctrl+O
Import data files Ctrl+D
Import INP File... Ctrl+I
Export INP File...
Save Ctrl+S
Save As...
Reopen PRO INP files
Reopen data files
Print Ctrl+P
Print Setup...
Exit


Select Data file(s) to load
查找范围(I):
D10
文件名(N):
*.raw
打开(O)
文件类型(T):
X-Ray data files (*.raw)
取消
X-Ray data files (*.raw)
X-Ray data files (*.xdd)
X-Ray data files (*.cal)
X-Ray data files (*.dat)
X-Y data files (*.xy)
xye files (*.xye)
Full-Prof data files (*.*)
GSAS CONST data files (*.*)
XYE data files (*.*)

可读入数据的格式

- 布鲁克衍射仪的数据(*.raw)

  Bruker AXS binaries (DIFFRAC AT and DIFFRAC*plus*)
- *.DAT

  Several ASCII file formats including LHPM/RIET7/CSRIET, GSAS ("std - const", "alt -ralf") and FullProf.
- *.XDD / *.CAL

  ASCII file format.

*.XY, *XYE

ASCII file formats. Can be used for non-equidistant x-axis steps.

File Type:	Format:	Explanation:

*.DAT

- **LHPM/RIET7/CSRIET**

Line 1-4	Comments
Line 5	Start angle, step width, finish angle
Line 6 onwards	Observed XRD data points (any number of rows)

- **GSAS** ("std - const", "alt - ralf")

Line 1	Legend
Line 2	Item 3: Number of data points
Line 3 onwards	Depending of item10 and item5

For item10 = "STD" and item5 = "CONST"

xmin = item6/div

step =item7/div

read(10(i2,F6.0) iww(i),y(i) i=1, npts

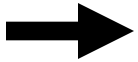
sigma(i)=sqr(y(i)/iww(i)) i=1, npts

rk (constant wavelength data): div = 100

rk (time of flight data): div = 1

岛津衍射仪的ASCII数据

```
*  Group     : YSH
*  Data      : Ti-c1
*  File Name : Ti-c1.RAW
*  Comment   :
*
5501    10.0000   0.02000
202      200      238      188      236
210      210      208      220      198
218      224      198      192      210
190      210      222      192      218
```



```
*  Group     : YSH
*  Data      : Ti-c1
*  File Name : Ti-c1.RAW
*  Comment   :
  10.0000   0.02000  120.00
202      200      238      188      236
210      210      208      220      198
218      224      198      192      210
190      210      222      192      218
196      186      196      216      186
```

理学衍射仪的ASCII数据

GSAS数据格式

5.000 0.020 120.000 050104 7.3.2006
BANK 1 5751 575 CONST 500 2 0 0 STD
1374 1294 1388 1368 1342 1366 1350 1364 1400 1360
1360 1410 1372 1338 1330 1308 1318 1372 1374 1314
1414 1346 1340 1348 1342 1318 1290 1314 1384 1348
1294 1316 1358 1280 1336 1294 1378 1268 1324 1374
1276 1356 1320 1280 1388 1300 1396 1386 1282 1306
1332 1336 1282 1328 1298 1374 1392 1350 1262 1310

- **GSAS** ("std - const", "alt - ralf")

Line 1	Legend
Line 2	Item 3: Number of data points
Line 3 onwards	Depending of item10 and item5

For item10 = "ALT" and item5 = "RALF"

```
xmin = item6/32
step = item7/32
read(4(F8.0,F7.4,F5.4) x(i), y(i), sigma(i)   i=1, npts
x(i) = x(i)/32                                i=1, npts
do i = 1, npts-1
  div = x(i+1)-x(i)
  y(i) =1000 * y(i)/div
  sigma(i) = 1000 * sigma(i)/div
end do
```

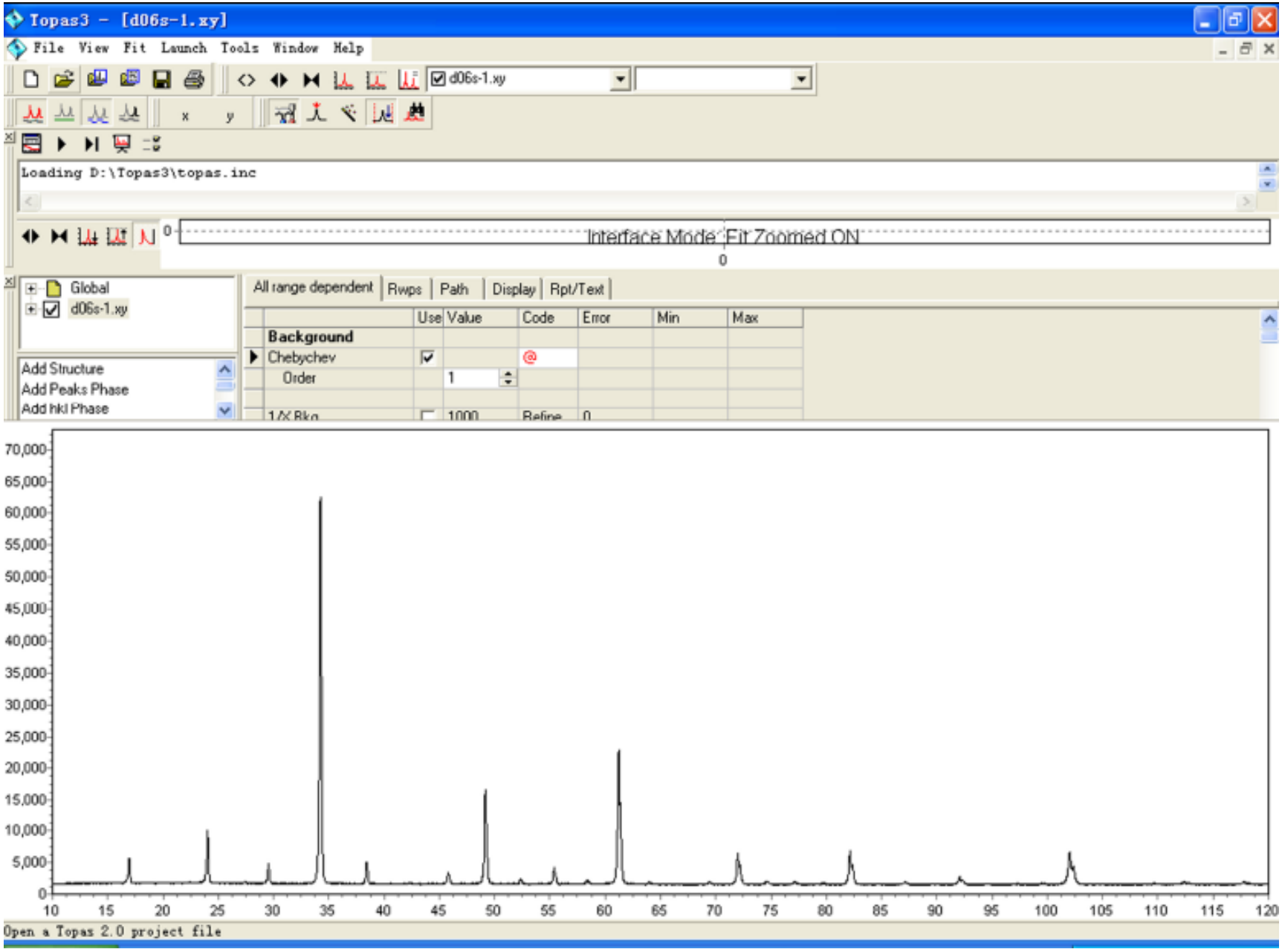
rk (constant wavelength data):	div = 100
rk (time of flight data):	div = 1

File Type:	Format:	Explanation:
*.DAT		
• **FullProf** (INSTRM = 0: free format file)		
	Line 1	Start angle, step width, finish angle, comments
	Line 2 onwards	Observed XRD data points (any number of rows)
*.XDD / *.CAL	Line 1	Optional line for comments
	Number 2	Start angle
	Number 3	Step width
	Number 4	Finish angle
	Number 5	Counting time
	Number 6	Unused
	Number 7	Unused
	Number 8 onwards	Observed XRD data points
*.XY	Number 1 onwards	Numbers corresponding to 2θ and intensity data values
*.XYE	Number 1 onwards	Numbers corresponding to 2θ, intensity and intensity error values

*.XY格式

050104 Original Data
5751
5 1372
5.02 1384
5.04 1370
5.06 1388
5.08 1384
5.1 1334
5.12 1378
5.14 1352
5.16 1372
5.18 1368
5.2 1378

5 1372
5.02 1384
5.04 1370
5.06 1388
5.08 1384
5.1 1334
5.12 1378


Topas3 - [d06s-1.xy]
File View Fit Launch Tools Window Help
d06s-1.xy
Loading D:\Topas3\topas.inc
Interface Mode: Fit Zoomed ON
Global
d06s-1.xy
All range dependent
Rwps
Path
Display
Rpt/Text
Use
Value
Code
Error
Min
Max
Background
Chebychev
Order
1
Add Structure
Add Peaks Phase
Add hkl Phase
70,000
65,000
60,000
55,000
50,000
45,000
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
Open a Topas 2.0 project file

界面简介（user interface）

- **Menubar**

Contains the names of submenus, which provide lists of all commands available together with their shortcuts respectively toolbar icons, if existing.

- **Toolbar**

Displays the most important commands in form of icons for fast access.

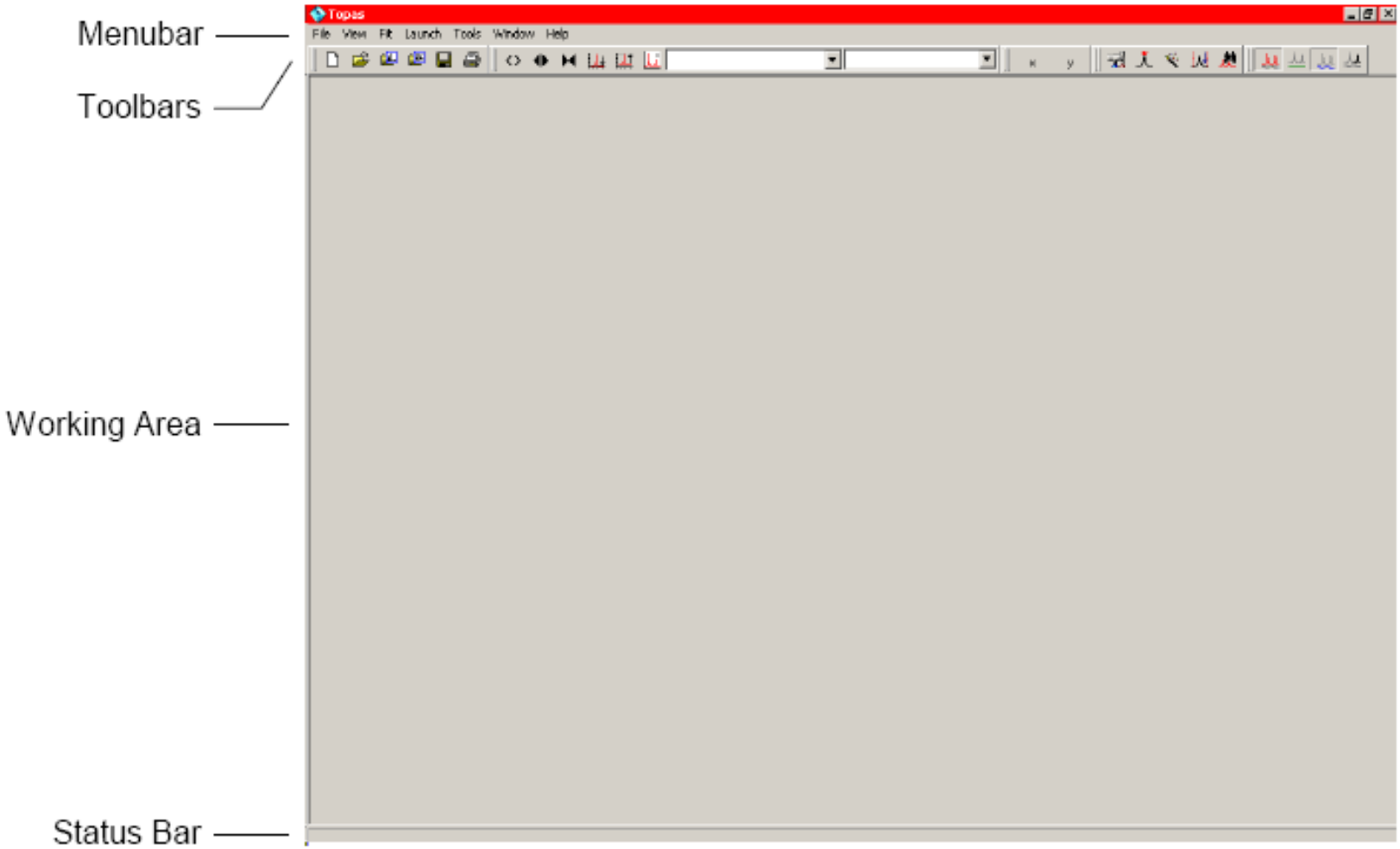
- **Working Area**

Contains all elements needed for profile fitting such as observed and calculated

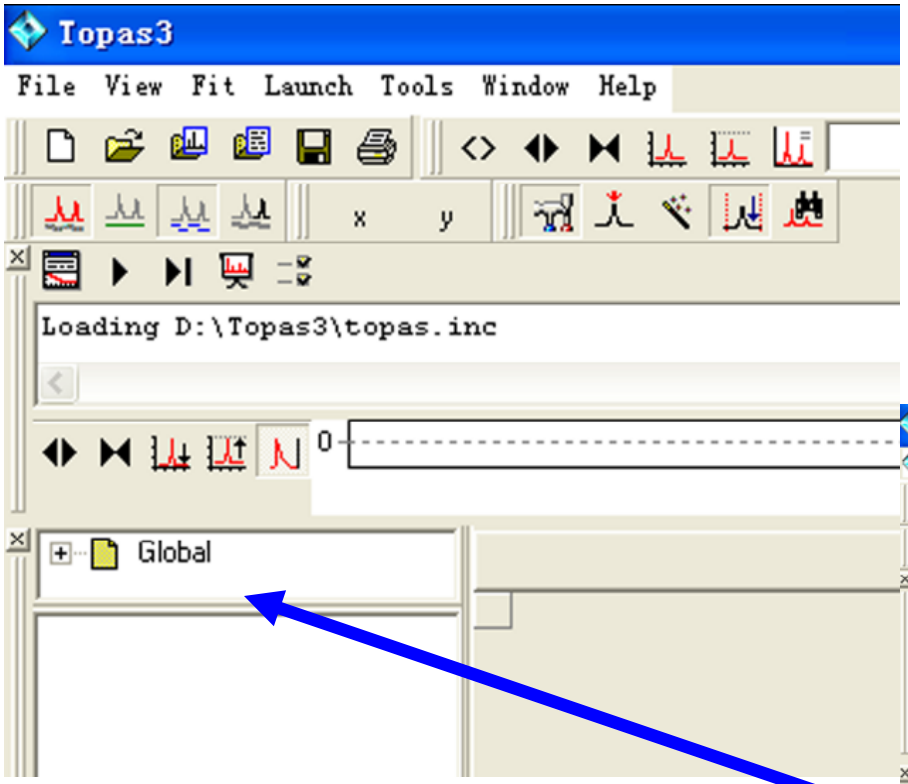
data, fit parameters, and fit results, which are displayed in separated views.

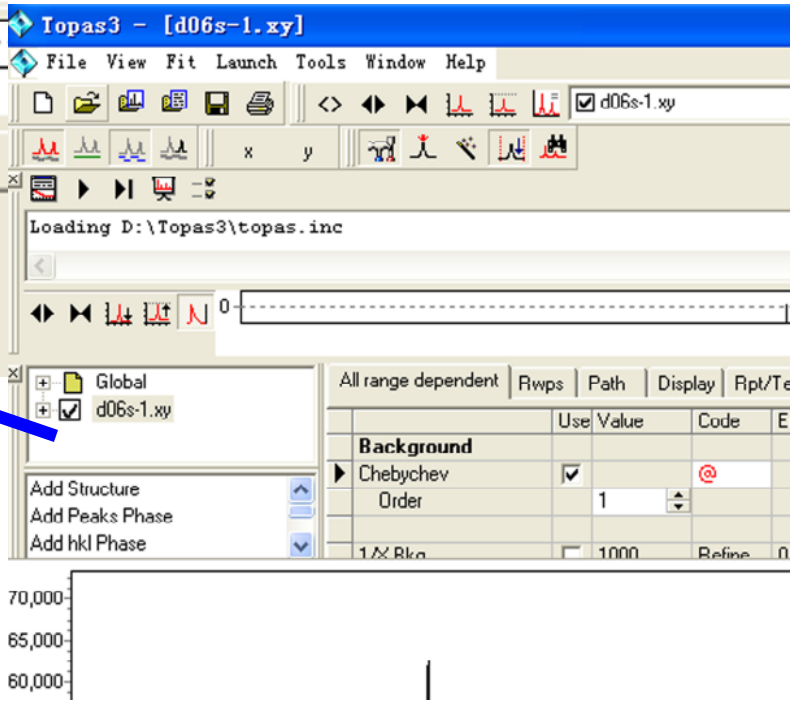
- **Status Bar**

Displays some context sensitive help information and the x- and y-coordinates of the data cursor in the active *Scan Window*, which is described in section 2.2.


Menubar
Toolbars
Working Area
Status Bar
Topas
File View Fit Launch Tools Window Help

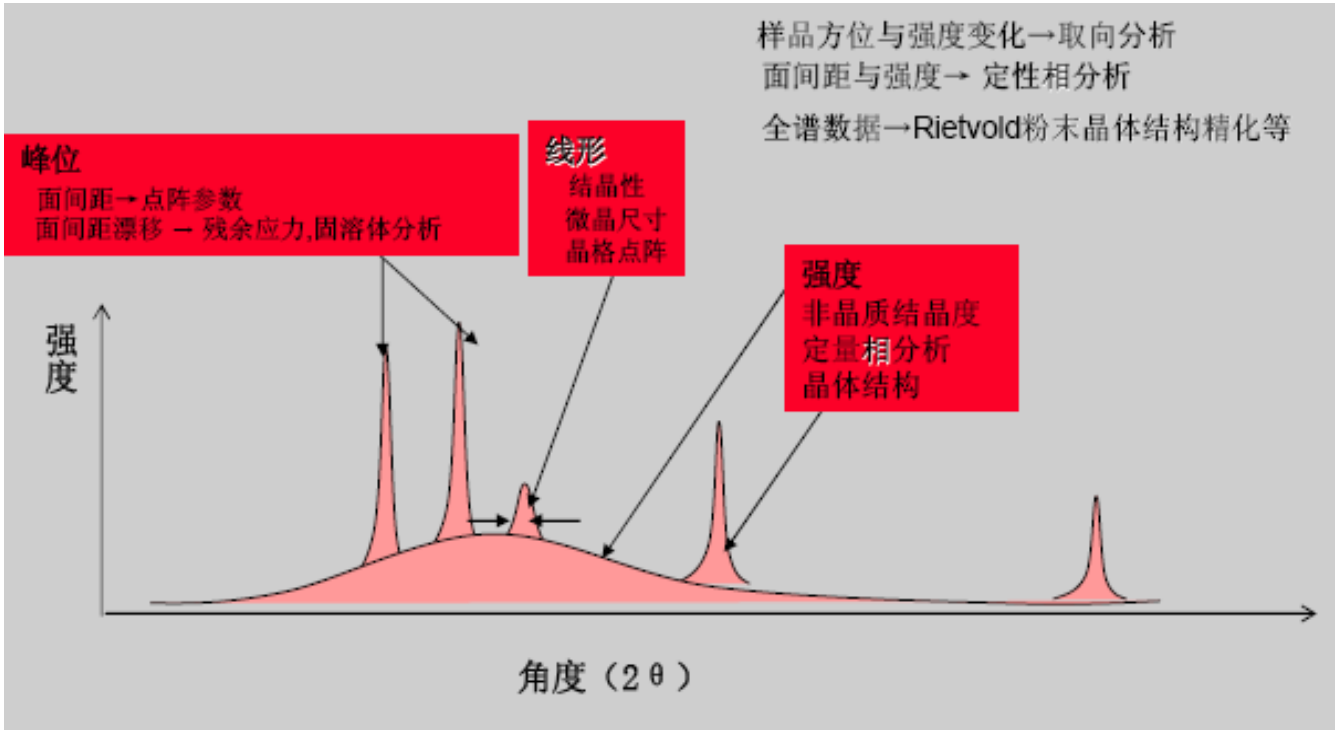
数据的处理


Topas3
File View Fit Launch Tools Window Help
x y
Loading D:\Topas3\topas.inc
0
Global


Topas3 - [d06s-1.xy]
File View Fit Launch Tools Window Help
d06s-1.xy
x y
Loading D:\Topas3\topas.inc
0
Global
d06s-1.xy
Add Structure
Add Peaks Phase
Add hkl Phase
All range dependent
Rwps
Path
Display
Use
Value
Code
Background
Chebychev
Order
1
70,000
65,000
60,000

数据的组成

背底　　峰位置　　峰形



Global item(全域项)

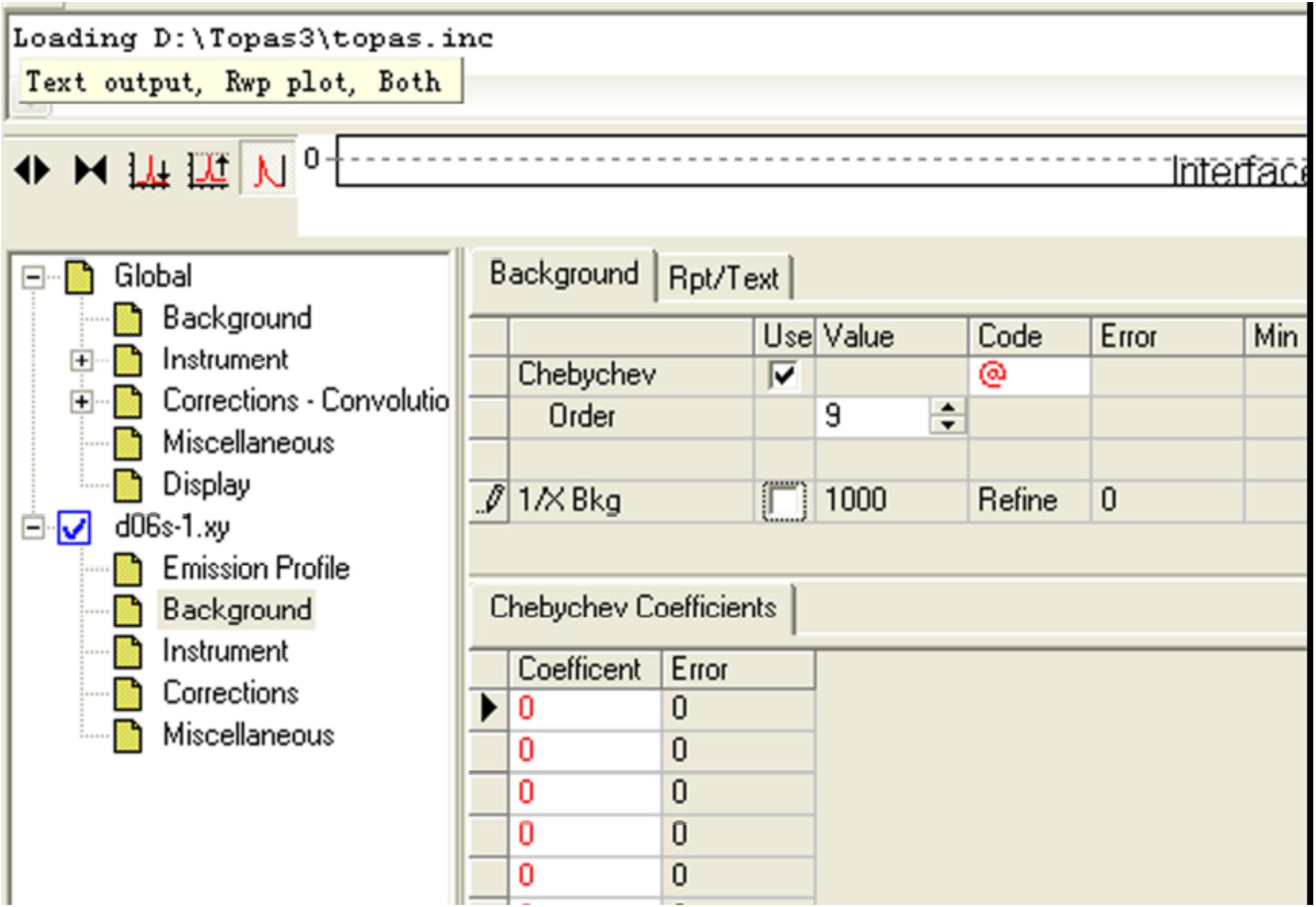
- ***Background*** **(section 2.3.2.4)**
- ***Instrument*** **(section 2.3.2.5)**
- ***Corrections*** **(section 2.3.2.6)**
- ***Miscellaneous*** **(section 2.3.2.7)**
- ***Display***
- ***All Peaks*** **(section 2.3.2.8)**
- ***All Structures / hkl Phases*** **(section 2.3.2.11)**

Background

Two background functions are provided

1. a Chebychev polynomial of any order
2. a 1/X function.

The *Chebychev Coefficients* page contains the coefficients of the polynomial.


Loading D:\Topas3\topas.inc
Text output, Rwp plot, Both
0
Interface
Global
Background
Instrument
Corrections - Convolutio
Miscellaneous
Display
d06s-1.xy
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Background
Rpt/Text
Use
Value
Code
Error
Min
Chebychev
Order
9
1/X Bkg
1000
Refine
0
Chebychev Coefficients
Coefficent
Error
0
0
0
0
0
0
0
0
0
0

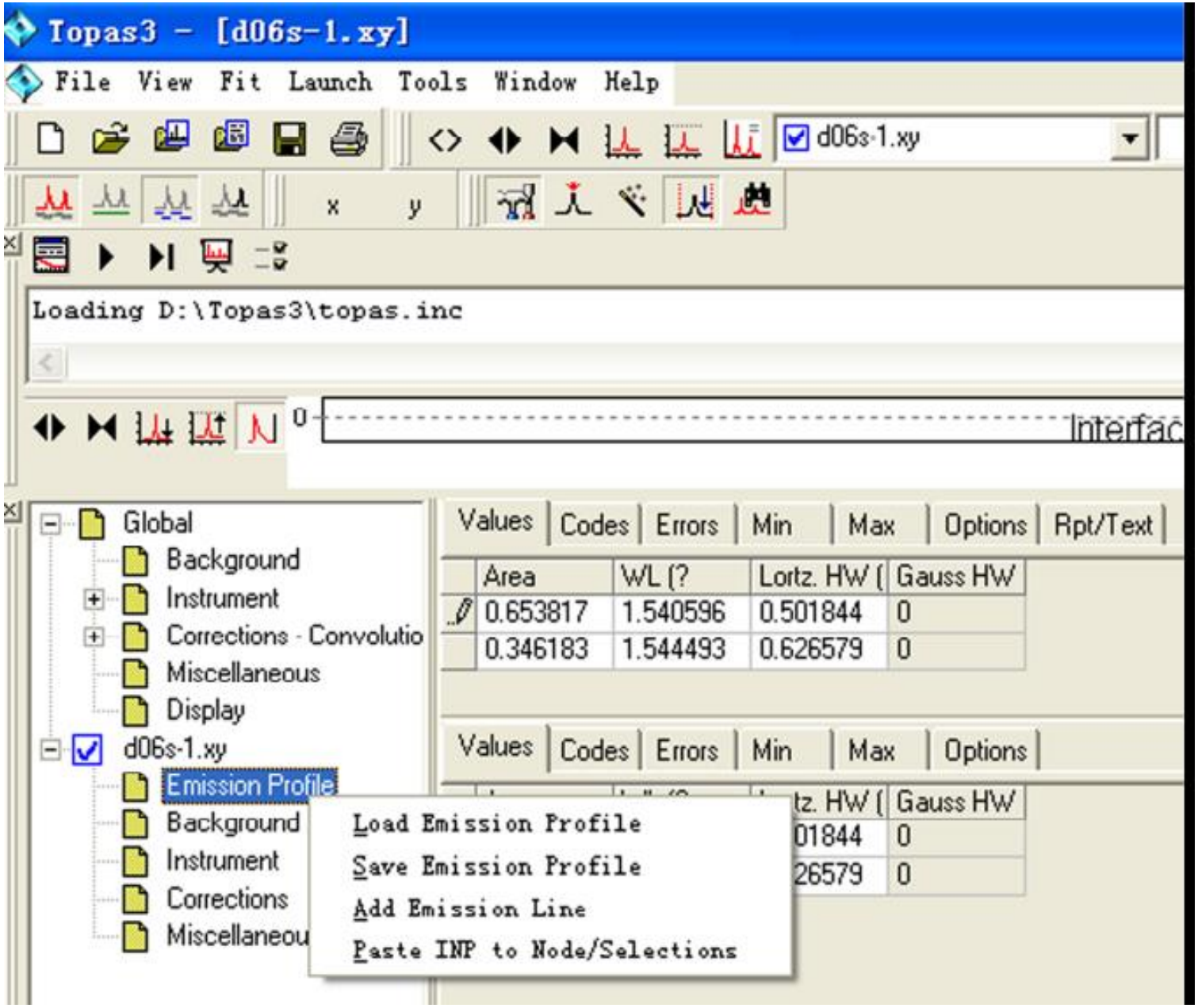
Emission profile
(光源的信息)

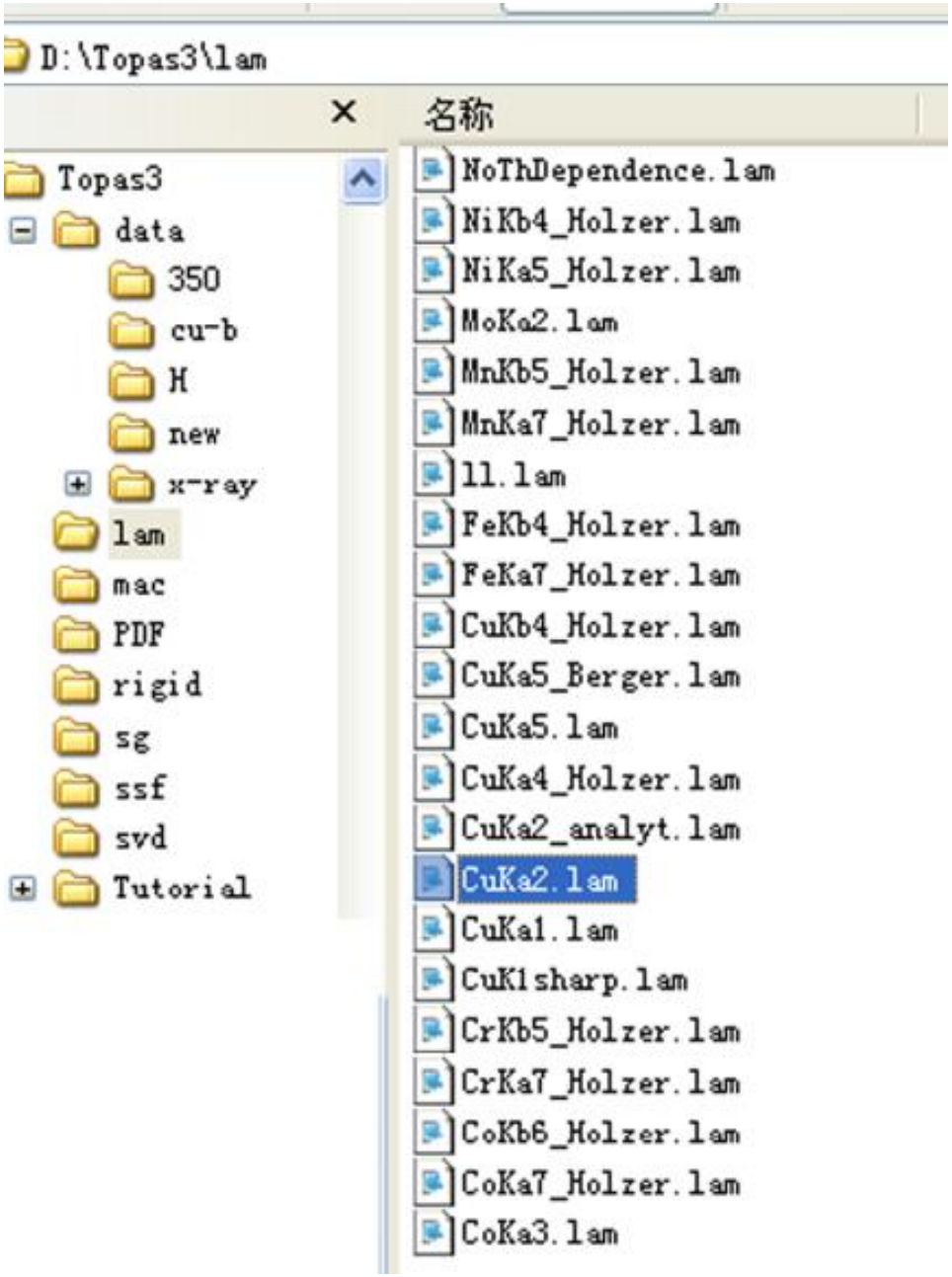
Gives the ability to add and delete emission lines which form the emission profile of the X-ray source.

The *Options* page contains the following options:

Option: Remarks:

- Ymin on Ymax Determines the x-axis extent to which peak tails are calculated (cut off)
- No Th dependence Defines an emission profile that is 2θ independent. Allows the use of non-X-ray data or fitting to negative 2θ values.
- For LAM cursor Switches the mouse cursor to a multi-line cursor representing the different emission lines of the current emission profile (Fig. 2-14)
- Lam for Bragg angle Only for expert users, refer to the Technical Reference manual
- Calculate Lam Only for expert users, refer to the Technical Reference manual


Topas3 - [d06s-1.xy]
File View Fit Launch Tools Window Help
d06s-1.xy
x y
Loading D:\Topas3\topas.inc
Global
Background
Instrument
Corrections - Convolutio
Miscellaneous
Display
d06s-1.xy
Emission Profile
Background
Instrument
Corrections
Miscellaneou
Load Emission Profile
Save Emission Profile
Add Emission Line
Paste INP to Node/Selections
Values Codes Errors Min Max Options Rpt/Text
Area WL (? Lortz. HW (Gauss HW
0.653817 1.540596 0.501844 0
0.346183 1.544493 0.626579 0
Values Codes Errors Min Max Options
Gauss HW
01844 0
26579 0


D:\Topas3\lam
名称
Topas3
data
350
cu-b
H
new
x-ray
lam
mac
PDF
rigid
sg
ssf
svd
Tutorial
NoThDependence.lam
NiKb4_Holzer.lam
NiKa5_Holzer.lam
MoKa2.lam
MnKb5_Holzer.lam
MnKa7_Holzer.lam
ll.lam
FeKb4_Holzer.lam
FeKa7_Holzer.lam
CuKb4_Holzer.lam
CuKa5_Berger.lam
CuKa5.lam
CuKa4_Holzer.lam
CuKa2_analyt.lam
CuKa2.lam
CuKa1.lam
CuK1sharp.lam
CrKb5_Holzer.lam
CrKa7_Holzer.lam
CoKb6_Holzer.lam
CoKa7_Holzer.lam
CoKa3.lam

*.lam文件的内容

普通衍射仪：

lam

ymin_on_ymax 0.0001

la 0.653817 lo 1.540596 lh 0.501844

la 0.346183 lo 1.544493 lh 0.626579

布鲁克的D8 Advance：

lam

ymin_on_ymax 0.0001

la 1 lo 1.540596 lh 0.401844

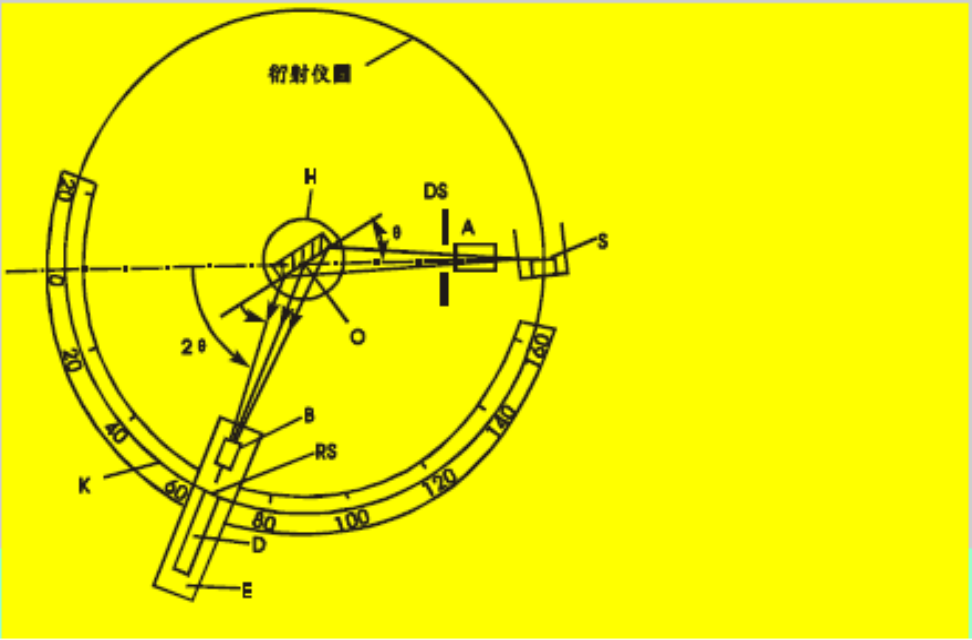
Instrument
（仪器参数）

- Bragg-Brentano geometry
- Additional Convolutions

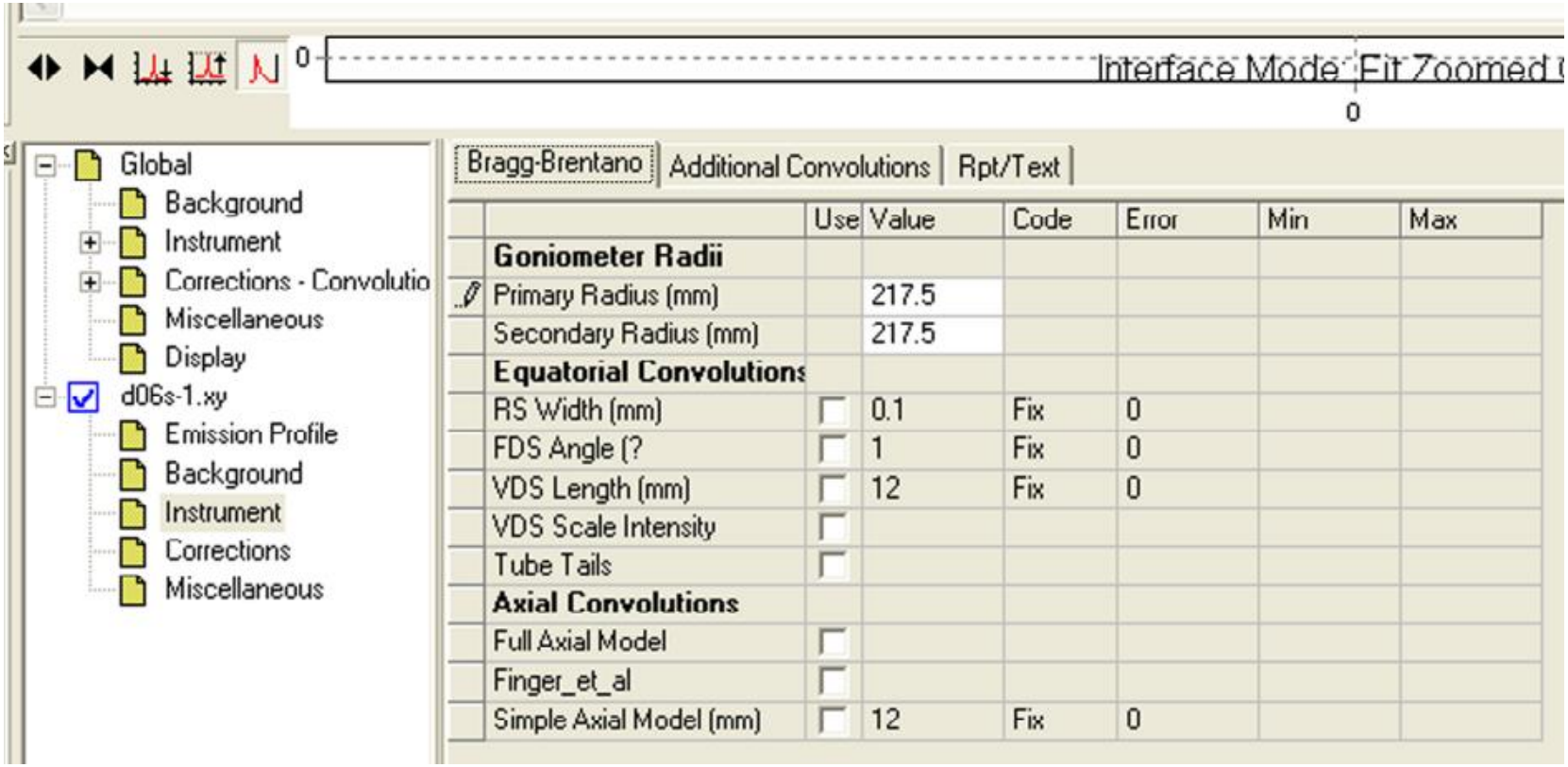
Bragg-Brentano 衍射几何

测角仪光路与聚焦圆

衍射仪通常使用线焦X射线，线焦应与与测角仪转动轴平行，而且，线焦到衍射仪转动轴O的距离与轴到接收狭缝RS的距离相等，平板试样的表面必须经过测角仪的轴线。按照这样的几何布置，当试样的转动角速度为探测器（接收狭缝）的角速度的1/2时，无论在何角度，线焦点、试样和接收狭缝都在一个圆上，而且试样被照射面总与该圆相切，此圆则称为聚焦圆，如图所示。



Bragg-Brentano geometry



The Bragg-Brentano page:

Contains all instrument details necessary to model the instrument function using the Fundamental Parameters Approach. This includes the following refinement models:

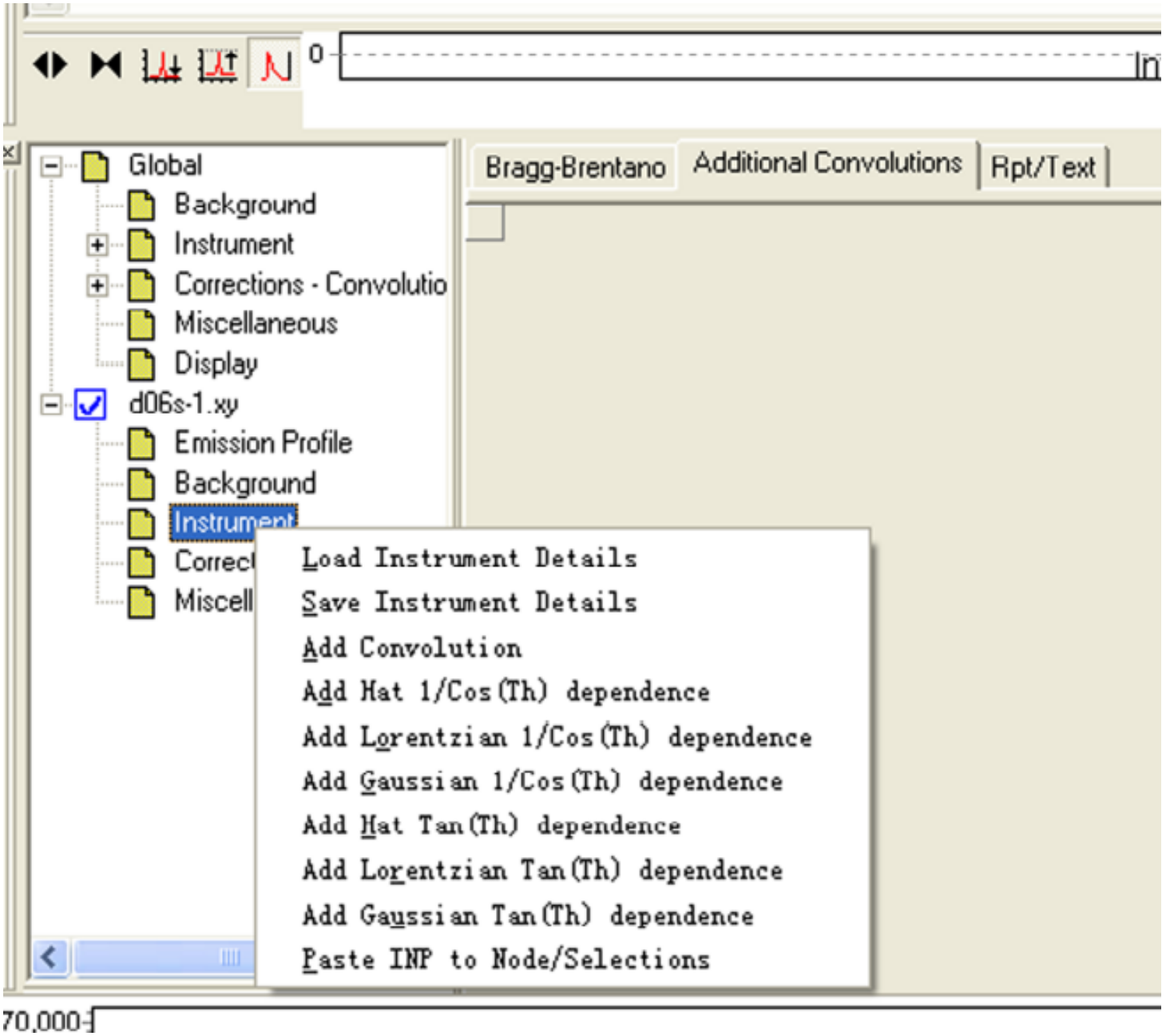
Parameter name:	Remarks:
Goniometer radii	
• Primary Radius	Primary goniometer circle radius [mm]
• Secondary Radius	Secondary goniometer circle radius [mm]
Equatorial Convolutions	
• RS Width	Receiving Slit (= detector slit) width [mm]
• FDS Angle	Fixed Divergence Slit angle [°]
• VDS Length	Irradiated sample length in beam direction for Variable Divergence Slits [mm]
• VDS Scale Intensity	1/sin(θ) intensity correction for Variable Divergence Slits
• Tube Tails	Tube tails correction (Bergmann, 2000)
• Source Width	Width of the tube filament [mm]
• Z1	Length of the left tail (negative) [mm]
• Z2	Length of the right tail [mm]
• Fraction	Fractional height of the tube tails relative to the main beam

Axial Convolutions

• Full Axial Model	Accurate model for describing peak asymmetry
• Source Length	Length of the tube focus [mm]
• Sample Length	Length of the irradiated sample [mm]
• RS Length	Receiving Slit length [mm]
• Prim. Soller	Primary Soller slit angle [°]
• Sec. Soller	Secondary Soller slit angle [°]
• N Beta	Only for expert users, refer to the Technical Reference manual
• Del	Only for expert users, refer to the Technical Reference manual
• Finger_et_al	Simplified model for describing peak asymmetry
• Simple Axial Model	Simplified model for describing peak asymmetry

Short cut menu options of the *Bragg Brentano* page are:

- **Load Instrument Details**
  Loads instrument details from a PAR file
- **Save Instrument Details**
  Saves instrument details to a PAR file


0
Global
Background
Instrument
Corrections - Convolutio
Miscellaneous
Display
d06s-1.xy
Emission Profile
Background
Instrument
Bragg-Brentano
Additional Convolutions
Rpt/Text
Load Instrument Details
Save Instrument Details
Add Convolution
Add Hat 1/Cos(Th) dependence
Add Lorentzian 1/Cos(Th) dependence
Add Gaussian 1/Cos(Th) dependence
Add Hat Tan(Th) dependence
Add Lorentzian Tan(Th) dependence
Add Gaussian Tan(Th) dependence
Paste INP to Node/Selections
70,000

The Additional Convolutions page:

Provides for empirical modelling of instrument functions. Available convolutions include the Hat, Lorentzian, Gaussian, Circles, Exponential, and One_on_X convolutions to be selected from the *Conv. Type* combo box. Predefined angular dependencies are Constant, 1/Cos(Th), Tan(Th), and Sin(2 Th) to be selected from the *2Th Dependence* combo box; alternatively, user-defined angular dependencies can be provided in the form of equations.

Short cut menu options of the *Additional Convolutions* page are:

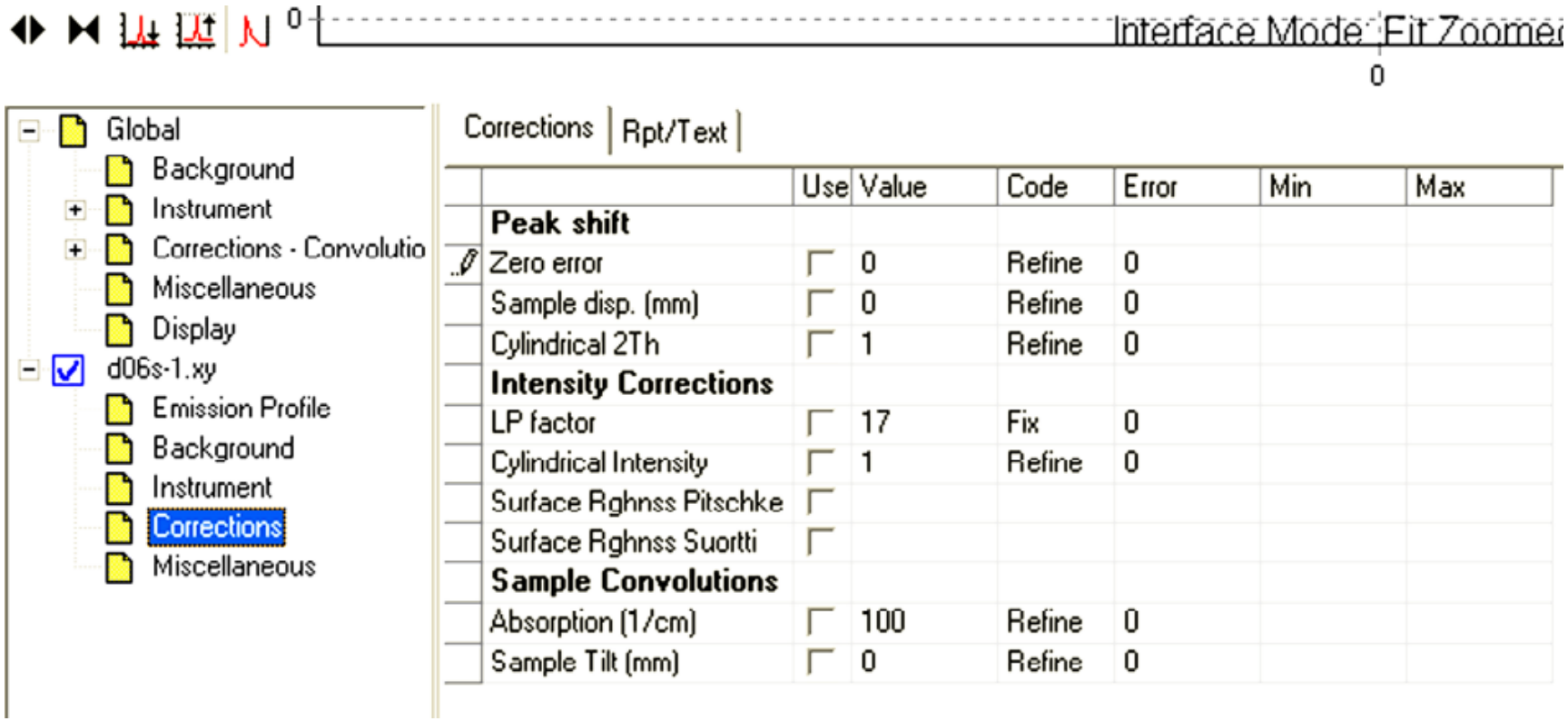
- **Load Instrument Details**
  Loads instrument details from a PAR file
- **Save Instrument Details**
  Saves instrument details to a PAR file
- **Add Convolution**
  Adds an additional convolution. Convolution type and angular dependence can be defined using the *Conv. Type* and *2Th Dependence* combo boxes.

Additionally it offers quick access to the following important convolutions:

- **Add Hat 1/cos(Th) dependence**
- **Add Lorentzian 1/cos(Th) dependence**
- **Add Gaussian 1/cos(Th) dependence**
- **Add Hat Tan(Th) dependence**
- **Add Lorentzian Tan(Th) dependence**
- **Add Gaussian Tan(Th) dependence**

Selected additional convolution rows can be deleted using the DEL key.

Corrections



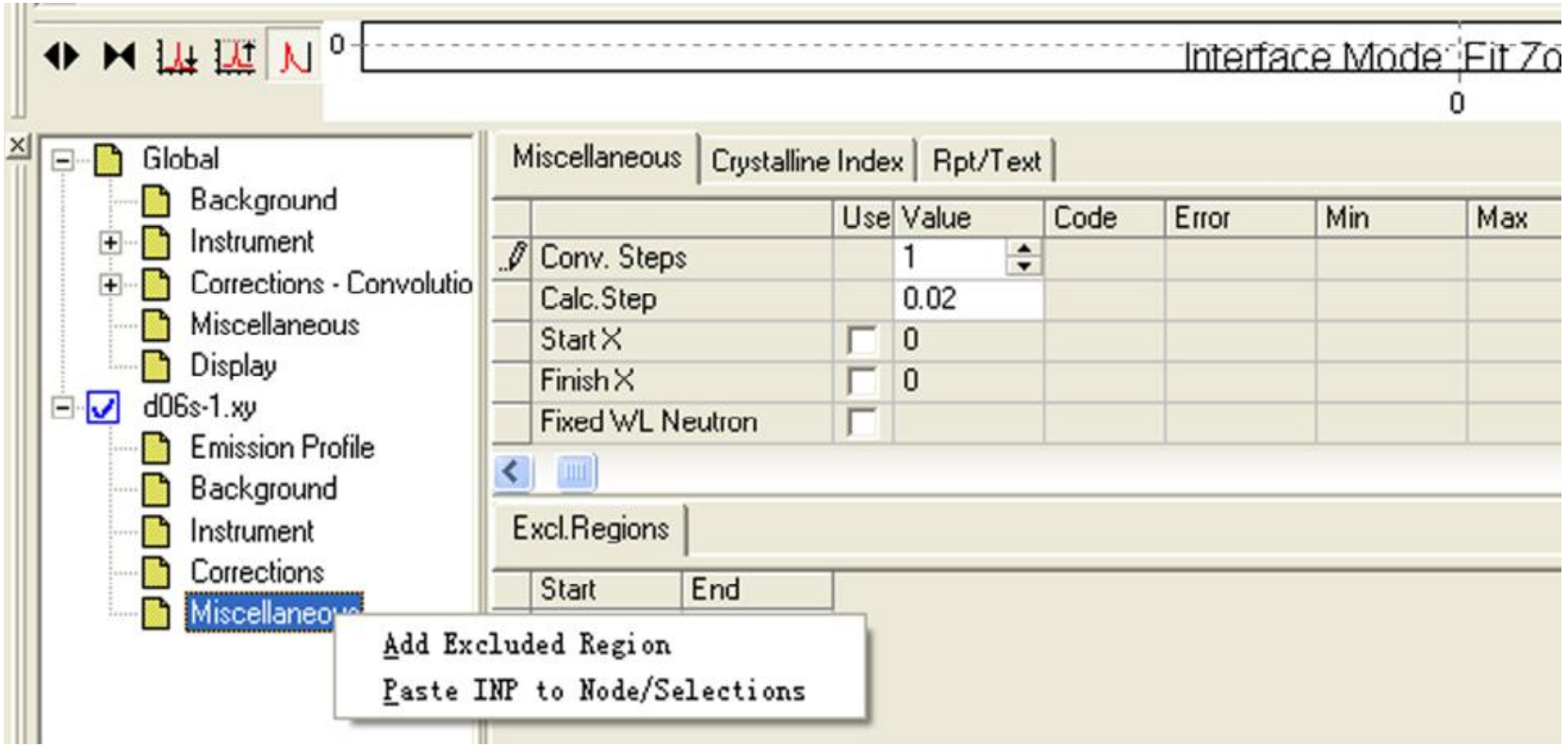
Parameter name:	Remarks:
• Zero Error	Zero point error in [° 2θ].
• Sample Disp.	Sample displacement in [mm].
• LP Factor	Lorentz-Polarisation factor using the monochromator angle in [°2θ].
• Absorption	Linear absorption coefficient used for adjusting the peak shape [cm^{-1}].
• Sample Thickness	Sample thickness in [mm] in the direction of the scattering vector
• Scale Intensity	Peak intensity correction for absorption effects
• Sample Tilt	Sample tilt in [mm].

The Lorentz-Polarisation factor for unpolarized radiation is 0 (e.g. X-ray diffractometers without any monochromator) and 90 for fully polarized radiation (e.g. synchrotron radiation). Values for most common monochromators (Cu radiation) are:

- Ge : 27.3
- Graphite : 26.4
- Quartz : 26.6

There is no polarization factor for neutron data and thus the angle for Lorentz Polarization should be set to 90; this gives the Lorentz only part.

Miscellaneous



Parameter name:	Remarks:
• Convolution Steps	An integer corresponding to the number of calculated data points per measured data point. It may be useful to increase this number when numerical instabilities are introduced. This can happen when a particular convolution has a small effect on the profile shape or when the measurement step is large.
• Start X, Finish X	Used to limit the refined X range independent on zooming
• Fixed WL Neutron	Signals the use of neutron atomic scattering lengths

The *Excl. Regions* page allows for a definition of an unlimited number of excluded regions, which may overlap. There is one option in the short cut menu:

- **Add Excluded Region**
  Adds an excluded region.

Selected excluded region rows can be deleted using the DEL key.

寻峰

Fit method Constraints and keywords 1)

SPF: Single peak fitting

No constraints by default. Optionally all profile parameters can be constrained (e.g. same shape, same width, relative intensity, ...)

Keywords: "*xo_I*", "*d_I*"

WPPF: Whole Powder pattern fitting.

• No constraints by default. Optionally all profile parameters can be constrained (e.g. same shape, same width, relative intensity, ...)

• Profile parameters constrained to be smoothly varying functions of 2θ

Keywords: "*xo_I*", "*d_I*"

WPPD: Whole powder pattern decomposition

Pawley and LeBail method

Number of peaks and their positions constrained by crystal system / spacegroup plus lattice parameters

Keyword: "*hkl_I*"

Rietveld: Rietveld structure refinement, ab-initio structure determination

Peak intensities constrained by the crystal structure

Keyword: "*str*"

1) For details refer to the Technical Reference manual

单谱线拟合

2.1.1.1 Single line fitting with a Split-PVII function

1. Start TOPAS.
2. Load the raw data by importing the file CEO2.RAW. By default this file is located in C:\TOPAS2\TUTORIAL\CEO2.

Menu:	Icon:	Shortcut:	Result:
File - *Import Data File(s)...*		n.a.	Imports measurement data

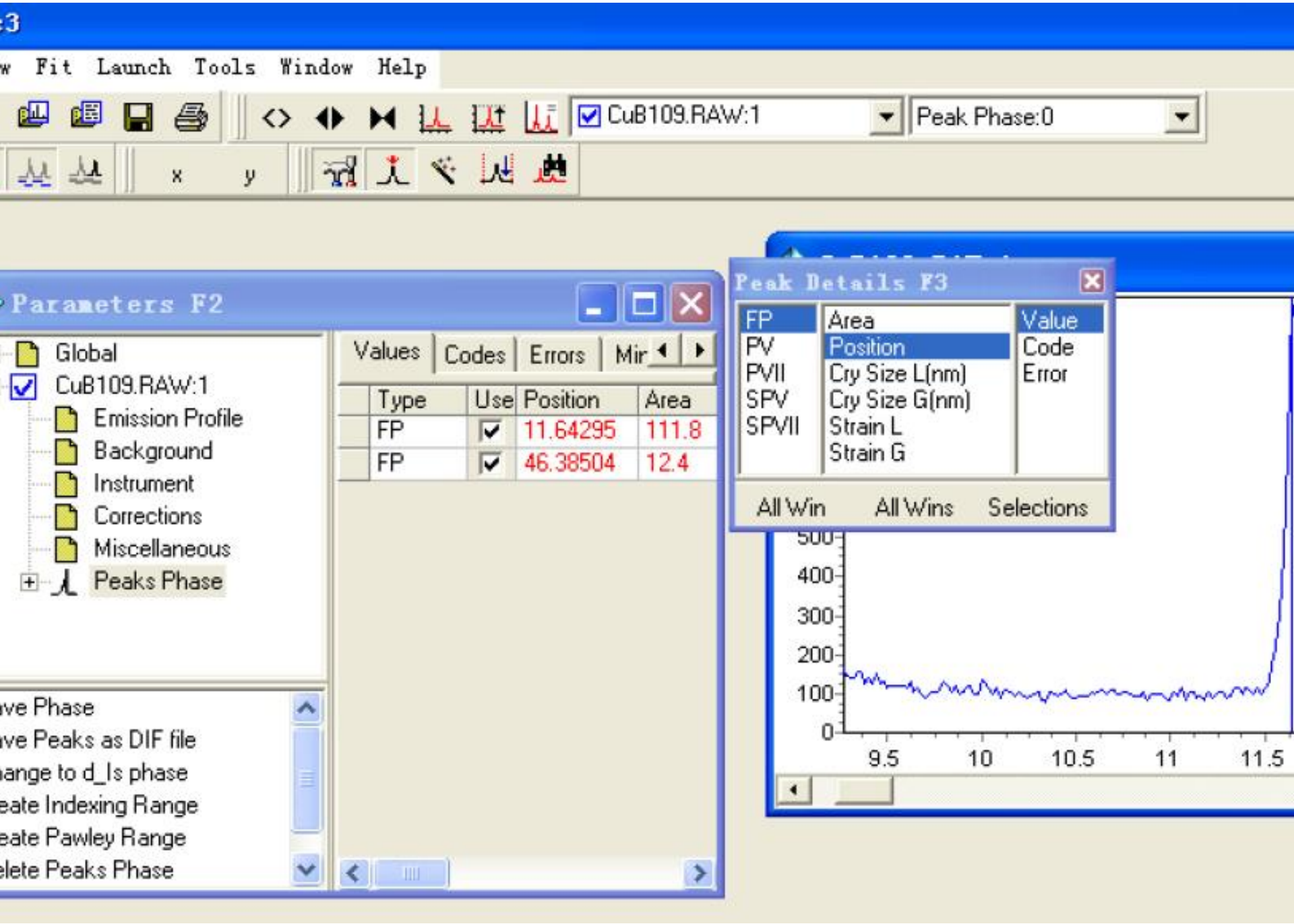
3. Zoom the first reflection in the region between 27.5° - 29.5° 2θ.

Hint! The *Chart Options Dialog* (found in the short cut menu of the *Scan Window*) is a powerful alternative for exact zooming. Its use for zooming is described in section 2.1.4.

4. Manually insert one peak at the desired 2θ position: Open the *Peak Details Dialog*, select the split-PVII function (SPVII), and insert one peak at the desired 2θ position by clicking the left mouse button. A stick indicates the peak position.

步骤

Menu:	Icon:	Shortcut:	Result:
View - *Peak Details Window*		F3	Displays or hides the *Peak Details Window*
View - *Parameters Window*		F2	Displays or hides the Parameters Window


Fit Launch Tools Window Help
CuB109.RAW:1
Peak Phase:0
x y
Parameters F2
Global
CuB109.RAW:1
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Peaks Phase
Values Codes Errors Mir
Type Use Position Area
FP 11.64295 111.8
FP 46.38504 12.4
ave Phase
ave Peaks as DIF file
hange to d_Is phase
eate Indexing Range
eate Pawley Range
elete Peaks Phase
Peak Details F3
FP PV PVII SPV SPVII
Area Position Cry Size L(nm) Cry Size G(nm) Strain L Strain G
Value Code Error
All Win All Wins Selections
500 400 300 200 100 0
9.5 10 10.5 11 11.5

2.2.3.5 Peak Details Dialog

Note: GUI mode only, not available in TOPAS R

Allows the insertion of different peak types as well as the direct editing of peak parameter values and refinement codes in the *Scan Window* (Fig. 2-6).

Peaks inserted into the *Scan Window* will be of the peak type selected in the left column. It is possible to insert different peak types into the same powder pattern. For each peak inserted a peak marker is displayed. In addition near to the top of the peak marker some peak properties such as profile parameter values or refinement codes for the associated peak can be shown depending on the selections in the second and third column of the *Peak Details Dialog*.

Note: The *Peak Details Dialog* is available in GUI mode only.

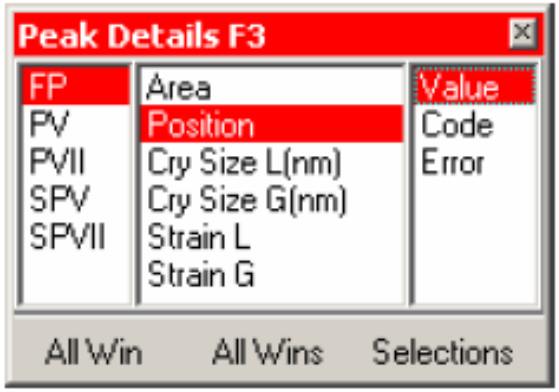


Fig. 2-6: *Peak Details Dialog*

When opening the *Peak Details Dialog* the cursor will change to peak insertion mode. The form of the cursor unambiguously reflects the selected peak type. A mouse click using the left mouse button in the *Scan Window* will insert a peak, when the *Peak Details Dialog* is open. Peaks can also be inserted anytime even when the Peak Details Window is closed by pressing the CTRL key when clicking the left mouse button.

An important feature of the Peak Details Window is the direct editing capability of peak parameter values and refinement codes in the *Scan Window*. A mouse click (LMB) on the text displayed nearby the peak using the left mouse button will open an edit field, which allows to change parameter values or refinement codes. Any changes have to be confirmed using the Enter key.

For changing the values of a peak group there are three buttons on the bottom of the Peak Details Window:

- **All Win**
  Overwrites the values of all peaks in the active *Scan Window* with the value in the edit field.

  Note: A change of the peak position moves all peaks to the same position!

- **All Wins**
  Same as All Win, but changes will be applied to all peaks in all *Scan Windows*.

- **Selections**
  Changes are applied to all selected peaks in the active *Scan Window*.

峰形函数

Topas Users Manual.pdf

TOPAS提供的两类峰形拟合方法

- **1. Analytical Profile Fitting:**

  analytical peak shape functions (PSF)

  Gaussian, Lorentzian, sums of Gaussians or Lorentzians, Voigt, pseudo-Voigt and Pearson VII functions

- **2. Direct Convolution Approach:**

$$Y(2\theta) = W \otimes F_1(2\theta) \otimes F_2(2\theta) \otimes \ldots \otimes F_i(2\theta) \otimes \ldots \otimes F_n(2\theta)$$

$Y(2\theta)$ is the observed line profile shape, W is the source emission profile, and $\otimes$ denotes the convolution process.

Source emission profiles
（衍射源谱线的描述）

Fig. 3-1: Phenomenological representation of the Cu Kα emission profile based on four Lorentzians (from Cheary et al., 2002).

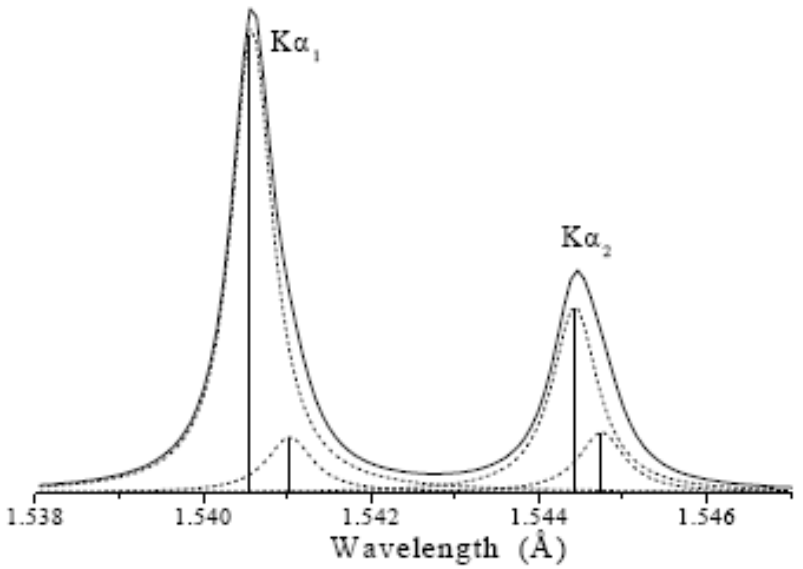


Fig. 3-2: CuKα emission profile showing the satellite group of lines and the extent of the tails from the $K\alpha_1$ and $K\alpha_2$ emission lines. This profile was recorded using the 400 line from a silicon single crystal wafer (from Cheary et al., 2002).

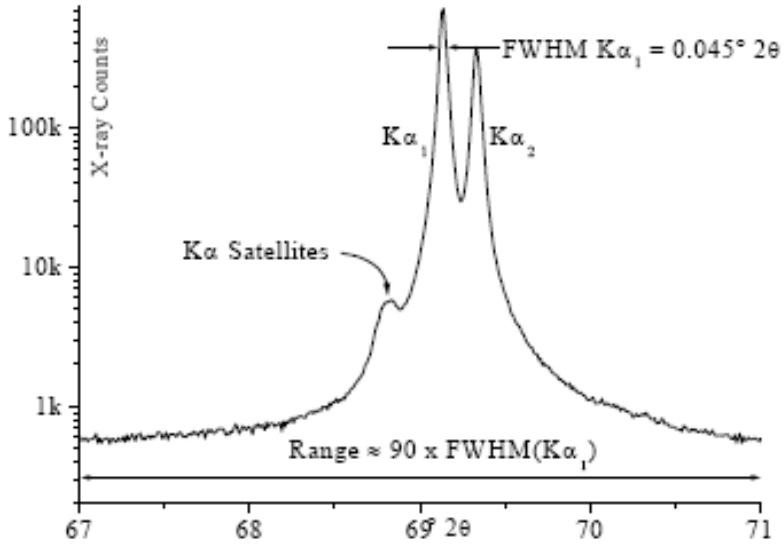
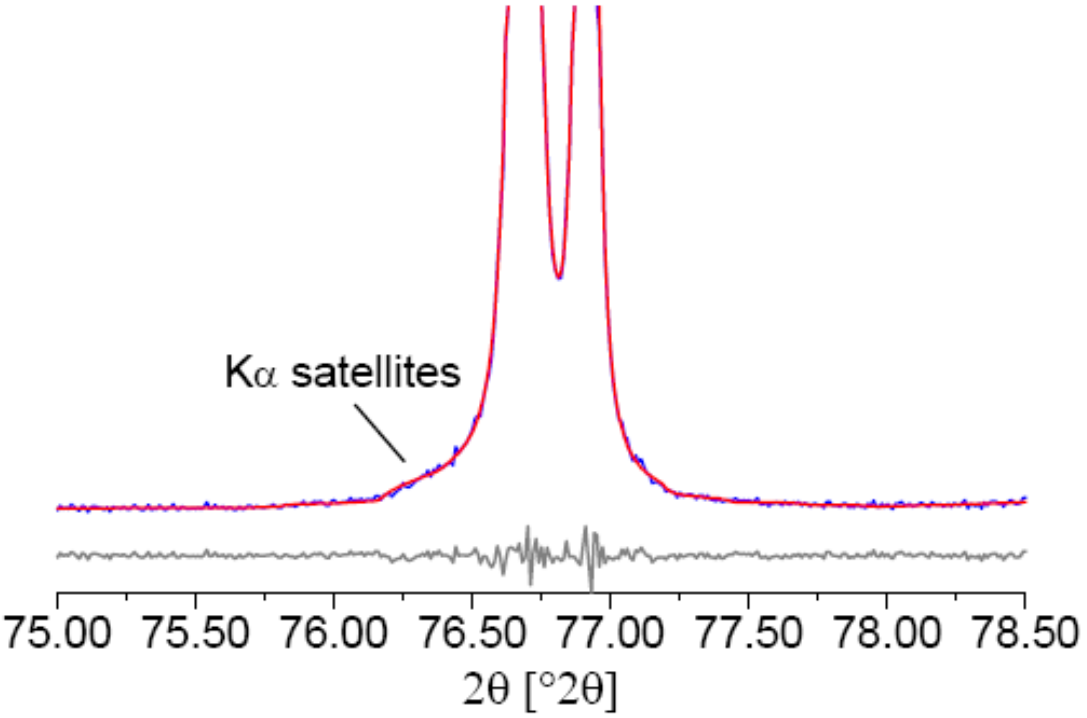
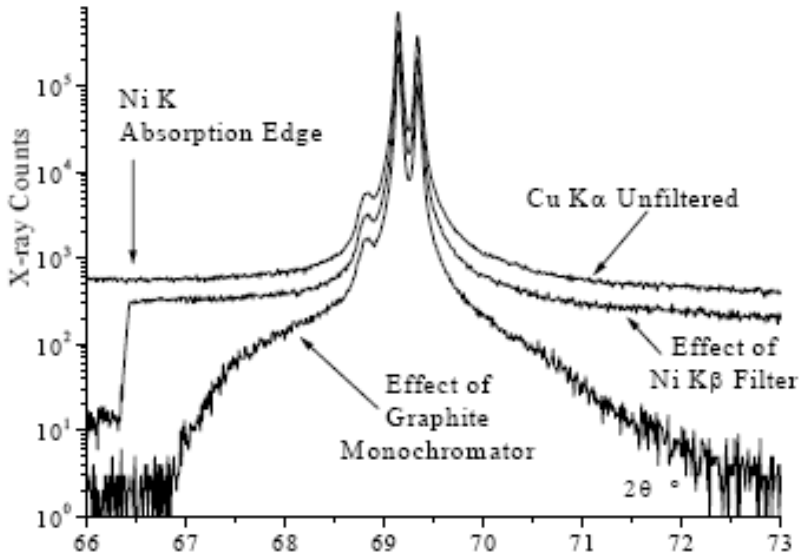


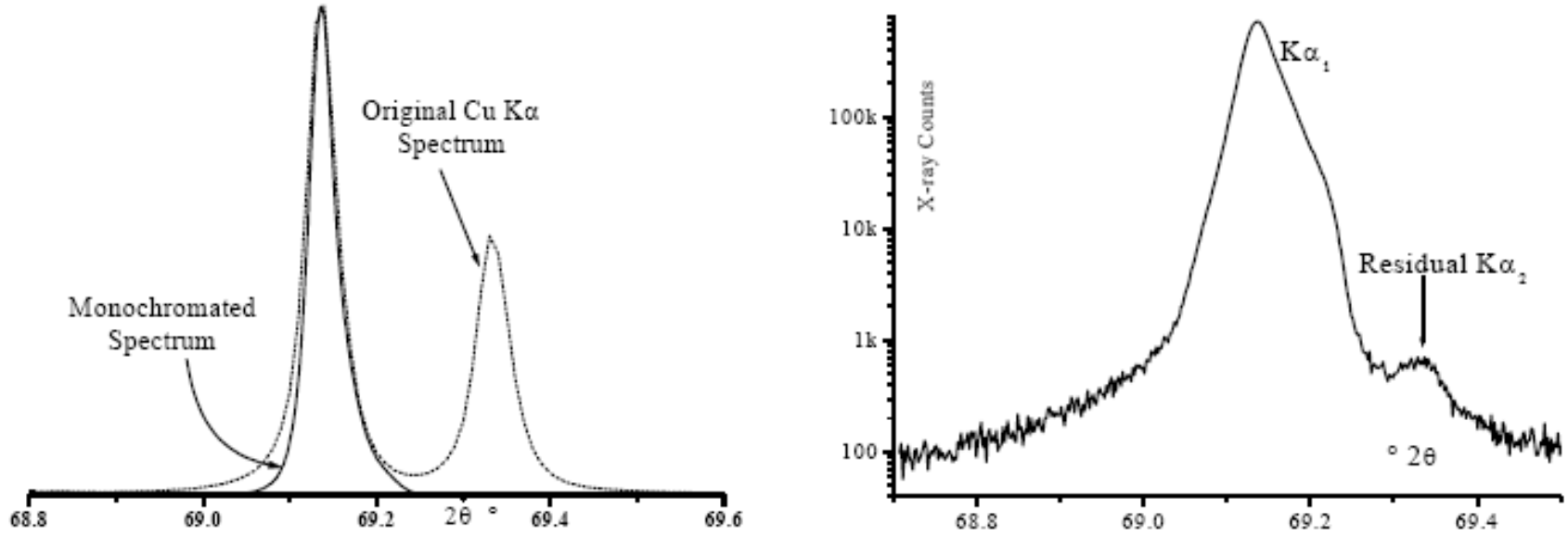
Fig. 3-3: Fundamental parameters fit to the 331 line of CeO_2 (Balzar, 2001) at about 76.7° 2θ. Divergent beam data have been taken with a D8 ADVANCE (Bruker AXS). The Kα satellites contribute significant intensity to the total profile, which is typically neglegted in analytical profile fitting approaches.



单色器对峰形的影响

Fig. 3-4: CuKα emission profile obtained using the 400 line from a silicon single crystal wafer. Each pattern was recorded sequentially using the same sample, first with no filter or monochromator in the beamline, then with a Ni Kβ filter, and finally with a standard curved graphite diffracted beam monochromator (from Cheary et al., 2002).





a) b)

Fig. 3-5: Wavelength spectrum emerging from an asymmetrically cut Ge111 ground and bent incident beam monochromator presented linearly (a) and logarithmically (b). The Kα satellites are completely removed, but the $K\alpha_2$ is still present at ≈0.02% of $K\alpha_1$ even in a well aligned system (from Cheary et al., 2002).

Table 3-1: Two examples for differently sophisticated descriptions of the Cu Kα emission profile. λ: wavelength; I_{Rel}: relative intensity; lh: Lorentzian halfwidth (parameters are described in the Technical Reference manual).

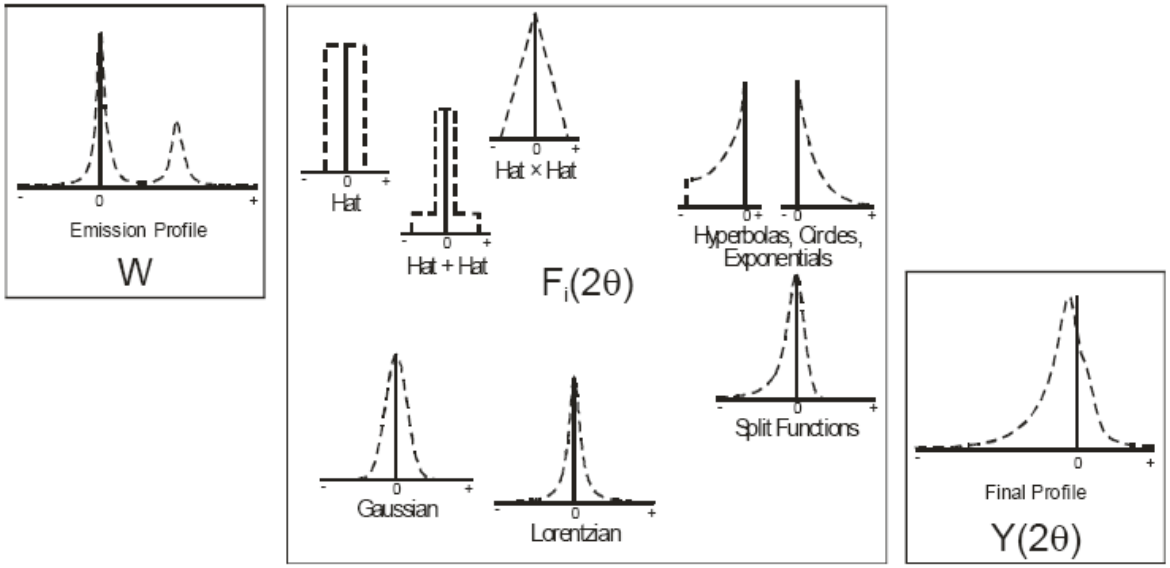
Emission profile	**Emission lines**	**λ [Å]**	**I_{Rel}**	**lh [Å x 10^{-3}]**
CuKa5	Satellites	1,534753	1,59	3,69
	$K\alpha_{1a}$	1,540596	57,91	0,44
	$K\alpha_{1b}$	1,541058	7,62	0,60
	$K\alpha_{2a}$	1,544410	24,17	0,52
	$K\alpha_{2b}$	1,544721	8,71	0,62
CuKa2_analyt	$K\alpha_1$	1,540596	66,05	0,50
	$K\alpha_2$	1,544493	33,95	0,50

Table 3-2: Predefined emission profiles in TOPAS. The name components "Holzer" and "Berger" denote source emission profiles taken from Hölzer et al. (1997) and Berger (1986) respectively.

Anode material	Kα	Kβ
Cu	CuKa1 [1)]	
	CuKa2	
	CuKa2_analyt	
	CuKa4_Holzer	CuKb4_Holzer
	CuKa5	
	CuKa5_Berger	
Co	CoKa3	
	CoKa7_Holzer	CoKb6_Holzer
Cr	CrKa7_Holzer	CrKb5_Holzer
Fe	FeKa7_Holzer	FeKb4_Holzer
Mn	MnKa7_Holzer	MnKb5_Holzer
Ni	NiKa5_Holzer	NiKb4_Holzer
Mo	MoKa2	

[1)] Monochromatic Cu emission profile for instruments equipped with Johannson-type Ge primary monochromator

Direct convolution approach
Empirical parameterisation
（直接卷积法：实验参数法）



$$Y(2\theta) = W \otimes F_1(2\theta) \otimes F_2(2\theta) \otimes \ldots \otimes F_i(2\theta) \otimes \ldots \otimes F_n(2\theta)$$

Fig. 3-6: Schematic representation of the convolution approach as given in equation 3-1. The final profile $Y(2\theta)$ is described by the selection of appropriate functions $F_i(2\theta)$ and convoluting them on top of the emission profile W. Note the capabilities of this approach to add functions before convoluting them as shown for the sum of two hat functions as well as to convolute split-type functions.

The explicit discrimination of instrument and specimen contributions (Jones, 1938):

$$Y(2\theta) = (W \otimes G) \otimes S, \qquad (3\text{-}2)$$

where

- G and S are instrument and sample contributions respectively which are modeled separately using appropriate $F_i(2\theta)$ functions according to equation 3-1.

In general, a particular target system or instrumental setup ($W \otimes G$) is seen as an entity called the instrument function $I(2\theta)$, which can be either measured (conventional approach) or calculated from first principles based on the known instrument geometry (fundamental parameters approach, which is discussed in detail later).

In the conventional convolution approach an instrument function I(2θ) is determined experimentally from a standard material, which ideally should (but does not) meet the following requirements: (i) large crystallite size to minimize size broadening, (ii) small crystallite size to give sufficient particle statistics, (iii) no strain and (iv) possess the same linear absorption coefficient as the specimen. The instrument function is then convoluted with specimen related functions to represent the "real" specimen properties. Obviously the requirement to have both large and small crystallites simultaneously is a contradiction and limits the accuracy of microstructure analysis at small levels of specimen broadening. In many approaches such as the Double-Voigt Approach (e.g. Balzar, 1999), Lorentzian and Gaussian functions are employed to describe both crystallite size and strain effects. For more information about the Double-Voigt Approach, which is supported by TOPAS, refer to the Technical Reference manual.

In principle any instrument function can be described using the conventional convolution approach in TOPAS. However, the quality of the instrument function is directly related to the quality of the standard material and thus additional broadening in the instrument function is unavoidable for reasons described above. As a result specimen broadening is underestimated resulting in erroneous specimen characteristics such as over-estimated crystallite size estimates.

A further drawback is that the instrument function needs re-determination when relevant instrument settings, such as slit settings, change. In addition the effects of sample penetration by the incident beam is often overlooked resulting in increased broadening in the instrument function. This is an intrinsic error to the conventional convolution approach whereby the instrument function is linked to sample preparation (packing density).

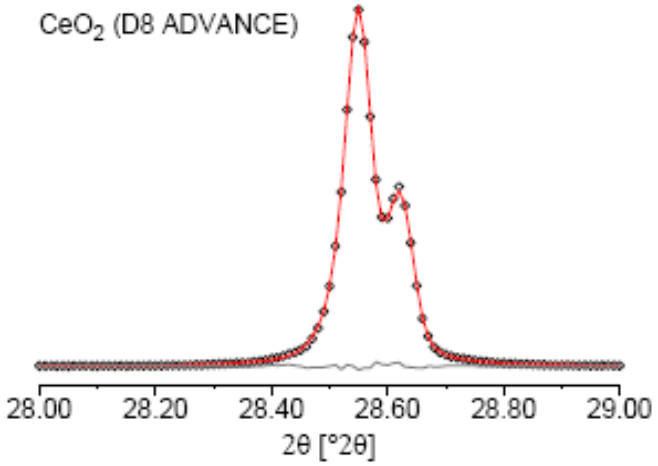


Fig. 3-7a: Laboratory X-ray data, measured instrument function (D8 ADVANCE, Bruker AXS).

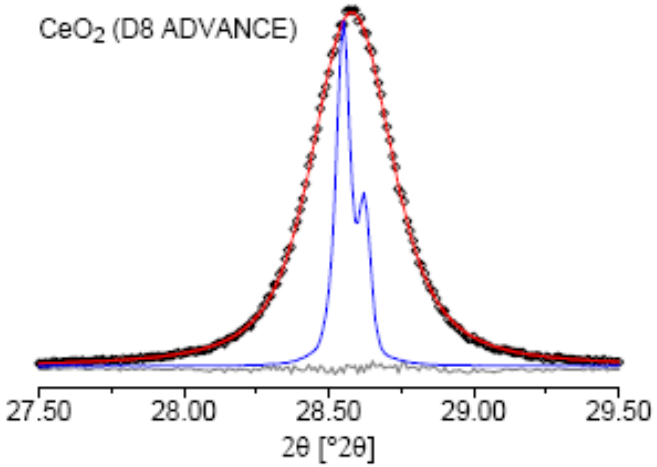


Fig. 3-7b: Laboratory X-ray data, broadened data (D8 ADVANCE, Bruker AXS).

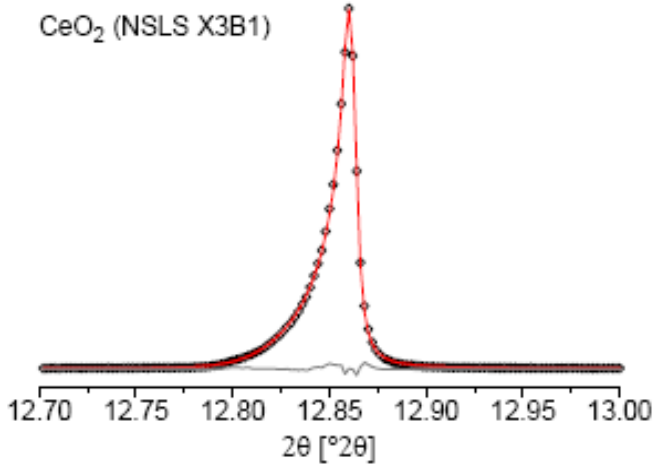


Fig. 3-8a: Synchrotron data, measured instrument function (NSLS X3B1).

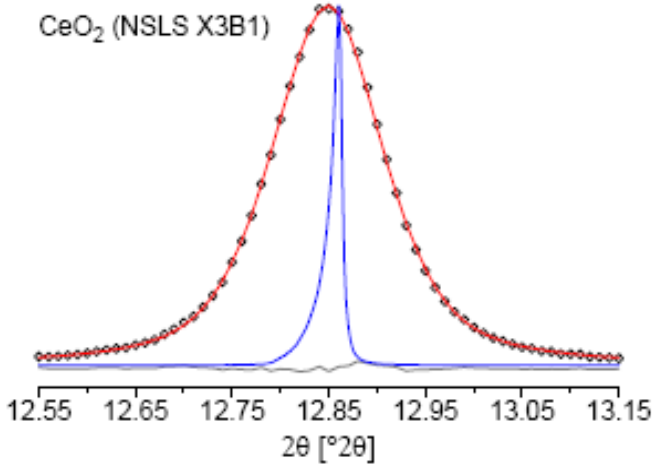


Fig. 3-8b: Synchrotron data, broadened data (NSLS X3B1).

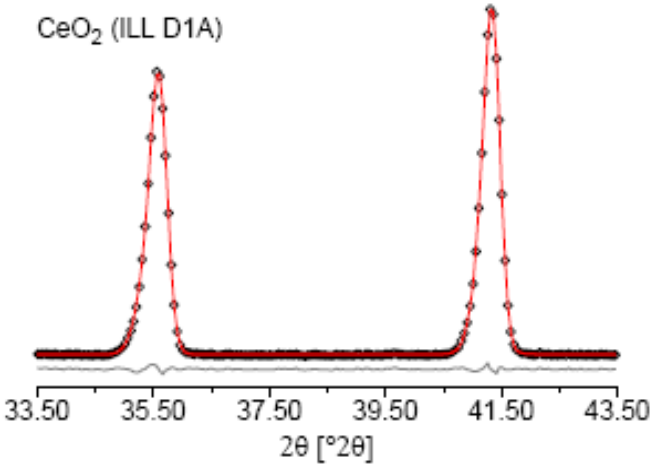


Fig. 3-9a: CW neutron data, measured instrument function (ILL D1A).

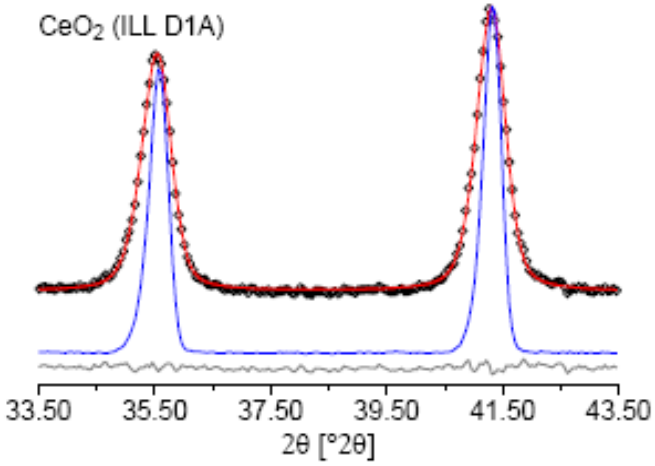


Fig. 3-9b: CW neutron data, broadened data (ILL D1A).

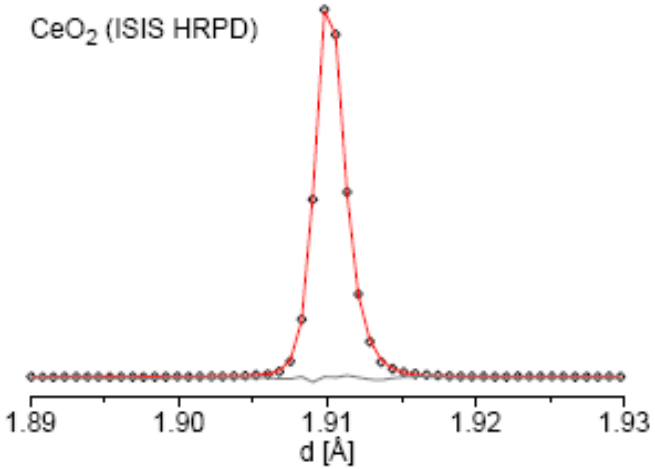


Fig. 3-10a: TOF neutron data, measured instrument function (ISIS HRPD).

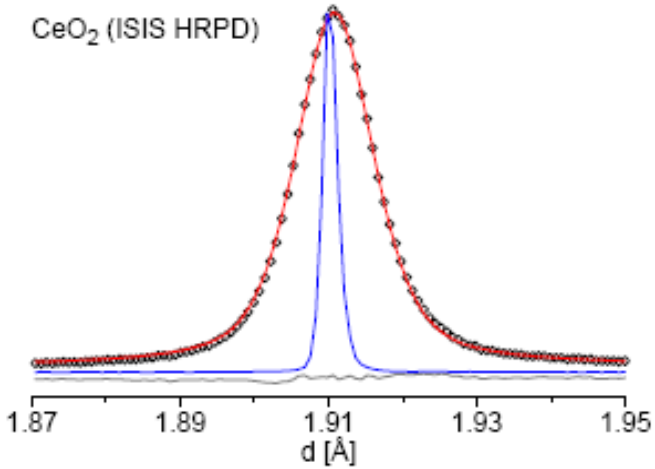


Fig. 3-10b: TOF neutron data, broadened data (ISIS HRPD).

经验函数

Table 3-4: Analytical PSFs supported in TOPAS. For generic unit area expressions and definitions of the PSF dependent parameters refer to the Technical Reference manual.

PSF:	Name:	PSF dependent parameters:
Single line fitting:		
Gaussian [1)]	G	*Ia*, $2\theta_k$, *fwhm*
Lorentzian [2)]	L	*Ia*, $2\theta_k$, *fwhm*
PearsonVII	PVII	*Ia*, $2\theta_k$, *fwhm*, *m*
Pseudo-Voigt	PV	*Ia*, $2\theta_k$, *fwhm*, η
Split PearsonVII	SPVII	*Ia*, $2\theta_k$, *fwhm*1, *fwhm*2, *m*1, *m*2
Split PseudoVoigt	SPV	*Ia*, $2\theta_k$, *fwhm*1, *fwhm*2, η1, η2
Whole pattern fitting:		
PearsonVII	PVII	*Ia*, *ha*, *hb*, *hc*, *ma*, *mb*, *mc*
Modified Pseudo-Voigt	PV_MOD	*Ia*, *ha*, *hb*, *hc*, *lora*, *lorb*, *lorc*
TCHZ Pseudo-Voigt	PV_TCHZ	*Ia*, *U*, *V*, *W*, *X*, *Y*, *Z*

[1)] PV function with mixing factor $\eta = 0$

[2)] PV function with mixing factor $\eta = 1$

Direct convolution approach: Fundamental parameters
（基本参数法）

$$Y(2\theta) = (W \otimes G) \otimes P \otimes S, \quad (3\text{-}3)$$

where

- P represents the sample contribution function
- G and S are instrument and sample contributions respectively which are modeled separately using appropriate $F_i(2\theta)$ functions according to equation 3-1.

The instrument function $I(2\theta)=(W\times G)$ in terms of the individual aberrations $G_i(2\theta)$ can be written as:

$$I(2\theta) = W \otimes G_1(2\theta) \otimes G_2(2\theta) \otimes \ldots \otimes G_i(2\theta) \otimes \ldots \otimes G_n(2\theta) \quad (3\text{-}4)$$

Thus it is seen from equations 3-1 and 3-4 that FPA is a special case of convolution based profile fitting. The important difference is that $I(2\theta)$ for FPA is determined from prior knowledge of the emission profile and diffractometer geometry resulting in far fewer refinable profile parameters. This results in decreased correlations between the profile, background and in particular microstructural parameters leading to an overall improvement of the refinement process within all profile fitting methods.

Diffractometer configurations and their geometrical aberrations

- **Divergent Beam Laboratory Diffractometers**

- **Parallel Beam Diffractometers**

Divergent Beam Laboratory Diffractometers

- the finite width of the X-ray source
- flat specimen error
- finite angular acceptance of the receiving optics (receiving slit)
- specimen transparency
- axial divergence

Position sensitive detectors (PSDs)

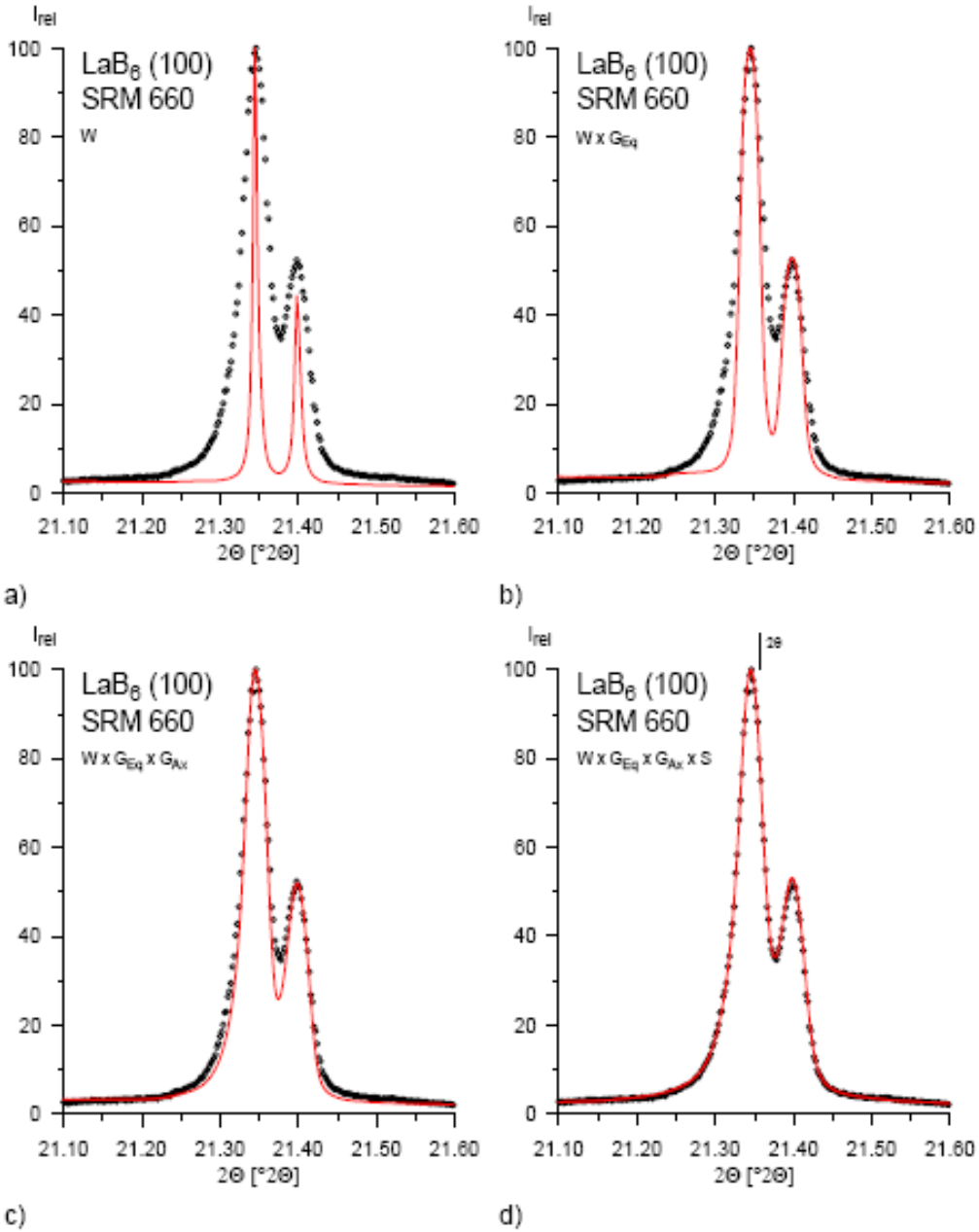
- defocusing due to asymmetric diffraction
- discharge resolution of the detector
- parallax error

Parallel Beam Diffractometers

- axial divergence
- finite angular acceptance of the receiving optics

Position sensitive detectors (PSDs)

- discharge resolution for both detector types
- parallax error for linear detectors


I rel
LaB6 (100)
SRM 660
W
W x GEq
W x GEq x GAx
W x GEq x GAx x S
2θ
100
80
60
40
20
0
21.10
21.20
21.30
21.40
21.50
21.60
2Θ [°2Θ]
a)
b)
c)
d)

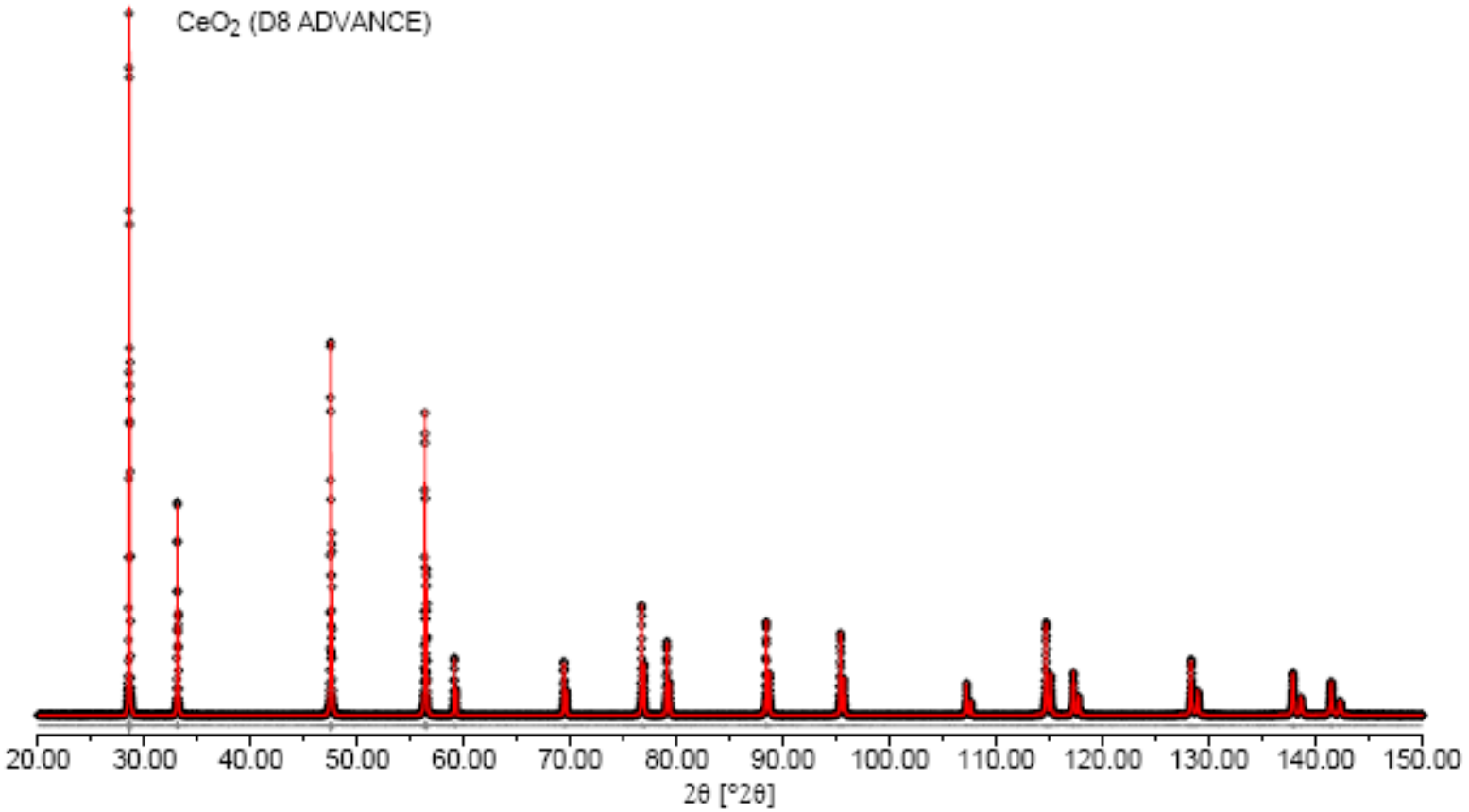
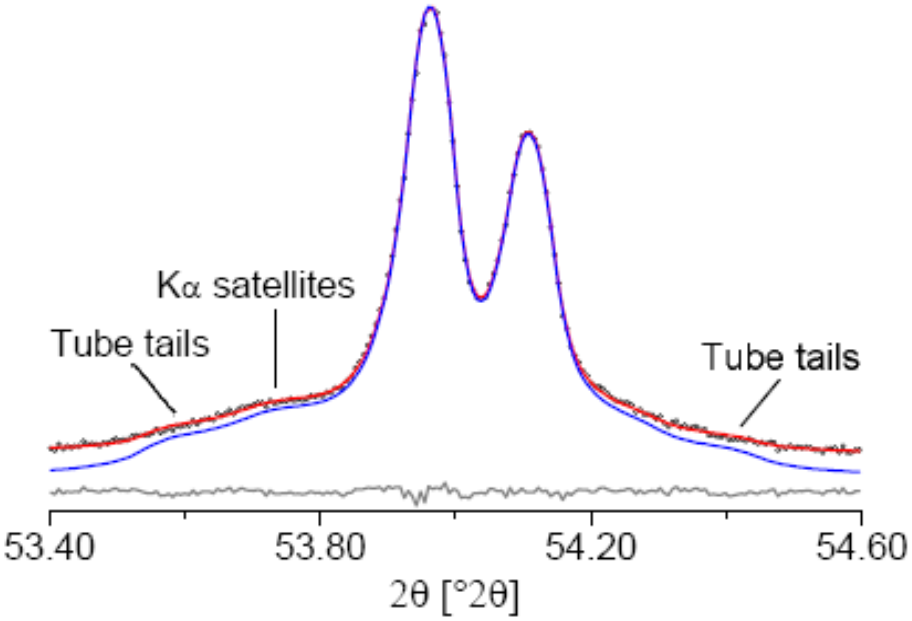


Fig. 3-12: Fundamental parameters based full pattern Pawley fit to the CeO_2 laboratory X-ray data (D8 ADVANCE, Bruker AXS), measured instrument function (Balzar, 2001).

Treatment of satellite peaks and tube tails

Fig. 3-14: Single line fundamental parameters fit to the 211 line of LaB_6 (NIST SRM 660a) at about 54° 2θ with tube tails (square root scale). The blue line represents the calculated data without background. Courtesy by Cline (2001).



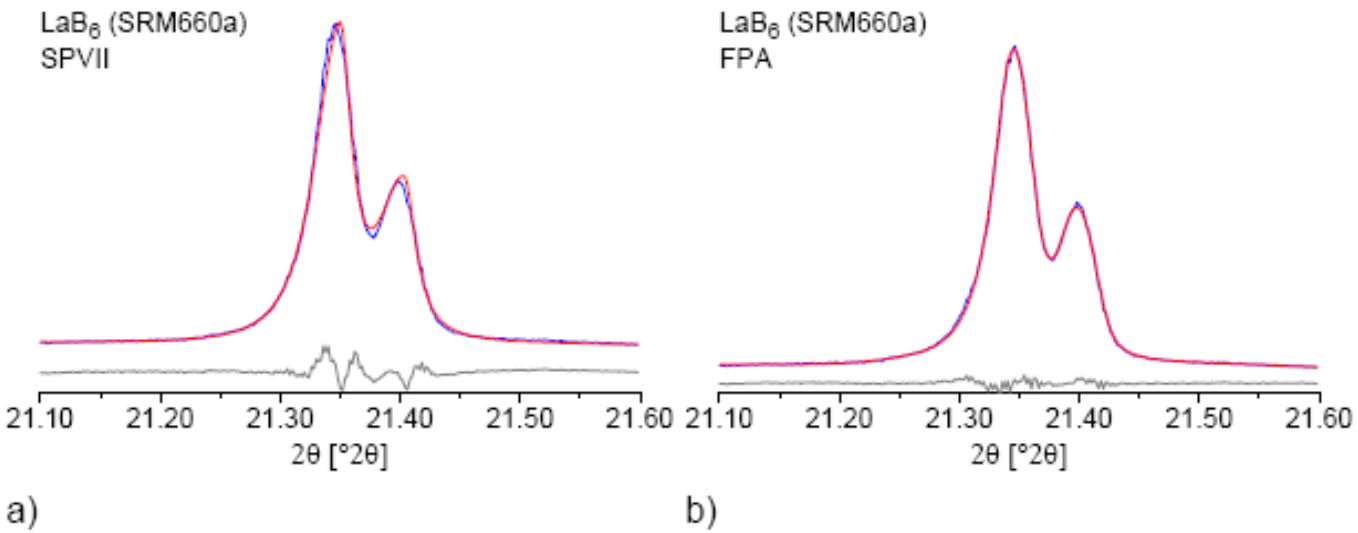


Fig. 3-15: Comparison of a single line fit to the 100 line of LaB_6 (SRM660a) with a SPVII function (a) versus a FPA fit of the same data in (b).

Table 3-5: Agreement indices obtained by the split-PearsonVII (SPVII) and fundamental parameters approach (FPA) in Fig. 3-15.

	R_P	R_{WP}	R_{Exp}	GOF	DW
SPVII	4.8	6.1	1.9	3.2	0.44
FPA	2.2	3.1	1.9	1.6	1.35

- improved refinement stability,
- increased refinement speed due to faster convergence, and
- reduced parameter correlations and therefore more physically meaningful parameters.

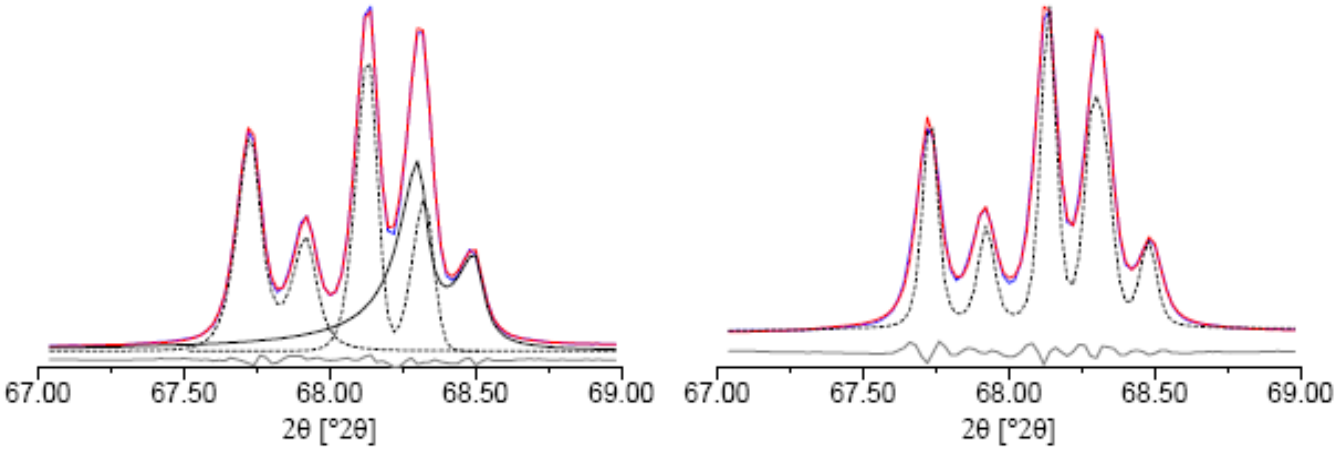
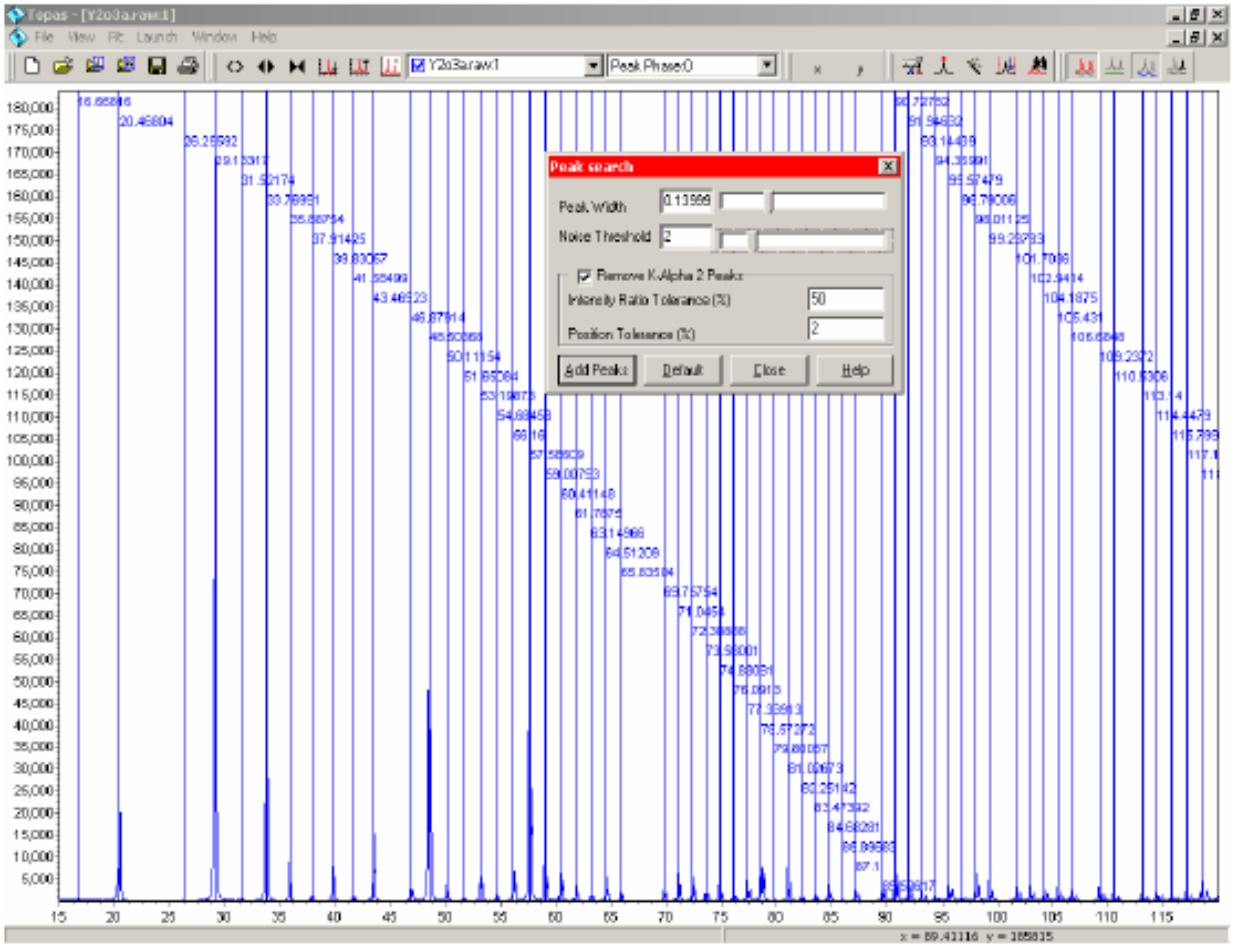


Fig. 3-16: Comparison of an unconstrained single line fit to the Quartz "5 finger peak" with SPVII functions (a) versus a FPA fit of the same data in (b).

全谱拟合

1. Start TOPAS.
2. Importing the file Y2O3A.RAW. By default this file is located in C:\TOPAS2-1\TUTORIAL\MISC.
3. Select FP as profile function.
4. Perform a peak search using the *Peak Search Dialog*. Define a *Peak Width* of about 0.14 (this value has to correspond approx. to the peak halfwidths) and a *Noise Threshold* of 2. Note the real time preview in the *Scan Window* showing the results of the peak search using peak markers. If you agree with the search result press the *Add Peaks* button. Check for missing or redundant peaks.

Menu:	**Icon:**	**Shortcut:**	**Result:**
View - *Search Peaks...*		n.a.	Displays the *Peak Search Dialog*

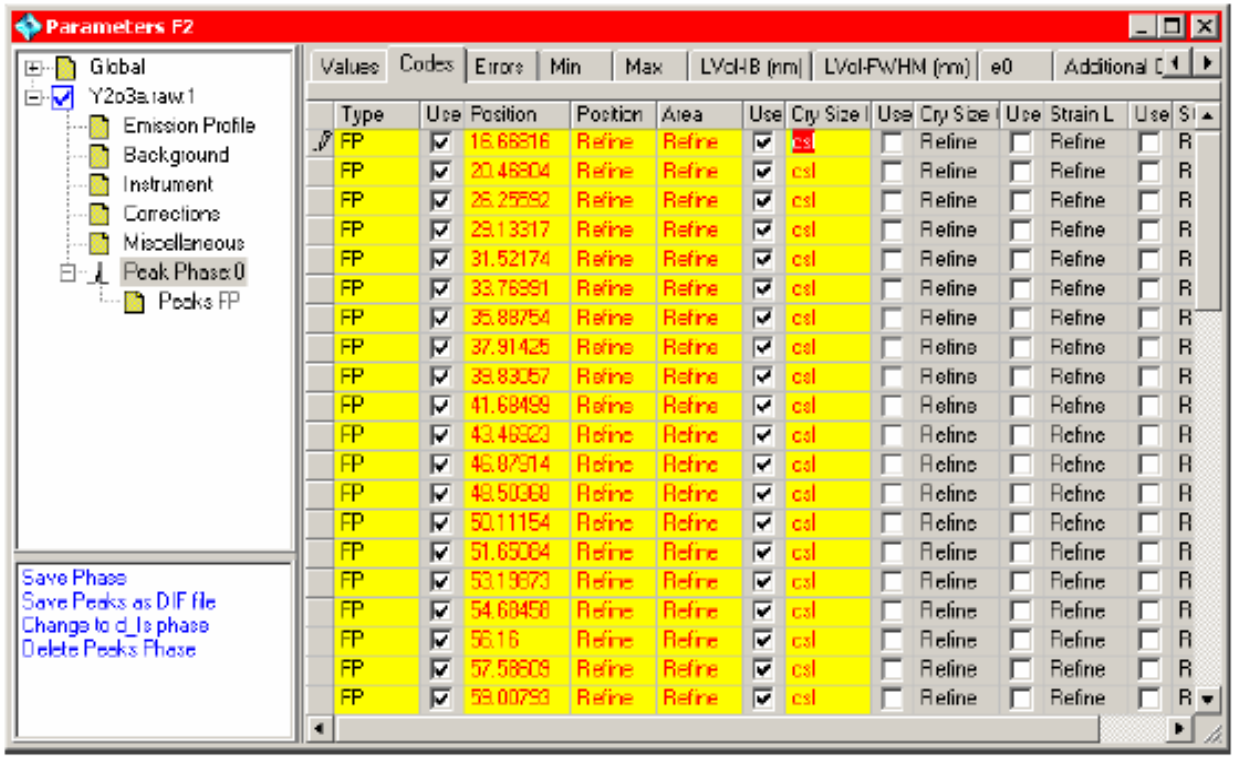


Hint! It is also possible to import peaks from DIF and UXD files. This feature allows the direct use of PDF data of the ICDD. DIF files can be created e.g. using DIFFRAC^{plus} EVA after a search/match operation.

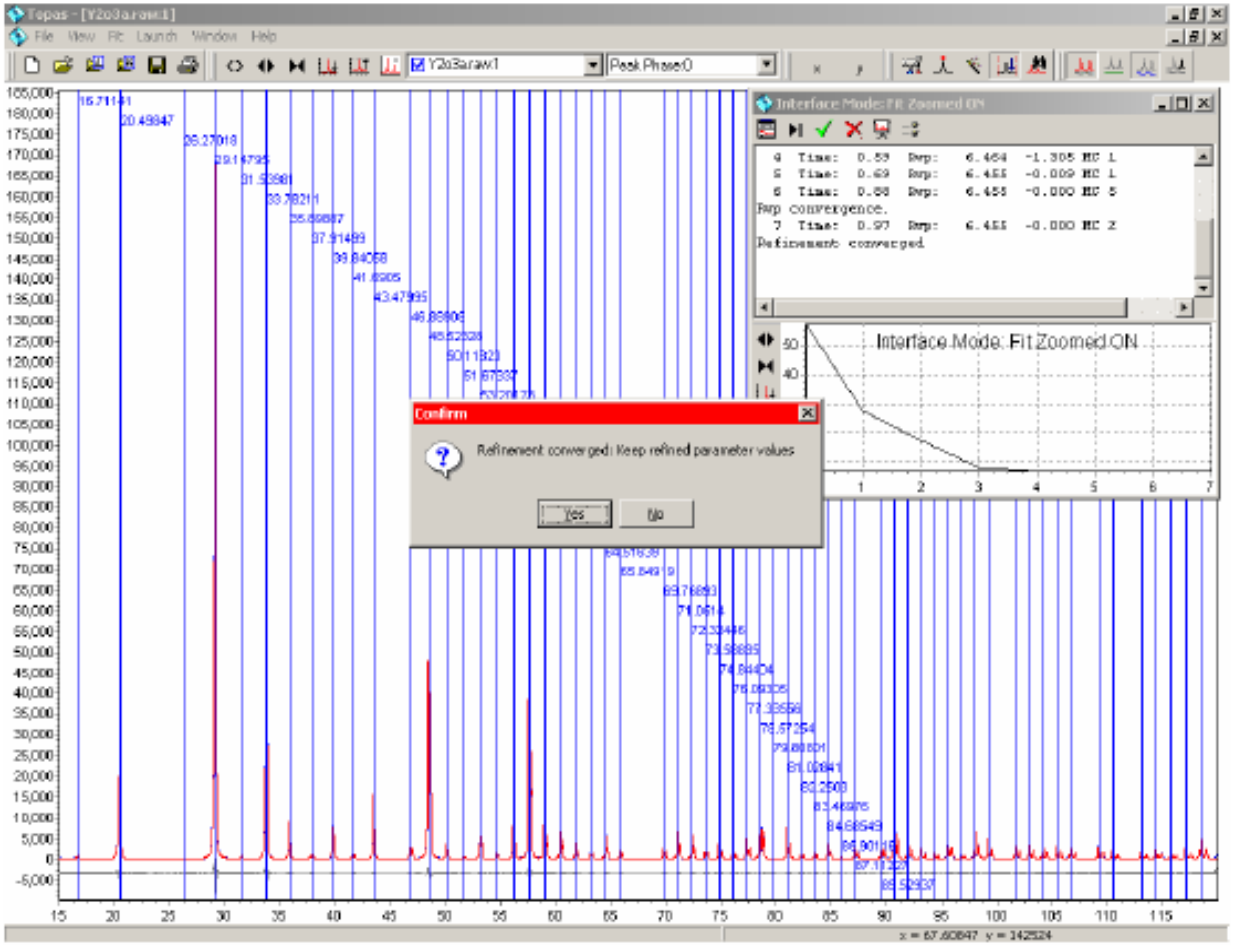
5. Load the predefined emission profile CUKA5. By default this file is located in C:\TOPAS2-1\LAM.
6. Apply the following instrument settings:

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	173 mm
	Secondary:	173 mm
RS	Width:	0.2 mm
FDS	Angle:	1°
Soller Slits	Primary:	5.1°
	Secondary:	8.6°

7. Refine on an isotropic crystallite size parameter. Focus the *Peak Phase* item, select the *Codes* page and constrain the *Cry Size L* parameter for all peaks to the same value by providing identical parameter codes.



8. Fit the data. Note the excellent fit to the observed line profiles.



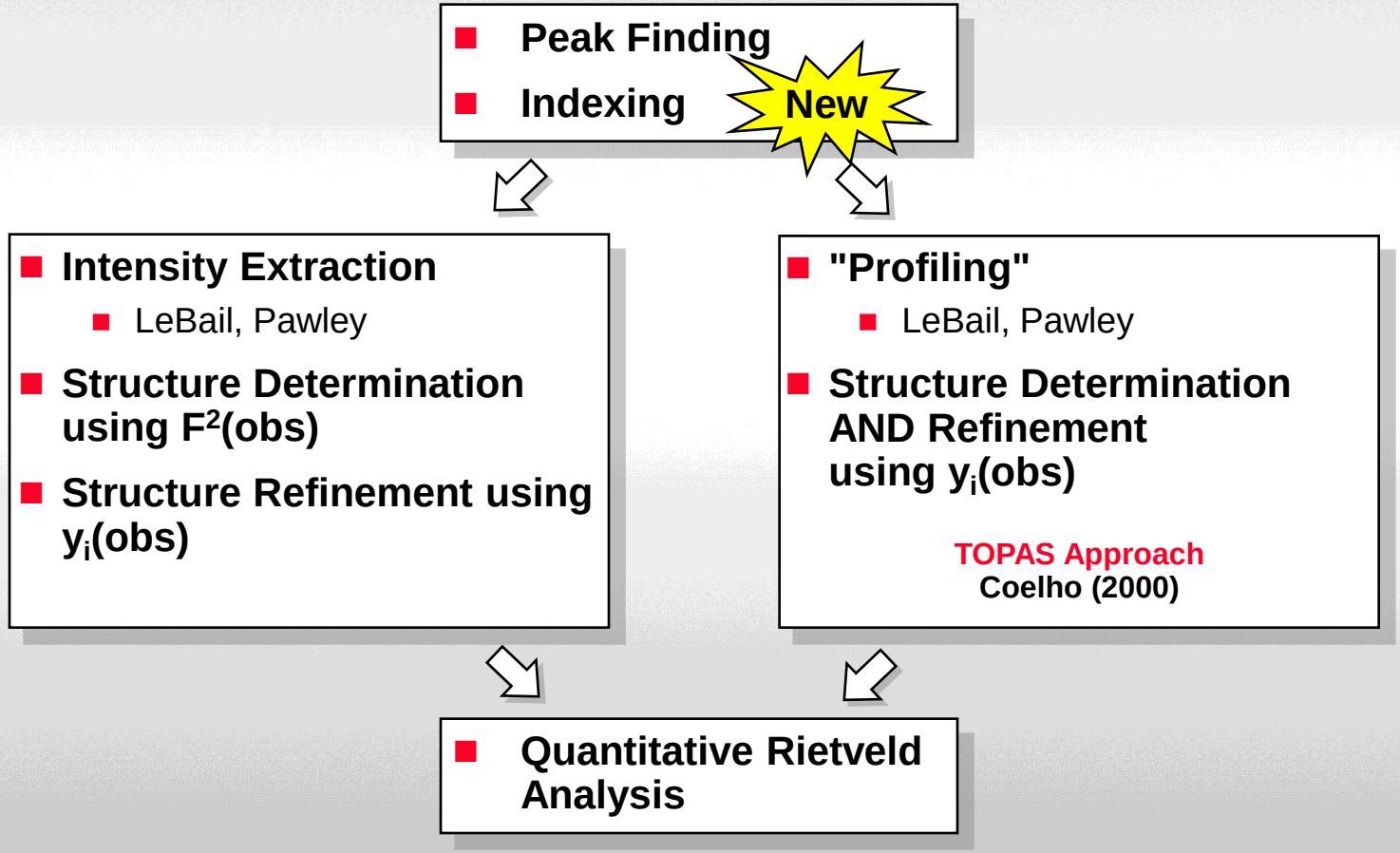
如何指标化

- LSI
- LP-Search

Advances in Indexing of Powder Diffraction Patterns: Iterative Use of Least Squares(LSI) and Monte-Carlo Based Whole Powder Pattern Decomposition

Arnt Kern

TOPAS V3
TOtal Pattern Analysis Solutions



TOPAS V3
LSI and LP-Search

- **LSI**
  - **Iterative use of least squares**
  - **Operates on d-values extracted from reasonable quality powder diffraction data**

- **LP-Search**
  - **Monte-Carlo Based Whole Powder Pattern Decomposition**
  - **Independent of d-spacing extraction and line profile shape and therefore suited for indexing of poor quality powder data**

! No d-values required !

TOPAS V3
LSI

- **Method**
  - **1. LSI Iterative Process**
    - **hkls assigned using present (random) lattice parameters**
    - **Reciprocal lattice relationship solved using least squares for <u>all hkl</u>**

$$X_{hh}\,\mathrm{h}^2 + X_{kk}\,\mathrm{k}^2 + X_{ll}\,\mathrm{l}^2 + X_{hk}\,\mathrm{hk} + X_{hl}\,\mathrm{h\,l} + X_{kl}\,\mathrm{k\,l} = 1/d^2_{\mathrm{hkl}}$$

  - **2. Monte-Carlo approach to searching parameter space**
    - **Randomize lattice parameters**
    - **Execution of the LSI iterative process until convergence**

TOPAS V3
LSI

- **Reciprocal lattice relationship:**

$$X_{hh}\,\mathrm{h}^2 + X_{kk}\,\mathrm{k}^2 + X_{ll}\,\mathrm{l}^2 + X_{hk}\,\mathrm{hk} + X_{hl}\,\mathrm{h\,l} + X_{kl}\,\mathrm{k\,l} = 1/d^2_{\mathrm{hkl}}$$

- **Modified to include a zero error and a weighting function:**

$$X_{hh}\,\mathrm{h}^2 + X_{kk}\,\mathrm{k}^2 + X_{ll}\,\mathrm{l}^2 + X_{hk}\,\mathrm{hk} + X_{hl}\,\mathrm{h\,l} + X_{kl}\,\mathrm{k\,l}$$
$$+ Ze\,(\pi/360)(4/\lambda^2)\sin(2\theta))\,\mathrm{W}_{\mathrm{hkl}} = \mathrm{W}_{\mathrm{hkl}} / d^2_{\mathrm{o}}$$

$$W_{\mathrm{hkl}} = d^{\mathrm{m}}_{\mathrm{o}}\,(\mathrm{C}_1 - \exp(-\mathrm{C}_2\,\Delta 2\theta_{\mathrm{hkl}}))$$

- **Objective function:**

$$S = \sum_i w_i \left[\frac{1}{d^2_{hkl}}(obs) - \frac{1}{d^2_{hkl}}(calc) \right]^2 \rightarrow \min$$

- **For large d-spacings as well as for high 2θ errors weightings are increased automatically**

TOPAS V3
LSI

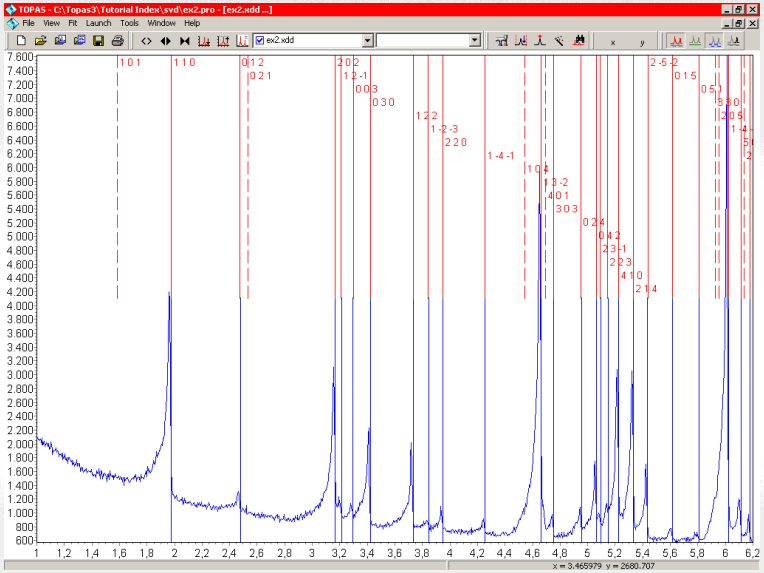
- **LSI is applied consecutively with hkls corresponding to minimum symmetry Bravais lattices from each crystal system and in decreasing order of symmetry.**
- **Monoclinic lattices are treated differently where a search is performed using the six unique sets of hkls corresponding to the space groups *P2*, *P21*, *Pc*, *P21/c*, *C2*, and *Cc* and not just the Bravais lattices.**
- **On present personal computers LSI searches all crystals systems down to the triclinic lattice in less than three minutes.**

TOPAS V3
LSI

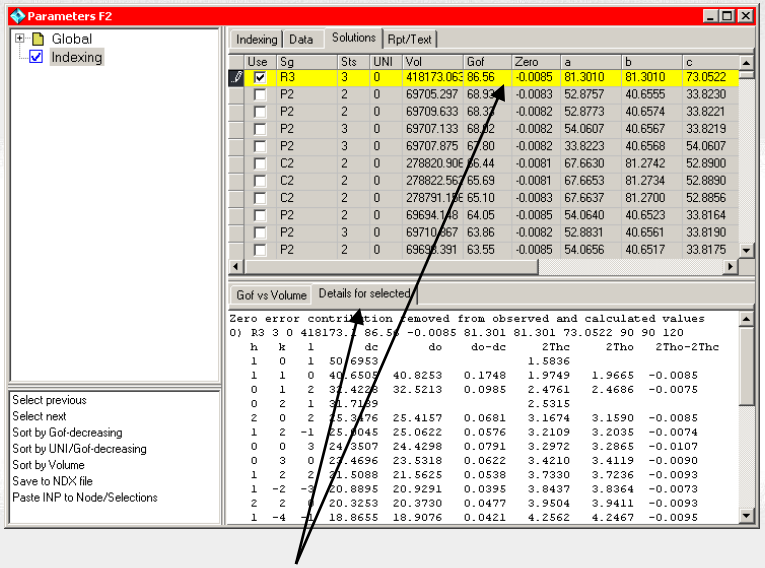
Most important features:

- **Seamless integration into TOPAS V3**
- **Zero-point error consideration**
- **Automatic determination of possible spacegroups**
- **Highly tolerant to impurity peaks, missing high d-spacings, extreme lattice parameter ratios as well as large d-spacing and zero point errors (> 0.05° 2θ)**
- **Particularily strong in indexing of very large cells (>> 100.000 A^3) and dominant zone problems**
- **Weighting of reflections using observed peak intensities or user-defined weights**
- **Fully automated Pawley or Le Bail fitting of all or user-selected solutions**
- **Goodness-of-fit versus volume plots**

TOPAS V3
LSI

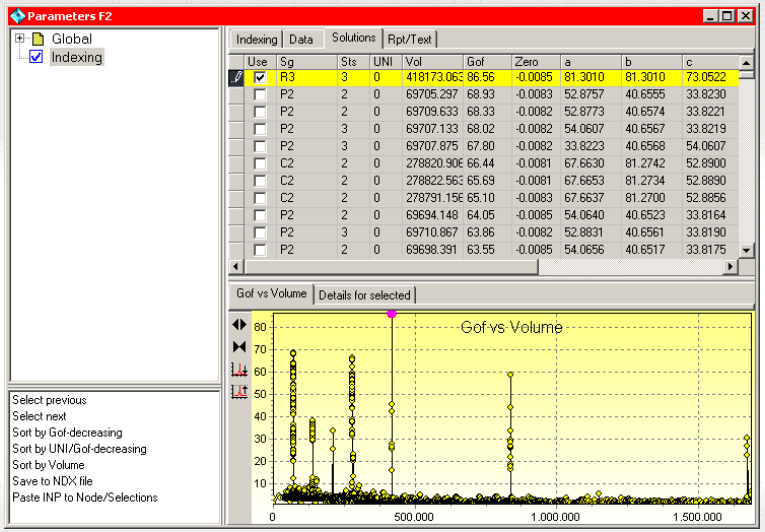


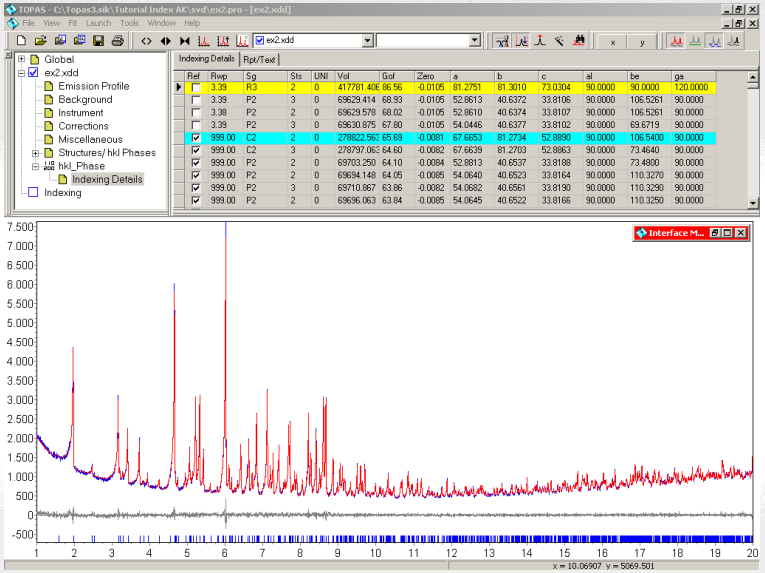
- Powder pattern overlaid with both observed (blue) and calculated (red) peak positions



- Detailed indexing results for all solutions

TOPAS V3
LSI





- **Goodness-of-fit versus volume display**
- **Easy identification of fractional and multiple volumes**
- **Fully automatic Pawley or Le Bail fitting of all or user selected solutions**

TOPAS V3
LSI Reference

electronic reprint

Journal of
Applied
Crystallography
ISSN 0021-8898

Indexing of powder diffraction patterns by iterative use of singular value decomposition

A. A. Coelho

Indexing of powder diffraction patterns by iterative use of singular value decomposition
A. A. Coelho
J. Appl. Cryst. (2003), **36**, 86–95

TOPAS V3
LP-Search

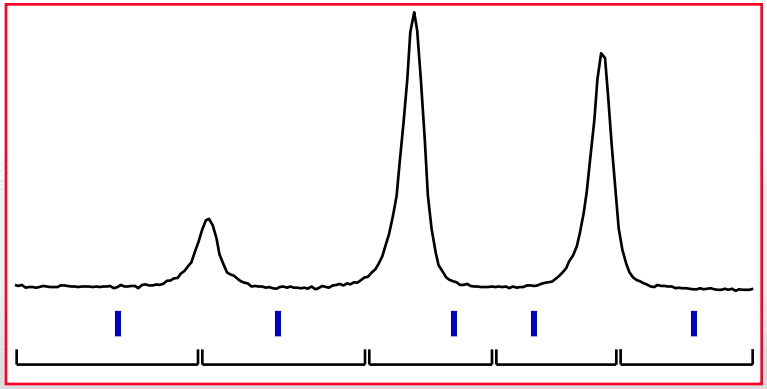
- LP-Search is a Monte-Carlo based Whole Powder Pattern Decomposition approach
- It minimizes on a new figure of merit function that gives a measure of correctness for a particular set of lattice parameters

$$\mathrm{FOM} = \sum_{\mathrm{j}} \sum_{\mathrm{i}} \mathrm{I}(2\theta_i) \left| 2\theta_i - 2\theta_{0,\mathrm{j}} \right|$$

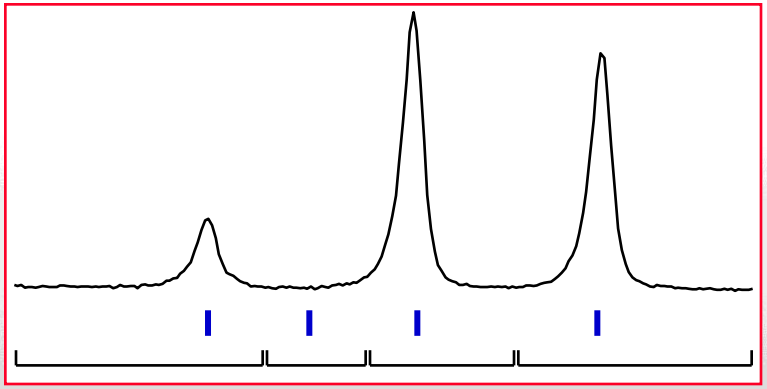
- The figure of merit function assigns parts of the diffraction pattern to calculated peak positions and then sums the absolute values of the products of the diffraction intensities multiplied by the distance to the calculated peak positions
- LP-Search avoids difficulties associated with extracting d-spacings from complex patterns comprising heavily overlapped lines

TOPAS V3
LP-Search

- **Generate sets of lattice parameters and calculate d-values**
  - **For each solution, for each calculated d-value**
    - **define pattern segments**
    - **sum the absolute values of (step intensities * distance to the d-value)**



Poor solution, high R-value



Good solution, low R-value

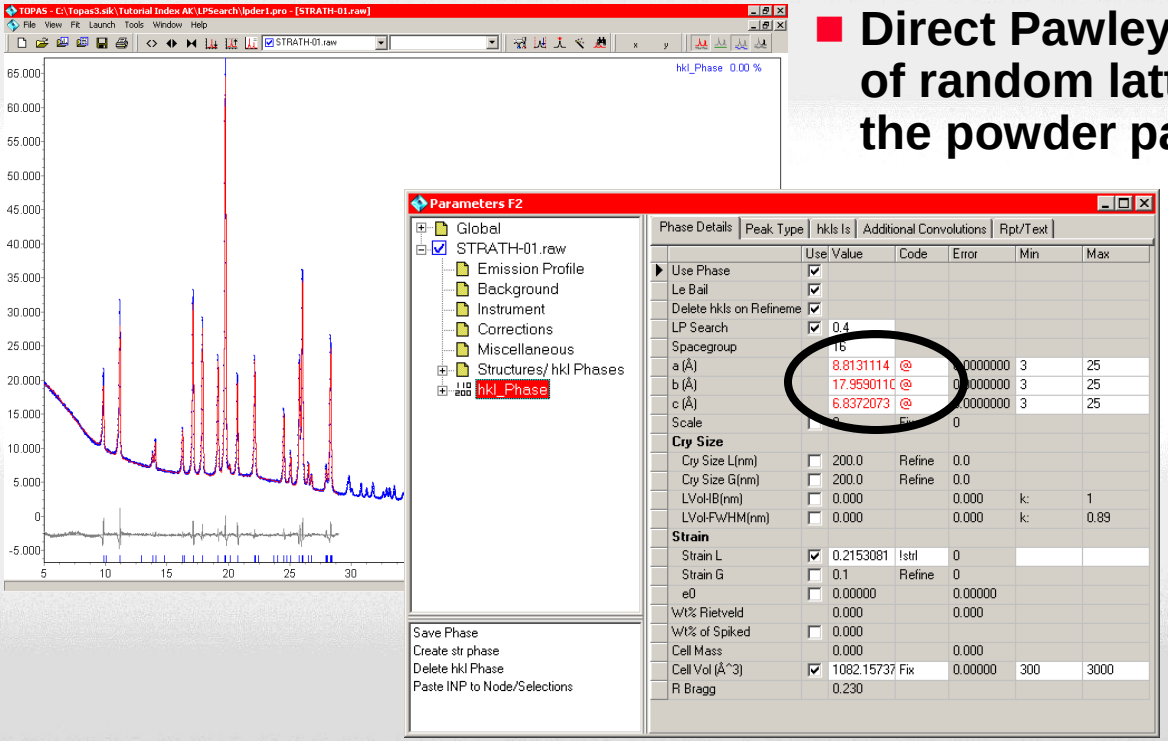
  - **Refine the best solution**
- **Reiterate**

TOPAS V3
LP-Search

Most important features:

- **Seamless integration into TOPAS V3**
- **Independent of 2θ or d-spacing extraction**
- **Independent of line profile shape**
- **Zero-point error consideration, highly tolerant to large zero point errors (> 0.05° 2θ)**
- **Particulary suited for indexing of poor quality powder data, where reliable 2θ or d-spacing extraction is difficult or even impossible**

TOPAS V3
LP-Search

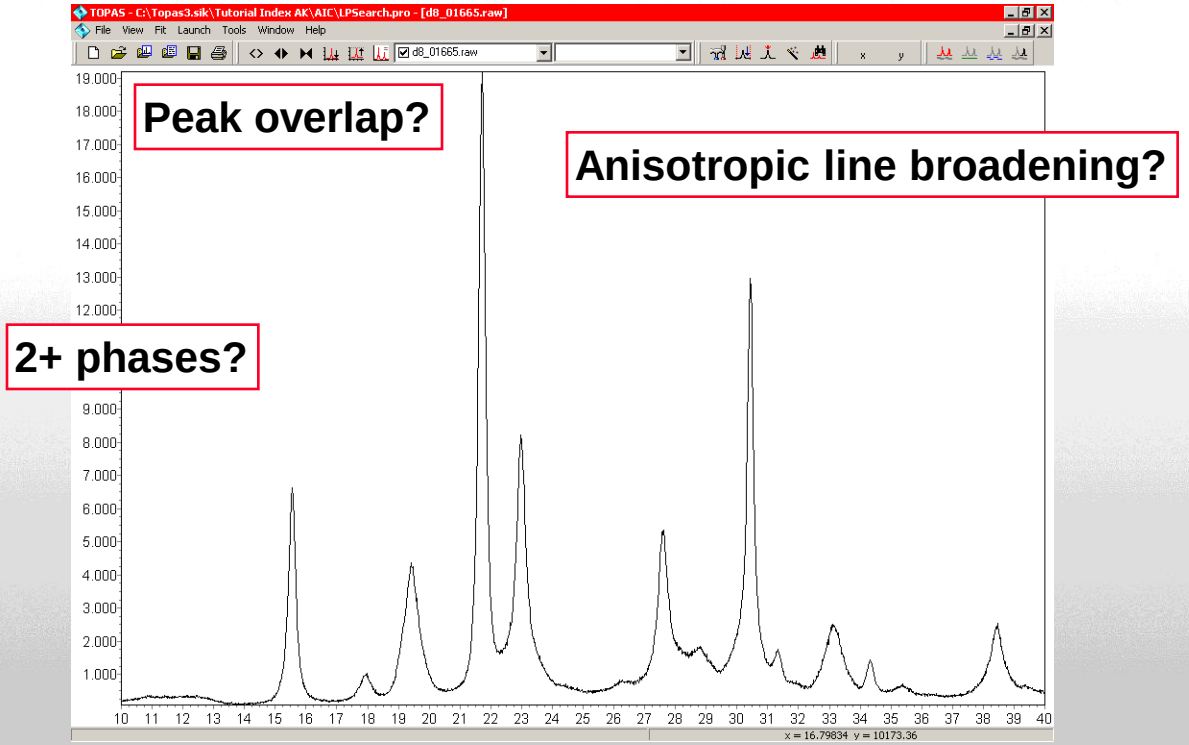


- **Direct Pawley or Le Bail fitting of random lattice parameters to the powder pattern**

! No d-values required !

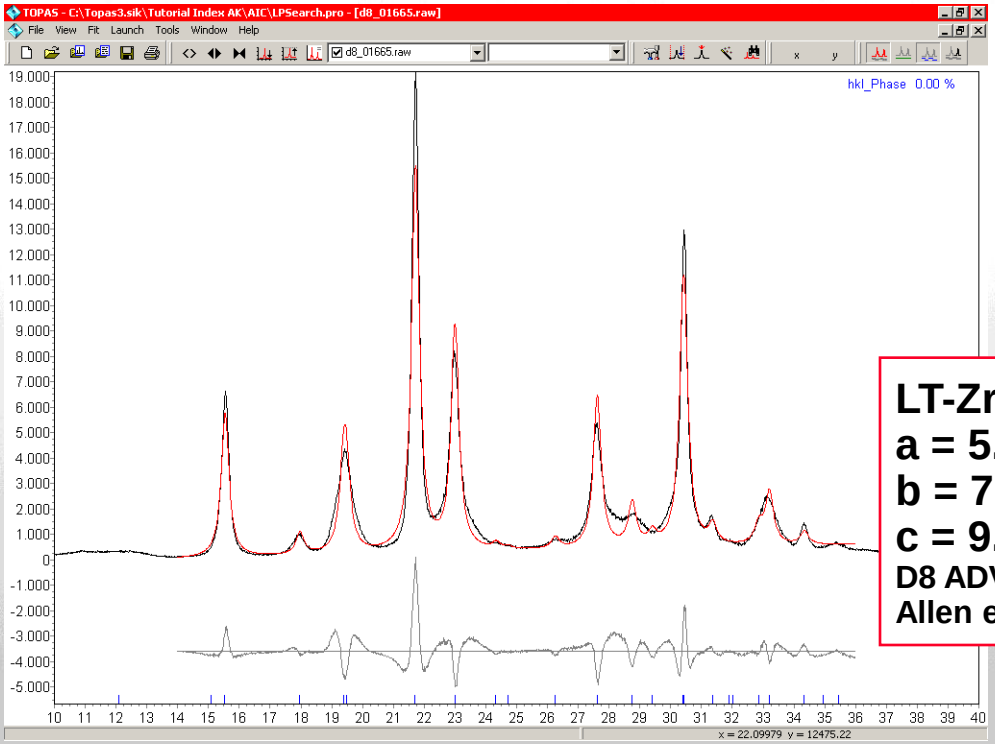
TOPAS V3
LP-Search: LT-$ZrMo_2O_8$

- **Particulary suited for indexing of poor quality powder data:**
  How many peaks are there?



TOPAS V3
LP-Search: LT-$ZrMo_2O_8$

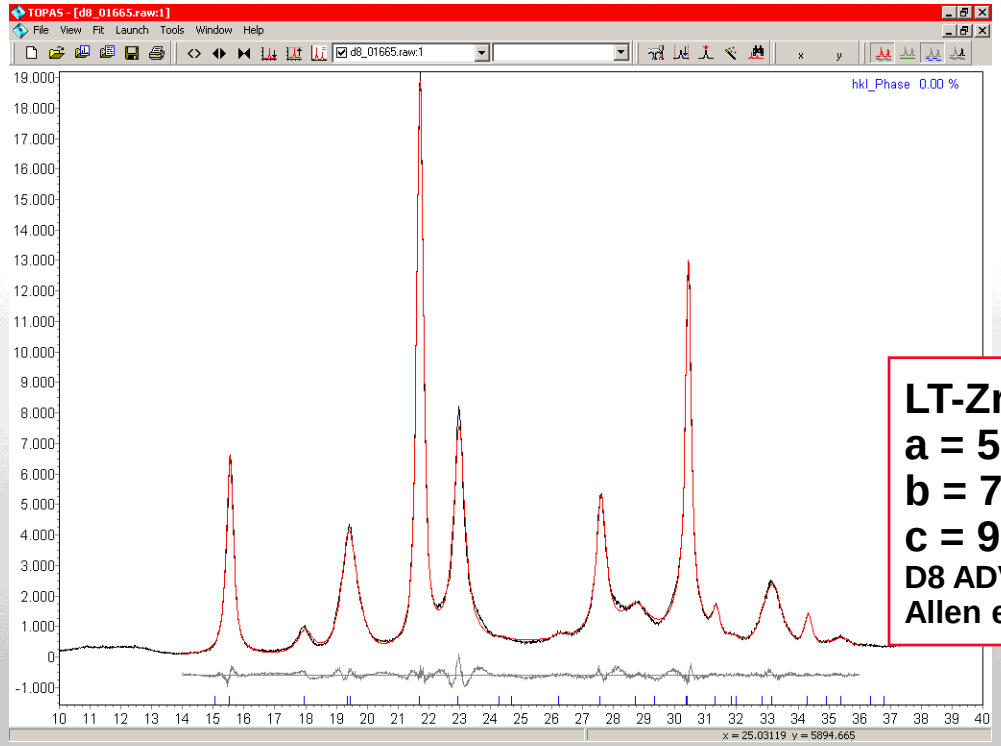
- Data are easily indexed with LP-Search
- LP-Search profile fit reveals strong anisotropic line broadening



$LT\text{-}ZrMo_2O_8$
a = 5.879 Å
b = 7.329 Å
c = 9.130 Å
D8 ADVANCE, $K\alpha_1$
Allen et al. (2003)

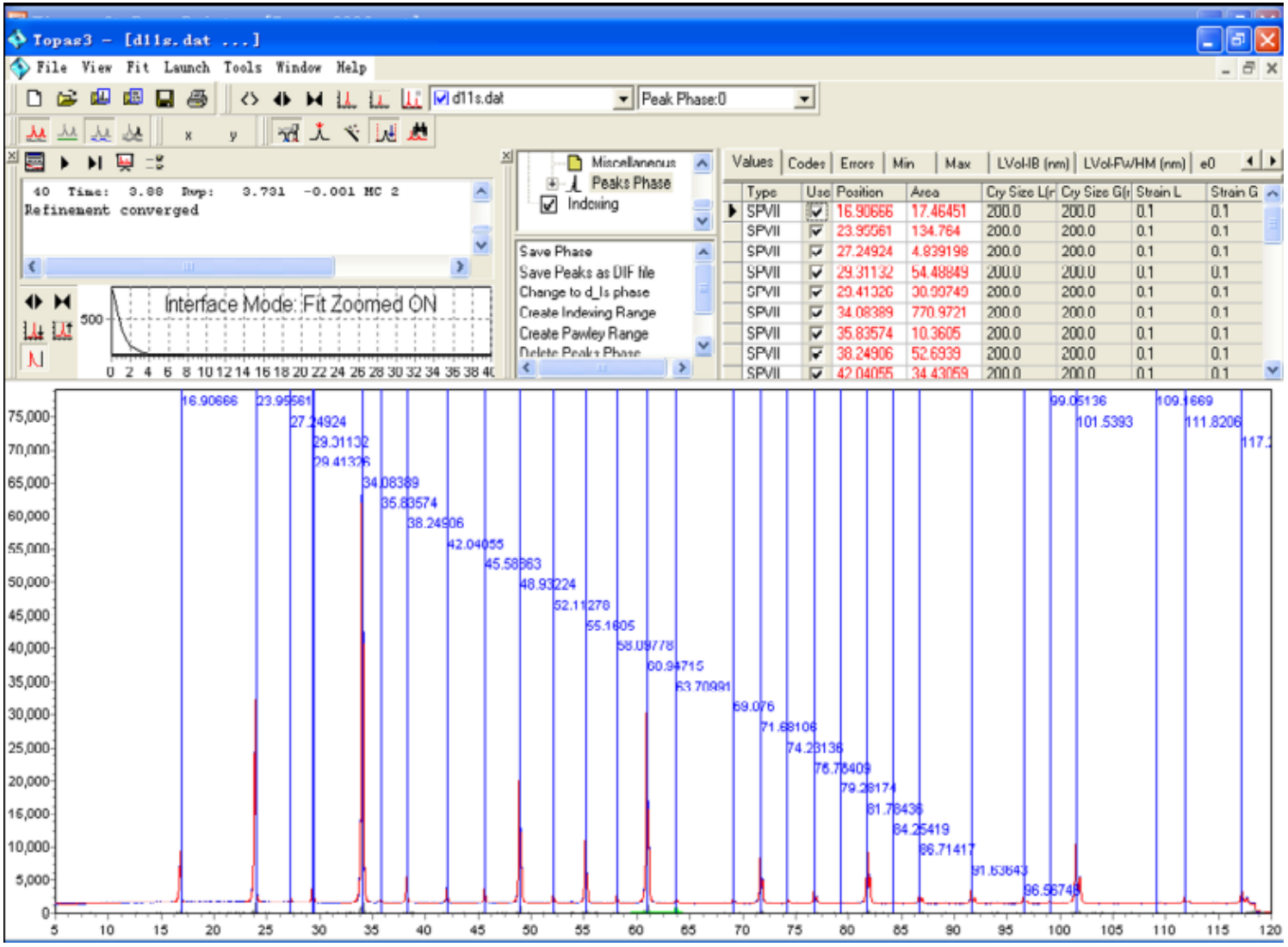
TOPAS V3
LP-Search: LT-$ZrMo_2O_8$

- Final Pawley fit taking anisotropic line broadening into account
- Spherical harmonics function used to model excess broadening



$LT\text{-}ZrMo_2O_8$
a = 5.879 Å
b = 7.329 Å
c = 9.130 Å
D8 ADVANCE, $K\alpha_1$
Allen et al. (2003)

具体操作


Topas3 - [d11s.dat ...]
File View Fit Launch Tools Window Help
d11s.dat
Peak Phase:0
Refinement converged
Interface Mode: Fit Zoomed ON
Miscellaneous
Peaks Phase
Indexing
Save Phase
Save Peaks as DIF file
Change to d_ls phase
Create Indexing Range
Create Pawley Range
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LVol-FW/HM (nm)
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Strain G
SPVII
16.90666
17.46451
23.95561
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4.839198
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52.11278
55.1605
58.09778
60.94715
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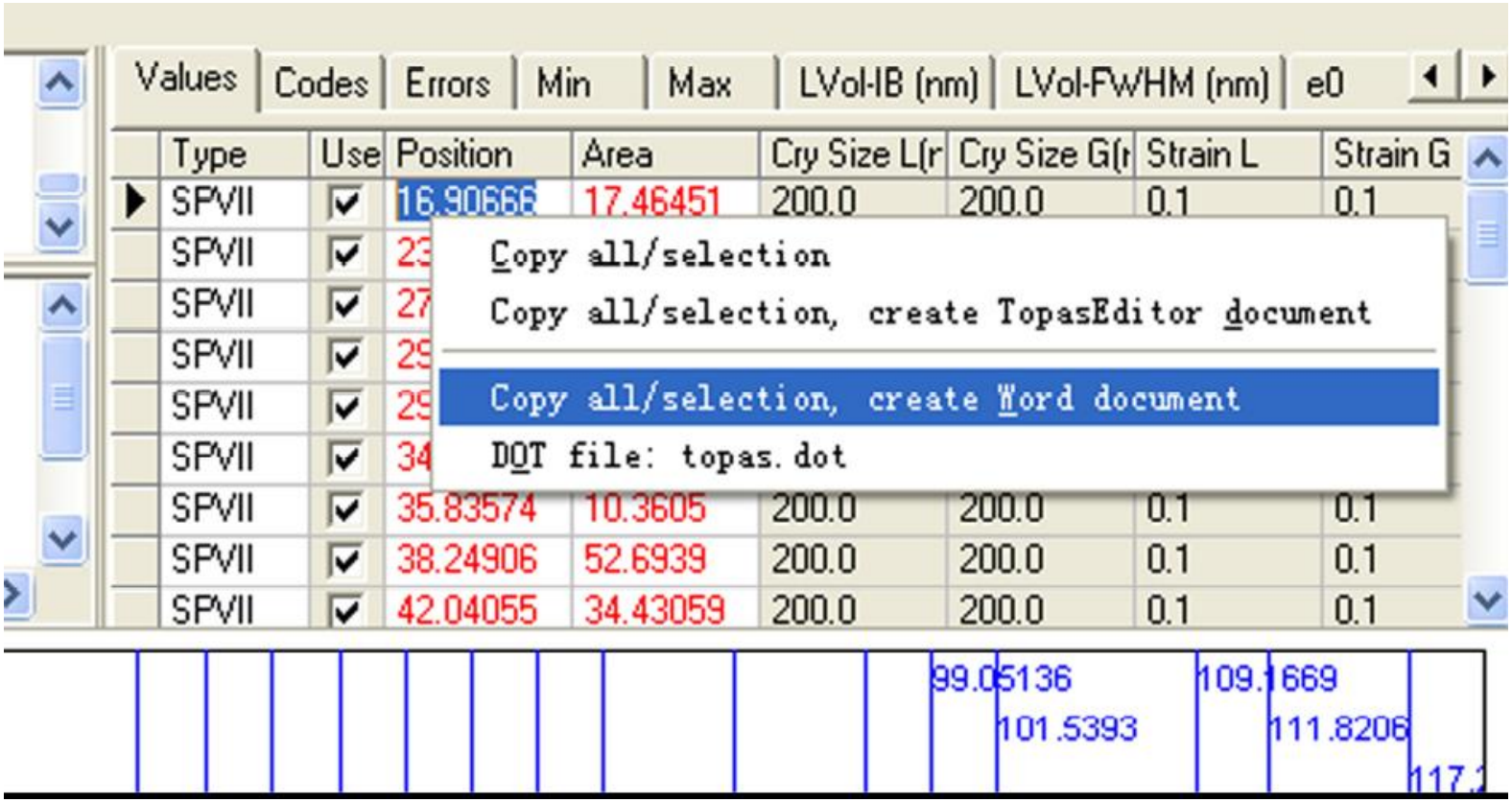
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Copy all/selection, create Word document
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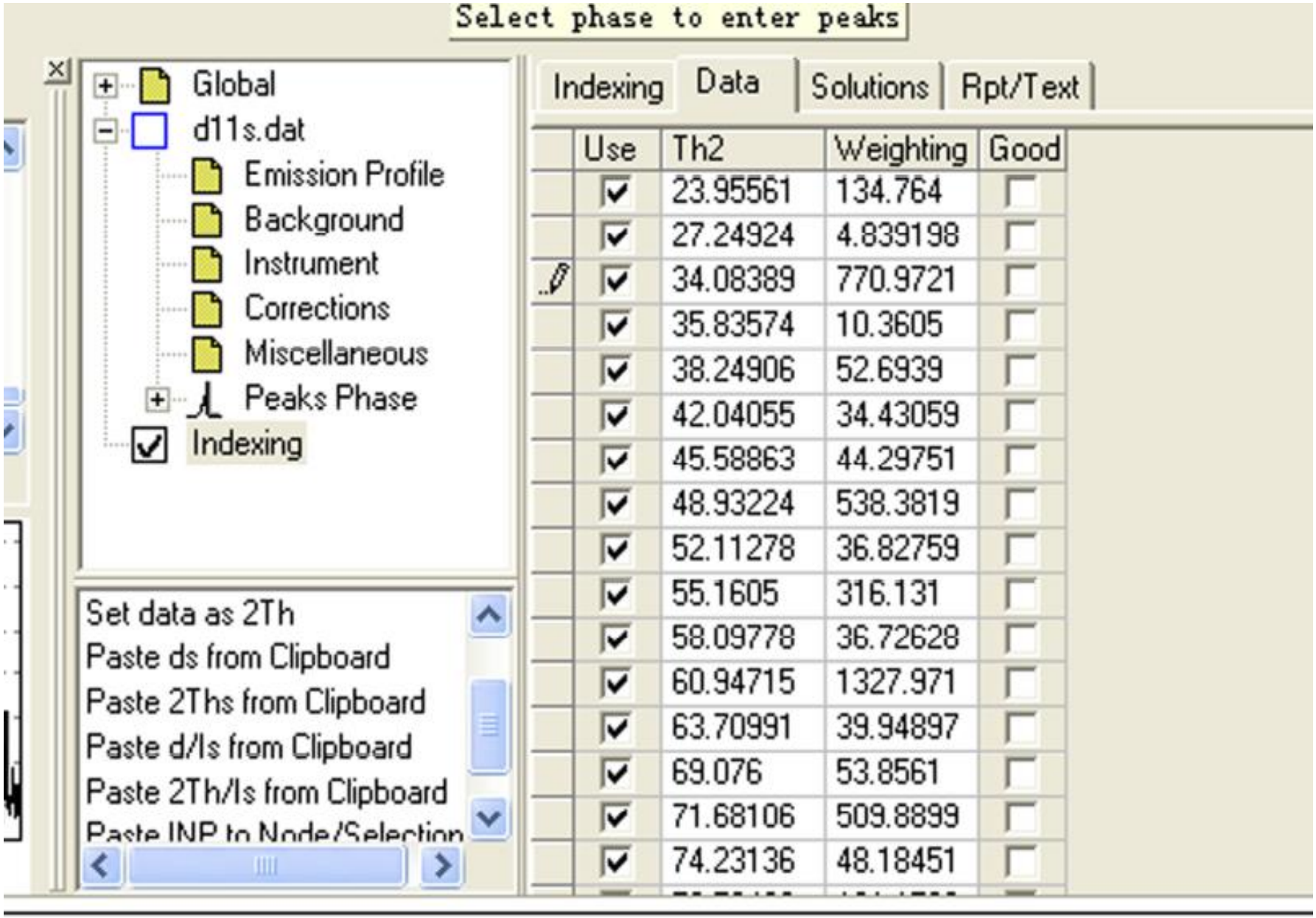
99.05136
101.5393
109.1669
111.8206

Type	Use	Position	Area	Cry Size L(nm)	Cry Size G(nm)	Strain L	Strain G
SPVII	**1**	**16.90666**	**17.46451**	**200.0**	**200.0**	**0.1**	**0.1**
SPVII	**1**	**23.95561**	**134.764**	**200.0**	**200.0**	**0.1**	**0.1**
SPVII	**1**	**27.24924**	**4.839198**	**200.0**	**200.0**	**0.1**	**0.1**

16.90666, 17.46451
23.95561, 134.764
27.24924, 4.839198

Copy the Data to Clipboard


Select phase to enter peaks
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Emission Profile
Background
Instrument
Corrections
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Solutions
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35.83574 10.3605
38.24906 52.6939
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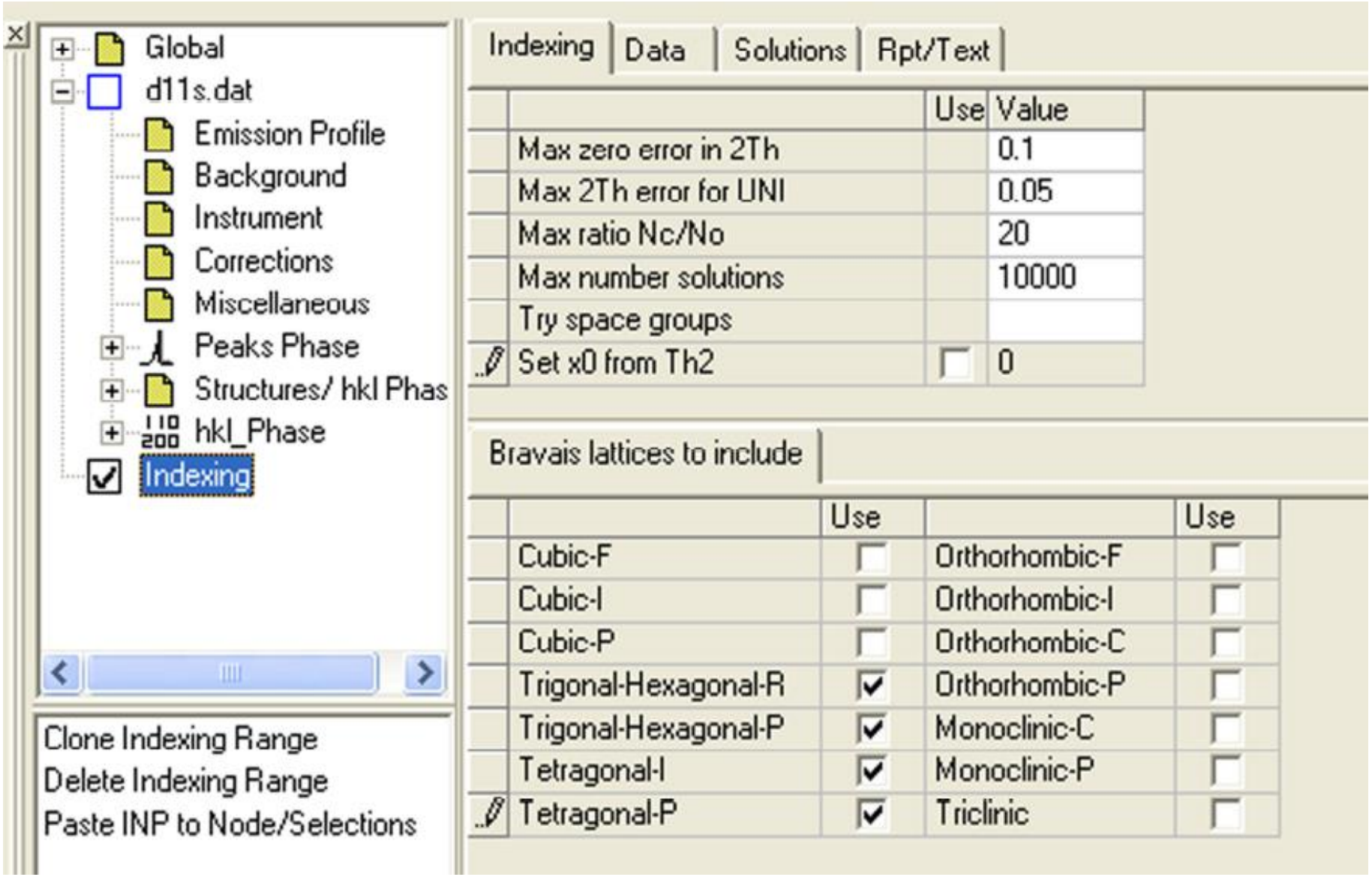
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Emission Profile
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Corrections
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Clone Indexing Range
Delete Indexing Range
Paste INP to Node/Selections
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Data
Solutions
Rpt/Text
Use
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Max zero error in 2Th
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Max ratio Nc/No
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Max number solutions
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Bravais lattices to include
Use
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Cubic-I
Cubic-P
Trigonal-Hexagonal-R
Trigonal-Hexagonal-P
Tetragonal-I
Tetragonal-P
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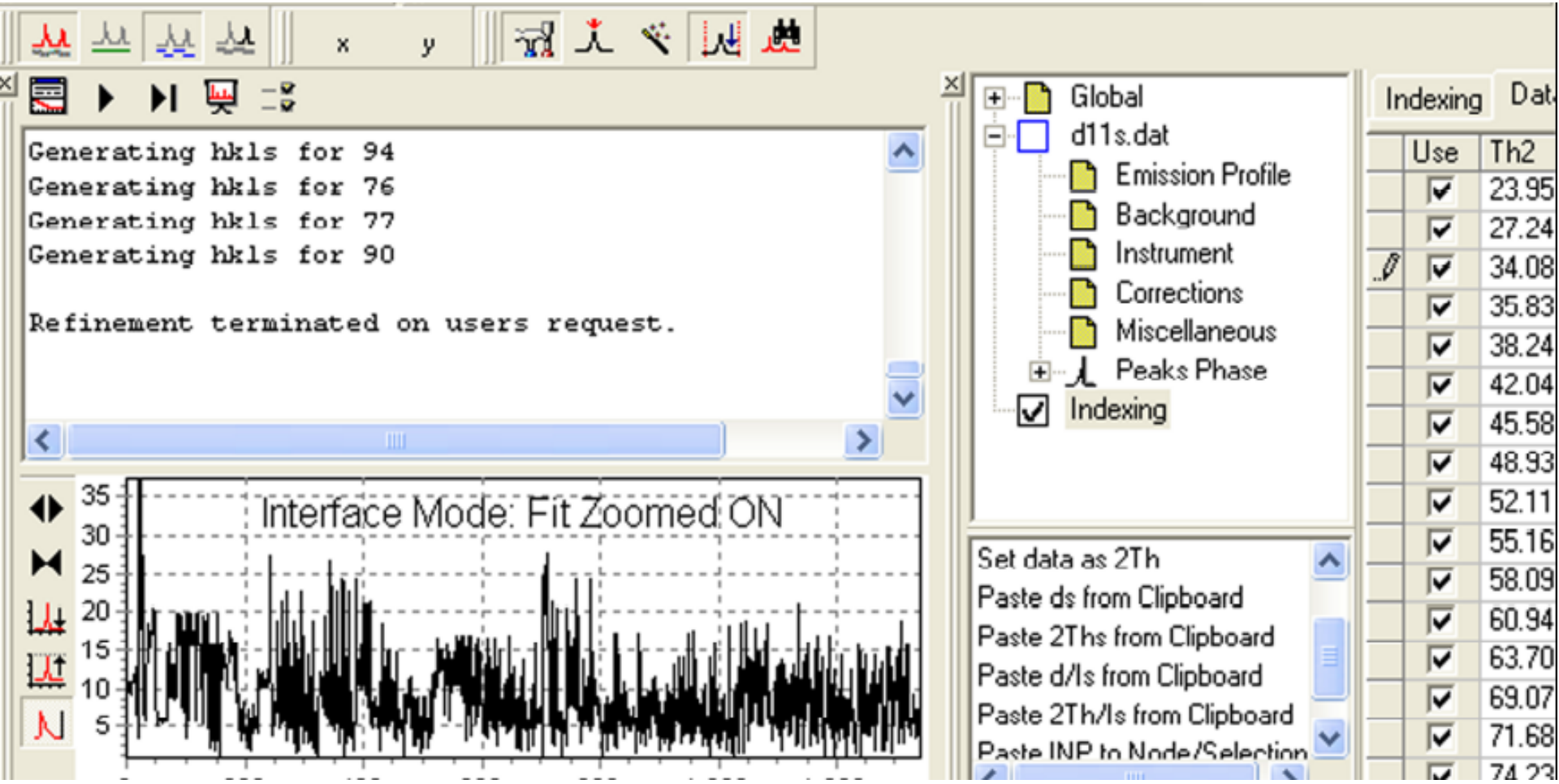
Orthorhombic-P
Monoclinic-C
Monoclinic-P
Triclinic


x
y
Generating hkls for 94
Generating hkls for 76
Generating hkls for 77
Generating hkls for 90
Refinement terminated on users request.
Interface Mode: Fit Zoomed ON
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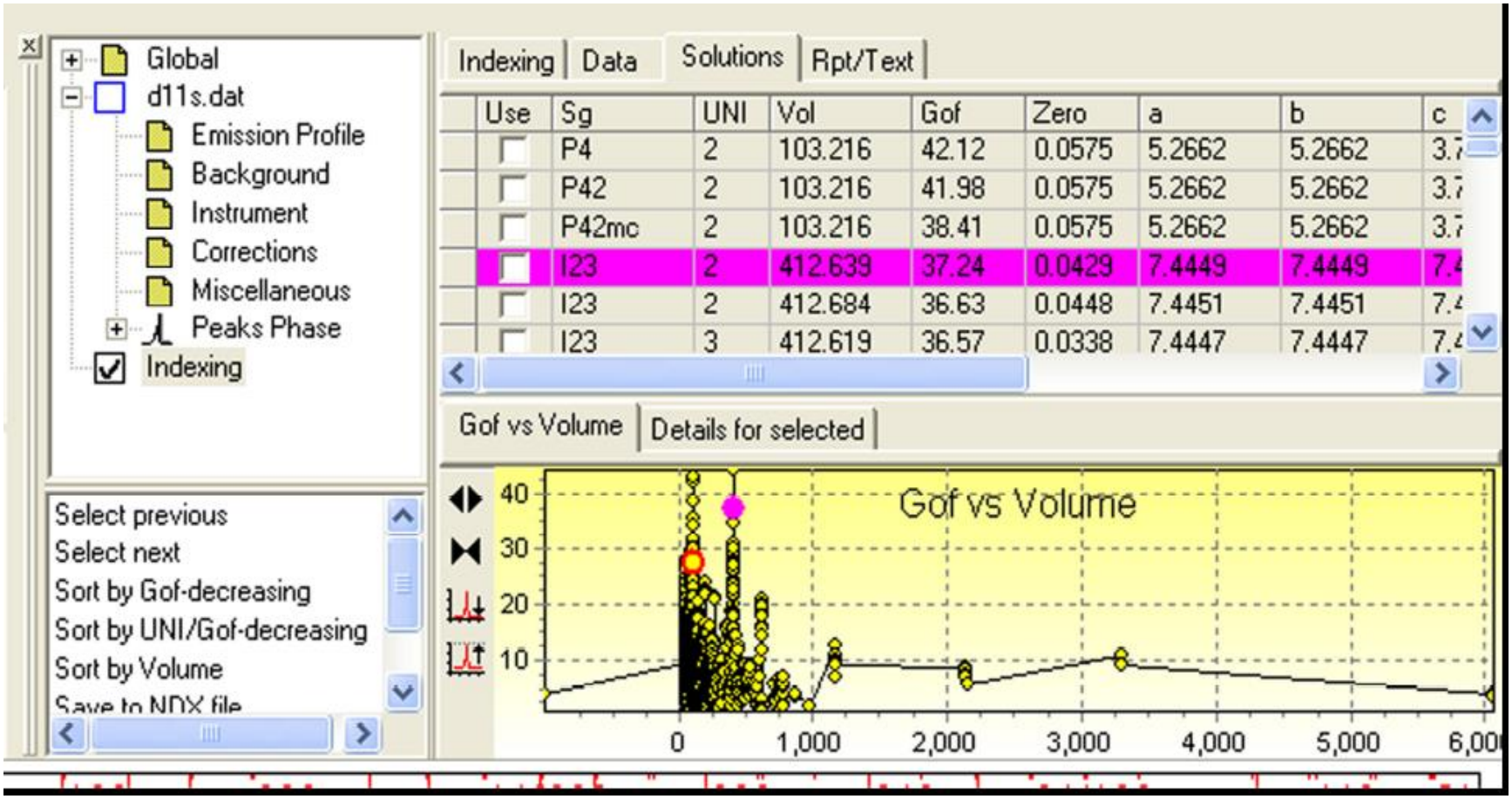
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Background
Instrument
Corrections
Miscellaneous
Peaks Phase
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Select next
Sort by Gof-decreasing
Sort by UNI/Gof-decreasing
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Solutions
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P42 2 103.216 41.98 0.0575 5.2662 5.2662
P42mc 2 103.216 38.41 0.0575 5.2662 5.2662
I23 2 412.639 37.24 0.0429 7.4449 7.4449
I23 2 412.684 36.63 0.0448 7.4451 7.4451
I23 3 412.619 36.57 0.0338 7.4447 7.4447
Gof vs Volume
Details for selected
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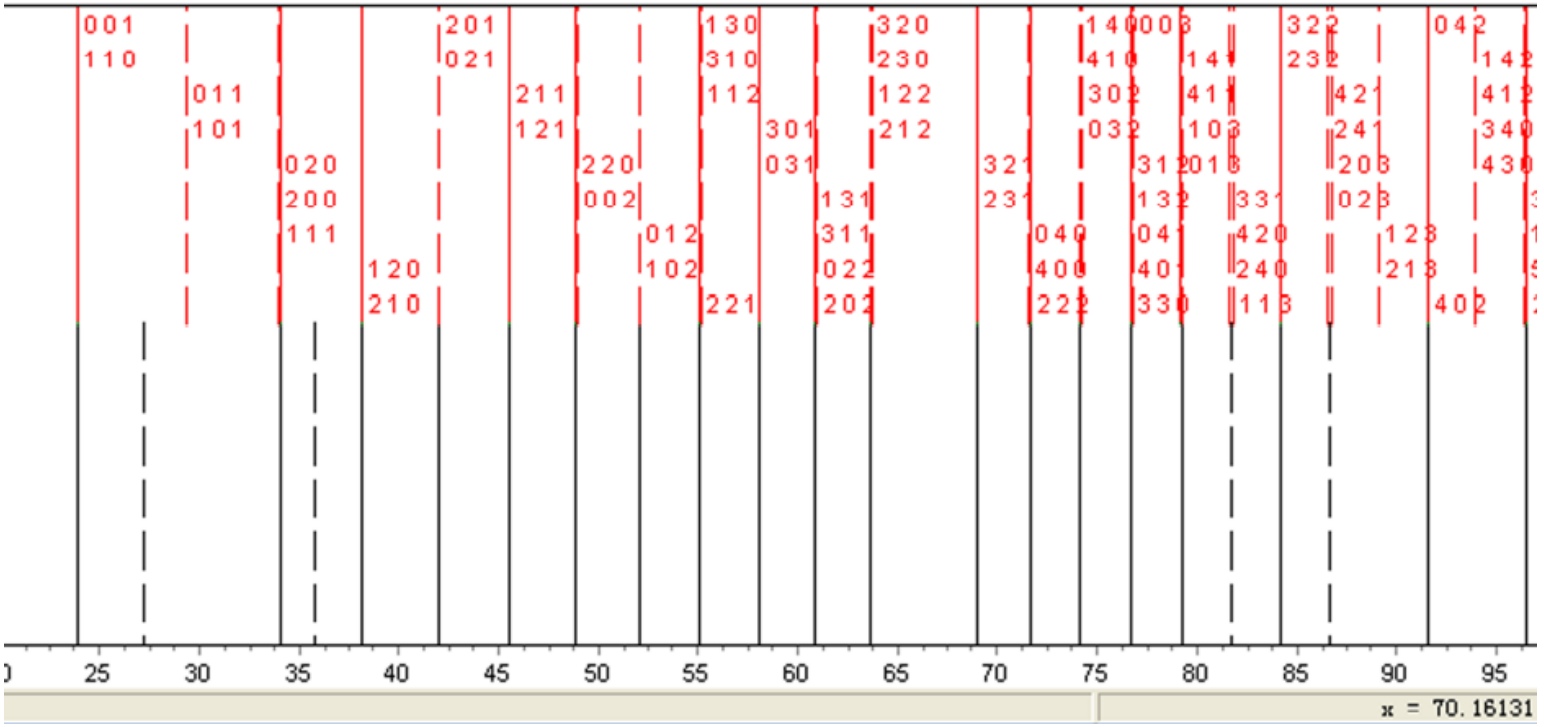
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411
103
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421
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042
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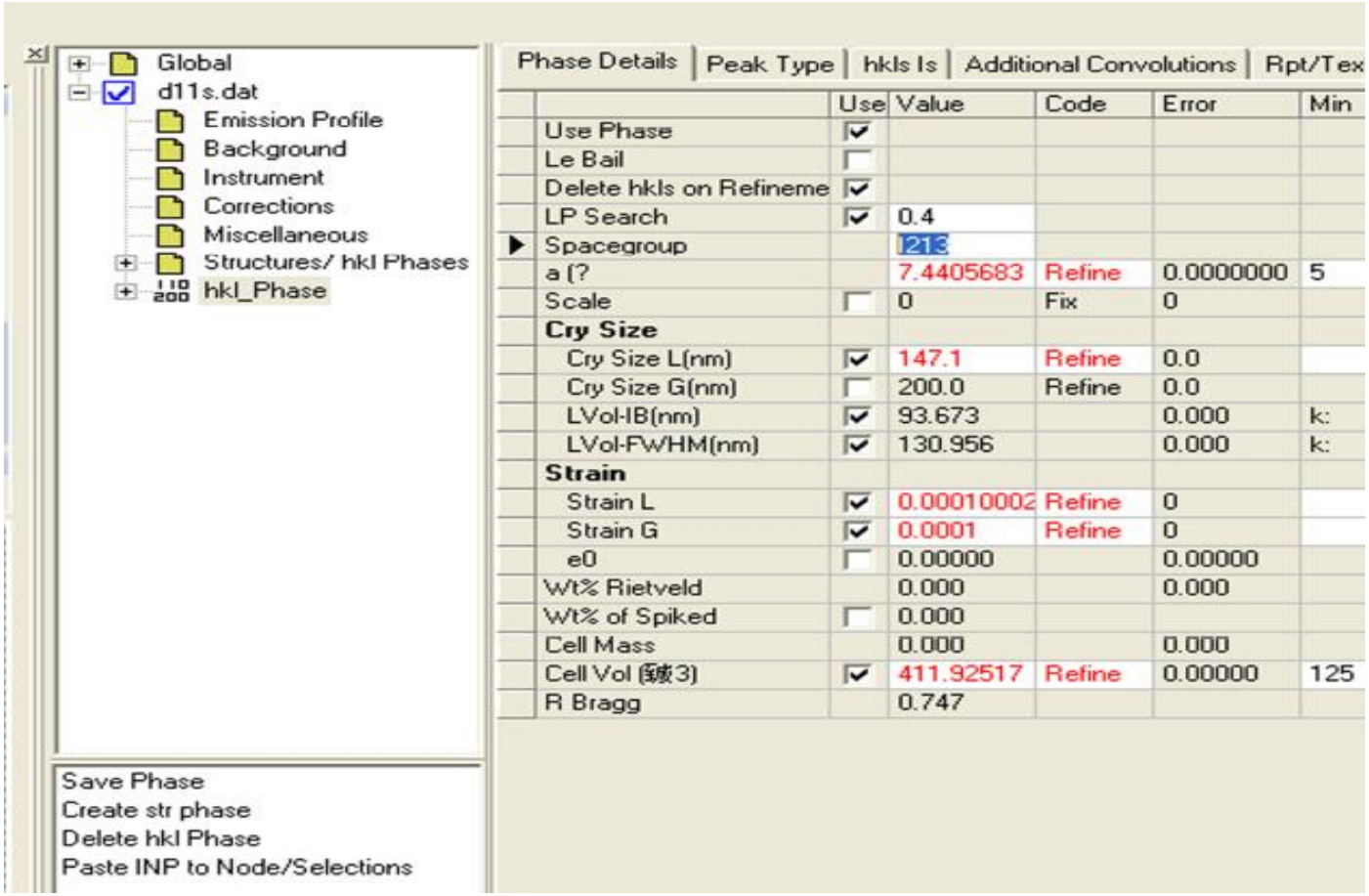
x = 70.16131

LP-Search方法


Global
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Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
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Save Phase
Create str phase
Delete hkl Phase
Paste INP to Node/Selections
Phase Details
Peak Type
hkls Is
Additional Convolutions
Rpt/Tex
Use
Value
Code
Error
Min
Use Phase
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213
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Refine
0.0000000
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Scale
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Refine
0.0
Cry Size G(nm)
200.0
Refine
0.0
LVol-IB(nm)
93.673
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LVol-FWHM(nm)
130.956
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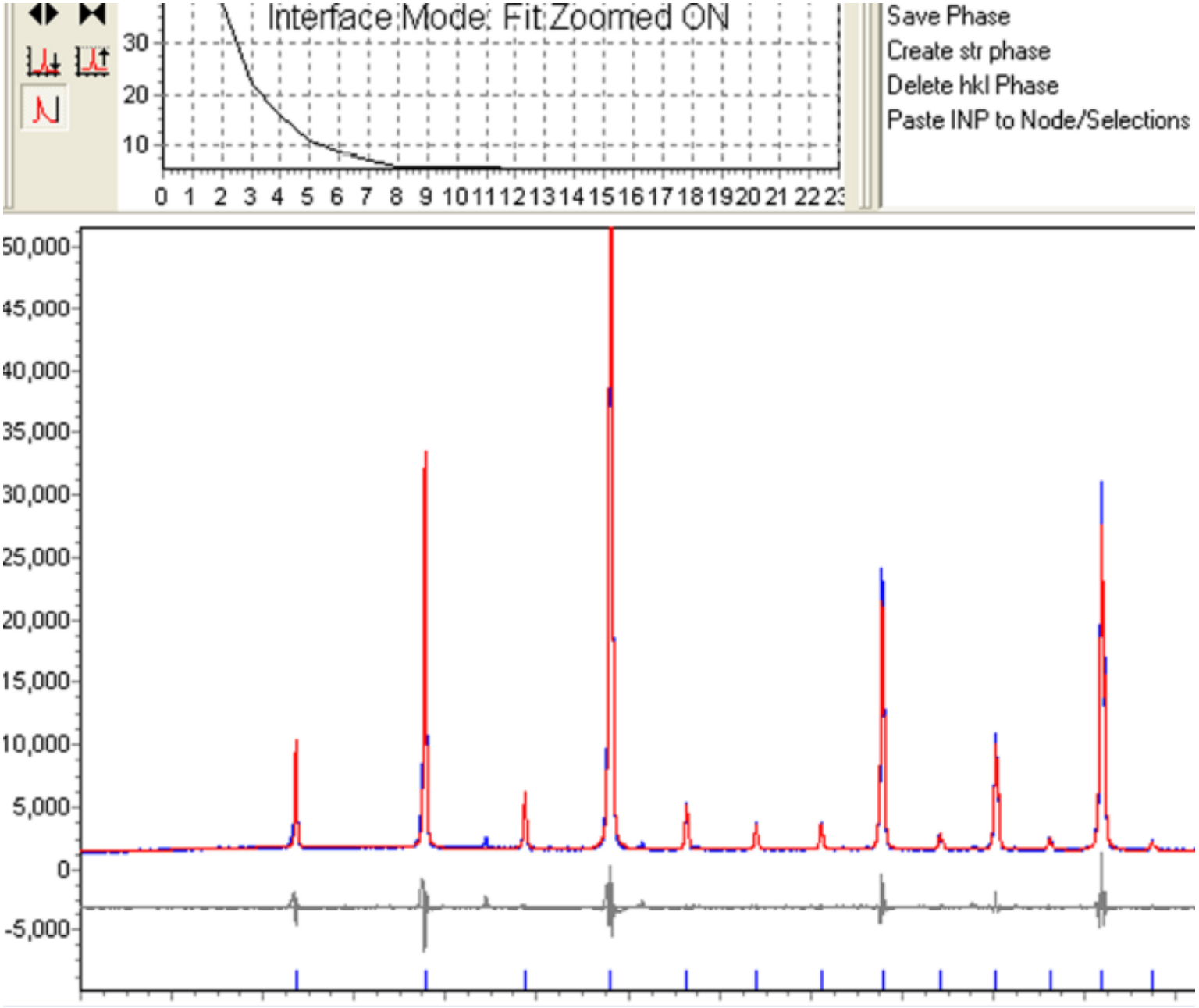
Interface Mode: Fit Zoomed ON
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Create str phase
Delete hkl Phase
Paste INP to Node/Selections
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0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
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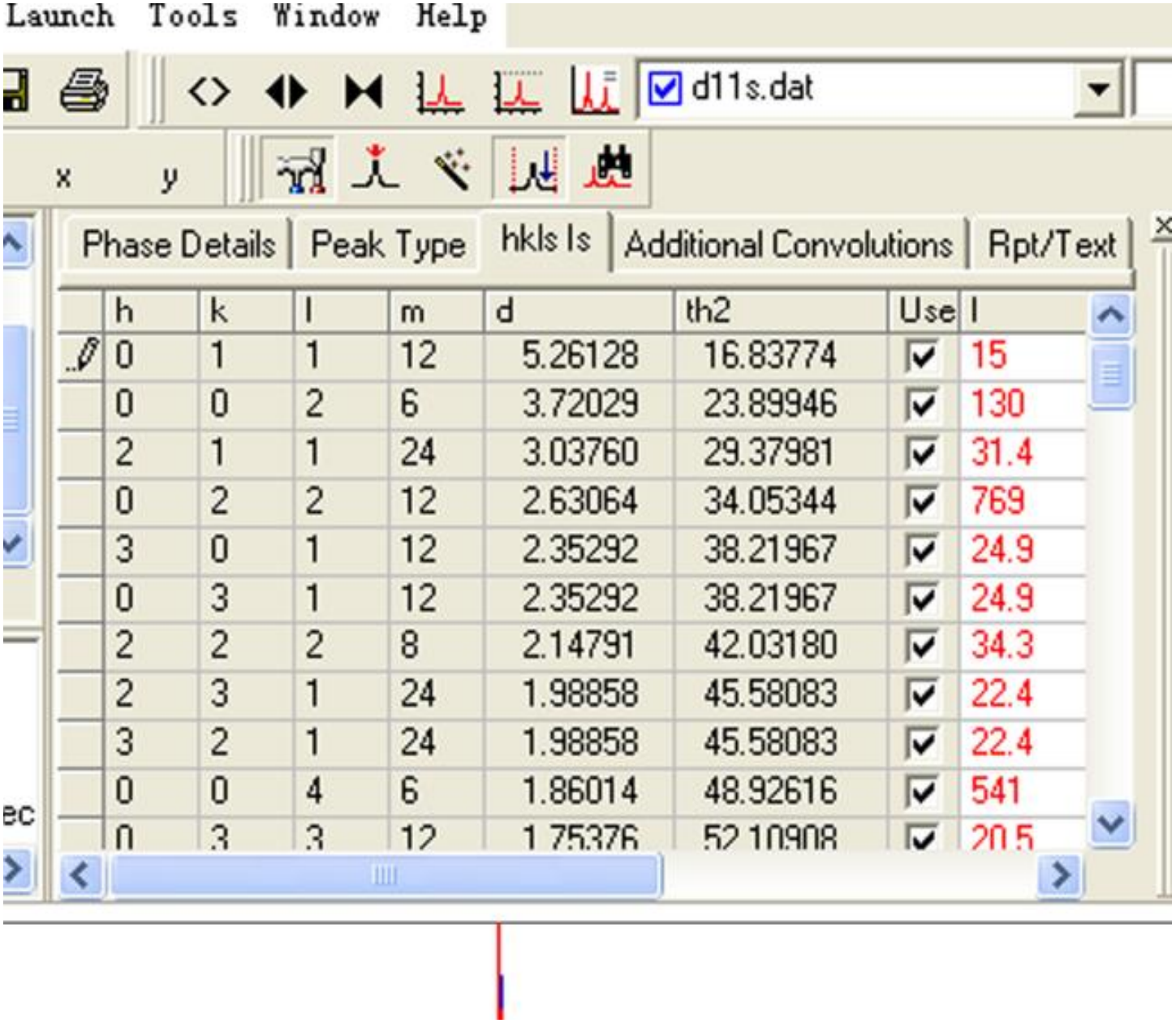
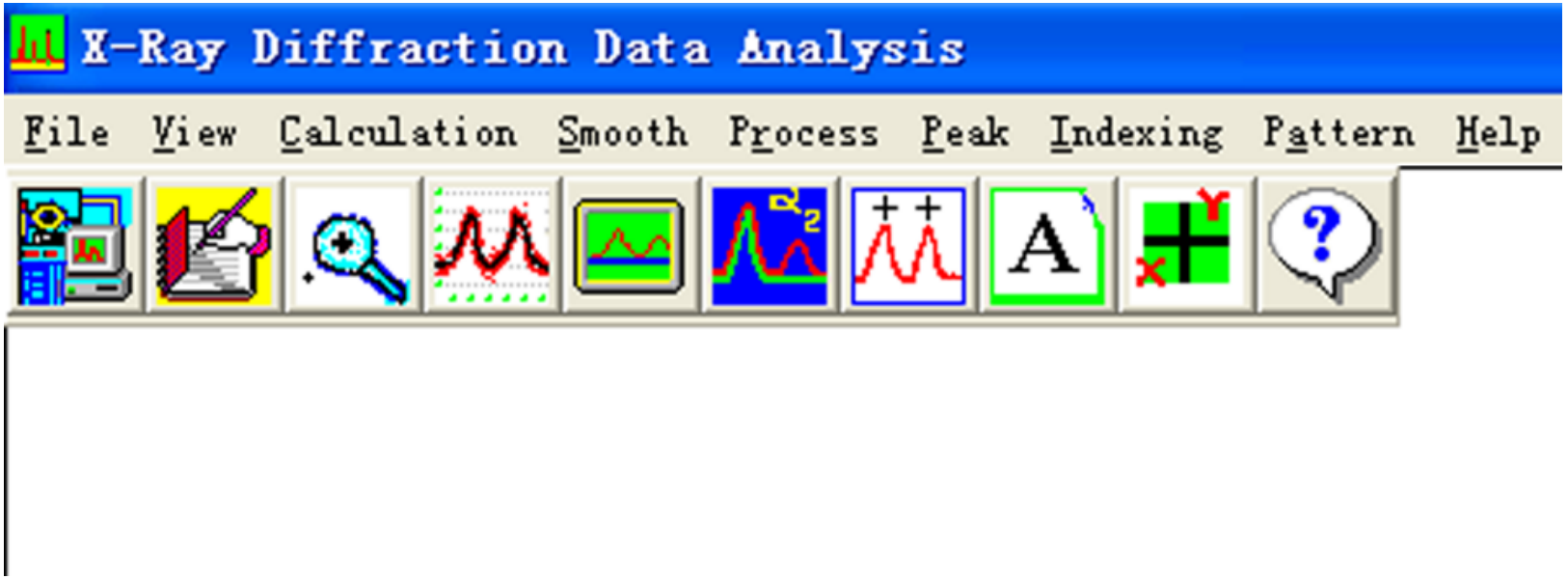
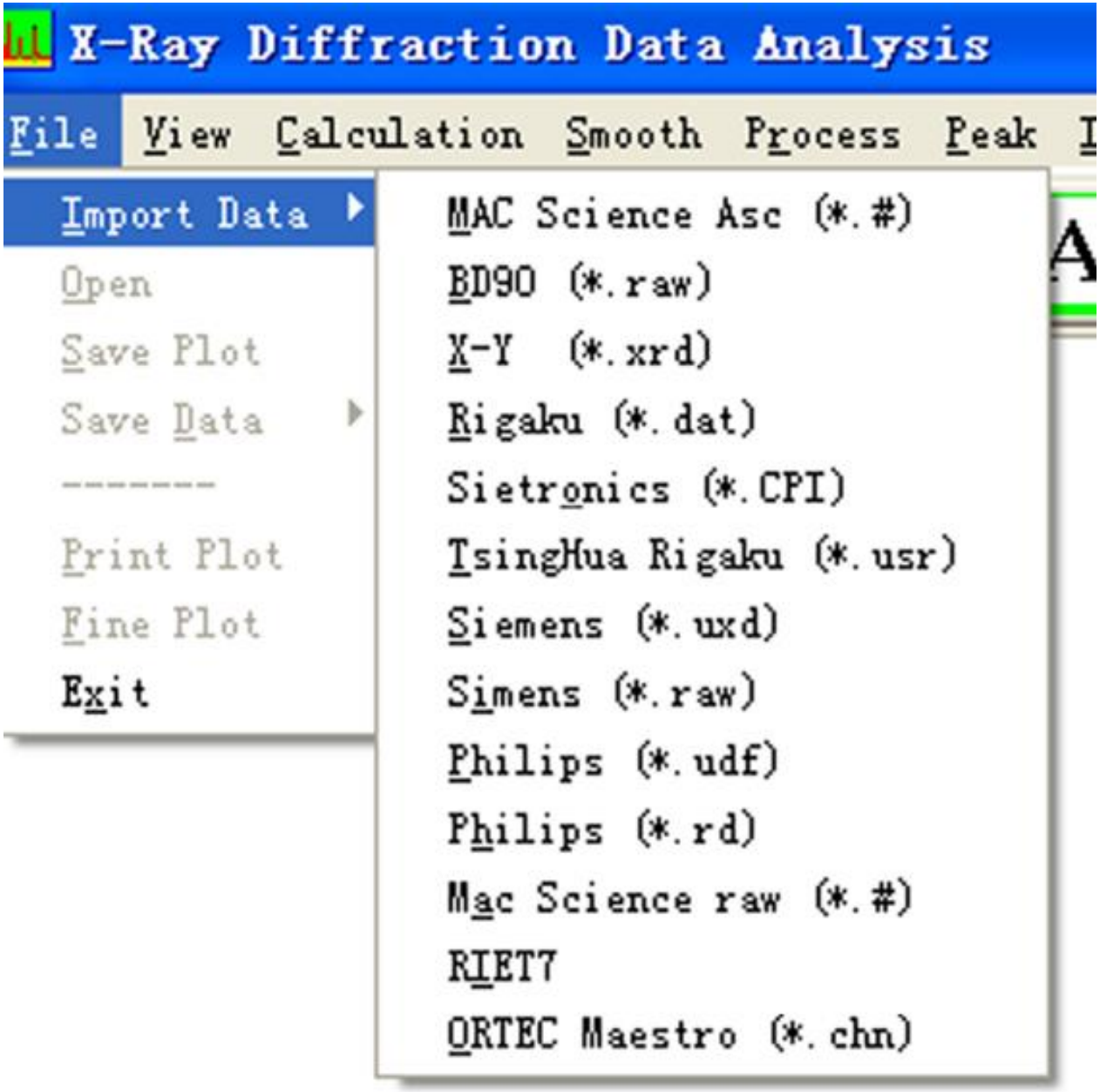
20,000
15,000
10,000
5,000
0
-5,000

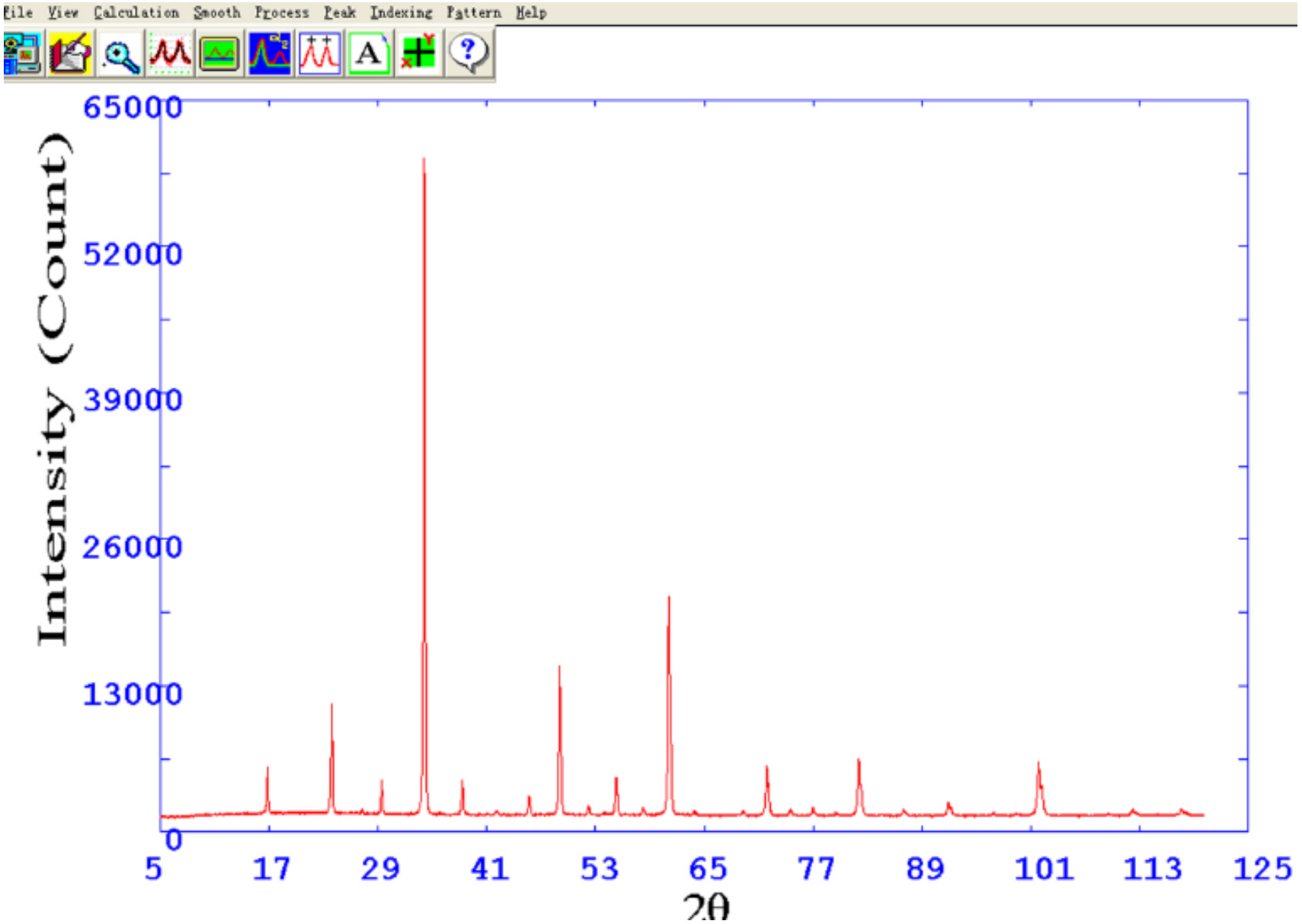

Launch Tools Window Help
d11s.dat
x y
Phase Details
Peak Type
hkls Is
Additional Convolutions
Rpt/Text
h k l m d th2 Use I
0 1 1 12 5.26128 16.83774 15
0 0 2 6 3.72029 23.89946 130
2 1 1 24 3.03760 29.37981 31.4
0 2 2 12 2.63064 34.05344 769
3 0 1 12 2.35292 38.21967 24.9
0 3 1 12 2.35292 38.21967 24.9
2 2 2 8 2.14791 42.03180 34.3
2 3 1 24 1.98858 45.58083 22.4
3 2 1 24 1.98858 45.58083 22.4
0 0 4 6 1.86014 48.92616 541
0 3 3 12 1.75376 52.10908 20.5

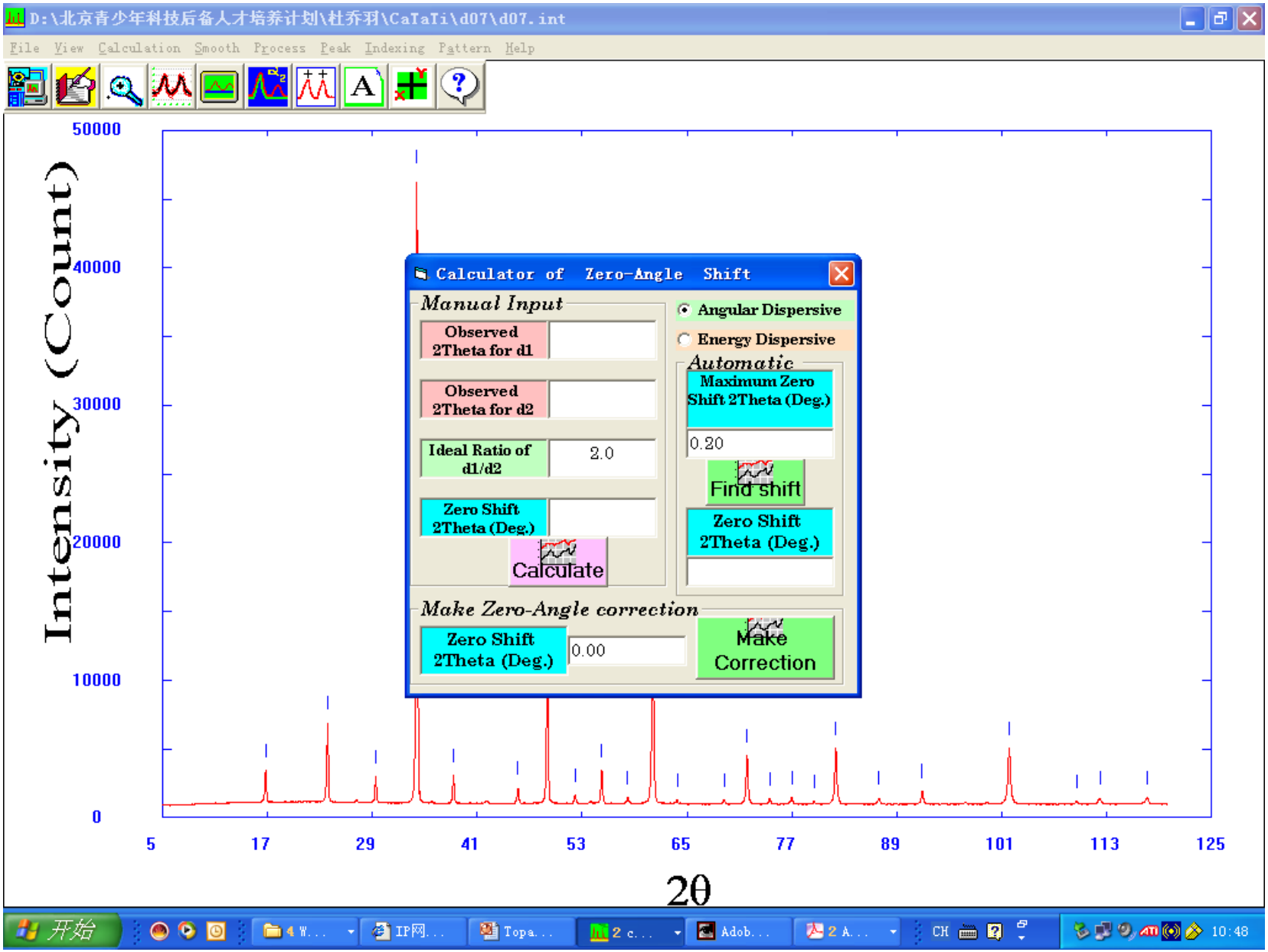
其他方法

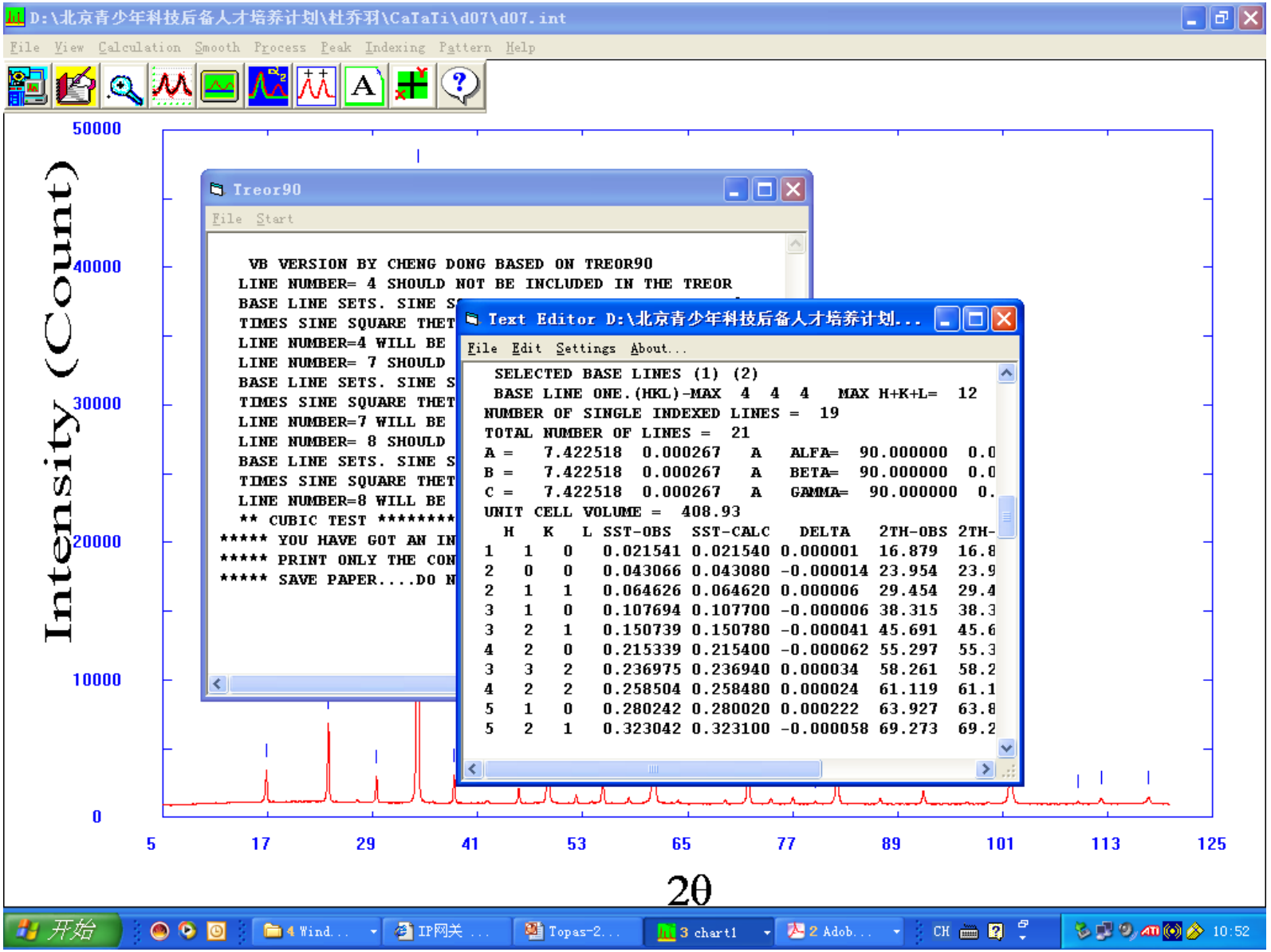
- Powder-X
- 中国科学院物理研究所
- 董成研究员

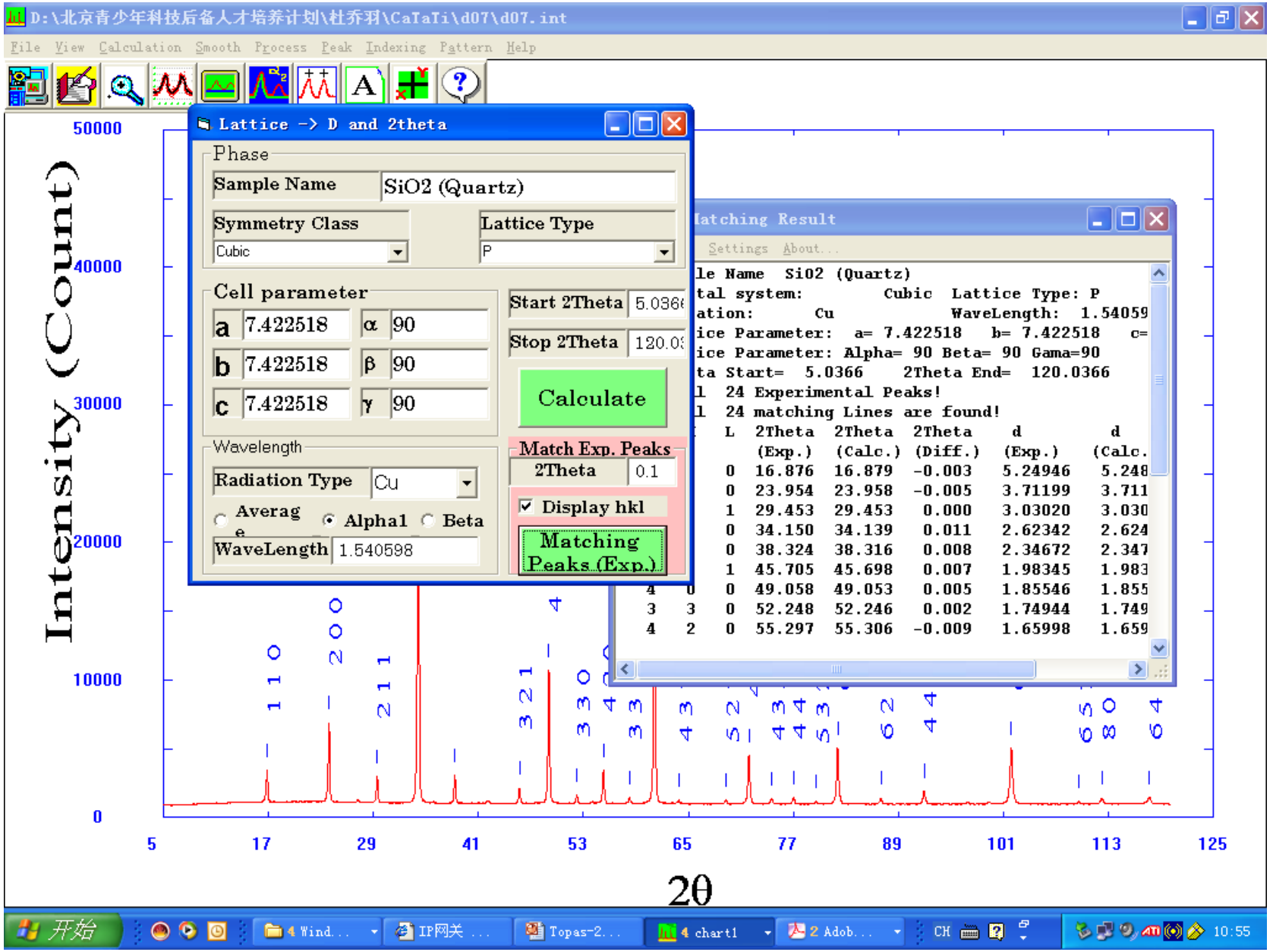


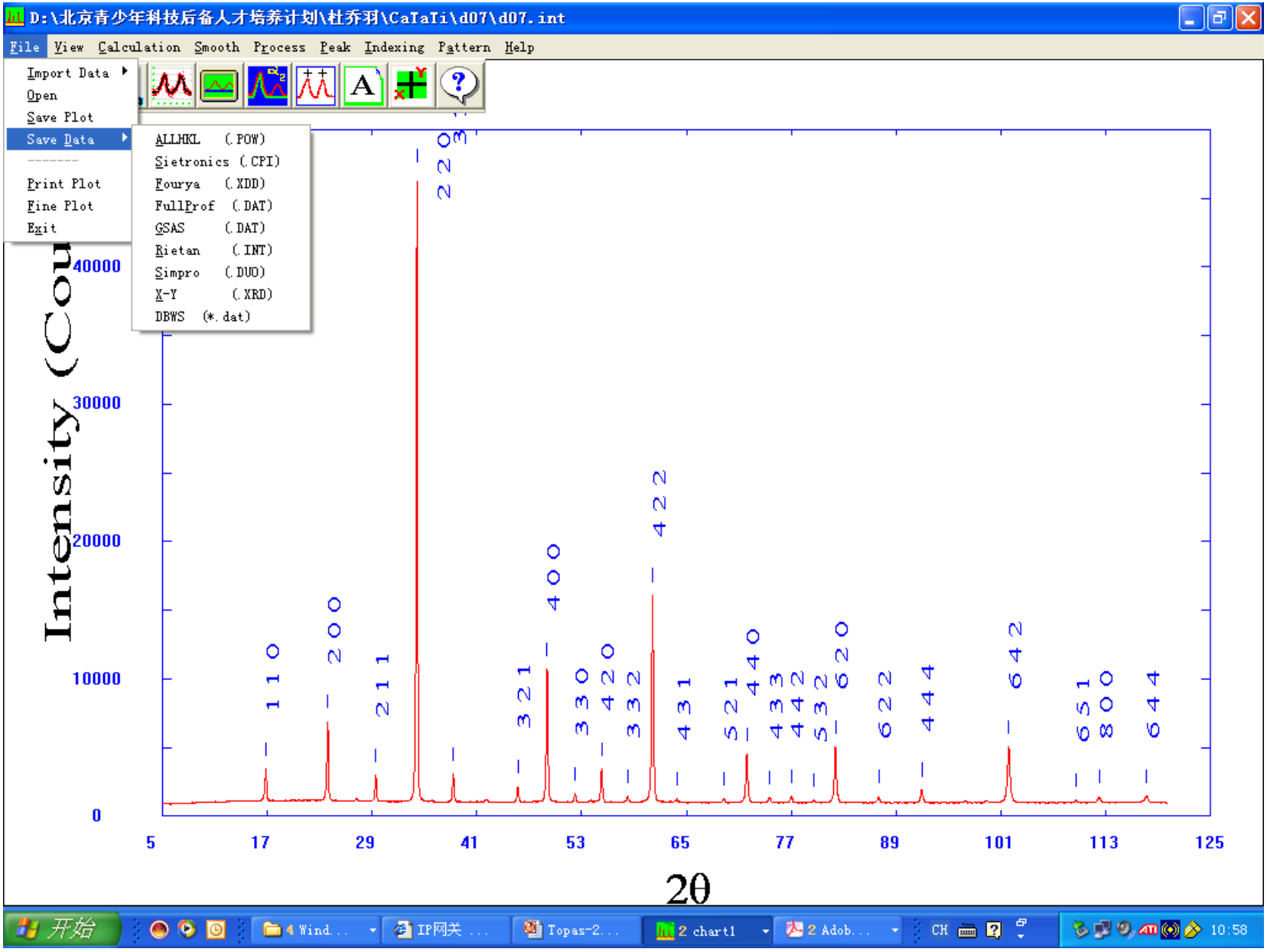

X-Ray Diffraction Data Analysis
File
View
Calculation
Smooth
Process
Peak
Import Data
Open
Save Plot
Save Data
Print Plot
Fine Plot
Exit
MAC Science Asc (*.#)
BD90 (*.raw)
X-Y (*.xrd)
Rigaku (*.dat)
Sietronics (*.CPI)
TsingHua Rigaku (*.usr)
Siemens (*.uxd)
Simens (*.raw)
Philips (*.udf)
Philips (*.rd)
Mac Science raw (*.#)
RIET7
ORTEC Maestro (*.chn)


File View Calculation Smooth Process Peak Indexing Pattern Help
Intensity (Count)
65000
52000
39000
26000
13000
0
5
17
29
41
53
65
77
89
101
113
125
2θ


D:\北京青少年科技后备人才培养计划\杜乔羽\CaTaTi\d07\d07.int
File View Calculation Smooth Process Peak Indexing Pattern Help
Intensity (Count)
50000
40000
30000
20000
10000
0
5
17
29
41
53
65
77
89
101
113
125
2θ
Calculator of Zero-Angle Shift
Manual Input
Observed 2Theta for d1
Observed 2Theta for d2
Ideal Ratio of d1/d2
2.0
Zero Shift 2Theta (Deg.)
Calculate
Angular Dispersive
Energy Dispersive
Automatic
Maximum Zero Shift 2Theta (Deg.)
0.20
Find shift
Zero Shift 2Theta (Deg.)
Make Zero-Angle correction
Zero Shift 2Theta (Deg.)
0.00
Make Correction
开始
10:48

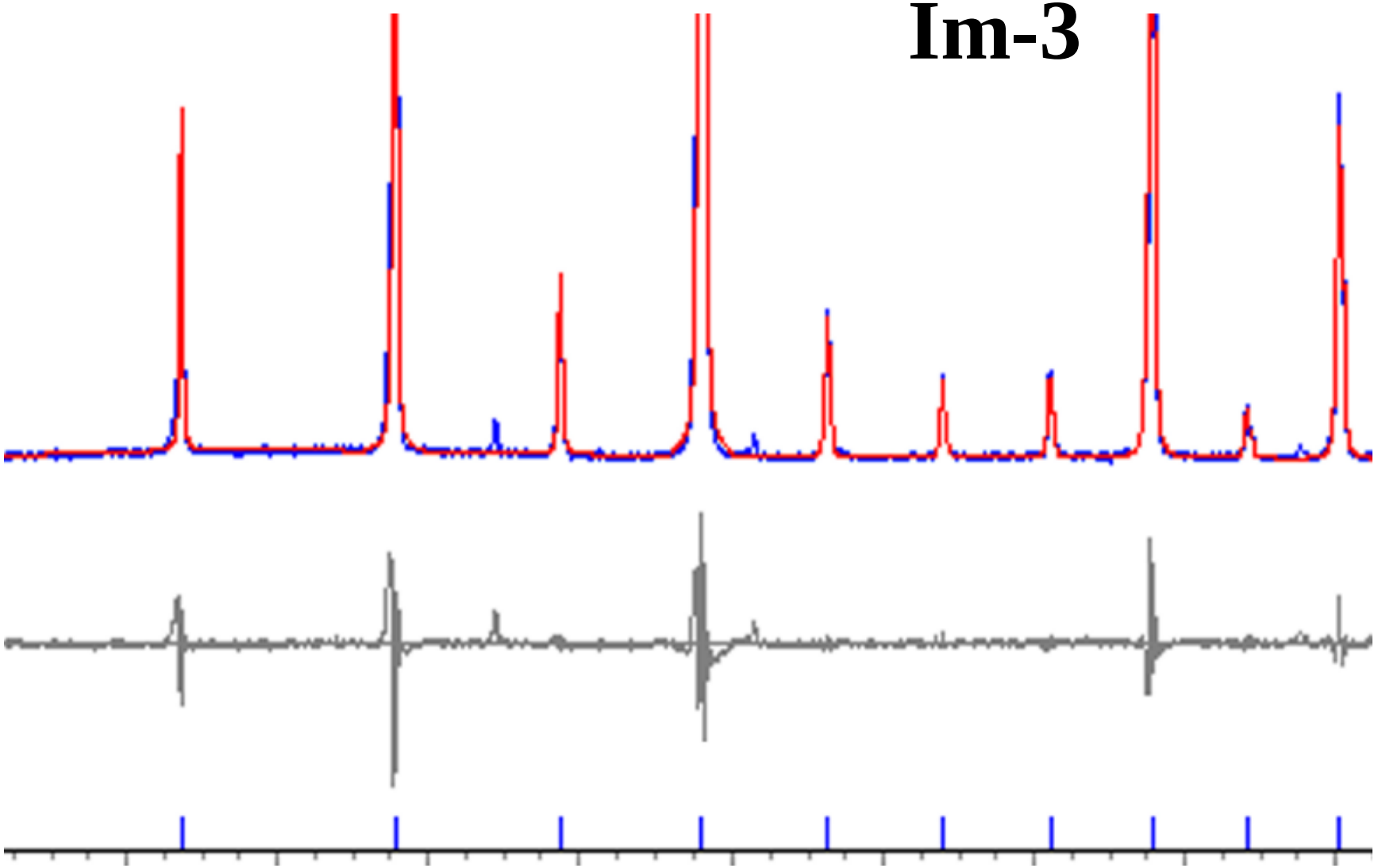

D:\北京青少年科技后备人才培养计划\杜乔羽\CaTaTi\d07\d07.int
File View Calculation Smooth Process Peak Indexing Pattern Help
Intensity (Count)
50000
40000
30000
20000
10000
0
5
17
29
41
53
65
77
89
101
113
125
2θ
Treor90
File Start
VB VERSION BY CHENG DONG BASED ON TREOR90
LINE NUMBER= 4 SHOULD NOT BE INCLUDED IN THE TREOR
BASE LINE SETS. SINE S
TIMES SINE SQUARE THET
LINE NUMBER=4 WILL BE
LINE NUMBER= 7 SHOULD
BASE LINE SETS. SINE S
TIMES SINE SQUARE THET
LINE NUMBER=7 WILL BE
LINE NUMBER= 8 SHOULD
BASE LINE SETS. SINE S
TIMES SINE SQUARE THET
LINE NUMBER=8 WILL BE
** CUBIC TEST ********
***** YOU HAVE GOT AN IN
***** PRINT ONLY THE CON
***** SAVE PAPER....DO N
Text Editor D:\北京青少年科技后备人才培养计划...
File Edit Settings About...
SELECTED BASE LINES (1) (2)
BASE LINE ONE.(HKL)-MAX 4 4 4 MAX H+K+L= 12
NUMBER OF SINGLE INDEXED LINES = 19
TOTAL NUMBER OF LINES = 21
A = 7.422518 0.000267 A ALFA= 90.000000 0.0
B = 7.422518 0.000267 A BETA= 90.000000 0.0
C = 7.422518 0.000267 A GAMMA= 90.000000 0.
UNIT CELL VOLUME = 408.93
H K L SST-OBS SST-CALC DELTA 2TH-OBS 2TH-
1 1 0 0.021541 0.021540 0.000001 16.879 16.8
2 0 0 0.043066 0.043080 -0.000014 23.954 23.9
2 1 1 0.064626 0.064620 0.000006 29.454 29.4
3 1 0 0.107694 0.107700 -0.000006 38.315 38.3
3 2 1 0.150739 0.150780 -0.000041 45.691 45.6
4 2 0 0.215339 0.215400 -0.000062 55.297 55.3
3 3 2 0.236975 0.236940 0.000034 58.261 58.2
4 2 2 0.258504 0.258480 0.000024 61.119 61.1
5 1 0 0.280242 0.280020 0.000222 63.927 63.8
5 2 1 0.323042 0.323100 -0.000058 69.273 69.2
开始
4 Wind...
IP网关 ...
Topas-2...
3 chart1
2 Adob...
CH
10:52


D:\北京青少年科技后备人才培养计划\杜乔羽\CaTaTi\d07\d07.int
File View Calculation Smooth Process Peak Indexing Pattern Help
Lattice -> D and 2theta
Phase
Sample Name
SiO2 (Quartz)
Symmetry Class
Cubic
Lattice Type
P
Cell parameter
a 7.422518
α 90
b 7.422518
β 90
c 7.422518
γ 90
Wavelength
Radiation Type
Cu
Averag e
Alpha1
Beta
WaveLength 1.540598
Start 2Theta 5.036
Stop 2Theta 120.0
Calculate
Match Exp. Peaks
2Theta 0.1
Display hkl
Matching Peaks (Exp.)
Matching Result
Settings About...
le Name SiO2 (Quartz)
tal system: Cubic Lattice Type: P
ation: Cu WaveLength: 1.54059
ice Parameter: a= 7.422518 b= 7.422518 c=
ice Parameter: Alpha= 90 Beta= 90 Gama=90
ta Start= 5.0366 2Theta End= 120.0366
l 24 Experimental Peaks!
l 24 matching Lines are found!
L 2Theta (Exp.) 2Theta (Calc.) 2Theta (Diff.) d (Exp.) d (Calc.
0 16.876 16.879 -0.003 5.24946 5.248
0 23.954 23.958 -0.005 3.71199 3.711
1 29.453 29.453 0.000 3.03020 3.030
0 34.150 34.139 0.011 2.62342 2.624
0 38.324 38.316 0.008 2.34672 2.347
1 45.705 45.698 0.007 1.98345 1.983
0 49.058 49.053 0.005 1.85546 1.855
0 52.248 52.246 0.002 1.74944 1.749
2 0 55.297 55.306 -0.009 1.65998 1.659
Intensity (Count)
50000
40000
30000
20000
10000
0
5
17
29
41
53
65
77
89
101
113
125
2θ
1 1 0
2 0 0
2 1 1
3 2 1
3 3 0
4 0 0
3 3 3
4 3 2
5 2 0
4 3 4
5 3 3
6 2 0
4 4 4
6 5 0
8 0 4
开始
4 Wind...
IP网关 ...
Topas-2...
4 chart1
2 Adob...
CH
10:55

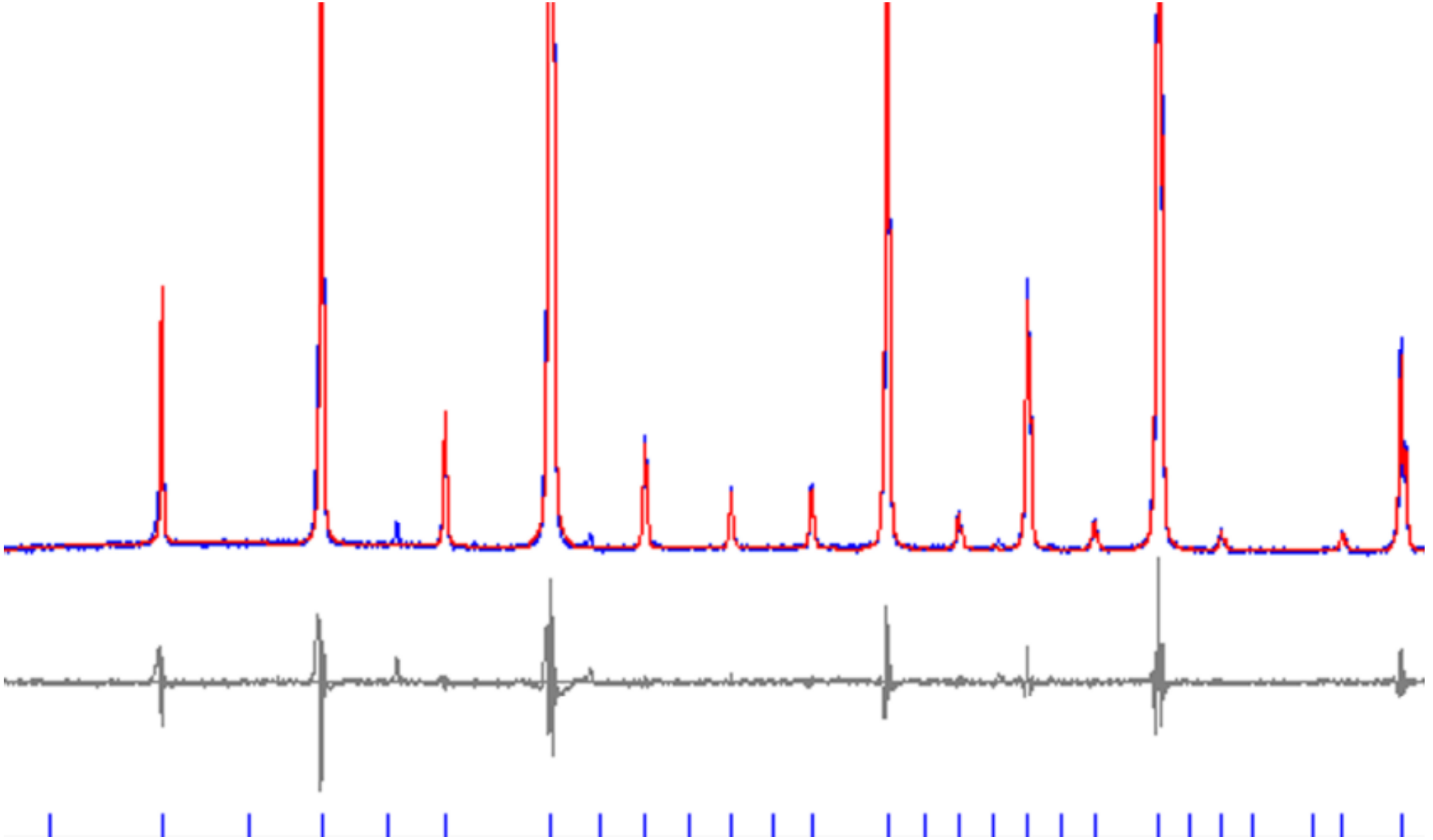

D:\北京青少年科技后备人才培养计划\杜乔羽\CaTaTi\d07\d07.int
File View Calculation Smooth Process Peak Indexing Pattern Help
Import Data
Open
Save Plot
Save Data
Print Plot
Fine Plot
Exit
ALLHKL (.POW)
Sietronics (.CPI)
Fourya (.XDD)
FullProf (.DAT)
GSAS (.DAT)
Rietan (.INT)
Simpro (.DUO)
X-Y (.XRD)
DBWS (*.dat)
Intensity (Cou
40000
30000
20000
10000
0
110
200
211
220
321
400
330
420
332
422
431
521
440
433
442
532
620
622
444
642
651
800
644
5
17
29
41
53
65
77
89
101
113
125
2θ
开始
4 Wind...
IP网关 ...
Topas-2...
2 chart1
2 Adob...
CH
10:58

如何确定空间群

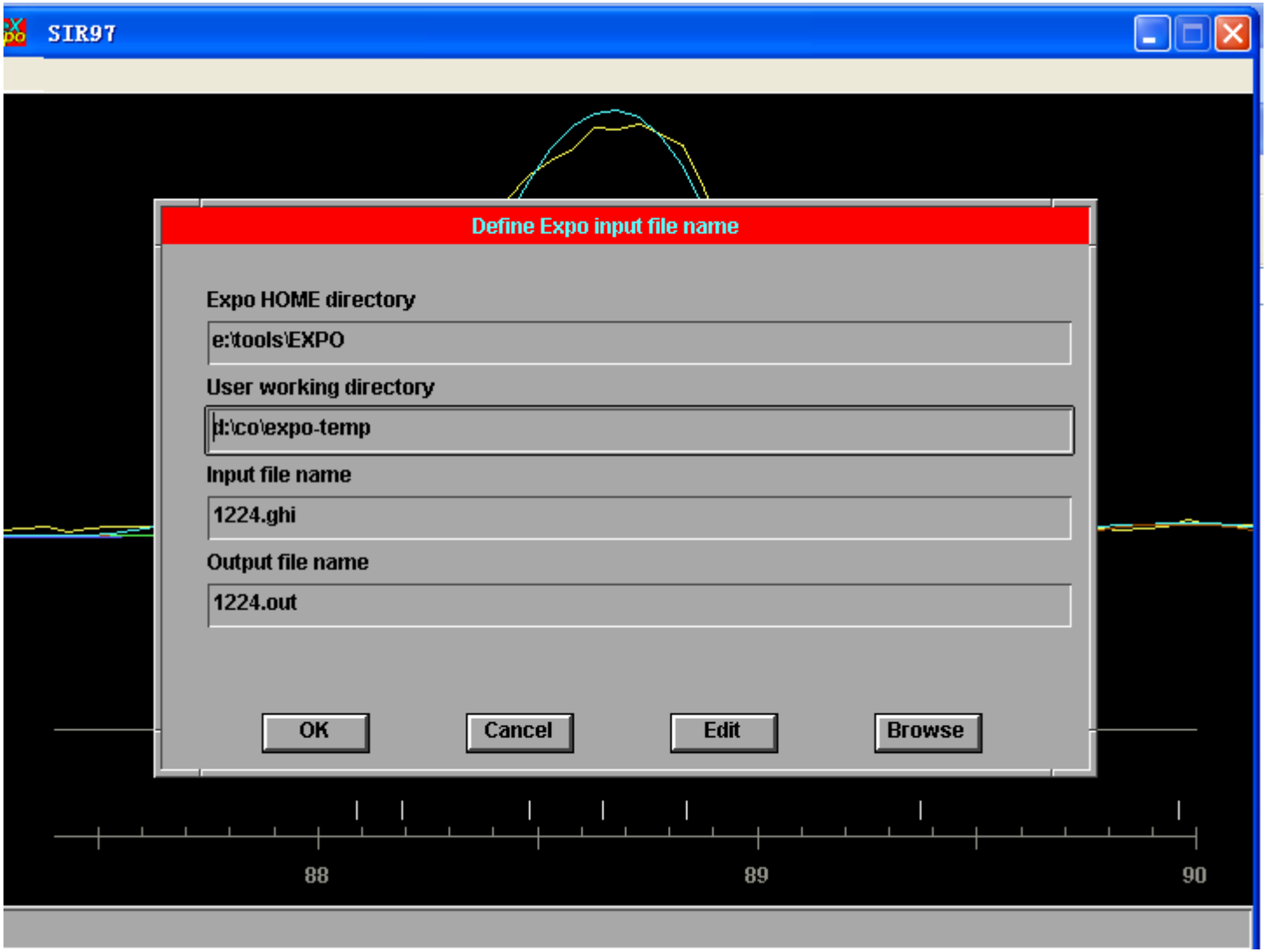
- 消光规律
- 简单尝试

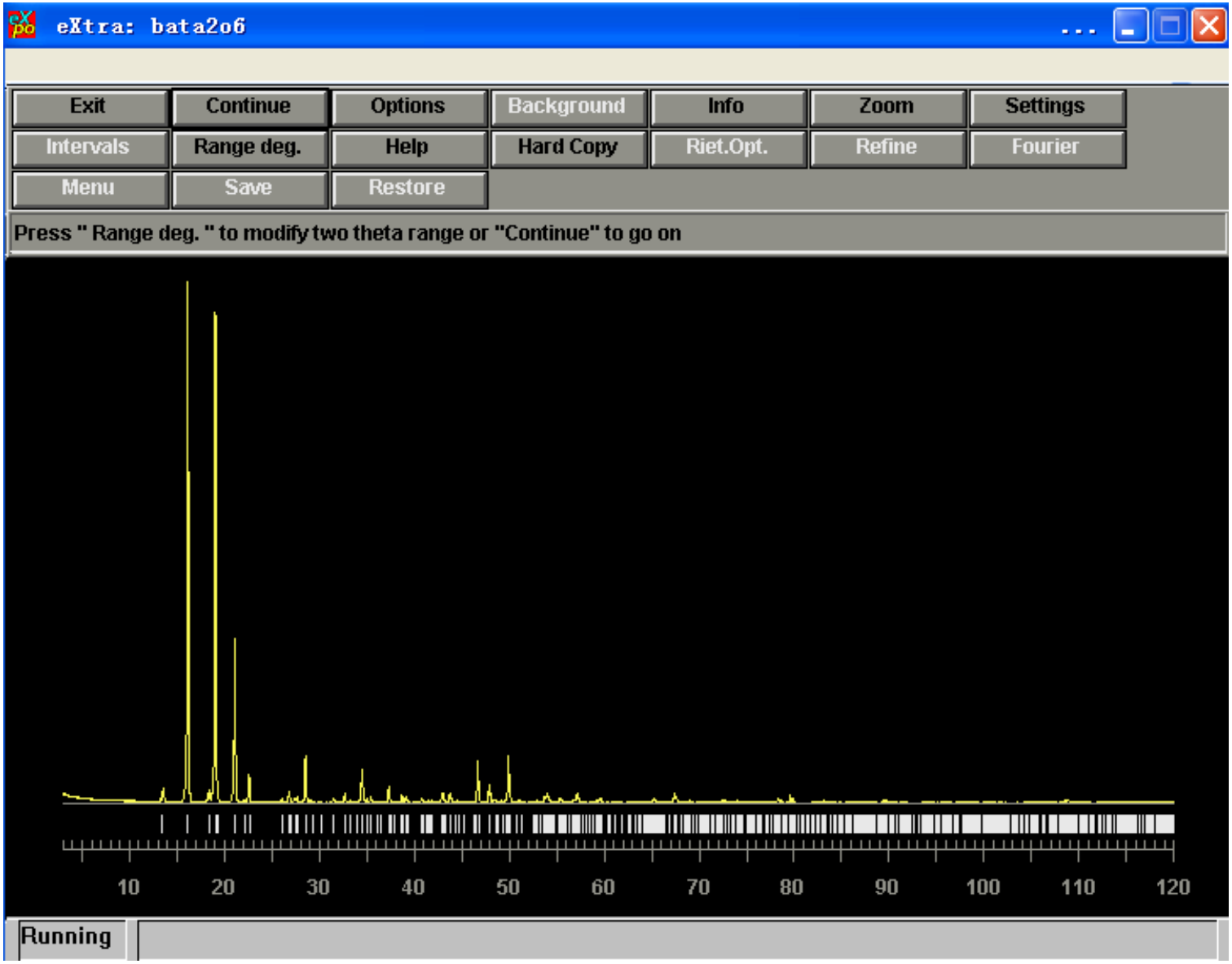

Im-3

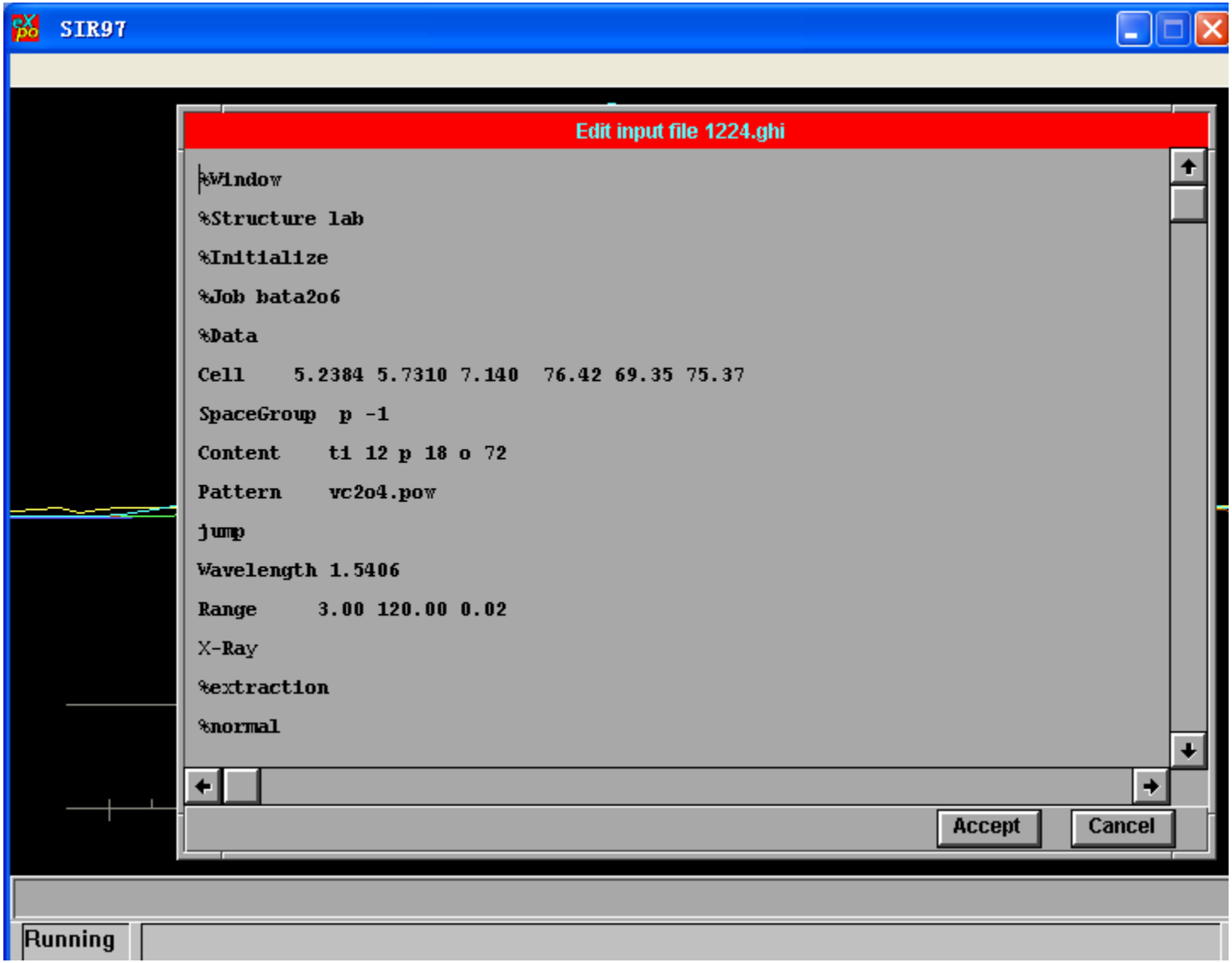
P23

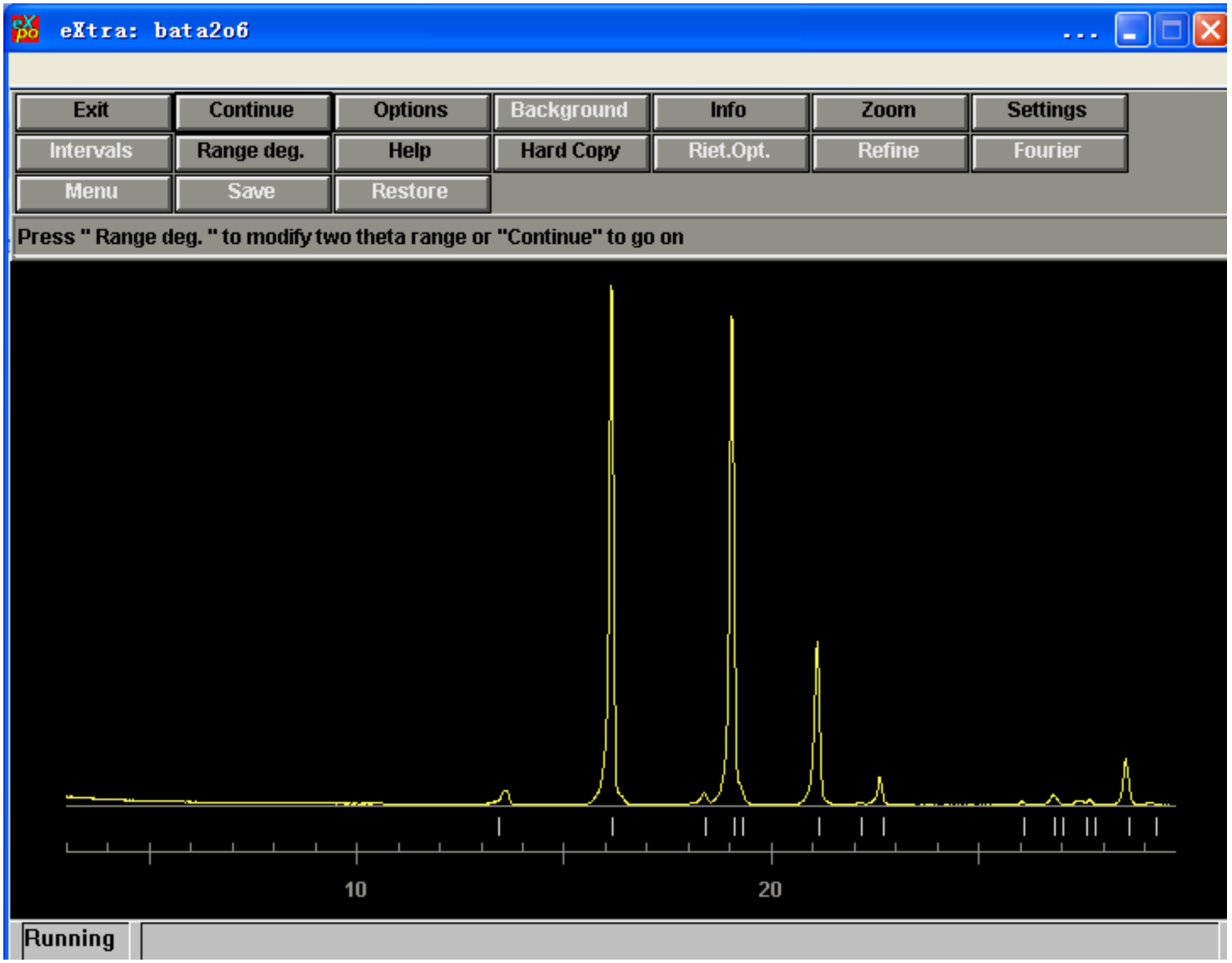


使用Sir97程序


SIR97
Define Expo input file name
Expo HOME directory
e:\tools\EXPO
User working directory
d:\co\expo-temp
Input file name
1224.ghi
Output file name
1224.out
OK
Cancel
Edit
Browse
88
89
90


eXtra: bata2o6
Exit
Continue
Options
Background
Info
Zoom
Settings
Intervals
Range deg.
Help
Hard Copy
Riet.Opt.
Refine
Fourier
Menu
Save
Restore
Press " Range deg. " to modify two theta range or "Continue" to go on
10
20
30
40
50
60
70
80
90
100
110
120
Running

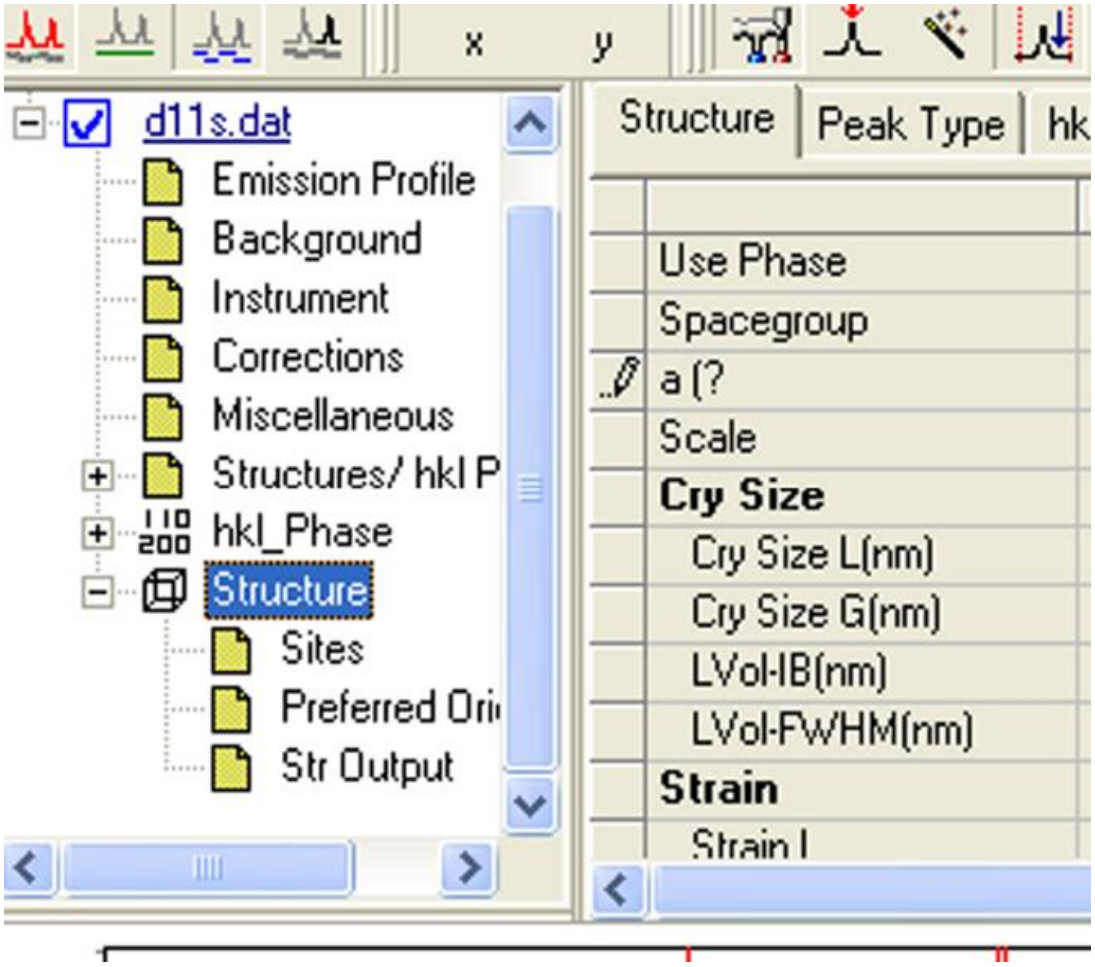

SIR97
Edit input file 1224.ghi
%Window
%Structure lab
%Initialize
%Job bata2o6
%Data
Cell 5.2384 5.7310 7.140 76.42 69.35 75.37
SpaceGroup p -1
Content t1 12 p 18 o 72
Pattern vc2o4.pow
jump
Wavelength 1.5406
Range 3.00 120.00 0.02
X-Ray
%extraction
%normal
Accept
Cancel
Running


eXtra: bata2o6
Exit
Continue
Options
Background
Info
Zoom
Settings
Intervals
Range deg.
Help
Hard Copy
Riet.Opt.
Refine
Fourier
Menu
Save
Restore
Press " Range deg. " to modify two theta range or "Continue" to go on
10
20
Running

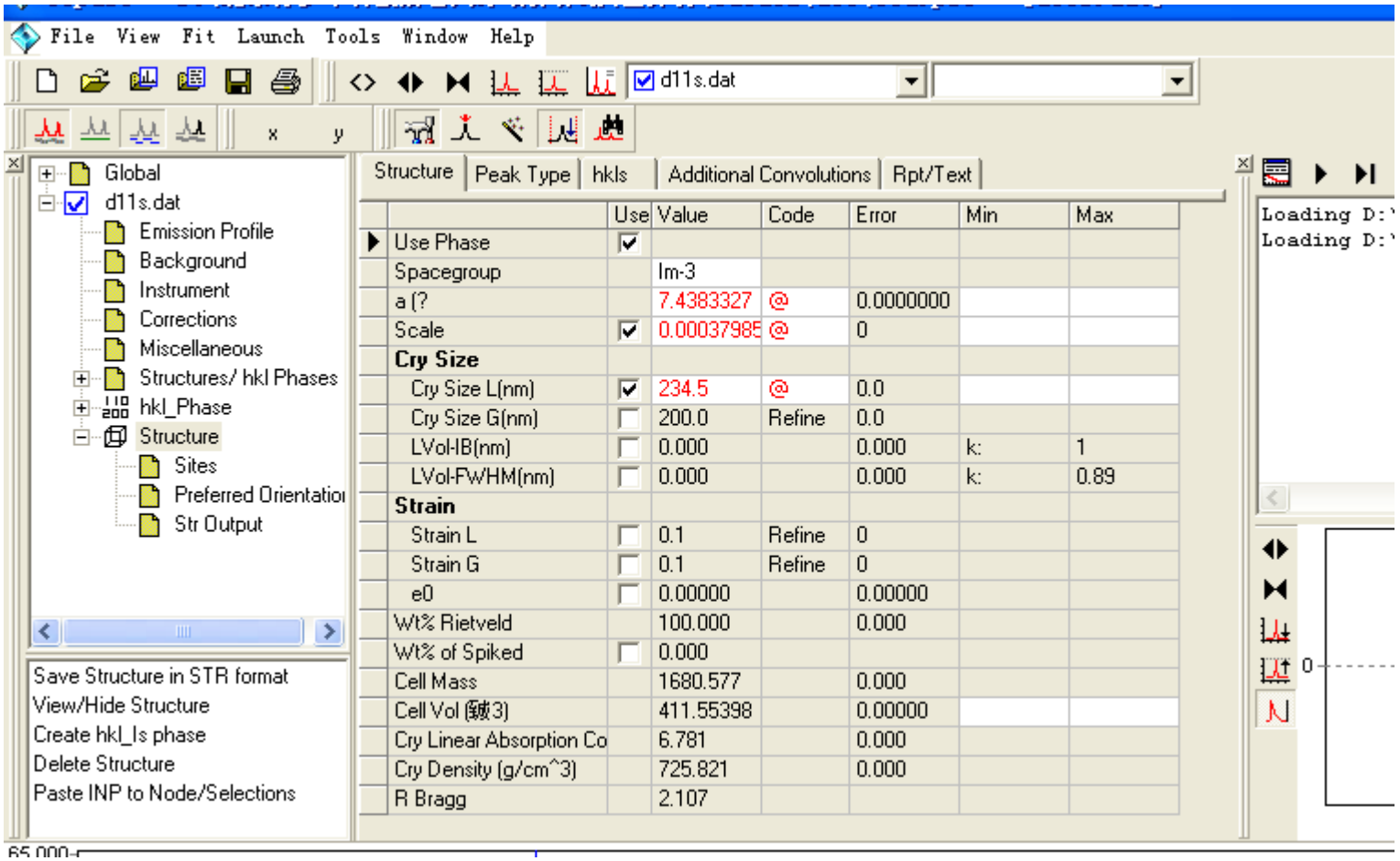
结构解析

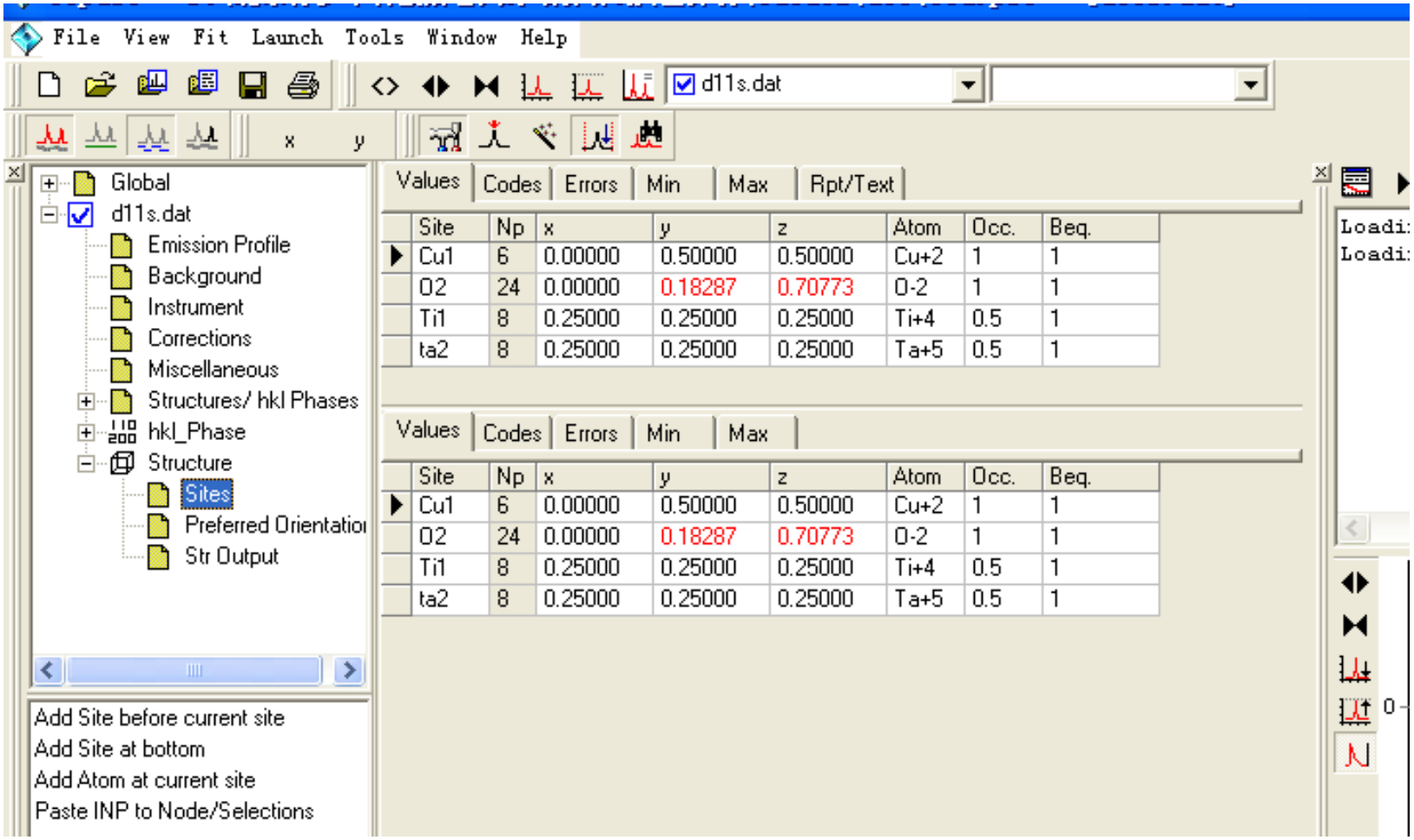
- **GUI模式**
- **Lauch模式**

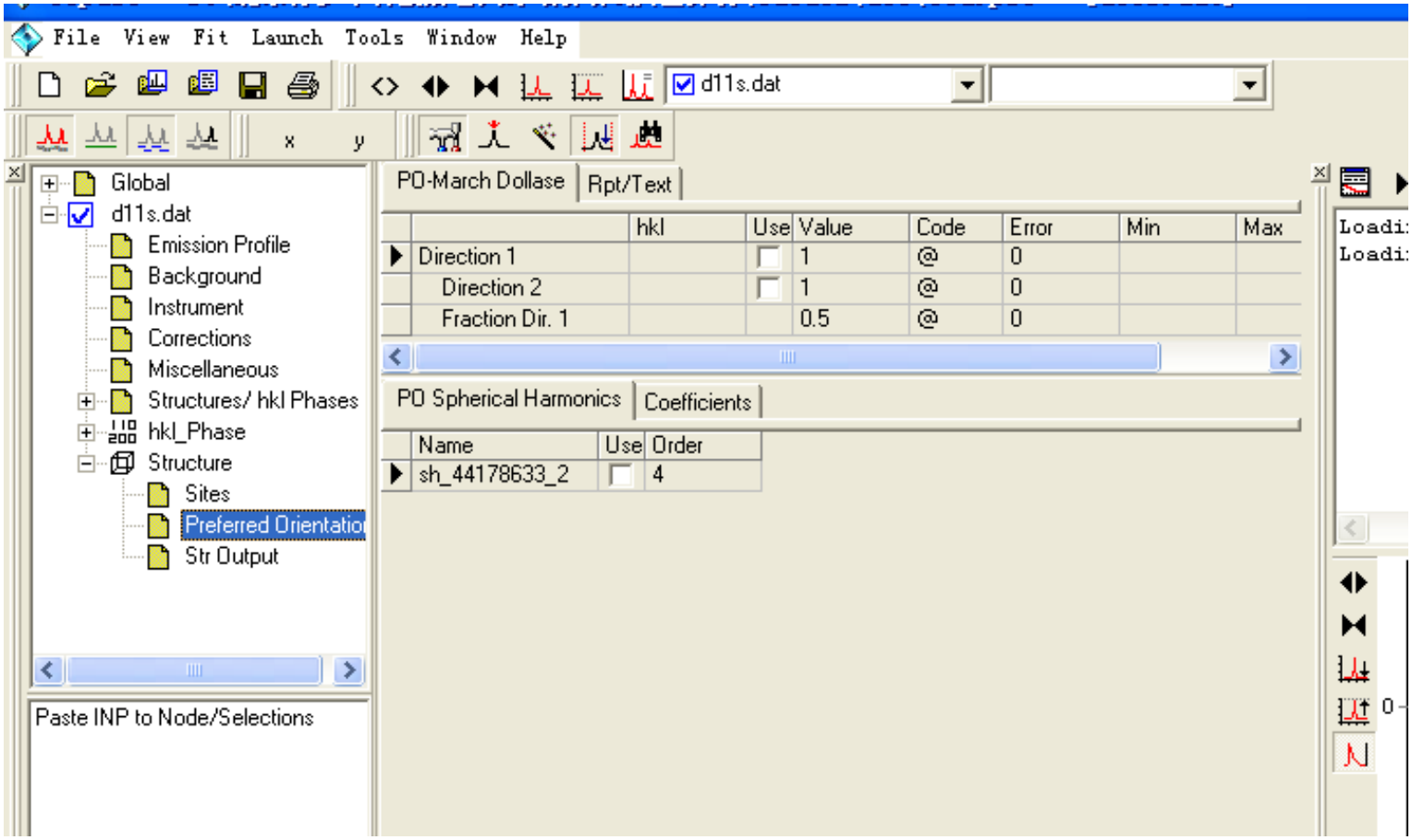
添加Structure项

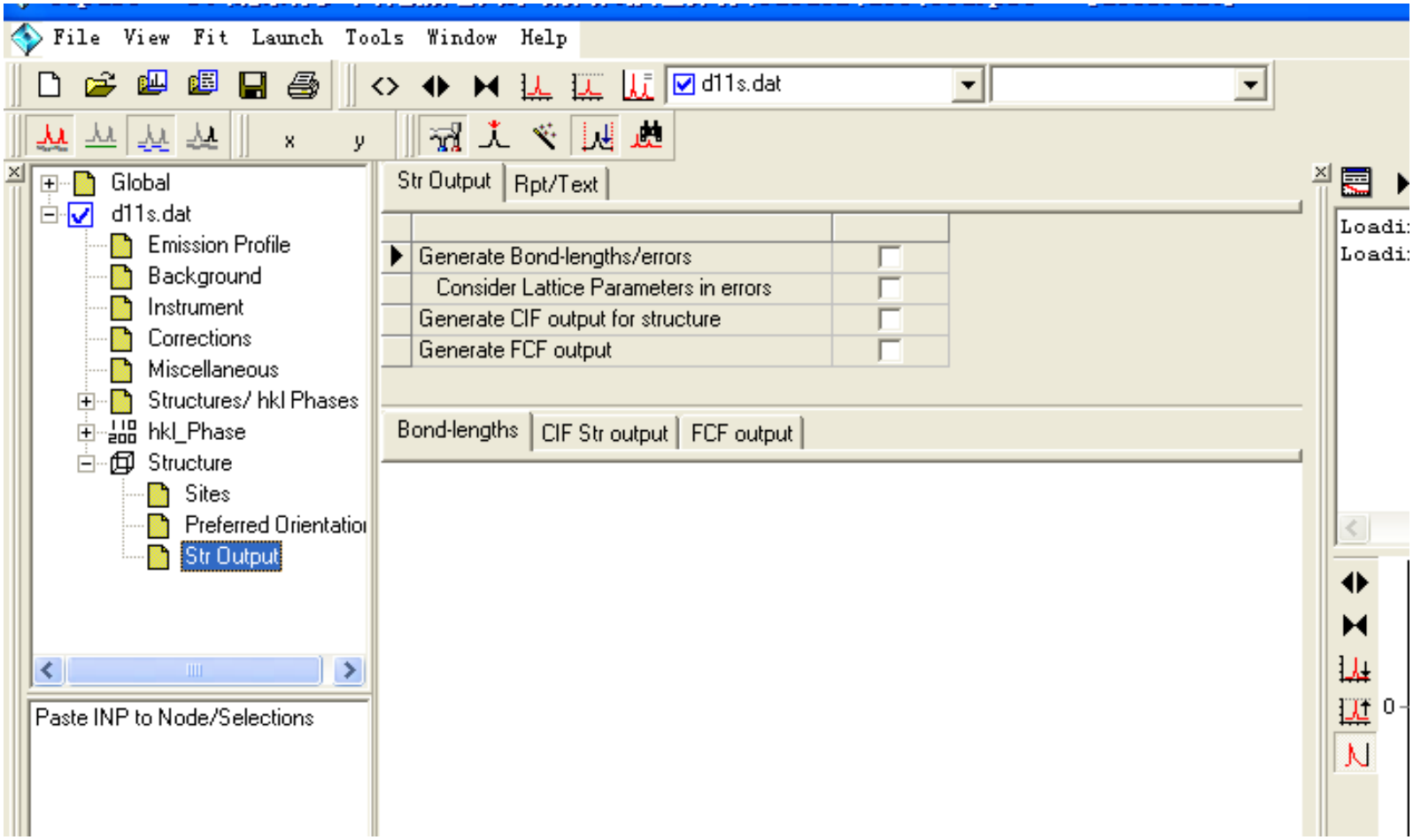


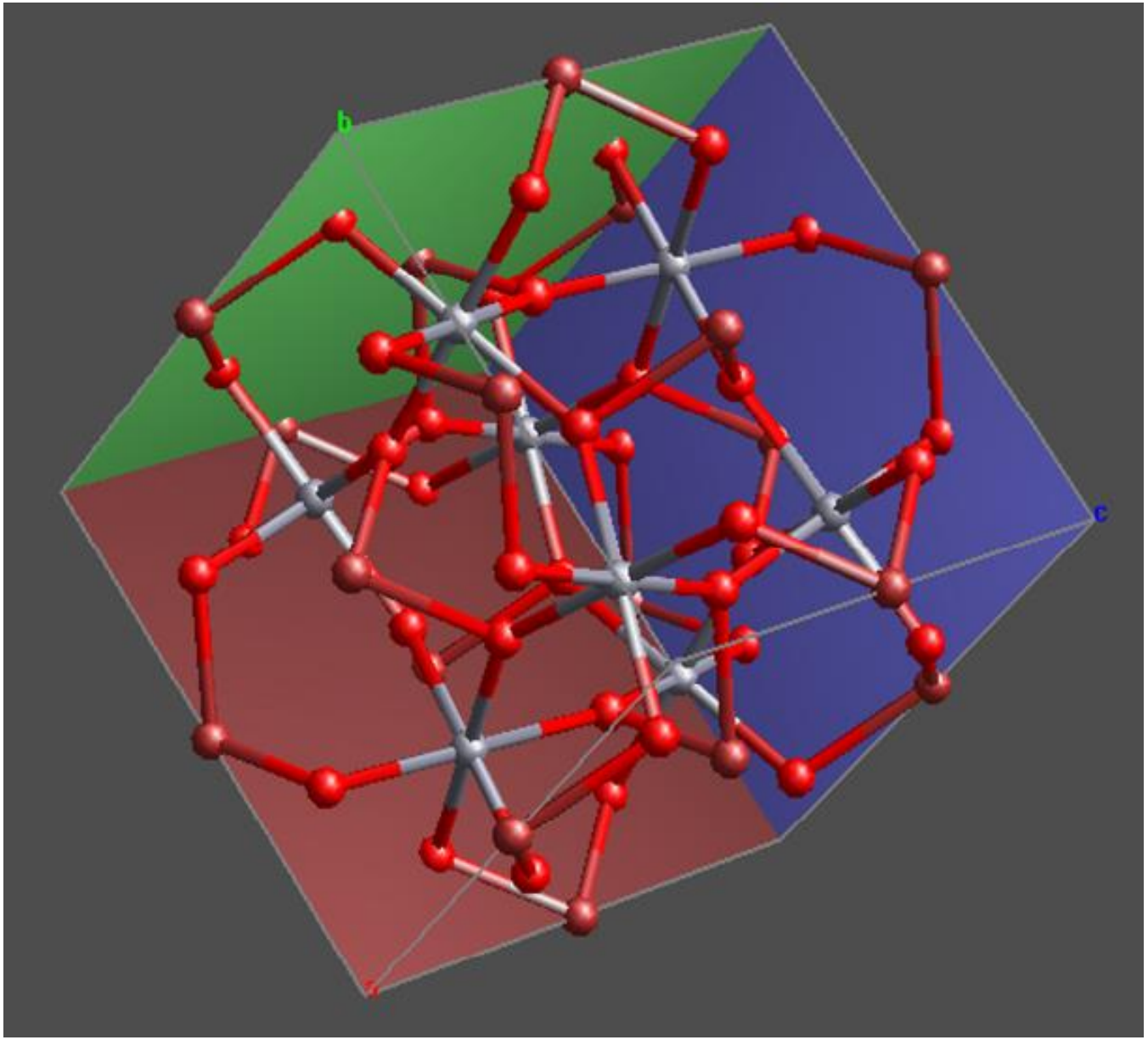
设定相关参数

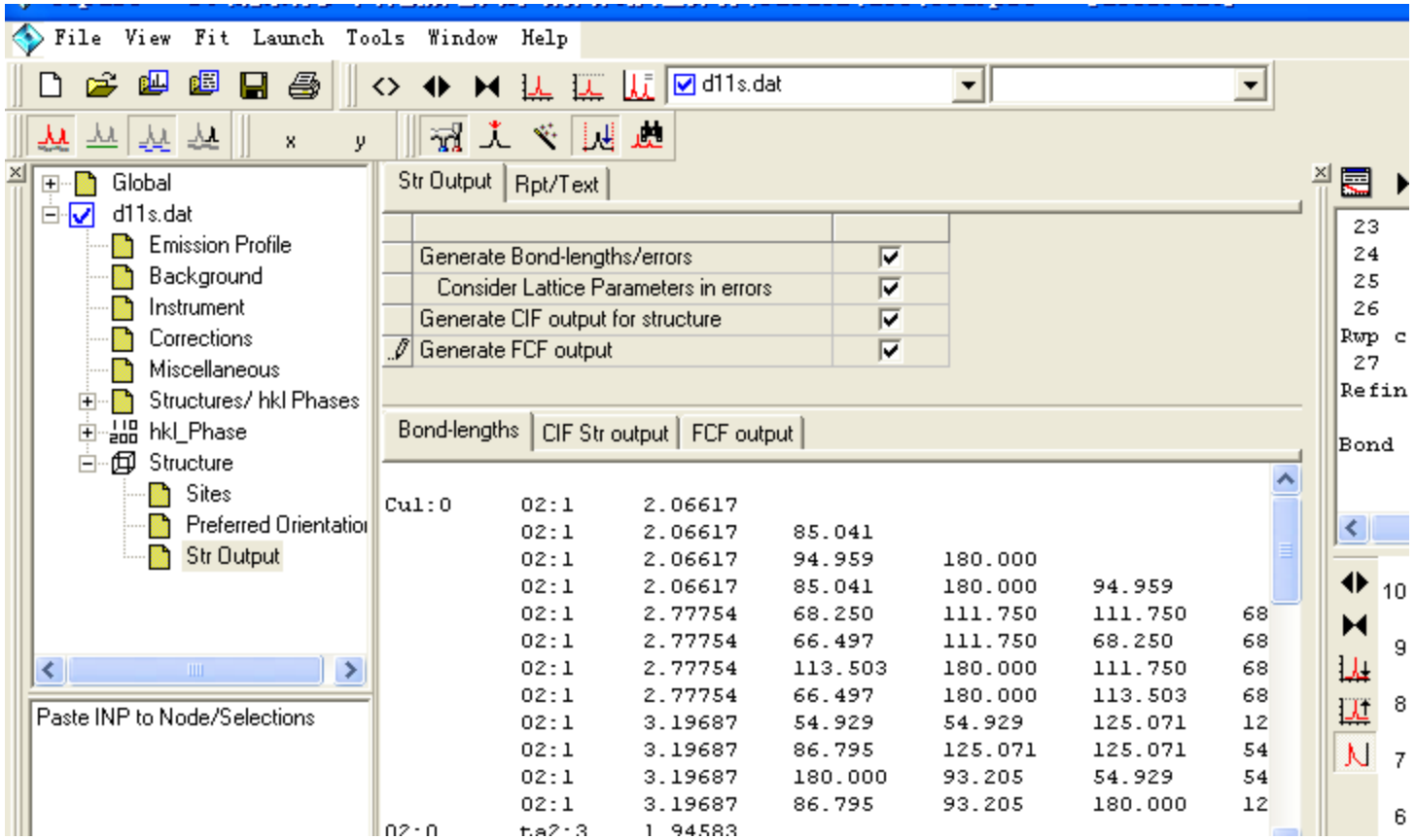

File View Fit Launch Tools Window Help
d11s.dat
x y
Global
d11s.dat
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
hkl_Phase
Structure
Sites
Preferred Orientatio
Str Output
Save Structure in STR format
View/Hide Structure
Create hkl_Is phase
Delete Structure
Paste INP to Node/Selections
Structure
Peak Type
hkls
Additional Convolutions
Rpt/Text
Use
Value
Code
Error
Min
Max
Use Phase
Spacegroup
Im-3
a (?
7.4383327
@
0.0000000
Scale
0.00037985
@
0
Cry Size
Cry Size L(nm)
234.5
@
0.0
Cry Size G(nm)
200.0
Refine
0.0
LVol-IB(nm)
0.000
0.000
k:
1
LVol-FWHM(nm)
0.000
0.000
k:
0.89
Strain
Strain L
0.1
Refine
0
Strain G
0.1
Refine
0
e0
0.00000
0.00000
Wt% Rietveld
100.000
0.000
Wt% of Spiked
0.000
Cell Mass
1680.577
0.000
Cell Vol (鍍3)
411.55398
0.00000
Cry Linear Absorption Co
6.781
0.000
Cry Density (g/cm^3)
725.821
0.000
R Bragg
2.107
Loading D:
Loading D:
0
65.000

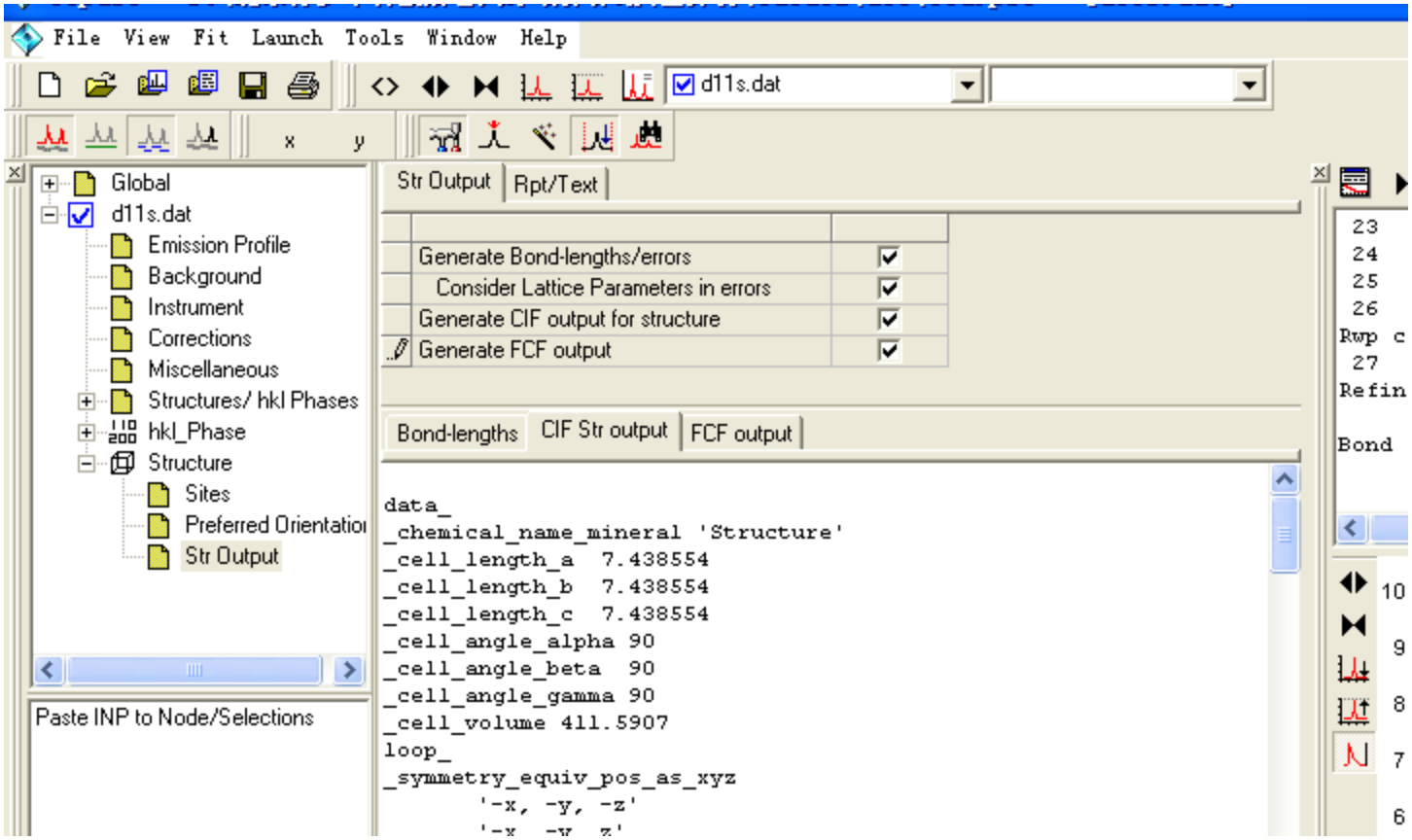

File View Fit Launch Tools Window Help
d11s.dat
x y
Global
d11s.dat
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
hkl_Phase
Structure
Sites
Preferred Orientatio
Str Output
Add Site before current site
Add Site at bottom
Add Atom at current site
Paste INP to Node/Selections
Values Codes Errors Min Max Rpt/Text
Site Np x y z Atom Occ. Beq.
Cu1 6 0.00000 0.50000 0.50000 Cu+2 1 1
O2 24 0.00000 0.18287 0.70773 O-2 1 1
Ti1 8 0.25000 0.25000 0.25000 Ti+4 0.5 1
ta2 8 0.25000 0.25000 0.25000 Ta+5 0.5 1
Values Codes Errors Min Max
Site Np x y z Atom Occ. Beq.
Cu1 6 0.00000 0.50000 0.50000 Cu+2 1 1
O2 24 0.00000 0.18287 0.70773 O-2 1 1
Ti1 8 0.25000 0.25000 0.25000 Ti+4 0.5 1
ta2 8 0.25000 0.25000 0.25000 Ta+5 0.5 1


File View Fit Launch Tools Window Help
d11s.dat
x y
Global
d11s.dat
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
hkl_Phase
Structure
Sites
Preferred Orientatio
Str Output
Paste INP to Node/Selections
PO-March Dollase
Rpt/Text
hkl
Use
Value
Code
Error
Min
Max
Direction 1
1
@
0
Direction 2
1
@
0
Fraction Dir. 1
0.5
@
0
PO Spherical Harmonics
Coefficients
Name
Use
Order
sh_44178633_2
4
Loadi
Loadi


File View Fit Launch Tools Window Help
d11s.dat
x y
Global
d11s.dat
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
hkl_Phase
Structure
Sites
Preferred Orientatio
Str Output
Paste INP to Node/Selections
Str Output
Rpt/Text
Generate Bond-lengths/errors
Consider Lattice Parameters in errors
Generate CIF output for structure
Generate FCF output
Bond-lengths
CIF Str output
FCF output
Loadi
Loadi
0

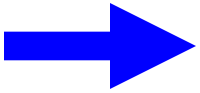

b
c


File View Fit Launch Tools Window Help
d11s.dat
x y
Global
d11s.dat
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
hkl_Phase
Structure
Sites
Preferred Orientatio
Str Output
Paste INP to Node/Selections
Str Output
Rpt/Text
Generate Bond-lengths/errors
Consider Lattice Parameters in errors
Generate CIF output for structure
Generate FCF output
Bond-lengths
CIF Str output
FCF output
Cu1:O 02:1 2.06617
02:1 2.06617 85.041
02:1 2.06617 94.959 180.000
02:1 2.06617 85.041 180.000 94.959
02:1 2.77754 68.250 111.750 111.750 68
02:1 2.77754 66.497 111.750 68.250 68
02:1 2.77754 113.503 180.000 111.750 68
02:1 2.77754 66.497 180.000 113.503 68
02:1 3.19687 54.929 54.929 125.071 12
02:1 3.19687 86.795 125.071 125.071 54
02:1 3.19687 180.000 93.205 54.929 54
02:1 3.19687 86.795 93.205 180.000 12
23
24
25
26
Rwp c
27
Refin
Bond
10
9
8
7
6


File View Fit Launch Tools Window Help
d11s.dat
x y
Global
d11s.dat
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
hkl_Phase
Structure
Sites
Preferred Orientatio
Str Output
Paste INP to Node/Selections
Str Output
Rpt/Text
Generate Bond-lengths/errors
Consider Lattice Parameters in errors
Generate CIF output for structure
Generate FCF output
Bond-lengths
CIF Str output
FCF output
data_
_chemical_name_mineral 'Structure'
_cell_length_a 7.438554
_cell_length_b 7.438554
_cell_length_c 7.438554
_cell_angle_alpha 90
_cell_angle_beta 90
_cell_angle_gamma 90
_cell_volume 411.5907
loop_
_symmetry_equiv_pos_as_xyz
'-x, -y, -z'
23
24
25
26
Rwp c
27
Refin
Bond
10
9
8
7
6

*.cif格式的变换

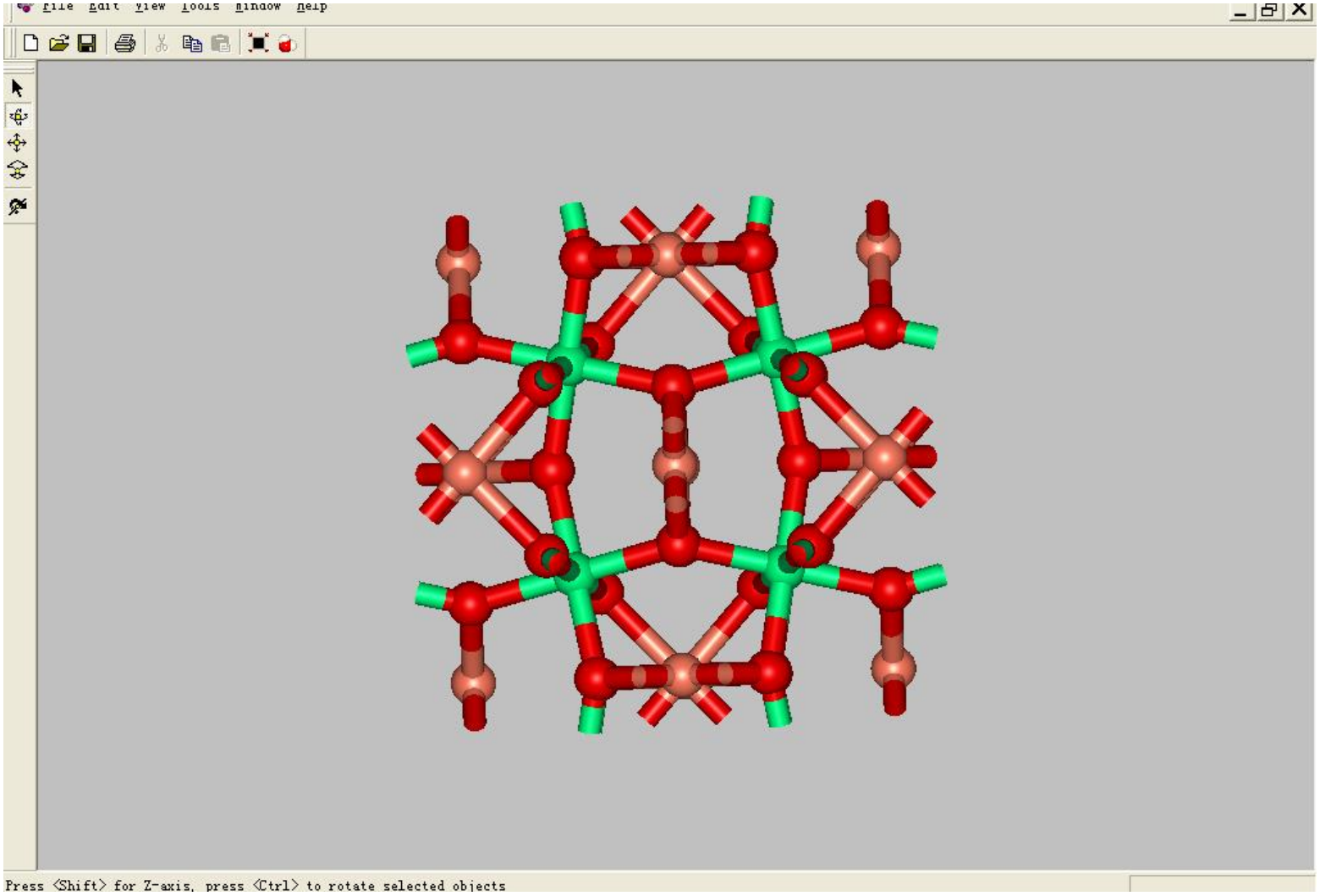
```
data_
_chemical_name_mineral 'Structure'
_cell_length_a  7.438554
_cell_length_b  7.438554
_cell_length_c  7.438554
_cell_angle_alpha 90
_cell_angle_beta  90
_cell_angle_gamma 90
_cell_volume 411.5907
loop_
_symmetry_equiv_pos_as_xyz
   '-x, -y, -z'
   '-x, -y, z'
   '-x, y, -z'
   '-x, y, z'
   '-y, -z, -x'
```

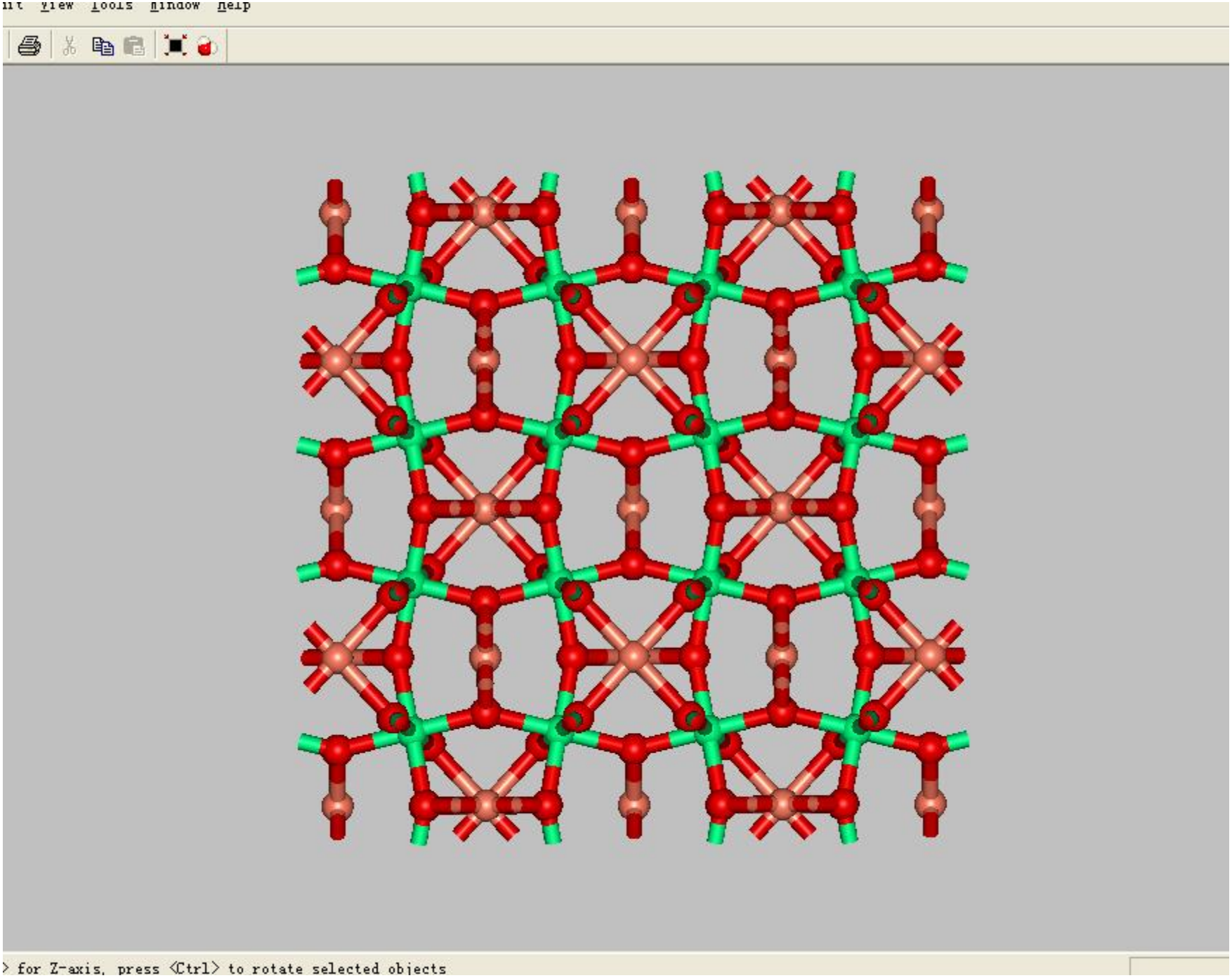


```
data_
_chemical_name_mineral 'Structure'

_symmetry_cell_setting            ?
_symmetry_space_group_name_H-M    Im-3

loop_
_symmetry_equiv_pos_as_xyz
            '-x, -y, -z'
……
_cell_length_a                    7.438554
_cell_length_b                    7.438554
_cell_length_c                    7.438554
_cell_angle_alpha                 90
_cell_angle_beta                  90
_cell_angle_gamma                 90
_cell_volume                      411.5907
```


File Edit View Tools Window Help
Press <Shift> for Z-axis, press <Ctrl> to rotate selected objects


lit View Tools Window Help
> for Z-axis, press <Ctrl> to rotate selected objects

GUI and Launch

一般特点

- Single line fitting up to whole powder pattern fitting
- Whole powder pattern decomposition according to Pawley (1981) and Le Bail et al. (1988), in the following referred to as "Pawley method" and "Le Bail method".
- Rietveld structure refinement (Rietveld, 1967, 1969) and quantitative Rietveld analysis (Hill & Howard, 1987)
- Ab-initio structure determination in direct space (Coelho, 2000)

Fit method	Constraints and keywords [1)]
SPF:	**Single peak fitting** No constraints by default. Optionally all profile parameters can be constrained (e.g. same shape, same width, relative intensity, ...) Keywords: "*xo_I*", "*d_I*"
WPPF:	**Whole Powder pattern fitting.** • No constraints by default. Optionally all profile parameters can be constrained (e.g. same shape, same width, relative intensity, ...) • Profile parameters constrained to be smoothly varying functions of 2θ Keywords: "*xo_I*", "*d_I*"
WPPD:	**Whole powder pattern decomposition** Pawley and LeBail method Number of peaks and their positions constrained by crystal system / spacegroup plus lattice parameters Keyword: "*hkl_I*"
Rietveld:	**Rietveld structure refinement, ab-initio structure determination** Peak intensities constrained by the crystal structure Keyword: "*str*"

[1)] For details refer to the Technical Reference manual

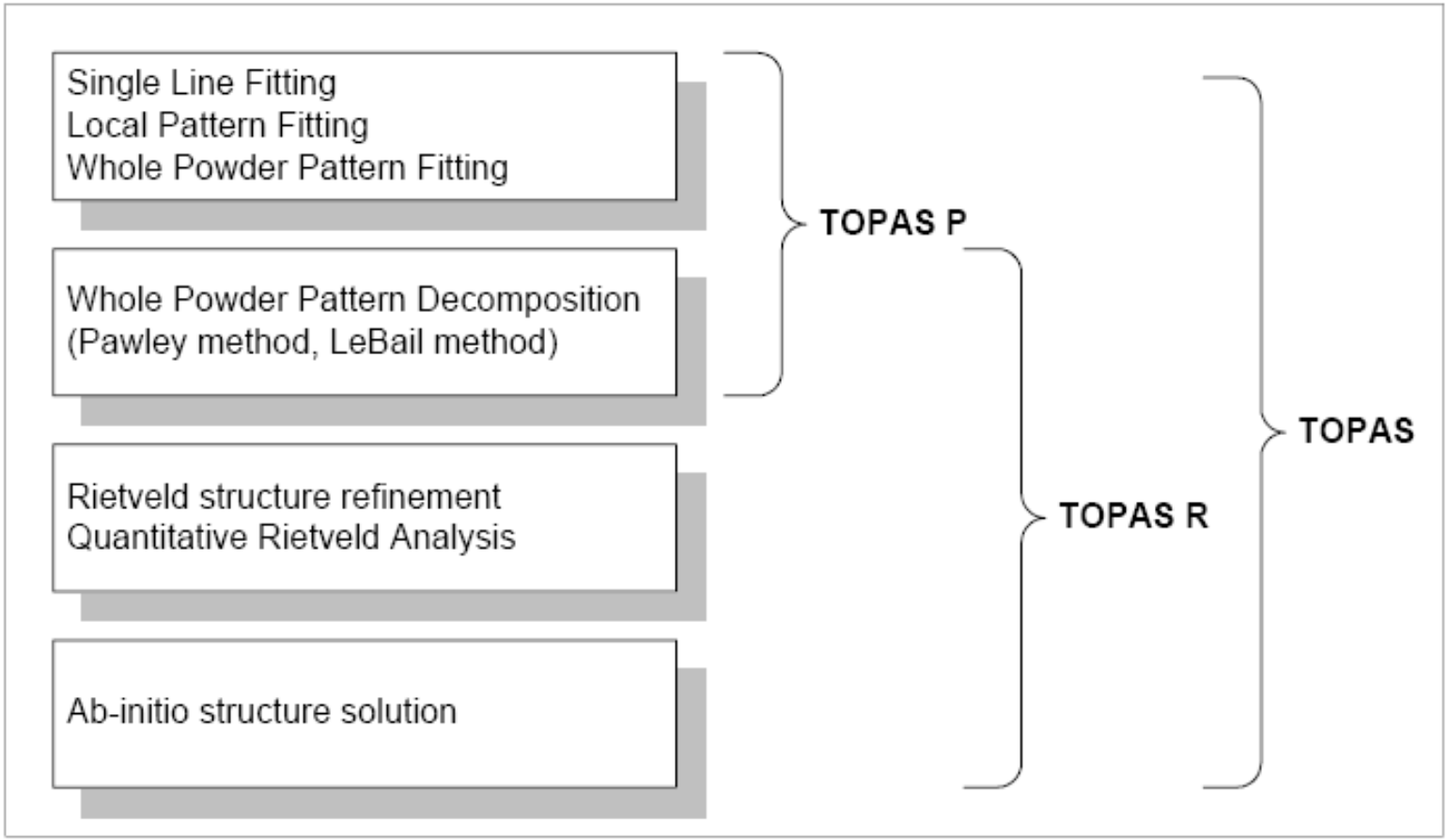


Fig. 1-1: Schematic representation of the basic differences between the functionality of TOPAS and its variants TOPAS P and TOPAS R

Two modes of operation are supported in TOPAS:

1. A Graphical User Interface mode for parameter input ("GUI mode")
2. Direct editing of an input file ("Launch mode")

In GUI Mode refinements are controlled using an intuitive and comfortable graphical user interface. Its clear design enables even the unexperienced user to get started in a short time. Most TOPAS features for single line and whole powder pattern fitting, whole powder pattern decomposition and Rietveld analysis are supported by the user interface. Remarkable are numerous import and export filters for measured and calculated data, peak profile parameters, structure data and much more, which make powder data analysis easy.

Operation in Launch Mode gives access to the full functionality of TOPAS including structure determination. In Launch Mode input to the kernel is through a text file. Advantageous is the possibility to include user-defined models into the refinement. Knowledge of the simple but extremely powerful TOPAS macro and equation language is required.

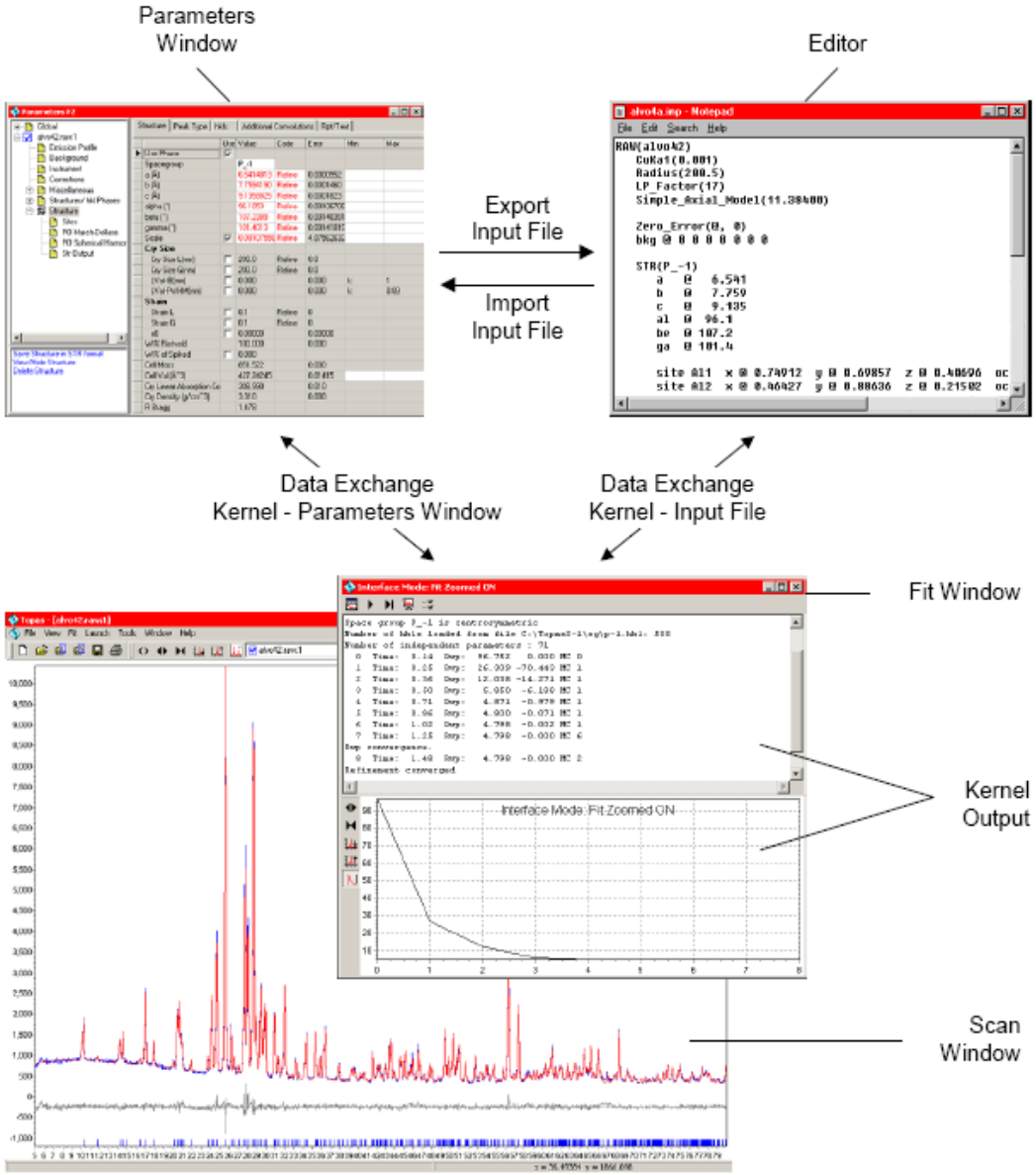


Fig. 1-2: Schematic representation of the GUI - Launch - Kernel architecture of TOPAS.

Features available in GUI and Launch Mode

Table 1-1: Functionality of TOPAS. Features marked with "GUI" available in GUI Mode. Features not available in TOPAS R or TOPAS P are marked with ~~R~~ or ~~P~~ respectively.

Features		
Profile Fitting Methods		
Single line up to whole powder pattern fitting	~~P~~	GUI
Whole powder pattern decomposition (Pawley method, LeBail method)		GUI
Rietveld structure analysis	~~P~~	GUI
Structure determination	~~R~~	
Measurement Data and Refinement Parameters		
Laboratory and synchrotron X-ray data, constant wavelength and TOF neutron data		GUI
Single crystal data	~~P~~	
Combined refinement of powder and single crystal data	~~P~~	GUI [1)]
Non dependence on X-ray data (all kinds of XY data can be fitted)		GUI
Support of non-equidistant x-axis steps		GUI
Support of negative x-axis values		GUI
Refines simultaneously on any number of diffraction patterns with any number of peaks, any number of datapoints, and any number of parameters		GUI
Refines on any number of structures per diffraction pattern with any number of sites per structure and atoms per site	~~P~~	GUI
All parameters can be fixed, refined, constrained and restrained		GUI

Peak Shape Models		
Analytical profile fitting:		GUI
Profile functions:		
PVII, Modified PV, TCHZ-type PV, Voigt		GUI
Asymmetry:		
SPV, SPVII (for single line fitting)		GUI
Simple and Full Axial Models (Cheary & Coelho, 1998a, b)		GUI
Finger asymmetry correction (Finger et al., 1994)		GUI
Crystallite size determination by Scherrer method		GUI
Direct convolution approach		GUI
Measured instrument functions		GUI
Fundamental Parameters Approach		GUI
Standardless crystallite size and strain analysis		GUI
Refinable instrument parameters		GUI
Determination of mean sample absorption coefficient and sample thickness		GUI
Tube tails correction		GUI
Support of user-defined convolutions		GUI
Background Models		
Chebychev polynomial of n'th order		GUI
Single peaks (PV, SPV, PVII, SPVII, Gauss, Lorentz, Voigt, FPA)		GUI
1/x-type background		GUI
Modulated background		
Preferred Orientation Models		
March-Dollase		GUI
Spherical Harmonics		GUI

Anisotropic Refinement Models		
Peak broadening		
Peak shifts		
Preferred orientation		
Temperature factors	+	
Occupancy factors	+	
Constraints and restraints		
Any linear and non-linear constraints		GUI
Penalty functions. Can be applied to all refineable parameters	+	
Bondlength restraints (Anti-Bump, Parabola, lattice energy minimization, user-defined)	+	
Rigid and soft bodies with all parameters refineable	+	
Minimization procedures		
Marquardt		GUI
Line minimisation		GUI
Extrapolation		GUI
Sparse matrix method		GUI
Miscallenous		
Simulated annealing	+	
Support of user-defined fit models		
Batch mode fitting capability		

[1] Single crystal data are not available in GUI

File types and formats

Table 1-2: File types used in TOPAS.

File Type	Comments
TOPAS files	
*.PRO	TOPAS documents (project files)
*.INP	TOPAS input file (see the Technical Reference manual)
*.OUT	TOPAS output file. Same format as *.INP.
*.STR	TOPAS structure data. Same format as *.INP.
*.PAR	TOPAS instrument parameters. Same format as *.INP.
*.LAM	TOPAS source emission profile data. Same format as *.INP.
*.DEF	TOPAS program defaults. Same format as *.INP.
*.LOG	TOPAS log file. Can be used for tracking input errors.
Measurement Data	
*.RAW	Bruker AXS binaries (DIFFRAC AT and DIFFRAC^{plus})
*.DAT	Several ASCII file formats including LHPM/RIET7/CSRIET, GSAS ("std - const", "alt - ralf") and FullProf. The file formats are described in Table 1-3.
*.XDD / *.CAL	ASCII file format. The file format is described in Table 1-3.
*.XY, *XYE	ASCII file formats. Can be used for non-equidistant x-axis steps. The file formats are described in Table 1-3.
Peak Profile Parameter Data	
*.DIF	Bruker DIF binaries. Can be used to import d-I data from the PDF (ICDD).
*.UXD	Bruker ASCII file format. Can be used to import d-I data from the PDF (ICDD).

Structure and structure factor data

*.CIF	Crystallographic Information File of the International Union for Crystallography (IUCr).
*.HKL	ShelX HKL4 format.
*.FCF	CIF file representation of structure factor details suitable for generating Fourier maps using ShelX.
*.SCR	ASCII file format. Consists of lines comprising h, k, l, m, d, 2θ, and Fo.

Some ASCII file formats as described in Table 1-3 can be used to import measurement data. "White Spaces" (= LF, Tab, Space, ...) are used as data separators. The files can contain comments in any part of the file of the following form:

/* Block and nested block comments are allowed. */

‘ text from this character to the end of the line is a comment.

TOPAS provides a powerful graphical user interface for working in both GUI and Launch Mode. Refinements in GUI Mode require input to a "*Parameters Window*", refinements in Launch Mode are controlled by an INP format file. Consequently, several windows and dialogs used in GUI mode will be not available or have no effect in Launch Mode.

The TOPAS screen (Fig. 2-1) consists of the following elements:

- **Menubar**
  Contains the names of submenus, which provide lists of all commands available together with their shortcuts respectively toolbar icons, if existing.
- **Toolbar**
  Displays the most important commands in form of icons for fast access.
- **Working Area**
  Contains all elements needed for profile fitting such as observed and calculated data, fit parameters, and fit results, which are displayed in separated views.
- **Status Bar**
  Displays some context sensitive help information and the x- and y-coordinates of the data cursor in the active *Scan Window*, which is described in section 2.2.

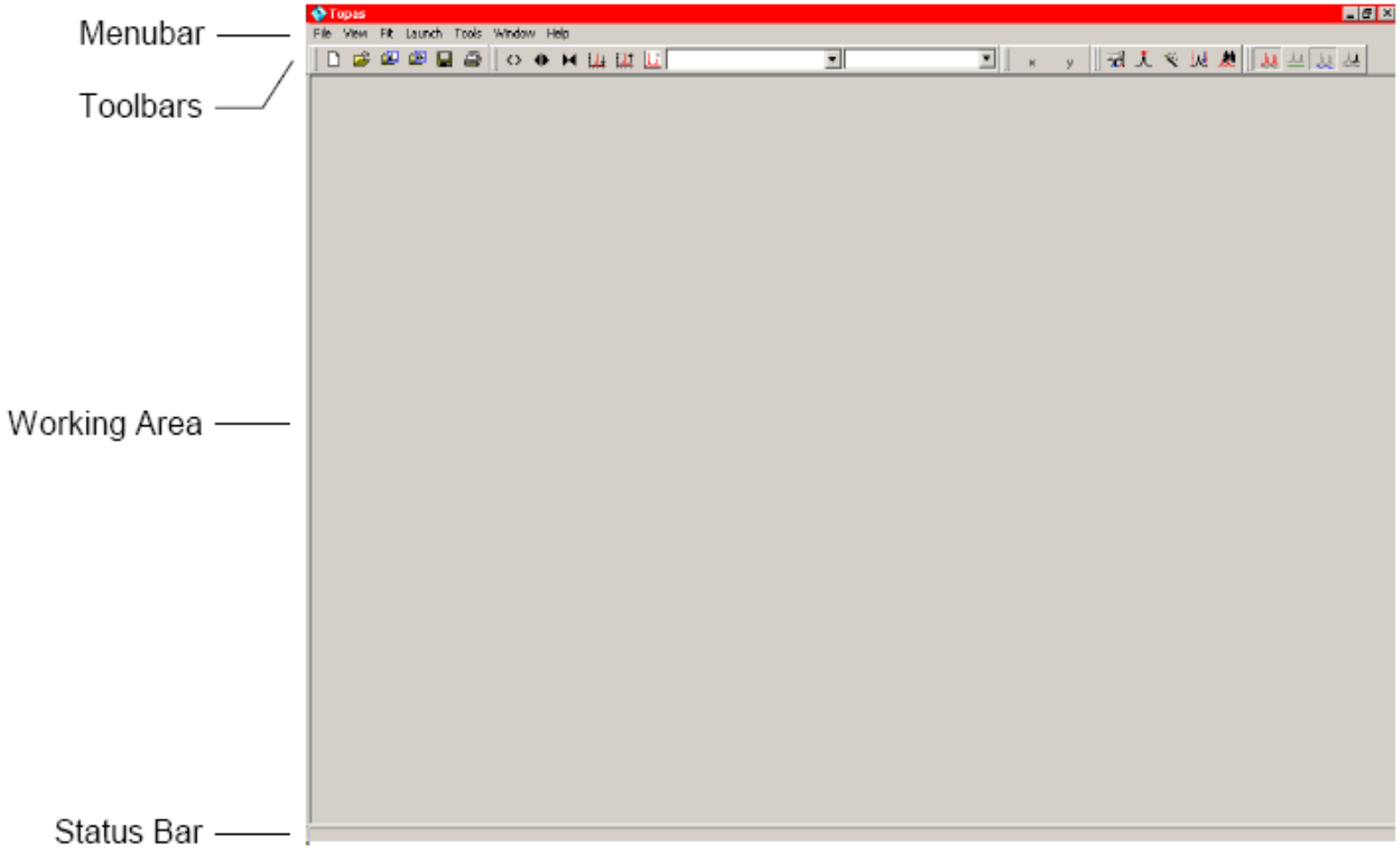
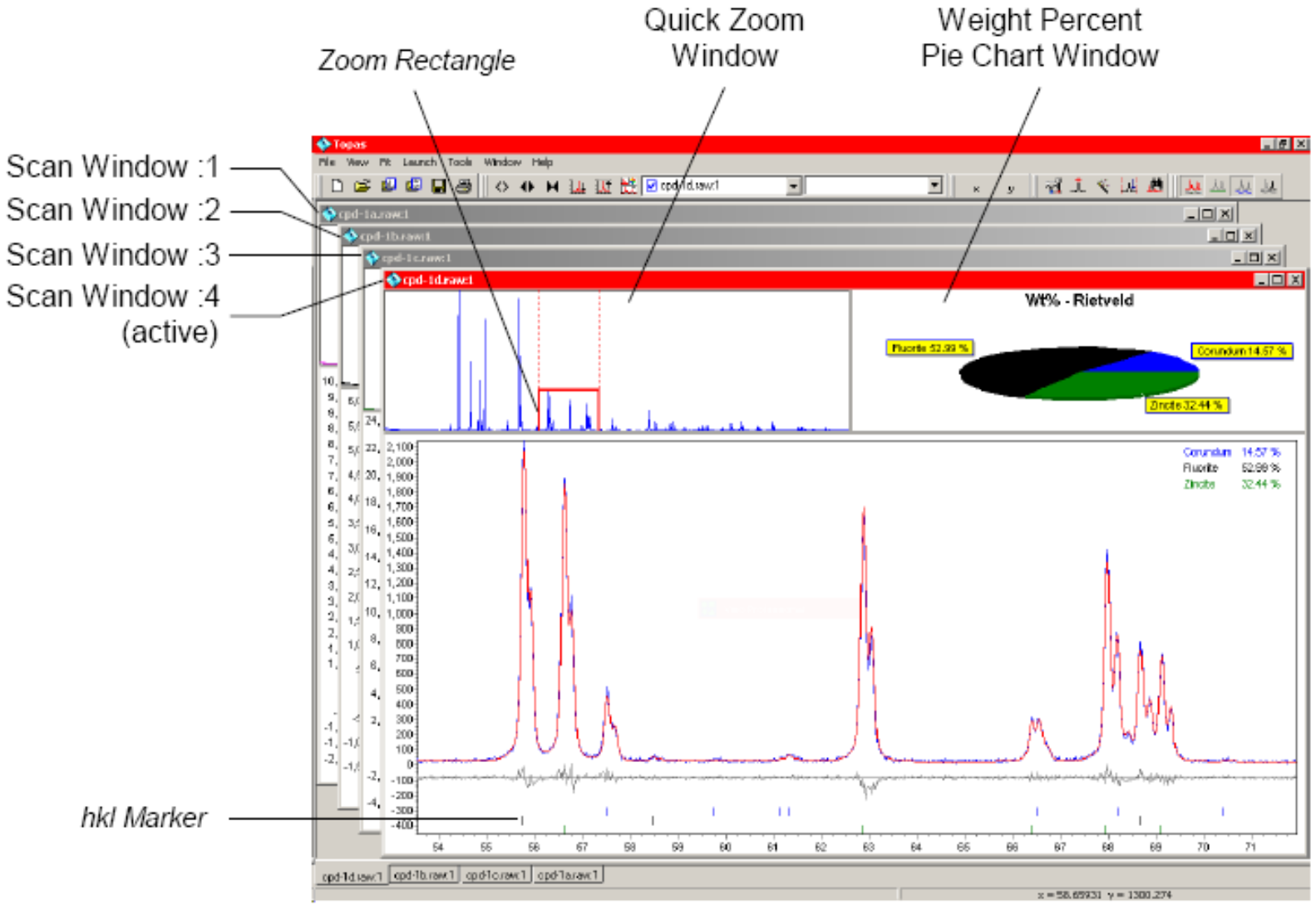


Fig. 2-1: TOPAS screen.

The *Working Area* serves as a container for several views, which are directly related to the profile fitting process. There are two main windows:

- **Scan Window**
  The *Scan Window* (Fig. 2-2) is the actual field of operation, and is available in both the GUI and the Launch Mode. It offers numerous graphical features for all kind of data evaluation by means of profile fitting. The following views are related to the *Scan Window*:
  - ***Quick Zoom Window***
  - ***Weight Percent Pie Chart Window***
  - ***Chart Options Dialog***
  - ***Peak Search Dialog*** (GUI mode only, not available in TOPAS R)
  - ***Peak Details Dialog*** (GUI mode only, not available in TOPAS R)
  - ***Options Dialog*** (most options available in GUI mode only)
  - ***Fit Window*** with its ***Refinement Options Dialog***

  The *Scan Window* is described in section 2.2.
- **Parameters Window**
  The *Parameters Window* represents all refinement parameters available in GUI Mode by a hierarchically organized tree view (Fig. 2-3). It can be docked at the left, right, top or bottom of the *Working Area*. For more details see section 2.3.


Zoom Rectangle
Quick Zoom Window
Weight Percent Pie Chart Window
Scan Window :1
Scan Window :2
Scan Window :3
Scan Window :4 (active)
hkl Marker
Wt% - Rietveld
Corundum 14.57 %
Fluorite 52.99 %
Zincite 32.44 %

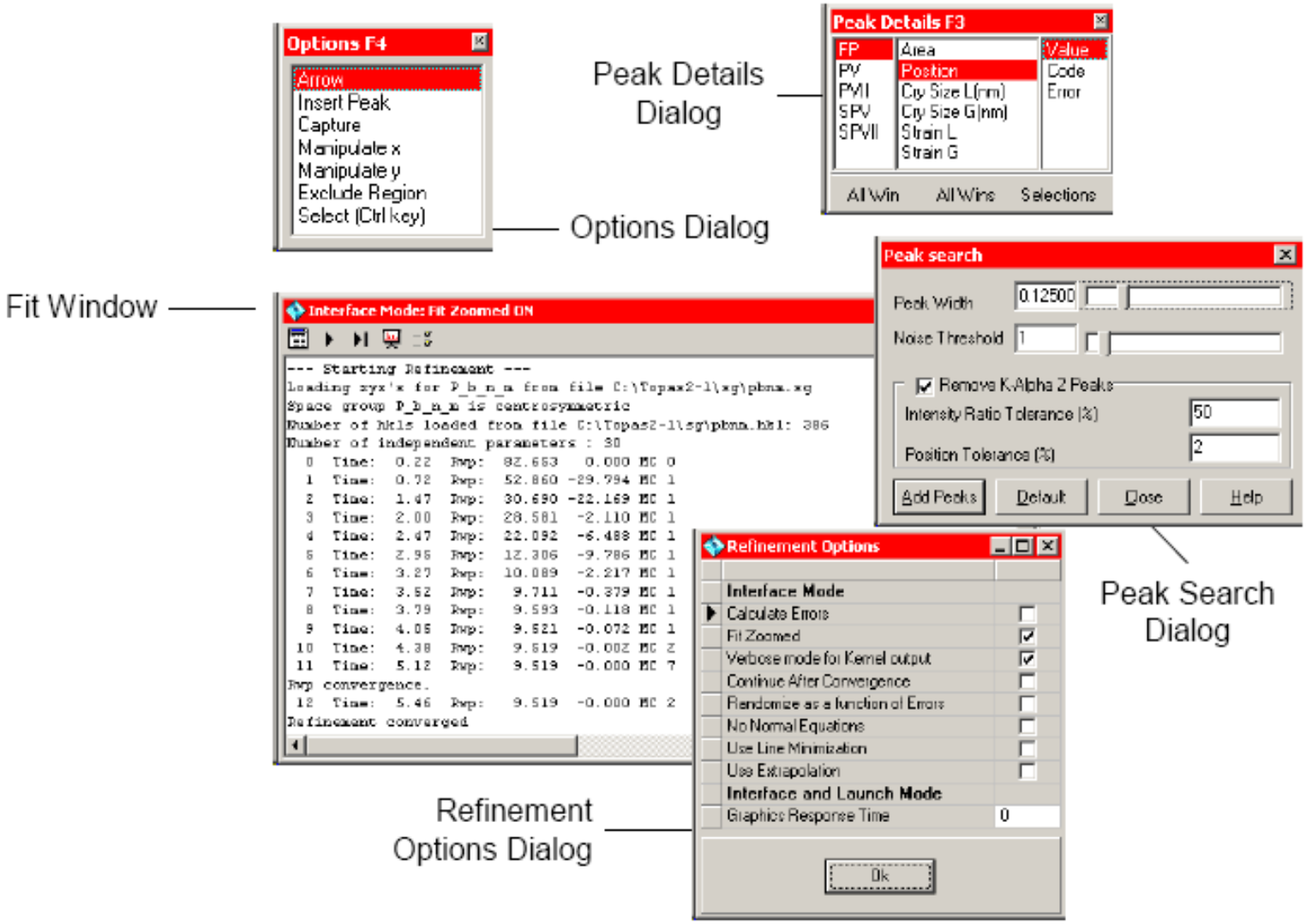


Fig. 2-2: *Scan Windows* with related views.

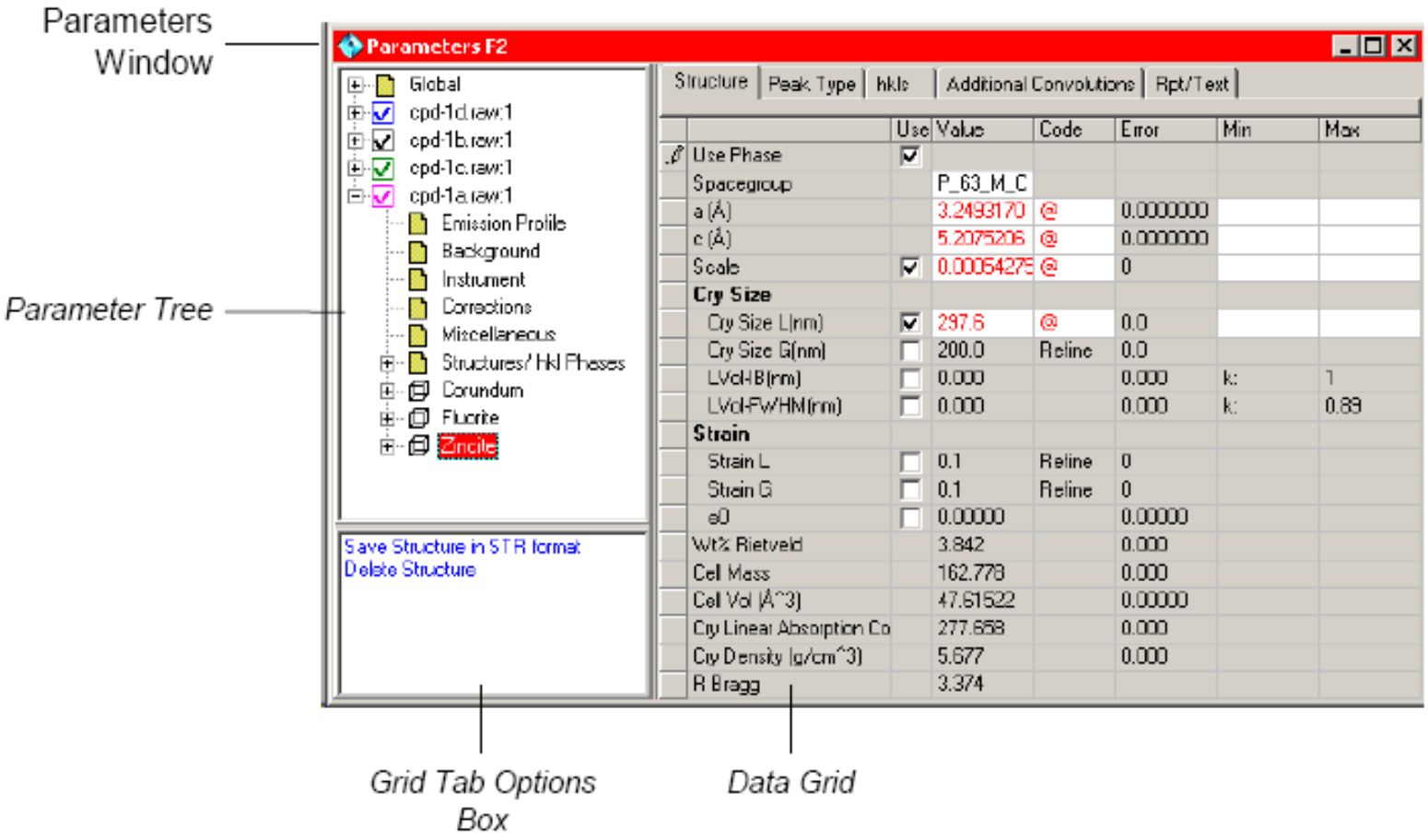
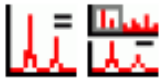


Fig. 2-3: *Parameters Window*.

The following menu commands and toolbar icons can be used to display or hide the various windows and dialogs:

Menu:	Icon:	Shortcut:	Result:
View - Quick Zoom			Displays / hides *Quick Zoom Window*
View - Pie Chart	n.a.		Displays / hides Pie Chart Windows
View - Parameters Window		F2	Displays / hides the *Parameters Window*
View - Peak Details Window		F3	Displays / hides the *Peak Details Dialog*
View - Options Window		F4	Displays / hides the *Options Dialog*
Fit - Fit Window		F5	Displays / hides the *Fit Window*
View - Search Peaks...			Displays / hides the *Peak Search Dialog*

The Scan Window

The following features concern the data displayed in the *Scan Window*:

- Axes scales comprise x (= 2θ), d, and 1/d for the x-axis and y (= linear), Sqrt(y) (= square root) and Ln(y) (= logarithmic) for the y-axis.
- Display of observed, calculated, difference, and background data
- Display of calculated intensities for individual single peaks or phases
- Animated display of the profile fitting process

For whole powder pattern decomposition (Pawley and LeBail method) and Rietveld refinement the following additional items are displayed:

- hkl markers at the bottom
- the phase name plus relative phase amounts in the upper right part of the window

Available menu commands and toolbar icons are:

Menu:	Icon:	Result:
View - X-Axis Scale -		Sets the x-axis scale to
Linear	x	x
d-spacing	d	d
1/d-spacing	1/d	1/d
View - Y-Axis Scale -		Sets the y-axis scale to
Linear	y	y
Sqrt(y)	Sqrt(y)	Sqrt(y)
Ln(y)	Ln(y)	Ln(y)
View - Curves - Calculated		Displays / hides calculated curves
View - Curves - Background		Displays / hides background curves
View - Curves - Difference		Displays / hides difference curves
View - Curves - Single Peaks		Displays / hides single peaks
View - Show hkl Ticks	n.a.	Displays / hides hkl ticks, phase names and amounts
n.a.		View previous / next *Scan Window* using LMB / RMB

Menu:	Icon:	Result:
View -		
Dont fix Y1		Does not fix Y1
Fix Y1 to zero		Fixes Y1 to zero
Fix Y1 to min value		Fixes Y1 to the minimum count value
View -		
Dont fix Y2		Does not fix Y2
Fix Y2 to max value		Fixes Y2 to the maximum count value
n.a.		Compresses the x-axis left / right using LMB / RMB
n.a.		Scrolls the x-axis left / right using LMB / RMB
View - Horizontal Scroll Bar	n.a.	Displays / hides the horizontal scroll bar
View - Unzoom	n.a.	Resets to the full X and Y scale

Clicking the RMB anywhere in the Scan Window will open a short cut menu offering fast access to the following features:

- **Set X1 / X2 / Y1 / Y2 to Mouse Position**
  Sets the x- and y-axis limits to the actual mouse position. Note: Fixed Y1 or Y2 axis limits will be automatically unfixed to allow setting of Y1 and Y2.
- **Reset Axies to Previous**
  Resets to the previously zoomed region
- **Unzoom**
  Resets axies to the full X and Y scale
- **Edit / Print / Chart Options**
  Opens the Chart Options Dialog (section 2.2.3.3) for defining various chart properties such as labels, ticks and fonts, which can be saved as default. Charts can be printed directly or copied to the clipboard.
- **Delete Selection**
  Deletes selected peaks and excluded regions
- **Delete Nearest Peak F9**
  Deletes the peak nearest to the actual mouse position

Note: As it is not possible in Launch Mode to graphically insert peak and excluded regions, the *Delete Selection* and *Delete Nearest Peak F9* will have no effect in Launch Mode (see also section 2.2.2).

The following features are available in GUI Mode only, as in Launch Mode the refinement is completely controlled by the input file:

- Graphical peak treatment such as manual peak insertion, automatic peak search, and the editing of peak properties
- Display of peak markers and profile parameters for single peaks
- Highlighting the intensity distribution of a peak with a bold line as the mouse is moved over its peak marker
- Graphical insertion of excluded regions
- Selection of peaks and excluded regions with the mouse (pressing the CTRL key allows multi-selection)
- Deletion of the selection with the DEL key

With respect to the fitting process it is important to understand the following features of the *Scan Window* in GUI Mode:

- In general all datasets in visible *Scan Windows* are fitted simultaneously.
- If several datasets are loaded in several *Scan Windows*, the data of minimized as well as closed windows will not be fitted.
- If several datasets are loaded in several *Scan Windows*, and one of these windows is maximized, then only the data within the maximized window are fitted.
- If the menu switch *Fit - Fit Zoomed* is selected only the data points displayed in the *Scan Window* are used for fitting. All data outside the zoomed area are ignored!

2.2.3 Views related to the Scan Window

2.2.3.1 Quick Zoom Window

Always displays the complete scan, which is particularly useful if the *Scan Window* only displays a zoomed area. Inside of the *Quick Zoom Window* a zoom rectangle represents the actually displayed data range within the active *Scan Window*. It allows a modification of the zoomed area by grabbing one of the red lines with the mouse and moving it. A double click on the Quick Zoom Window resets the Scan Window to full scale.

2.2.3.2 Weight Percent Pie Chart Window

Displays a weight percent pie chart providing quantitative analysis results.

Chart Options Dialog

This Dialog (Fig. 2-4) is linked to the short cut menu of the *Scan Window* (RMB) and provides two pages allowing to copy and print the chart as well as to define properties of the chart title and axes. Settings can be saved in STARTUP.DEF (see section 4.1) with the exception of the x- and y-axis limits, which cannot be kept as defaults. Note: Definition of Y1 or Y2 axis limits requires them to be unfixed.

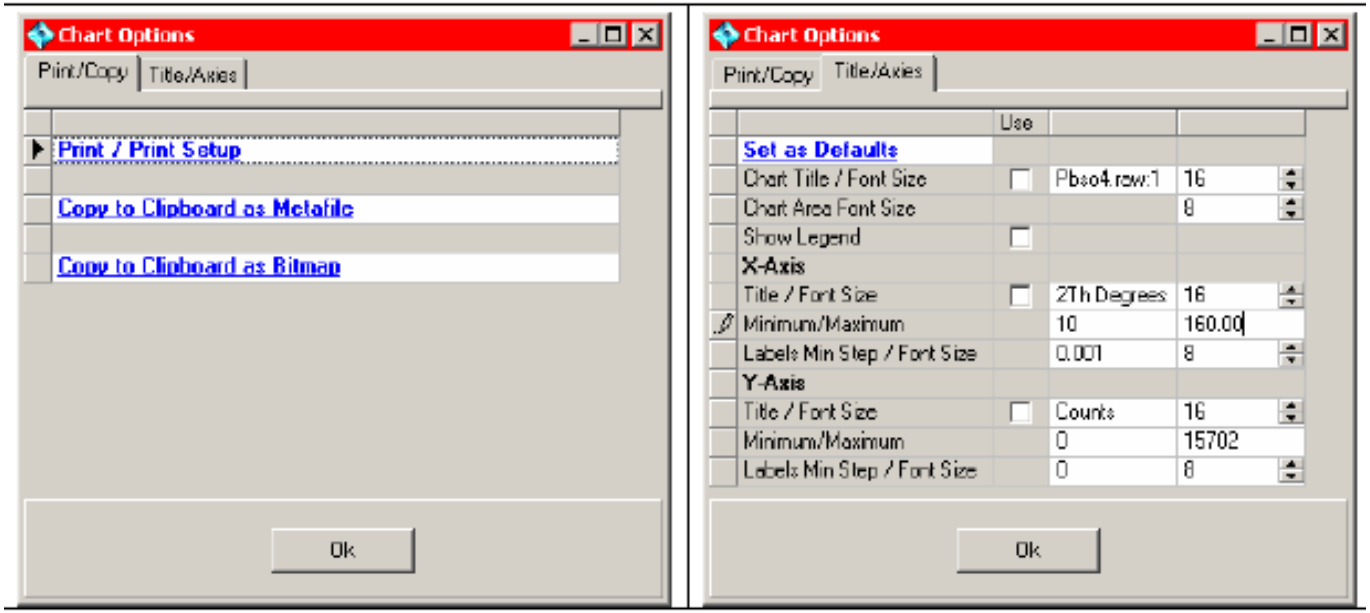


Fig. 2-4: *Chart Options Dialog*

Peak Search Dialog

Note: GUI mode only, not available in TOPAS R

Offers an automatic peak search according to Savitzky & Golay, 1964 (Fig. 2-5). $K\alpha_2$ peaks can be removed automatically.

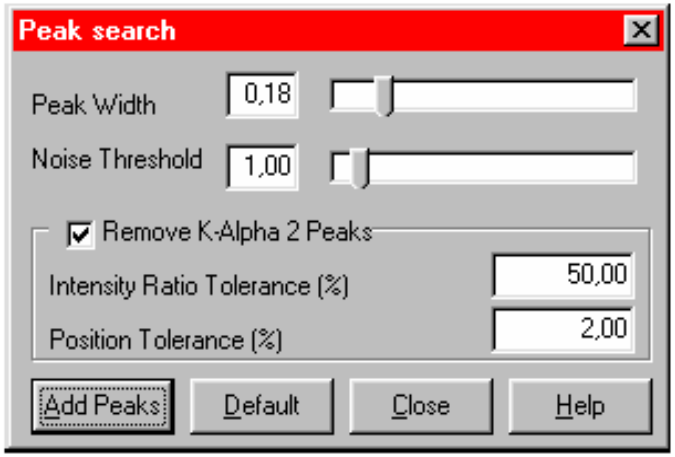


Fig. 2-5: *Peak Search Dialog*

Peak Details Dialog

Note: The *Peak Details Dialog* is available in GUI mode only.

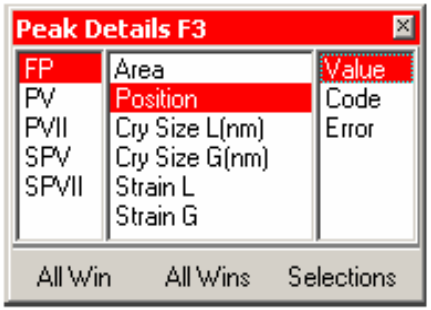


Fig. 2-6: *Peak Details Dialog*

- **All Win**
  Overwrites the values of all peaks in the active *Scan Window* with the value in the edit field.

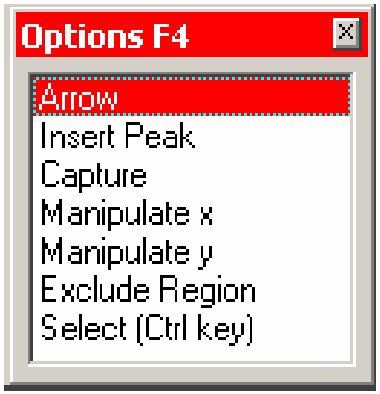
  Note: A change of the peak position moves all peaks to the same position!
- **All Wins**
  Same as All Win, but changes will be applied to all peaks in all *Scan Windows*.
- **Selections**
  Changes are applied to all selected peaks in the active *Scan Window*.

Options Dialog

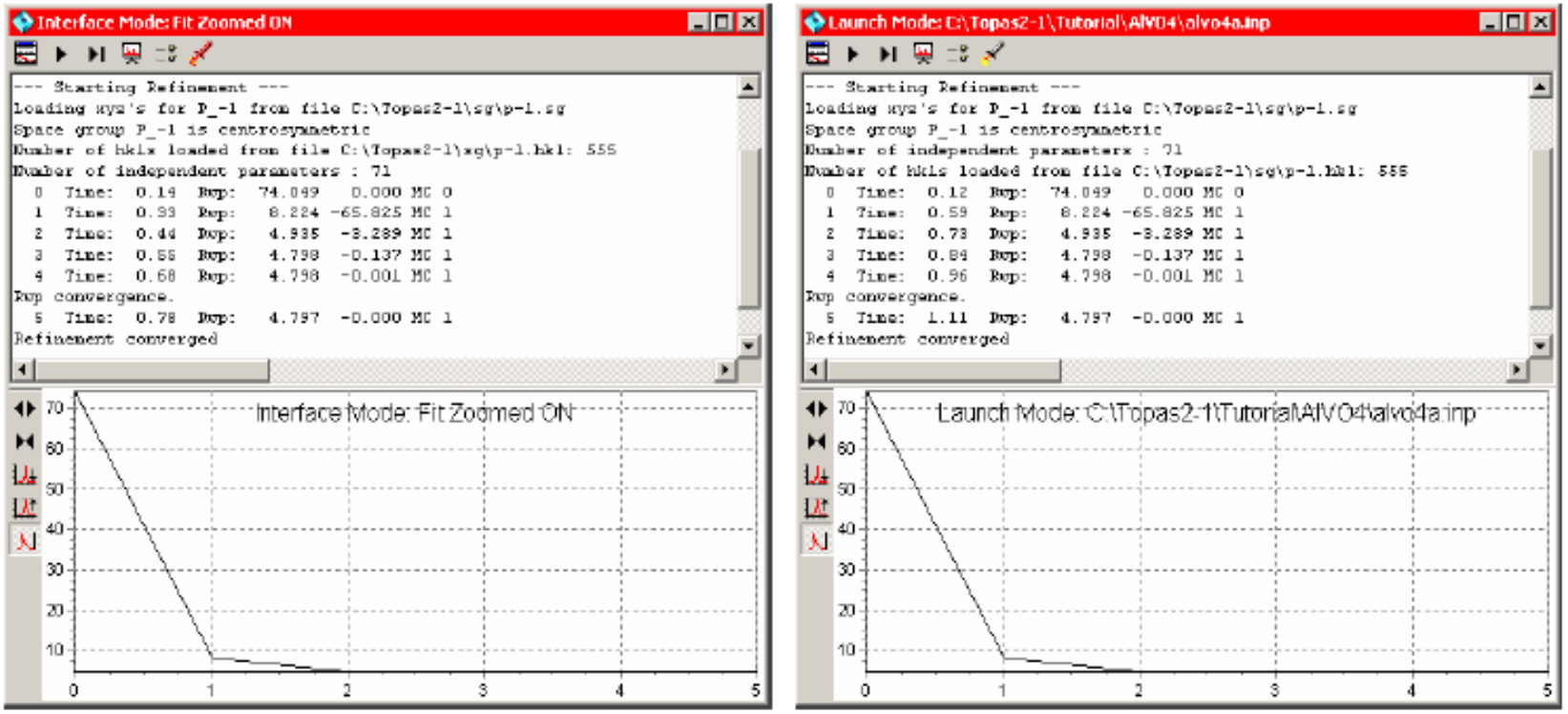
- **Arrow**
  Normal mouse operation for zooming and panning.
- **Insert Peak**
  Shows the *Peak Details Dialog* and switches the mouse to peak insertion mode.
- **Capture**
  Any observed or calculated data including difference plots in a *Scan Window* can be captured by the mouse. After clicking on the diagram line a new *Scan Window* is opened which contains the captured data. This feature allows for the export of any calculated data in a separate data file.
- **Manipulate X**
  Allows the movement of a selected scan in the positive or negative x-direction. This feature is useful for comparing different data sets or for visualisation of 2θ errors.

  Note: The data set in memory which constitute loaded data is directly manipulated; the original data file remains unchanged. Subsequent calculations are performed on the modified data.
- **Manipulate Y**
  Similar to Manipulate X but in the y-direction.

  Note: The data set in memory which constitute loaded data is directly manipulated; the original data file remains unchanged. Subsequent calculations are performed on the modified data.
- **Exclude Region**
  Allows the exclusion of selected data ranges from calculations. Excluded regions are defined with the mouse by clicking and dragging. An unlimited number of excluded regions are allowed including the case of overlap.
- **Select**
  Allows the selection of peaks and excluded regions in the *Scan Window*.



Fit Window



a) b)

Fig. 2-8: *Fit Window* in a) GUI Mode and b) Launch Mode.

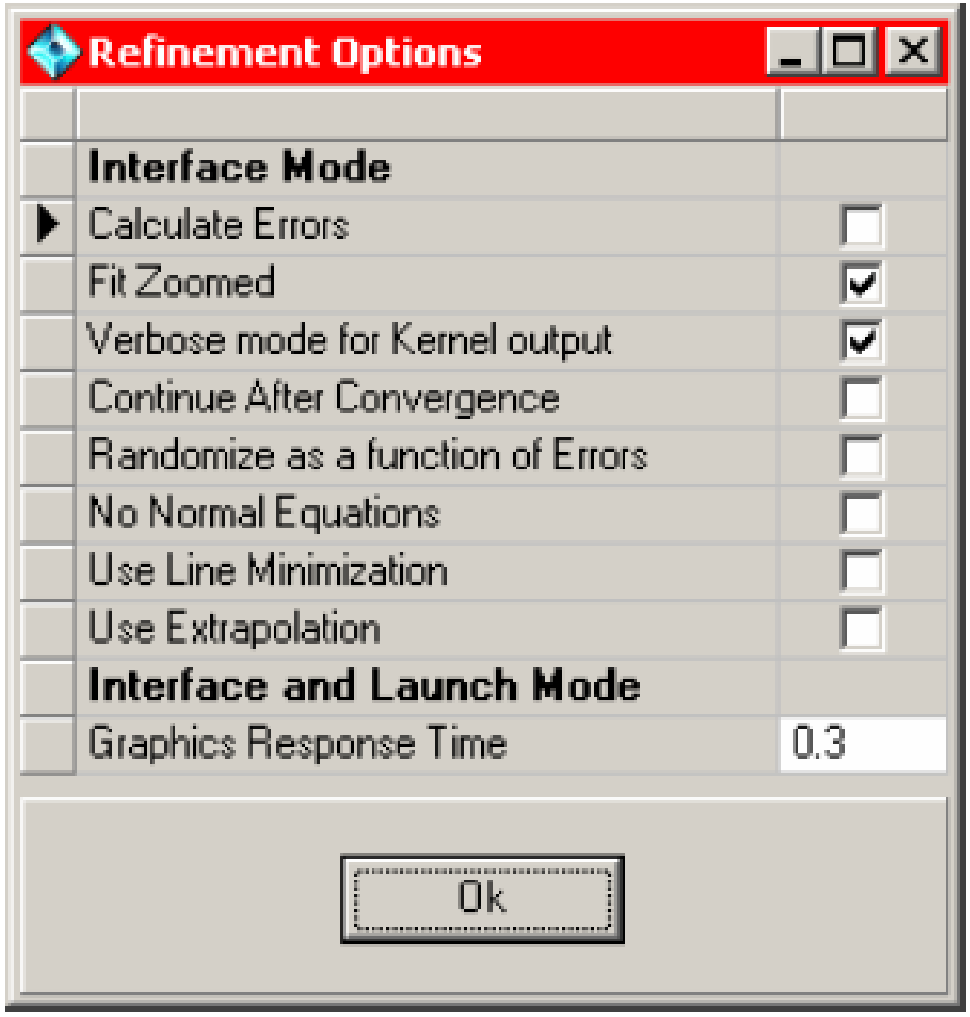
Icon:	Shortcut:	Result:
	n.a.	Displays or hides the text and / or the R_{WP} plot
	F6	Starts the refinement
	F7	Performs one refinement iteration
	F8	Stops the refinement and asks for saving the results
	Shift + F8	Cancels the refinement without saving results
	n.a.	Cancels the current refinement cycle.
	n.a.	Animation of the graphics in the *Scan Window* on/off
	n.a.	Shows the *Refinement Options Dialog*

An additional toolbar icon available in Launch Mode only is:

Icon:	Shortcut:	Result:
	n.a.	Switches between GUI Mode and Launch Mode

The *Refinement Options Dialog* (Fig. 2-9) offers several options to control the refinement mainly in GUI mode.

Note: All options provided in the "Interface Mode" section of the *Refinement Options Dialog* will have no effect in Launch Mode, as the refinement will be completely controlled by the input file.


Refinement Options
Interface Mode
Calculate Errors
Fit Zoomed
Verbose mode for Kernel output
Continue After Convergence
Randomize as a function of Errors
No Normal Equations
Use Line Minimization
Use Extrapolation
Interface and Launch Mode
Graphics Response Time
0.3
Ok

Interface Mode

- **Calculate Errors**
  Calculates errors, if checked
- **Fit Zoomed**
  If checked, only the zoomed region will be fitted
- **Verbose mode for Kernel output**
  Toggles kernel output in the text field between verbose and brief
- **Continue After Convergence**
  Refinement is continued after convergence
- **Randomize as a function of Errors**
  Useful if Continue After Convergence is used. Performs a random parameter change based on its error and then continues the refinement.
- **No Normal Equations**
  Prevents the use of normal equations in the minimization routine; useful if only effects of line minimization are sought
- **Use Line Minimization**
  Invokes the use of line minimization. Faster convergence and often to a lower minima is observed if the refinement is far from the global minimum.
- **Use Extrapolation**
  Often increases the convergence rate if used with Line Minimization

Interface and Launch Mode

- **Graphics Response Time**
  Defines the update frequency of the *Scan Window* and the R_{wp} plot window. Reducing the update frequency will leave more CPU time for numerical calculations.

The Parameters Window

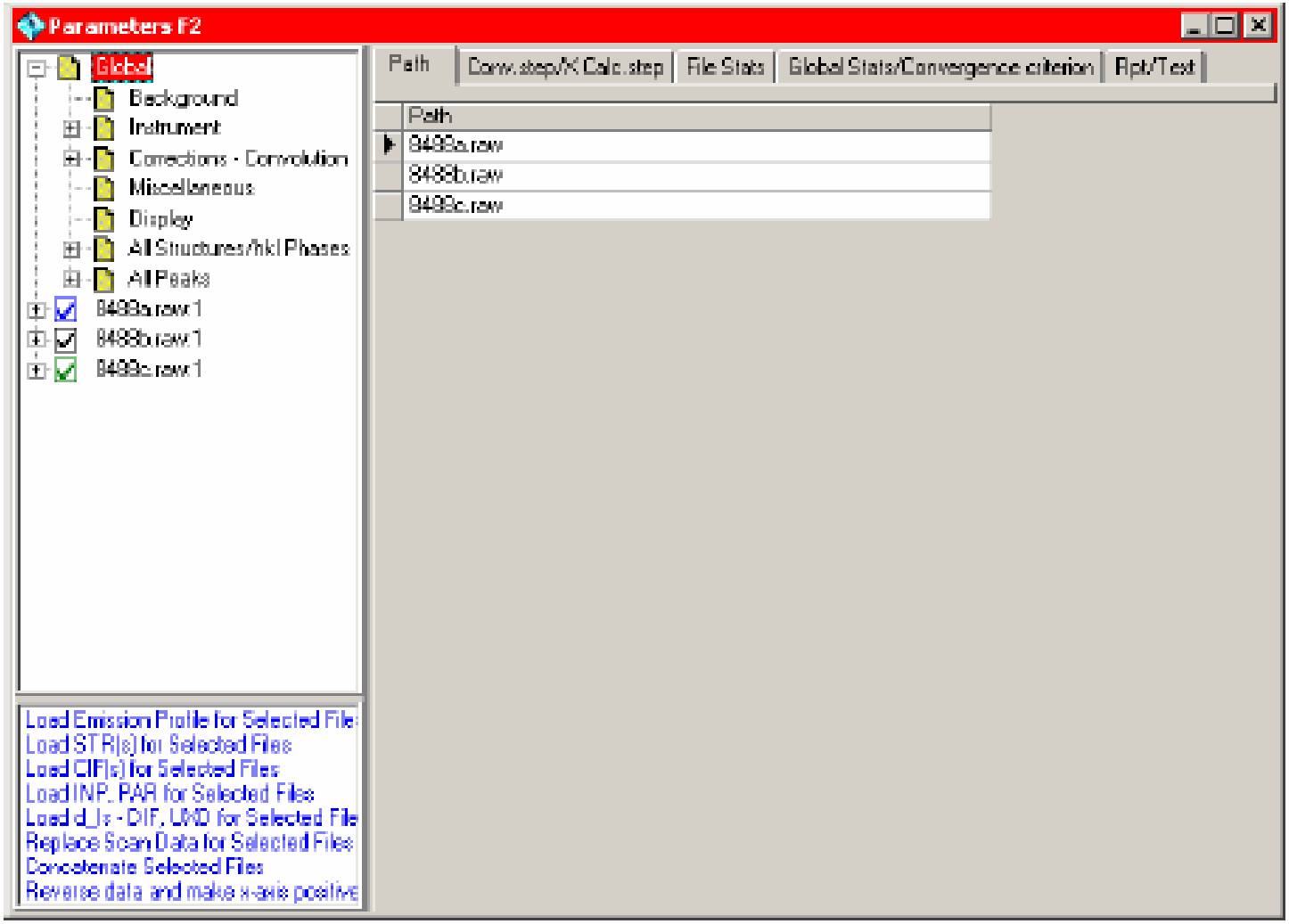
- **Global item**
- **Range item(s)**
- **Peak Phase**
- **hkl Phase**
- **Structure**
- **Structures / hkl Phases**

Global item

- *Background* (section 2.3.2.4)
- *Instrument* (section 2.3.2.5)
- *Corrections* (section 2.3.2.6)
- *Miscellaneous* (section 2.3.2.7)
- *Display*

Additionally the following items may be displayed as well:

- *All Peaks* (section 2.3.2.8)
- *All Structures / hkl Phases* (section 2.3.2.11)


Parameters F2
Global
Background
Instrument
Corrections - Convolution
Miscellaneous
Display
All Structures/hkl Phases
All Peaks
8488a.raw:1
8488b.raw:1
8488c.raw:1
Path
Conv.step/K Calc.step
File Stats
Global Stats/Convergence criterion
Rpt/Test
Path
8488a.raw
8488b.raw
8488c.raw
Load Emission Profile for Selected File
Load STR[s] for Selected Files
Load CIF[s] for Selected Files
Load INP, PAR for Selected Files
Load d_[s - DIF, UNO for Selected File
Replace Scan Data for Selected Files
Concatenate Selected Files
Reverse data and make x-axis positive

- **Load Emission Profile for Selected Files**
  Loads a source emission profile from a LAM file for all selected files
- **Load STR(s) for Selected Files**
  Loads structure information from STR file(s) for all selected files
- **Load CIF(s) for Selected Files**
  Loads structure information from CIF file(s) for all selected files
- **Load INP, PAR for Selected Files**
  Loads information from INP and PAR file(s) for all selected files; while PAR files are intended for instrument parameters only, with INP files any keywords and macros supported by the GUI can be loaded
- **Load d_Is – DIF, UXD for Selected Files**
  Loads peak information from DIF or UXD files for all selected files, providing a link to the ICDD PDF via DIFFRAC^{plus} EVA and SEARCH
- **Replace Scan Data for Selected Files**
  Allows to exchange scan data for selected files to be refined using the same refinement model
- **Concatenate Selected Files**
  Concatenates non-overlapping scan data files; excluded regions will be automatically created to tide over regions without data

Range item(s)

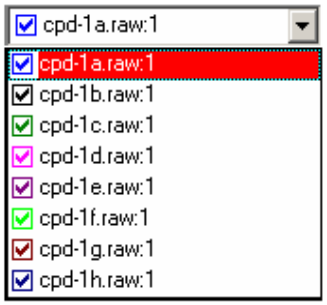


Fig. 2-11: *Range Combo Box* with eight ranges loaded.

Single clicking (LMB) a checkbox in the *Range Combo Box* enables or disables the associated range, a double click enables the associated range and disables all other ranges.

Range dependent second level items of the *Range* item are:

- *Emission Profile* (section 2.3.2.3)
- *Background* (section 2.3.2.4)
- *Instrument* (section 2.3.2.5)
- *Corrections* (section 2.3.2.6)
- *Miscellaneous* (section 2.3.2.7)

Additionally the following items may be displayed as well:

- *Peak Phase* (section 2.3.2.8)
- *hkl Phase* (section 2.3.2.9)
- *Structure* (section 2.3.2.10)
- *Structures / hkl Phases* (section 2.3.2.11)

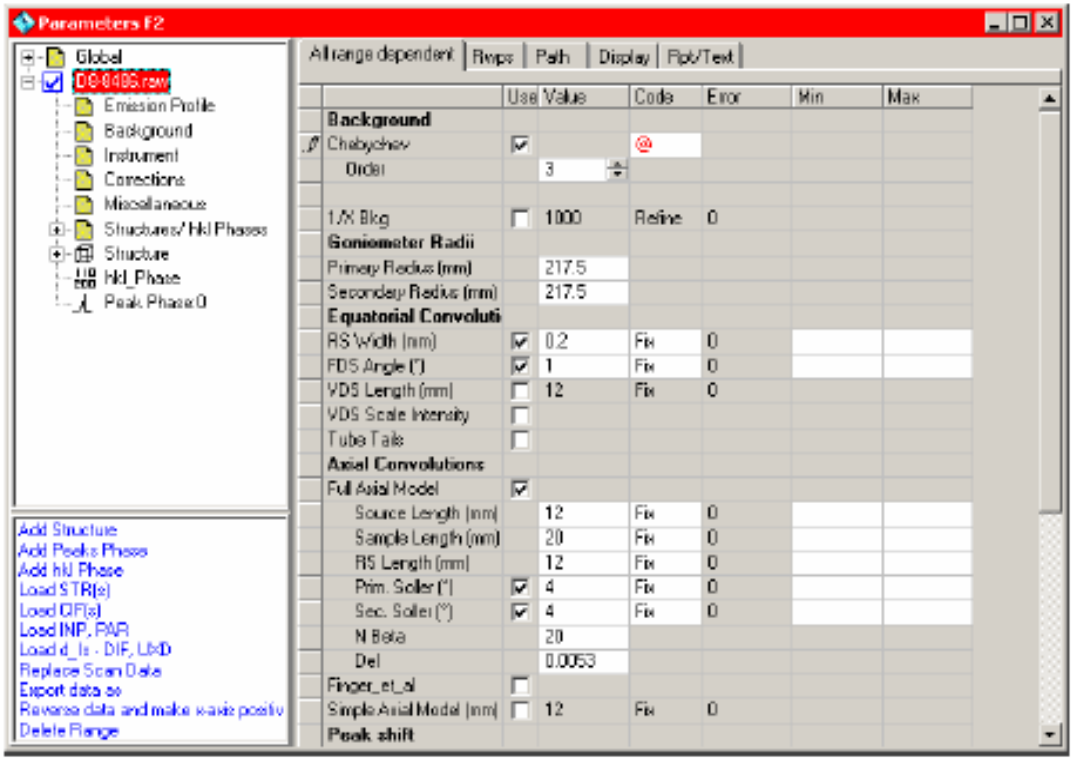


Fig. 2-12: *Range* item with its associated data grid showing the *All Range Dependent* page. All range dependent parameter values and codes can be viewed and manipulated in this data grid as well as in the respective second level items.

- **Add Structure**
  Adds an empty structure; default values are predefined in the file STR.DEF, see section 4.1
- **Add Peaks Phase**
  Adds an empty peaks phase; default peak type is fundamental parameters
- **Add hkl Phase**
  Adds an empty hkl phase; default values are predefined in the file HKLI.DEF, see section 4.1
- **Load STR(s)**
  Loads structure information from STR file(s)
- **Load CIF(s)**
  Loads structure information from CIF file(s)
- **Load INP, PAR**
  Loads information from INP and PAR file(s); while PAR files are intended for instrument parameters only, with INP files any keywords and macros supported by the GUI can be loaded
- **Load d_Is – DIF, UXD**
  Loads peak information from DIF or UXD files, providing a link to the ICDD PDF via DIFFRAC*plus* EVA and SEARCH
- **Replace Scan Data**
  Allows to exchange scan data for selected files to be refined using the same refinement model
- **Export Data as**
  Allows to export the scan data as RAW or ASCII files
- **Reverse Data and make X-axis positive**
  Allows the use of data obtained from scans in negative x-axis regions
- **Delete Range**
  Deletes the selected range

Emission profile

The *Options* page contains the following options:

Option:	Remarks:
• Ymin on Ymax	Determines the x-axis extent to which peak tails are calculated (cut off)
• No Th dependence	Defines an emission profile that is 2θ independent. Allows the use of non-X-ray data or fitting to negative 2θ values.
• For LAM cursor	Switches the mouse cursor to a multi-line cursor representing the different emission lines of the current emission profile (Fig. 2-14)
• Lam for Bragg angle	Only for expert users, refer to the Technical Reference manual
• Calculate Lam	Only for expert users, refer to the Technical Reference manual

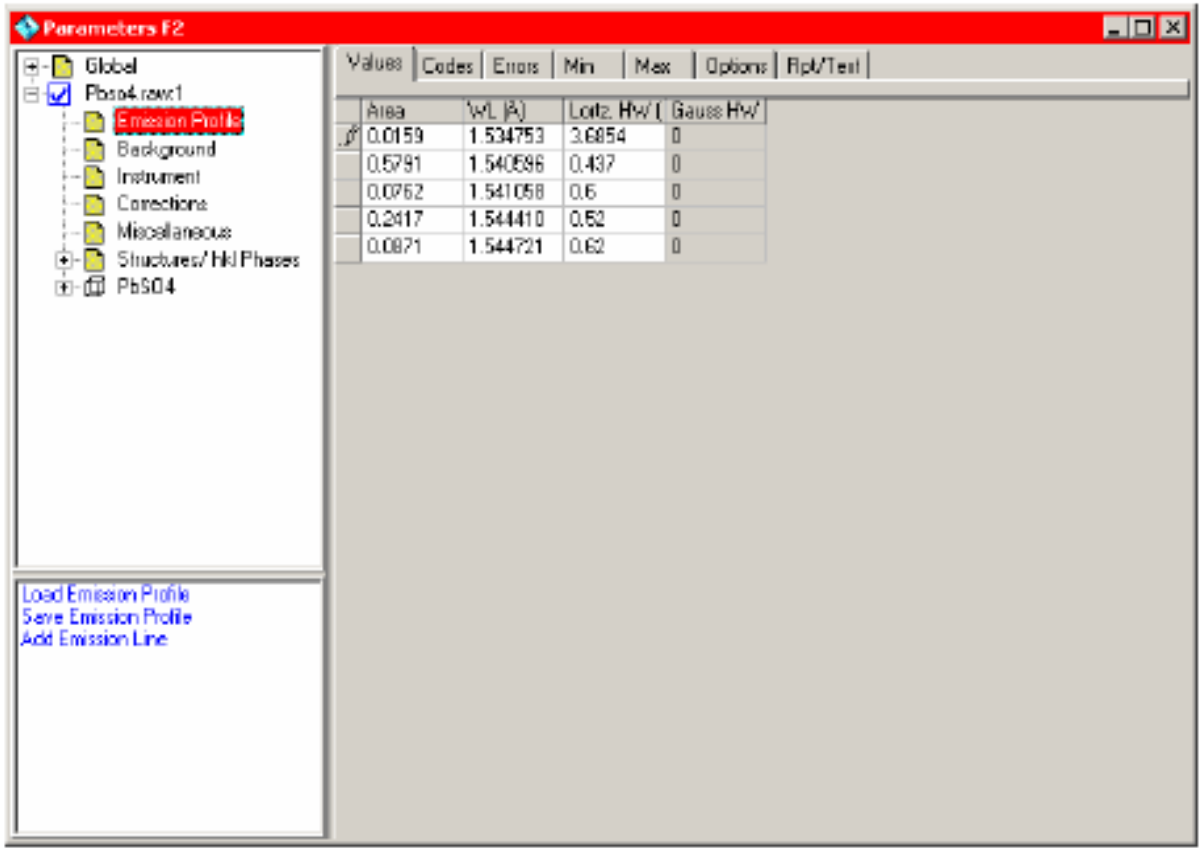


Fig. 2-13: *Emission Profile* item with its associated data grid showing a list of emission lines of the current emission profile (here CuKa5).

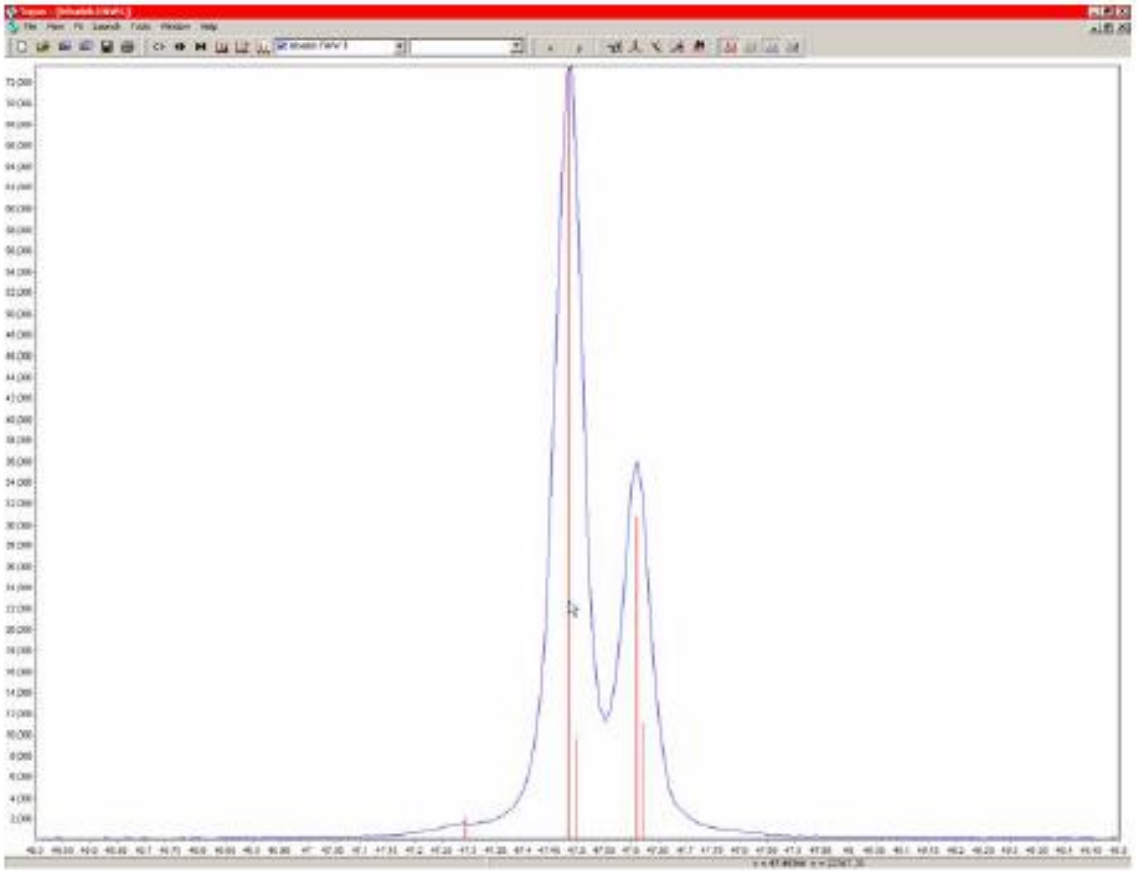


Fig. 2-14: With *For Lam cursor* switched on, a multi-line cursor representing the different emission lines of the current emission profile (here CuKa5) will be shown.

The short cut menu of the *Emission Profile* item offers the following options:

- **Load Emission Profile**
- **Save Emission Profile**
- **Add Emission Line**

Selected emission rows can be deleted using the DEL key.

For laboratory diffractometer systems a selection of predefined emission profiles is available in the LAM directory covering the most common anode target materials, see also section 3.1.

For other target materials as well as for synchrotron and neutron sources it is necessary to define a suitable emission profile. For accurate work it is necessary to refine on the emission profile shape using e.g. the NIST SRM 660a (LaB6) standard.

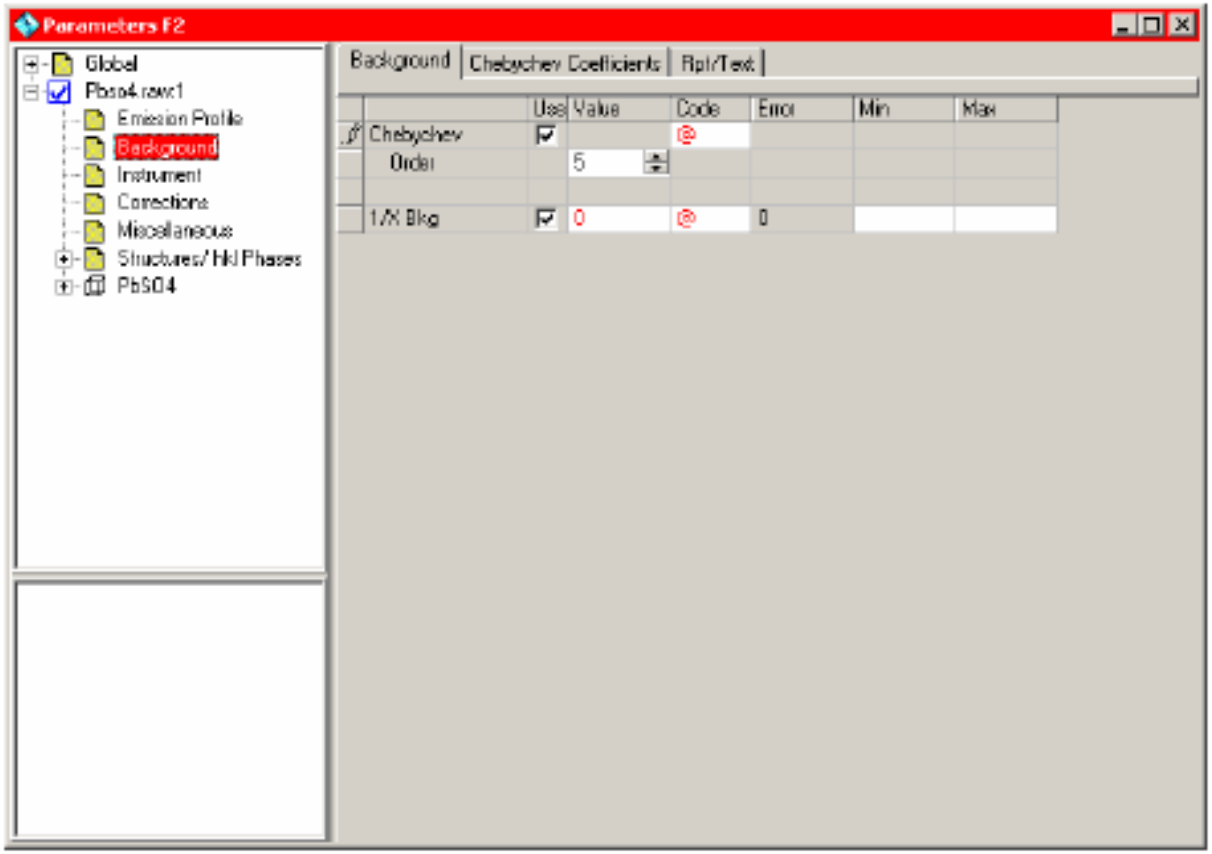


Fig. 2-15: *Background* item with its associated data grid

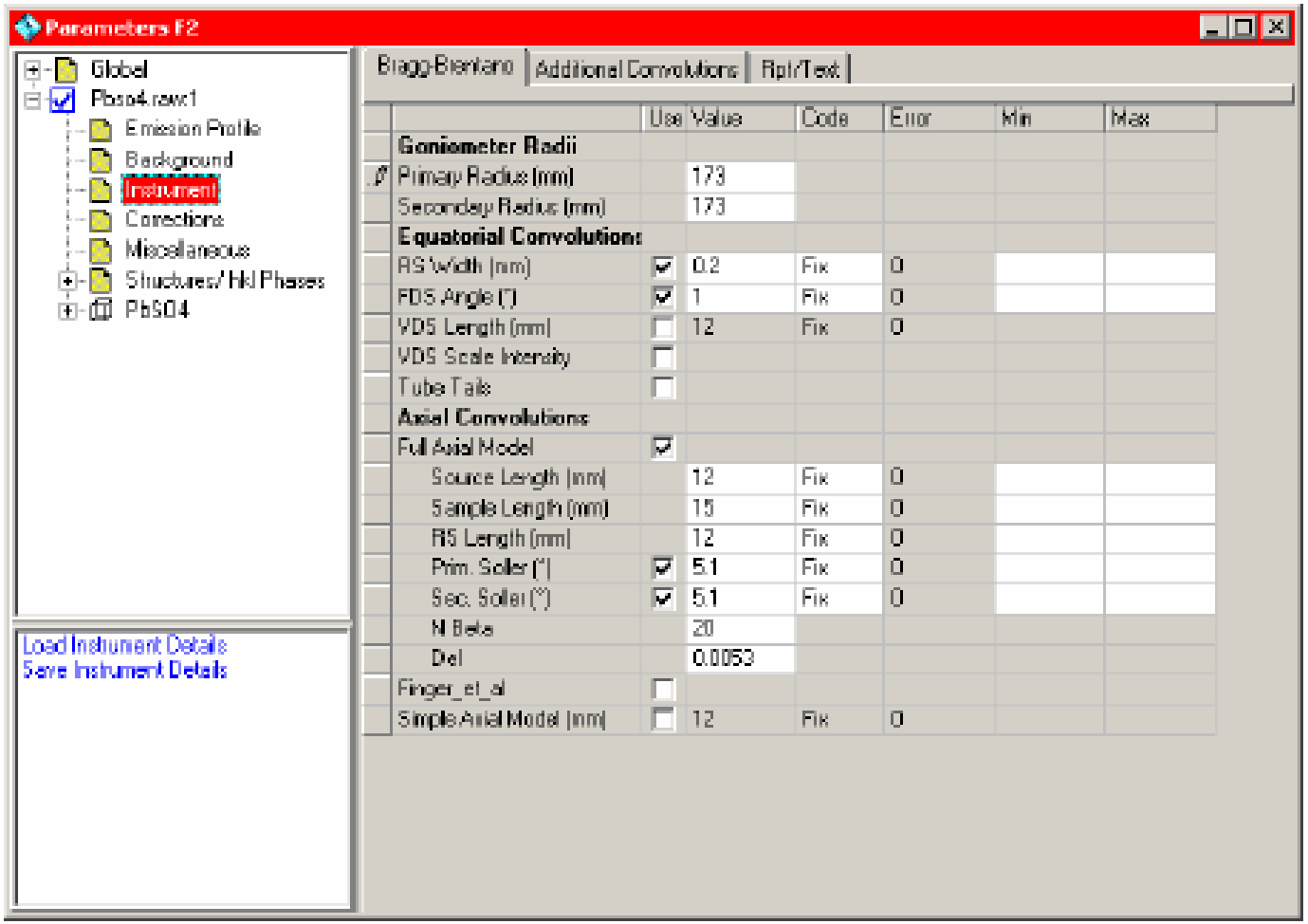


Fig. 2-16: *Instrument* item with its associated data grid showing the *Bragg-Brentano* page. Note: *Tube Tails* and *Full Axial Model* are "Use" dependent expand/collapse grid items.

The Bragg-Brentano page:

Contains all instrument details necessary to model the instrument function using the Fundamental Parameters Approach. This includes the following refinement models:

Parameter name:	Remarks:
Goniometer radii	
• Primary Radius	Primary goniometer circle radius [mm]
• Secondary Radius	Secondary goniometer circle radius [mm]
Equatorial Convolutions	
• RS Width	Receiving Slit (= detector slit) width [mm]
• FDS Angle	Fixed Divergence Slit angle [°]
• VDS Length	Irradiated sample length in beam direction for Variable Divergence Slits [mm]
• VDS Scale Intensity	1/sin(θ) intensity correction for Variable Divergence Slits
• Tube Tails	Tube tails correction (Bergmann, 2000)
• Source Width	Width of the tube filament [mm]
• Z1	Length of the left tail (negative) [mm]
• Z2	Length of the right tail [mm]
• Fraction	Fractional height of the tube tails relative to the main beam

Axial Convolutions

• Full Axial Model	Accurate model for describing peak asymmetry
• Source Length	Length of the tube focus [mm]
• Sample Length	Length of the irradiated sample [mm]
• RS Length	Receiving Slit length [mm]
• Prim. Soller	Primary Soller slit angle [°]
• Sec. Soller	Secondary Soller slit angle [°]
• N Beta	Only for expert users, refer to the Technical Reference manual
• Del	Only for expert users, refer to the Technical Reference manual
• Finger_et_al	Simplified model for describing peak asymmetry
• Simple Axial Model	Simplified model for describing peak asymmetry

Short cut menu options of the *Bragg Brentano* page are:

- **Load Instrument Details**
  Loads instrument details from a PAR file
- **Save Instrument Details**
  Saves instrument details to a PAR file

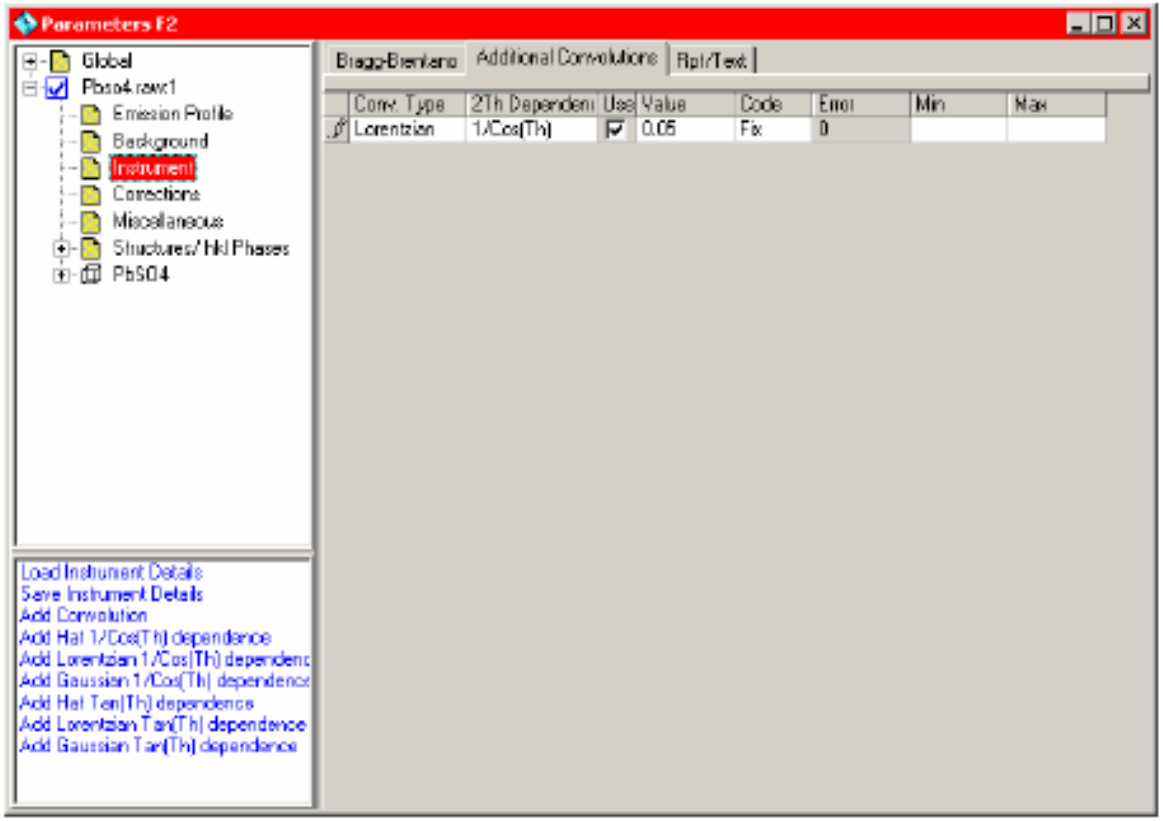


Fig. 2-17: *Instrument* item with its associated data grid showing the *Additional Convolutions* page with one example convolution added.

The Additional Convolutions page:

Provides for empirical modelling of instrument functions. Available convolutions include the Hat, Lorentzian, Gaussian, Circles, Exponential, and One_on_X convolutions to be selected from the *Conv. Type* combo box. Predefined angular dependencies are Constant, 1/Cos(Th), Tan(Th), and Sin(2 Th) to be selected from the *2Th Dependence* combo box; alternatively, user-defined angular dependencies can be provided in the form of equations.

Short cut menu options of the *Additional Convolutions* page are:

- **Load Instrument Details**
  Loads instrument details from a PAR file
- **Save Instrument Details**
  Saves instrument details to a PAR file
- **Add Convolution**
  Adds an additional convolution. Convolution type and angular dependence can be defined using the *Conv. Type* and *2Th Dependence* combo boxes.

Additionally it offers quick access to the following important convolutions:

- **Add Hat 1/cos(Th) dependence**
- **Add Lorentzian 1/cos(Th) dependence**
- **Add Gaussian 1/cos(Th) dependence**
- **Add Hat Tan(Th) dependence**
- **Add Lorentzian Tan(Th) dependence**
- **Add Gaussian Tan(Th) dependence**

Selected additional convolution rows can be deleted using the DEL key.

The *Corrections* item (Fig. 2-18) provides the following correction functions:

Parameter name:	Remarks:
• Zero Error	Zero point error in [° 2θ].
• Sample Disp.	Sample displacement in [mm].
• LP Factor	Lorentz-Polarisation factor using the monochromator angle in [°2θ].
• Absorption	Linear absorption coefficient used for adjusting the peak shape [cm^{-1}].
• Sample Thickness	Sample thickness in [mm] in the direction of the scattering vector
• Scale Intensity	Peak intensity correction for absorption effects
• Sample Tilt	Sample tilt in [mm].

The Lorentz-Polarisation factor for unpolarized radiation is 0 (e.g. X-ray diffractometers without any monochromator) and 90 for fully polarized radiation (e.g. synchrotron radiation). Values for most common monochromators (Cu radiation) are:

- Ge : 27.3
- Graphite : 26.4
- Quartz : 26.6

There is no polarization factor for neutron data and thus the angle for Lorentz Polarization should be set to 90; this gives the Lorentz only part.

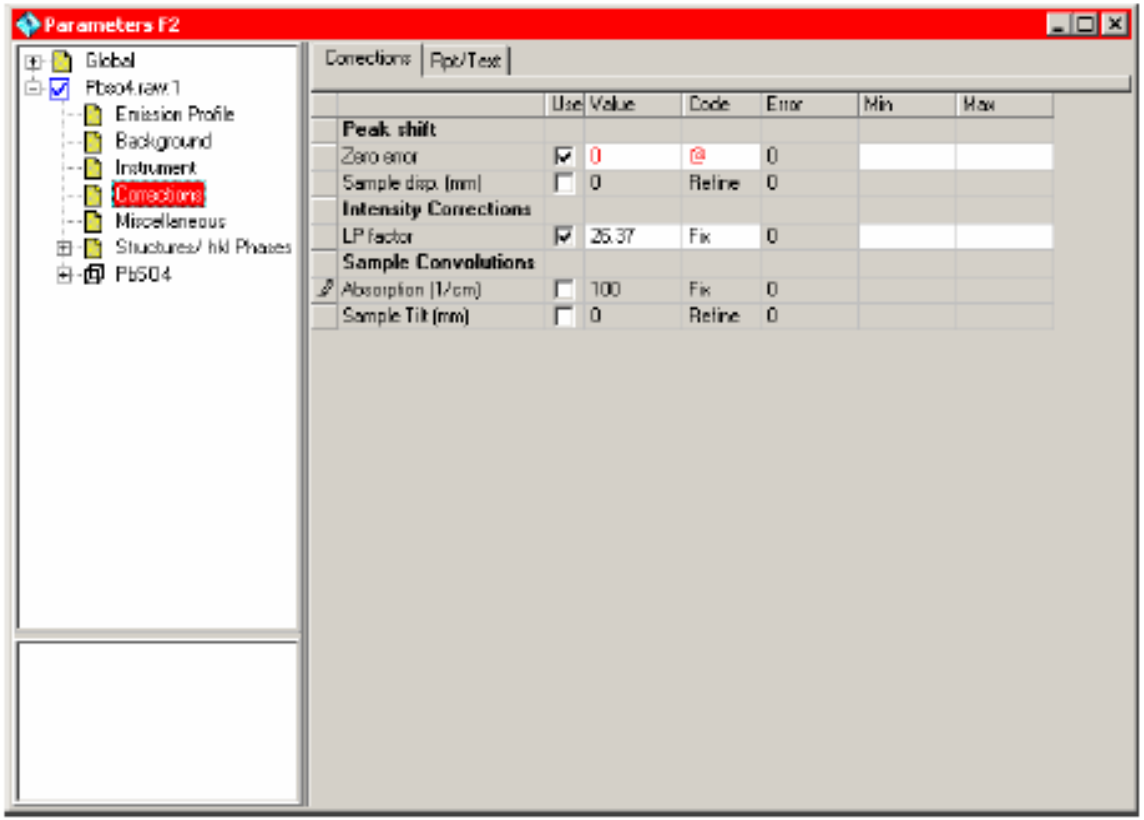


Fig. 2-18: *Corrections* item with its associated data grid. Note: *Absorption* is a "Use" dependent expand/collapse grid item.

2.3.2.7 Miscellaneous

Provides the following options (Fig. 2-19):

Parameter name:	Remarks:
• Convolution Steps	An integer corresponding to the number of calculated data points per measured data point. It may be useful to increase this number when numerical instabilities are introduced. This can happen when a particular convolution has a small effect on the profile shape or when the measurement step is large.
• Start X, Finish X	Used to limit the refined X range independent on zooming
• Fixed WL Neutron	Signals the use of neutron atomic scattering lengths

The *Excl. Regions* page allows for a definition of an unlimited number of excluded regions, which may overlap. There is one option in the short cut menu:

- **Add Excluded Region**
  Adds an excluded region.

Selected excluded region rows can be deleted using the DEL key.

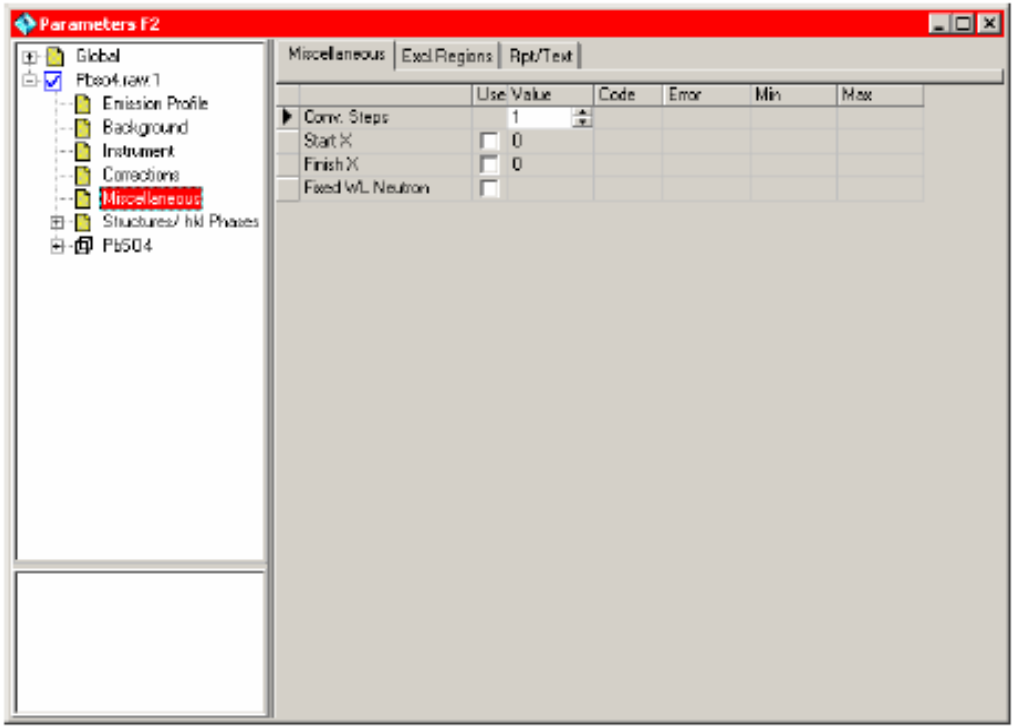


Fig. 2-19: *Miscellaneous* item with its associated data grid.

Peak Phase

Note: Not available in TOPAS R

Peak Phase items provide all parameters required for single line up to whole powder pattern fitting.

The first *Peak Phase* item will be created automatically, if a peak has been inserted manually or if a peak search has been performed. *Peak Phase* items can also be created manually using the short cut menu, see below.

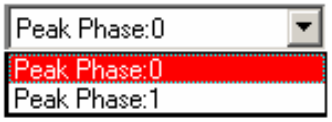


Fig. 2-20: *Peak Phase Combo Box* showing two *Peak Phases*.

With more than one *Peak Phase* item present, additional peaks, either inserted manually or found by peak search, will be moved to the *Peak Phase* item selected in the *Peak Phase Combo Box* (Fig. 2-20), which is located in the *Toolbar*.

A new *Peak Phase* item is always created when importing a peak list (d-I values) from a DIF or a UXD file.

Individual peaks of a *Peak Phase* can be of the type *FP*, *PV*, *PVII*, *SPV*, and *SPVII*. Furthermore there are several grid pages related to microstructure parameters as well as another *Additional Convolutions* page. For information about the microstructure parameters refer to section 3 and the Technical Reference manual. The *Additional Convolutions* page provides for empirical modelling of the observed

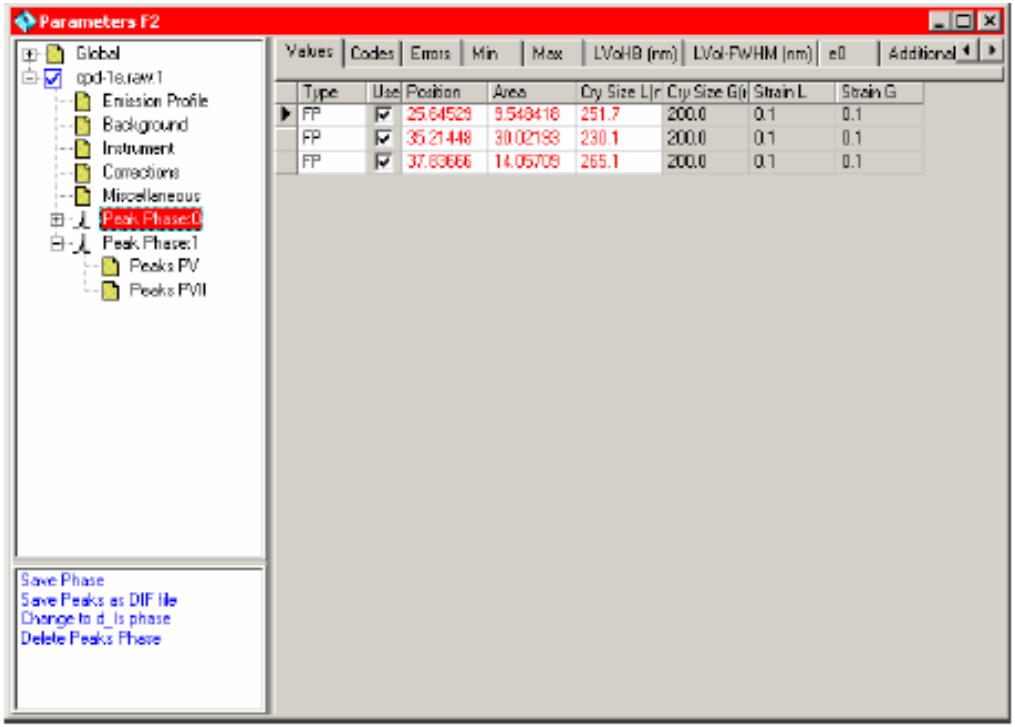


Fig. 2-21: *Peak Phase* items. The associated data grid only shows the profile function specific refinement parameters, which are different for the peak types *FP*, *PV*, *PVII*, *SPV*, and *SPVII*. The peak type can be changed for each peak at any time using the *Type* combo box (refined profile parameters will be lost). The "Use" checkbox enables/disables individual peaks.

hkl Phase

hkl Phase items (Fig. 2-22) provide all parameters required for whole powder pattern decomposition including both the Pawley and the Le Bail method. The data grid comprises the following pages: *Phase Details*, *Peak Type*, *hkl_Is*, and *Additional Convolutions*.

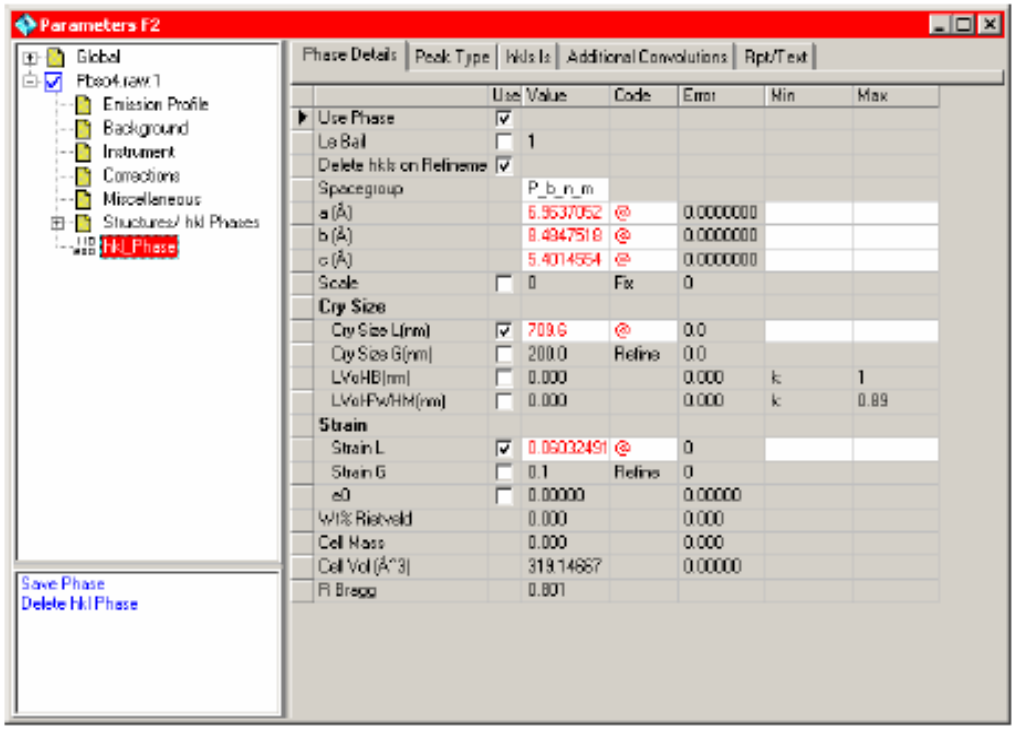


Fig. 2-22: *hkl Phase* item with its associated data grid showing the *Phase Details* page.

Parameter name:	Remarks:
• Use Phase	Includes or excludes the phase from the refinement
• Le Bail	If checked, the Le Bail method will be used for refinement of peak intensities
• Delete hkls on Refinement	If checked (default), the current hkls will be replaced by new hkls calculated for the actual spacegroup and data range, everytime a new refinement is started (refined intensities will be lost). This option should be used, if the spacegroup or the data range has been changed.
• Spacegroup	Space group symbol or space group number. When selecting the field, a drop down button opens a dialog for space group selection.
• a, b, c, alpha, beta, gamma	Lattice parameters. Spacegroup depend symmetry constraints are automatically applied including removal of redundant lattice parameters from the grid.
• Scale	Scale factor
• Cry Size Cry Size L Cry Size G LVol-IB LVol-FWHM	Microstructure parameters related to crystallite size; refer to section 3 and the Technical Reference manual
• Strain Strain L Strain G e0	Microstructure parameters related to strain; refer to section 3 and the Technical Reference manual
• Wt % Rietveld, Cell Mass, Cell Vol	Relative phase amount, cell mass, and cell volume
• R Bragg	R-Bragg value

Structure

Structure items (Fig. 2-22) provide all parameters required for Rietveld structure refinement as well as for quantitative Rietveld analysis. The structure dependent items of *Sites*, *PO March-Dollase*, *PO-Spherical Harmonics*, and *Str Output* are described below.

The *Structure* item data grid comprises the following pages: *Structure*, *Peak Type*, *hkl_Is*

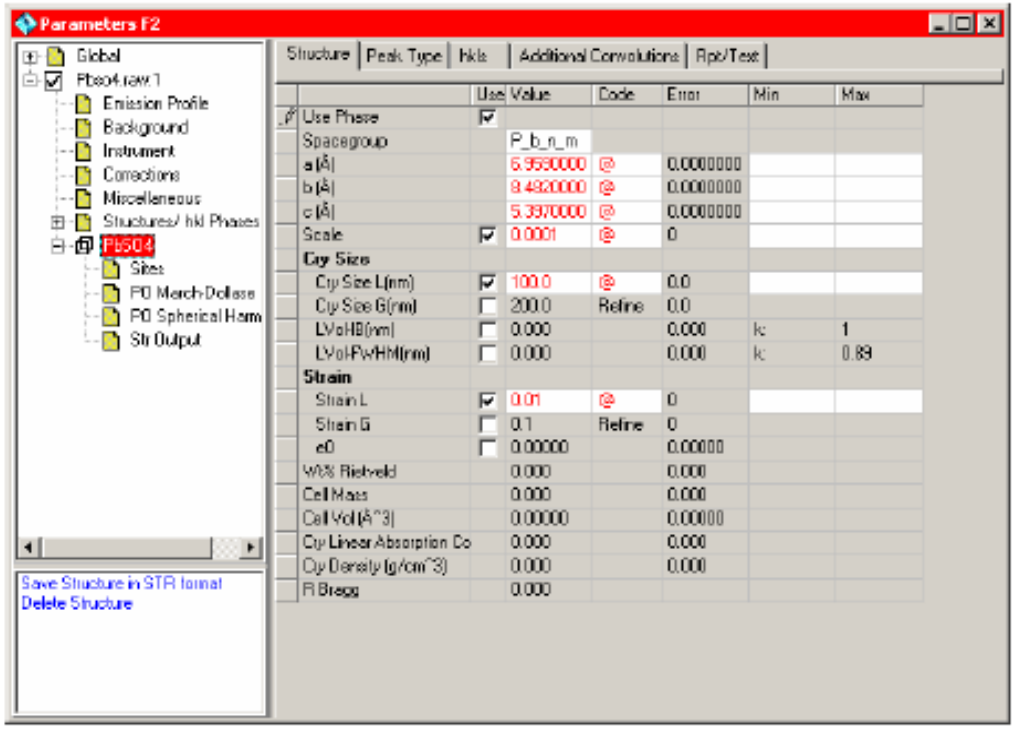


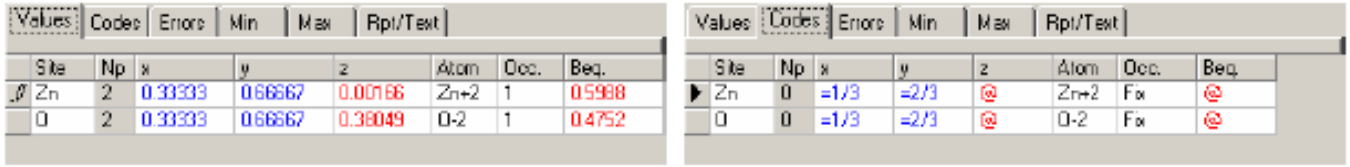
Fig. 2-23: *Structure* item with its associated data grid showing the *Structure* page.

Parameter name:	Remarks:
• Use Phase	Includes or excludes the phase from the refinement
• Spacegroup	Space group symbol or space group number. When selecting the field, a drop down button allows to open a dialog for space group selection.
• a, b, c, alpha, beta, gamma	Lattice parameters. Spacegroup depend symmetry constraints are automatically applied including removal of redundant lattice parameters from the grid.
• Scale	Scale factor
• Cry Size Cry Size L Cry Size G LVol-IB LVol-FWHM	Microstructure parameters related to crystallite size; refer to section 3 and the Technical Reference manual
• Strain Strain L Strain G e0	Microstructure parameters related to strain; refer to section 3 and the Technical Reference manual
• Wt % Rietveld, Cell Mass, Cell Vol	Relative phase amount, cell mass, and cell volume
• Cry Linear Absorption Coeff	Displays the phase linear absorption coefficient (for a packing density of 1)
• Cry Density	Displays the phase X-ray density (for a packing density of 1)
• R Bragg	R-Bragg value

The Sites item

The *Sites* item contains the following information concerning atomic sites:

Parameter name:	Remarks:
• Site	Customizable site name
• x, y, z	Fractional atomic coordinates
• Atom	X-ray data: Chemical species (atom/ion) determining the scattering factor Neutron data: Chemical symbol / isotope to determine the scattering length Both can be selected from a drop down list
• Occ.	Site occupancy factor; 0 <= Occ. <= 1
• Beq.	Isotropic temperature factor



a) b)

Fig. 2-24: *Sites* item data grids showing the *Values* (a) and *Codes* page (b) for a structure example requiring atomic coordinates provided in form of equations.

Short cut menu options of the *Sites* item are:

- **Add Site Before Current Site**
  Adds a new site before the current site
- **Add Site at Bottom**
  Adds a new site at the bottom of the list
- **Add Atom at Current Site**
  Adds a new atom at the current site

The PO March-Dollase item

March-Dollase (March, 1932) preferred orientation correction for up to two directions. hkls provided in the *hkl* field needs to be separated with spaces as shown in Fig. 2-26.

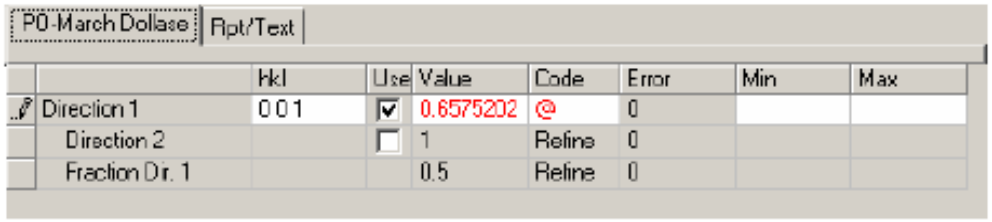


Fig. 2-26: *PO March Dollase* page.

The PO Spherical Harmonics item

A correction for preferred orientation effects using a spherical harmonics series, its coefficients can be viewed and manipulated in the *Coefficients* page. The *Order* parameter corresponds to the order of the spherical harmonics series, which must be an even integer ranging from 2 to 8.

The Str Output item

Allows for the output of the following structure details (Fig. 2-27):

- **Generate Bondlengths/Errors**
  If checked, bondlengths and bondangles will be calculated. Additionally errors for bondlengths and bondangles will be provided, if *Calculate Errors* has been turned on in the *Fit* menu or in the *Refinement Options Dialog* (section 2.2.3.7). The results will be displayed in the *Bondlengths* page.
  - **Consider Lattice Parameters in Errors**

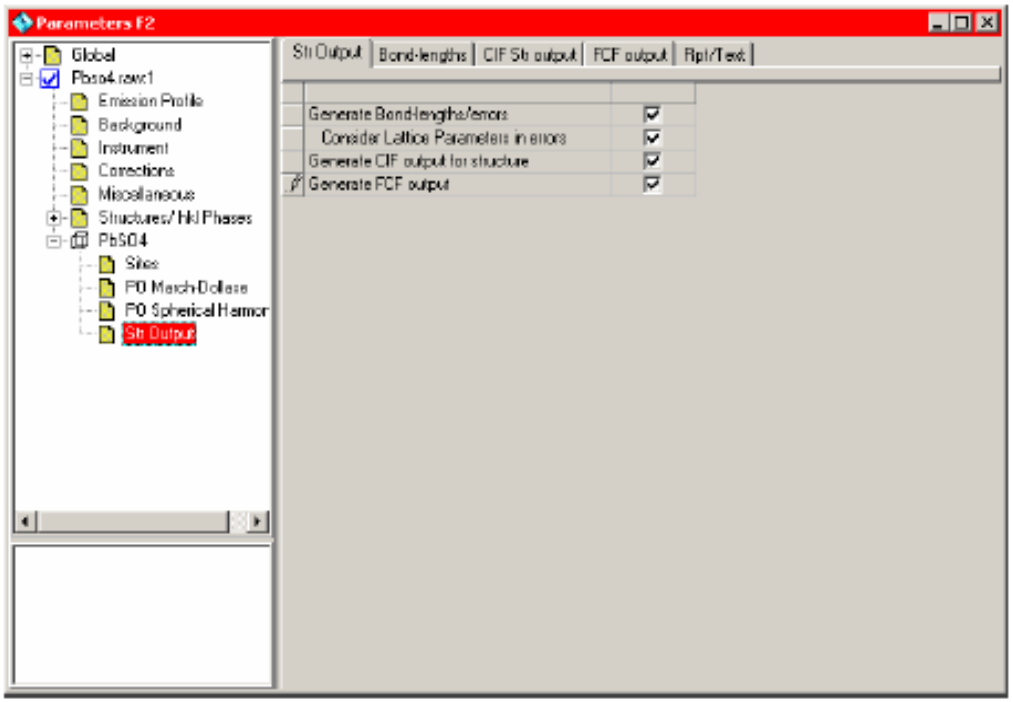
- **Consider Lattice Parameters in Errors**
  If checked, lattice parameter errors will be considered for calculation of bondlength and bondangle errors

- **Generate CIF Output for Structure**
  If checked, crystal structure details will be generated in CIF format and displayed in the *CIF Str Output* page

- **Generate FCF Output**
  If checked, structure factor details will be generated in FCF format and displayed in the *FCF Output* page

An example bond lengths output is as follows:

```
Y1:0     O1:0     2.23143
         O2:0     2.23143     88.083
         O3:0     2.28045     109.799     99.928
```



Structures / hkl Phases

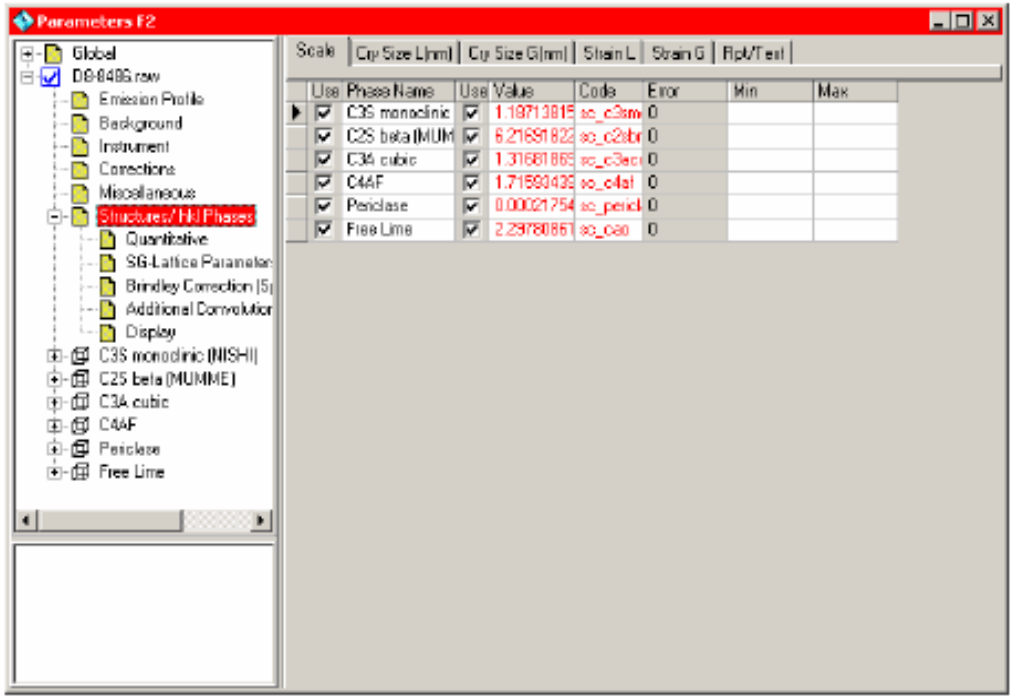
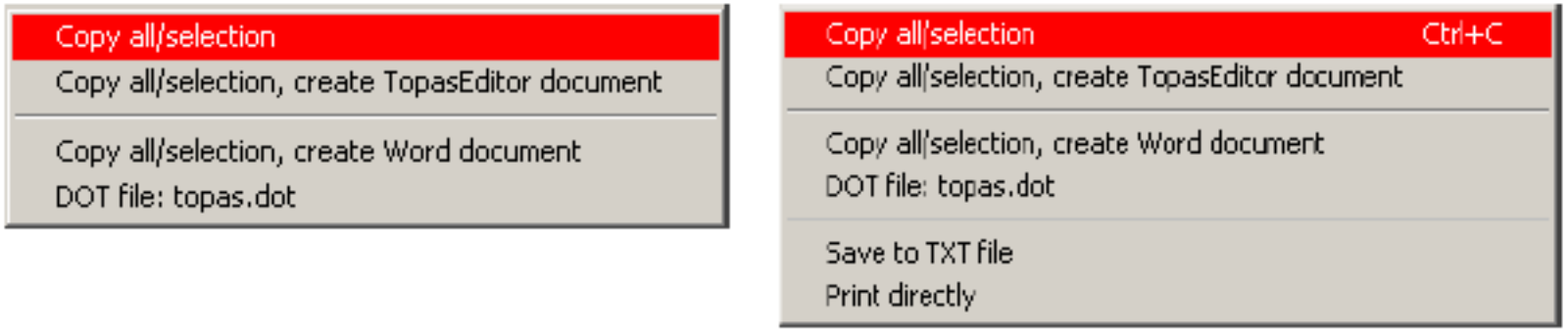


Fig. 2-28: *Structures / hkl Phases* item with its associated datagrid.

3rd level items of the *Global* item are:

- *Quantitative*
  Displays quantitative phase amounts for all phases included in the refinement
- *SG Lattice Parameters*
  Displays lattice parameters for all phases included in the refinement
- *Brindley Correction (Spherical Particles)*
  Corrects microabsorption effects for spherical particles (Brindley, 1945)
- *Additional Convolutions*
  Provides for empirical modelling of the observed line profile shapes; its options are identical to the *Additional Convolutions* page of the *Instrument* item, see section 2.3.2.5.
- *Display*
  Allows customization of display properties including colors, data point size and line width for each range

Printing and reporting



a) b)

Fig. 2-29: Short cut menu of the data grid showing available options for (a) grid pages and (b) text fields.

- **Copy all/selection**
  Copies the full page or the selection to the clipboard
- **Copy all/selection, create TopasEditor document**
  Launches the TopasEditor and transfers the full page or the selection into a new document in RTF format
- **Copy all/selection, create Word document**
  Launches Microsoft Word (if available) and transfers the full page or the selection into a new document in DOC format based on the currently defined document template (default is TOPAS.DOT)
- **DOT file: topas.dot**
  Allows to define a document template file for Microsoft Word (if available). This feature allows for the creation of customized reports with, for example, user-defined headers, footers, page numbering and more.

  Note: Topas.dot does not contain macros, however to use DOT files containing macros the security level of Microsoft Word for opening files must be set to either "low" (not recommended) or "medium"; if set to "high" any macros will be automatically disabled. For more information please refer to the Microsoft Word user's manual.

Operation in GUI and Launch Mode

The GUI Mode is active by default. Launch Mode becomes active if an input file (*.INP) is set by the menu command *Launch - Set INP File*.

Input files contain all information for controlling TOPAS in Launch Mode and can be modified by a text editor (for details please refer to the Technical Reference manual). Notepad is set as the default editor, user specified can be made permanently active by selecting *Launch - Editor*. Editing can be performed by selecting *Launch - Edit INP File*. In Launch mode refinement results are always written to an output file (*.OUT) which has the same format as the INP file. The output file can be inspected by selecting *Launch - Edit OUT File*.

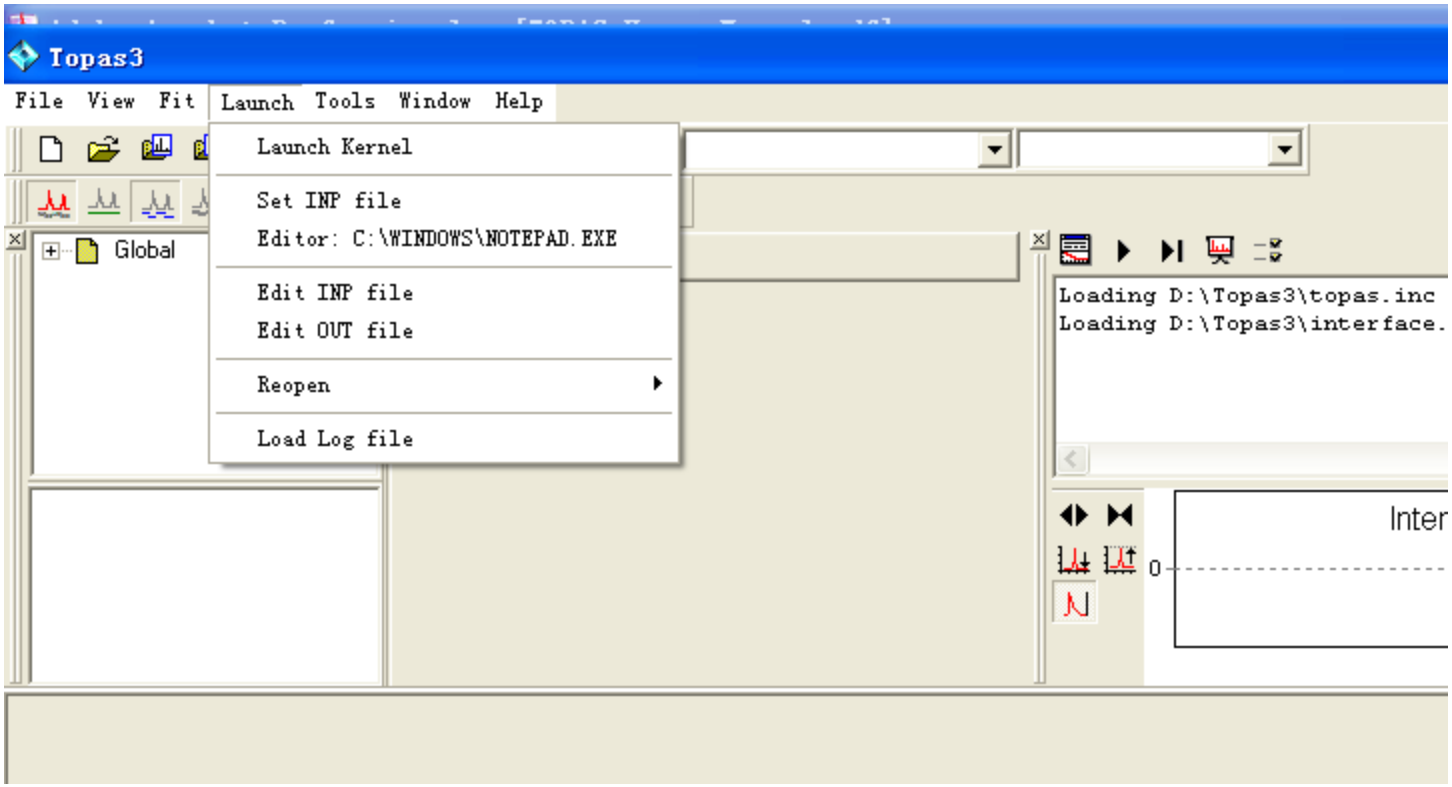
As in Launch Mode the refinement will be completely controlled by the input file, the following windows in the *Working Area* will have no effect:

- *Peak Search Dialog* (section 2.2.3.4)
- *Peak Details Dialog* (section 2.2.3.5)
- *Parameters Window* (section 2.3)

Scans loaded from Launch mode are placed into the *Parameters Window* for graphical display purposes. Editing of these entries has no bearing on the fitting process which is controlled entirely from the INP file.

Note: It is possible to work in GUI and Launch Mode at the same time. Once an input file is set the *Launch* button in the *Fit Window* allows for the switching between GUI and Launch Mode.

Lauch模式



Set INP file

*.inp的来源

- GUI模式的输出文件
- 已有的模版

r_exp 2.186 r_exp_dash 4.660 r_wp 2.922 r_wp_dash 6.227 r_p 2.275 r_p_dash 6.184 weighted_Durbin_Watson 1.333 gof 1.336
iters 1000
chi2_convergence_criteria 0.001
xdd D:\北京青少年科技后备人才培养计划\杜乔羽\CaTaTi\d11\d11s.dat
r_exp 2.186 r_exp_dash 4.660 r_wp 2.922 r_wp_dash 6.227 r_p 2.275 r_p_dash 6.184 weighted_Durbin_Watson 1.333 gof 1.336
bkg @ 1215.64401 208.701692 -188.17575 298.679653 -151.780171 59.956008 -87.3989484 39.2693905 16.2762255
One_on_X(@, 6118.28199)
Zero_Error(@, -0.20911)
Specimen_Displacement(@, -0.00575)
LP_Factor(26.4)
Rp 217.5
Rs 217.5
Cylindrical_2Th_Correction(@, 0.63346)
Absorption(@, 31.40650)
Specimen_Tilt(@, 0.37208)

lam

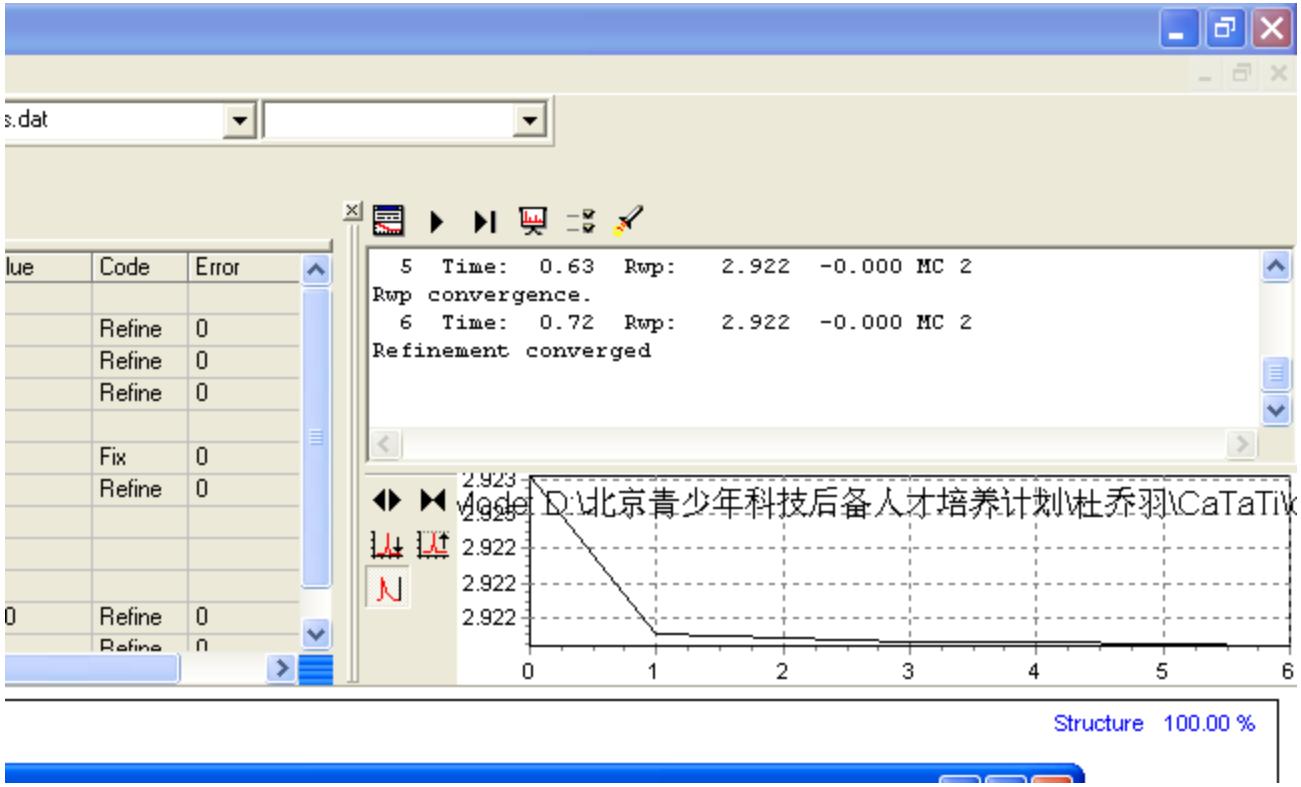
ymin_on_ymax 0.001
la 0.653817 lo 1.540596 lh 0.501844
la 0.346183 lo 1.544493 lh 0.626579

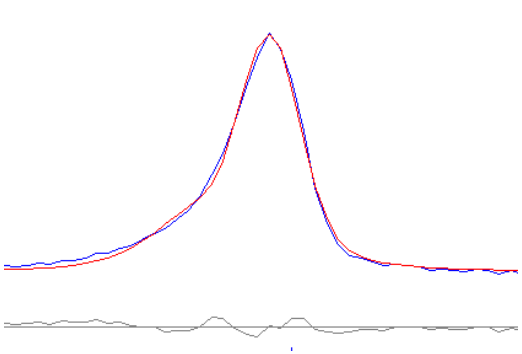
str

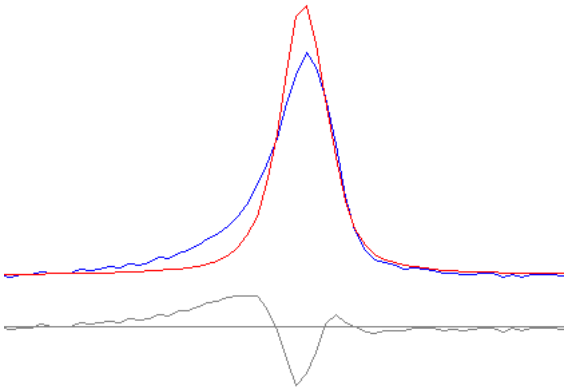
CS_L(@, 120.54707)
PVII_Peak_Type(@, 0.03757,@, 0.00372,@, 0.12792,@, 0.00010,@, 1.56236,@, 0.39528)
r_bragg 0.490306945
phase_name Structure
MVW(1680.577, 411.7866, 100.000)
scale @ 0.0001260772
space_group "I_m_-3"
Phase_LAC_1_on_cm(725.41115)
Phase_Density_g_on_cm3(6.77697)
Cubic(@ 7.43973)
site Cu1 num_posns 6 occ Cu+2 1 beq 1 x 0 y 0.5 z 0.5
site O2 num_posns 24 occ O-2 1 beq 1 x 0 y @ 0.29392 z @ 0.22710
site Ti1 num_posns 8 occ Ti+4 0.5 beq 1 x 0.25 y 0.25 z 0.25
site ta2 num_posns 8 occ Ta+5 0.5 beq 1 x 0.25 y 0.25 z 0.25

xo_Is

xo @ 16.9550599
I @ 13.078614
CS_L(@, 216.24903)
peak_type fp


.dat
lue
Code
Error
Refine 0
Refine 0
Refine 0
Fix 0
Refine 0
Refine 0
Refine 0
5 Time: 0.63 Rwp: 2.922 -0.000 MC 2
Rwp convergence.
6 Time: 0.72 Rwp: 2.922 -0.000 MC 2
Refinement converged
2.923
2.922
2.922
2.922
0
1
2
3
4
5
6
Structure 100.00 %





"keywords" and "macros"

- *bkg* : background
- *str...* : structure information for Rietveld refinement and structure determination
- *xo_Is...* : 2θ - I values for single line or whole powder pattern fitting
- *d_Is...* : d - I values for single line or whole powder pattern fitting
- *hkl_Is...* : lattice information for LeBail or Pawley fitting
- *fit_obj...* : user-defined fit models
- *hkl_Is_from_hkl4...* : Structure factores $(F_{obs})^2$ for creating a powder pattern from single crystal data

str, *xo_Is*, *d_Is* and *hkl_Is* will be referred to as "phases" and the peaks of these "phase peaks".

```
xdd filename

   CuKa5(0.001)
   Radius(217.5)
   LP_Factor(26.4)
   Full_Axial_Model(12, 15, 12, 2.3, 2.3)
   Slit_Width(0.1)
   Divergence(1)

   ZE(@, 0.0)
   bkg @ 0 0 0 0 0 0

   str
      space_group R_-3_C
      Trigonal(a_cor 4.759, c_cor 12.992)
      site Al x 0         y 0         z @ 0.3521  occ Al+3 1  beq @ 0.3
      site O  x @ 0.3062  y 0         z   0.25    occ O-2  1  beq @ 0.3
      scale @ 0.001
      CS(@, 100)
      r_bragg 0

   str
      space_group F_M_-3_M
      Cubic(a_fl 5.464)
      site Ca    x 0        y 0        z 0       occ Ca   1   beq @ 0.5
      site F     x 0.25     y 0.25     z 0.25    occ F    1   beq @ 0.5
      scale @ 0.001
      CS(@, 100)
      r_bragg 0
```

*.inp

r_exp 2.186 r_exp_dash 4.660 r_wp 2.922 r_wp_dash 6.227 r_p 2.275 r_p_dash 6.185 weighted_Durbin_Watson 1.333 gof 1.336

iters 1000

chi2_convergence_criteria 0.001

精修的参数

r_p, *r_p_dash*, *r_wp*, *r_wp_dash*, *r_exp*, *r_exp_dash*, *gof*

Syntax	[*r_p* #] [*r_p_dash* #] [*r_wp* #] [*r_wp_dash* #] [*r_exp* #] [*r_exp_dash* #] [*gof* #]
Description	File or global scope refinement indicators. Keywords ending in "_dash" correspond to background subtracted indicators.

weighted_Durbin_Watson

Syntax	[*weighted_Durbin_Watson* #]
Description	File or global scope refinement indicator.

Rp, *Rs*

Syntax	[*Rp* #] [*Rs* #]
Description	Defines the primary and secondary radius of the diffractometer in mm.
Hint	The default for *Rp* and *Rs* is set to 217.5 mm.

iters

Syntax	[*iters* #]
Description	The maximum number of refinement cycles requested.
Hint	*iters* is set to 20000 by default

do_errors

Syntax	[*do_errors*]
Description	Errors for refined parameters (ESD's) and a correlation matrix are calculated at the end of refinement. The correlation matrix is appended to the end of the *.OUT file.

relax

Syntax	[*relax* #]
Description	A global relaxation constant that dampens the change in parameters.
Hint	*relax* is set to 1 by default

chi2_convergence_criteria

Syntax	[*chi2_convergence_criteria* #]
Description	Convergence of the minimization routine is determined when the change in χ^2 is less than *chi2_convergence_criteria* for three consequitive cycles and when all defined *stop_when* parameter attributes evaluate to true.
Hint	For a detailed description of the TOPAS minimization routines refer to section 5.

randomize_on_errors

Syntax	[*randomize_on_errors*]
Description	This process is initiated after convergence, ie. when *continue_after_convergence* is defined. *randomize_on_errors* changes the parameter values according to the error in the parameter and the following equation: new_Val = Val + Rand(2, 4) Min(ESD, 3 Abs(Val)) Sign(Rand(-1, 1)); where ESD is the error in the parameter.

use_tube_dispersion_coefficients

Syntax	[*use_tube_dispersion_coefficients*]
Description	Instructs TOPAS to use Laboratory tube anomalous dispersion coefficients instead of the more accurate data from http://www-cxro.lbl.gov/optical_constants/asf.html.

out_rwp

Syntax	[*out_rwp* $file_name]
Description	Outputs a list of R_{wp} values encountered during refinement to the file $file_name.

out_chi2

Syntax	[*out_chi2* $file_name]
Description	Outputs a list of Chi^2 values encountered during refinement to the file $file_name.

randomize_file_out_normal

Syntax	[*randomize_file_out_normal* $file_name]
Description	Instructs TOPAS to randomize the calculated pattern Y_c using a Normal distribution and writes Y_c to the file $file_name.

seed

Syntax	[*seed*]
Description	Initialises the random number generator with a different seed based on the computer clock.

file_name_for_best_solutions

Syntax	[*file_name_for_best_solutions* $file]
Description	Appends INP file details to $file during refinement with independent parameter values updated. The operation is performed every time a particular convergence gives the best Rwp. For example, suppose that at convergence the following was obtained:

Rwp:

30	All prms appended to file in INP format
20	All prms appended to file in INP format
35	
40	
15	All prms appended to file in INP format
18	
10	All prms appended to file in INP format
15	

out

Syntax

[*out* $file [*append*]]...
    [*out_record*]
        [*out_eqn* !E]
        [*out_fmt* $c_fmt_string]
        [*out_fmt_err* $c_fmt_string]...

Description

Used for writing parameter details to a file. The details are appended to $file when *append* is defined. *out_eqn* defines the equation or parameter to be written to $file using the *out_fmt*. $c_fmt_string describes a format string in c syntax containing a single format specifier for a double precision number. *out_fmt_err* defines the $c_fmt_string used for formatting the error of *eqn*.

Both *out_fmt* and *out_fmt_err* requires an *out_eqn* definition. *out_fmt* can be used without *out_eqn* for writing strings. The order of *out_fmt* and *out_fmt_err* determines which is written to file first; thus if *out_fmt_err* is defind first then it will be operated on first.

Example

The following example illustrates the use of *out* using the Out macros.

```
xdd...
   out "sample output.txt" append
   str...
      CS_L(cs_l, 1000)
      Out_String("\tCrystallite Size Results:\n")
      Out_String("\t=========================\n")
      Out(cs_l, "\tCrystallite Size (nm):\t%11.5f",
              "\tError in Crystallite Size:\t%11.5f\n")
```

Hint

out provides a means of defining individual refinement result files.

*.inp

xdd D:\北\杜\CaTaTi\d11\d11s.dat

r_exp 2.186 r_exp_dash 4.660 r_wp 2.922 r_wp_dash 6.227 r_p 2.275 r_p_dash 6.185 weighted_Durbin_Watson 1.333 gof 1.336

bkg @ 1215.64267 208.70024 -188.175586 298.679649 -151.780757 59.9557014 -87.3990974 39.2693852 16.2758868

One_on_X(@, 6118.28036)

数据文件名及背底函数

xdd

Syntax	[*xdd* $file_name [{ $data }] [*range* #] [*xye_format*] [*gsas_format*] [*fullprof_format*]]...
Description	Defines the start of *xdd* dependent keywords and the file containing the observed data. [{$data}] allows the insertion of ASCII data directly into an input file. [*range* #] applies to Bruker AXS *.RAW data files; in multi-range files it defines the range to be refined with the first range starting at 1. *range* is set to 1 by default. [*xye_format*] [*gsas_format*] [*fullprof_format*]. *xye_format* signals the loading of columns of x, y and error values; additional columns are ignored. *gsas_format* and *fullprof_format* signals the loading of GSAS and FullProf file formats.

Example	The following instruction will refine on the first range in the data file pbso4.raw:
	`xdd pbso4.raw`
	
	To refine on the 3rd range within pbso4.raw, the *range* keyword has to be used:
	`xdd pbso4.raw range 3`
	
	To read data from an Input file, the following statements can be used:
	`xdd`
	`{`
	`1 1 10 ' start, step and finish (equidistant data )`
	`1 2 3 4 5 6 7 8 9 10`
	`}`
	
	`xdd`
	`{`
	`_xy ' switch indicating x-y format`
	`0.1 1 0.2 2 ...`
	`}`

Hint	The macro "XDD" simplyfies the use of *xdd*. Section 2.3 describes the different file formats supported by TOPAS.

9.3.1 xdd file input macros

RAW, DAT, XDD, XY, SCR, SHELX_HKL4

Syntax	RAW(path) RAW(path, range_num) DAT(path) XDD(path) XY(path, calc_step) SCR(path) SHELX_HKL4(path)
Description	Import measured data in different file formats (see section 2.3). [path]: Filename. Can include drive and path. [range_num]: The range number to be loaded (RAW files only). [calc_step]: Step size to be interpolated (XY files only).

bkg

Syntax	[*bkg* [@] # # #...]
Description	Defines a Chebyshev polynomial where the number of coefficients are equal to the number of numeric values appearing after the keyword *bkg*.
Hint	The number of coefficients is not limited.

Background functions using fit_objects

One_on_X

Syntax	One_on_X(c, v)
Description	1/X background function ideal to describe background intensity at low angles due to air scattering
	[c, v]: Parameter name and value.

Bkg_Diffuse

Syntax	Bkg_Diffuse(b, bv, bb, bbv)
Description	Defines a function to describe short range order effects.
	[b, bv]: Parameter name, refineable weight.
	[bb, bbv]: Parameter name, correlation shell radii.

*.inp

Zero_Error(@, -0.20911)
Specimen_Displacement(@, -0.00575)
LP_Factor(26.4)
Rp 217.5
Rs 217.5
Specimen_Tilt(@, 0.37208)
Cylindrical_2Th_Correction(@, 0.63346)
Absorption(@, 31.40664)
lam
ymin_on_ymax 0.001
la 0.653817 lo 1.540596 lh 0.501844
la 0.346183 lo 1.544493 lh 0.626579

9.3.7 2θ corrections

Zero_Error, ZE

Syntax	Zero_Error(c, v), ZE(c, v)
Description	Zero point error.
	[c, v]: Parameter name, zero point error in [° 2θ].

Specimen_Displacement, SD

Syntax	Specimen_Displacement(c, v), SD(c, v)
Description	Specimen displacement error.
	[c, v]: Parameter name, sample displacement in [mm].

9.3.8 Intensity corrections

LP_Factor, Lorentz_Factor

Syntax

Lorentz_Factor
LP_Factor(c, v)

Description

Lorentz and Lorentz-Polarisation factor.

[c, v]: Parameter name, monochromator angle in [°2θ].

For unpolarized radiation v is 0 (e.g. X-ray diffractometers without any monochromator), for fully polarized radiation v is 90 (e.g. synchrotron radiation).

Values for most common monochromators (Cu radiation) are:

Ge	: 27.3
Graphite	: 26.4
Quartz	: 26.6

There is no polarization factor for neutron data and thus the angle for Lorentz Polarization should be set to 90; this gives the Lorentz only part. Alternatively the Lorentz_Factor macro can be used for fixed wavelength neutron data.

9.3.4 Instrument and instrument convolutions

Radius

Syntax	Radius(rp, rs)
Description	Instrument radius.
	[rp, rs]: Primary and secondary instrument radii in [mm]. For most diffractometers rp equals rs.

Specimen_Tilt

Syntax	Specimen_Tilt(c, v)
Description	Specimen tilt.
	[c, v]: Parameter name, Specimen tilt in [mm].

Slit_Width, SW

Syntax	Slit_Width(c, v), SW(c, v)
Description	Aperture of the detector (= receiving) slit.
	[c, v]: Parameter name, detector slit aperture in [mm]..

Sample_Thickness

Syntax	Sample_Thickness(dc, dv)
Description	Describes the sample thickness in the direction of the scattering vector.
	[dc, dv]: Parameter name, sample thickness in [mm].

Divergence

Syntax	Divergence(c, v)
Description	Horizontal divergence of the beam for fixed slits.
	[c, v]: Parameter name, beam divergence in [°].

Variable_Divergence(c, v)

Syntax	Variable_Divergence(c, v)
Description	Constant illuminated sample length for variable slits (i.e. variable beam divergence). This macro considers the peak shape and corrects intensity deviations inherent to variable slits. [c, v]: Parameter name, illuminated sample length in [mm].

Variable_Divergence_Shape

Syntax	Variable_Divergence_Shape(c, v)
Description	Constant illuminated sample length for variable slits (i.e. variable beam divergence). This macro considers the peak shape inherent to variable slits. [c, v]: Parameter name, illuminated sample length in [mm].

Variable_Divergence_Intensity

Syntax	Variable_Divergence_Intensity
Description	Constant illuminated sample length for variable slits (i.e. variable beam divergence). This macro corrects intensity deviations inherent to variable slits.

Tube_Tails

Syntax	Tube_Tails(source_width_c, source_width_v, z1_c, z1_v, z2_c, z2_v, z1_z2_h_c, z1_z2_h_v)
Description	Model for description of tube tails (Bergmann, 2000).
	[source_width_c, source_width_v]: Parameter name, tube filament width in [mm].
	[z1_c, z1_v]: Parameter name, effective width of tube tails in the equatorial plane perpendicular to the X-ray beam - negative z-direction [mm].
	[z2_c, z2_v]: Parameter name, effective width of tube tails in the equatorial plane perpendicular to the X-ray beam - positive z-direction [mm].
	[z1_z2_h_c, z1_z2_h_v]: Parameter name, fractional height of the tube tails relative to the main beam.

UVW

Syntax	UVW(u, uv, v, vv, w, wv)
Description	Cagliotti relation (Cagliotti et al., 1958).
	[u, v, w]: Parameter names.
	[uv, vv, wv]: Halfwidth parameters.

lam

ymin_on_ymax 0.001
la 0.653817 lo 1.540596 lh 0.501844
la 0.346183 lo 1.544493 lh 0.626579

lam

Syntax	[*lam* [*ymin_on_ymax* #] [*no_th_dependence*] [*la* E *lo* E [*lh* E *lg* E]]...] [[*Lam* !N] [*calculate_Lam*]]
Description	Defines an emission profile where each "[*la* E *lo* E [*lh* E *lg* E]]" determines an emission profile line, where • *la* : Area under the emission profile line. • *lo* : Wavelength in Angstroms of the emission profile line. • *lh* : Lorentzian HW of the emission profile line in mili-Angstroms. • *lg* : Gaussian HW of the emission profile line in mili-Angstroms. [*ymin_on_ymax* #]: Determines the x-axis extent to which an emission profile line is calculated. [*no_th_dependence*]: Defines an emission profile that is 2θ independent. Allows the use of non-X-ray data or fitting to negative 2θ values. [*Lam* !N]: Defines the value to be used for the reserved parameter Lam. When *Lam* is not defined then the reserved parameter Lam is defined as the wavelength of the emission profile line with the largest *la* values. Note that Lam is used to determine the Bragg angle. [*calculate_Lam*]: Calculates *Lam* such that it corresponds to the wavelength at the peak of the emission profile. *Lam* needs to be set to an approximate value corresponding to the peak of the emission profile.
Hint	*ymin_on_ymax* is set to 0.001 by default. For more details about *lam* refer to section 6.

9.3.3 Emission profile macros

No_Th_Dependence

Syntax	No_Th_Dependence
Description	Defines an emission profile that is 2θ independent. Allows the use of non-X-ray data or fitting to negative 2θ values.

CuKa1, CuK1sharp,
CuKa2_analyt, CuKa2, CuKa4_Holzer, CuKa5, CuKa5_Berger,
CuKb4_Holzer

CoKa3, CoKa7_Holzer,
CoKb6_Holzer

CrKa7_Holzer,
CrKb5_Holzer

FeKa7_Holzer,
FeKb4_Holzer

MnKa7_Holzer,
MnKb5_Holzer

NiKa5_Holzer,
NiKb4_Holzer

MoKa2

Syntax	CuKa1(yminymax) and so forth
Description	Defines a source emission profile.
	[yminymax]: Determines the x-axis extent to which an emission profile line is calcultated.

CuKa5(0.001)

*.inp

str

CS_L(@, 120.54619)

PVII_Peak_Type(@, 0.03757,@, 0.00372,@, 0.12792,@, 0.00010,@, 1.56236,@, 0.39524)

r_bragg 0.489677278

phase_name Structure

MVW(1680.577, 411.7860, 100.000)

scale @ 0.0001260781

space_group "I_m_-3"

str

Syntax	[*str*]... *space_group* $symbol
Description	Defines the start of structure information. [*space_group* $symbol]: $symbol can be any space group symbol occurring in the ICSD, it can also be a space group number.
Hint	*space_group* is also used by the *hkl_ls* construct. The macro "STR" simplifies the use of *str*.

Temperature_Regime

Syntax	Temperature_Regime
Description	Defines a temperature regime. See the *temperature* keyword.

STR

Syntax	STR(sg)
Description	Signals the start of structure information. [sg]: Space group symbol.

Exclude

Syntax	Exclude
Description	Defines excluded regions. See the *exclude* keyword.

Sample convolutions

CS_L, Crystallite_Size, CS

Syntax	CS_L(c, v), Crystallite_Size(c, v), CS(c, v)
Description	Applies a Lorentzian convolution with a FWHM that varies according to the relation lor_fwhm = c / Cos(Th). [c, v]: Parameter name, crystallite size in [nm].

CS_G

Syntax	CS_G(c, v)
Description	Applies a Gaussian convolution with a FWHM that varies according to the relation gauss_fwhm = c / Cos(Th). [c, v]: Parameter name, crystallite size in [nm].

Strain_L, Microstrain, MS

Syntax	Strain_L(c, v)
Description	Applies a Lorentzian convolution with a FWHM that varies according to the relation lor_fwhm = c Tan(Th). [c, v]: Parameter name, strain.

Absorption, AB

Syntax	Absorption(c, v), AB(c, v)
Description	Linear absorption coefficient used for adjusting the peak shape.
	[c, v]: Parameter name, linear absorption coefficient in cm^{-1}.

Absorption_With_Sample_Thickness_mm_Shape

Syntax	Absorption_With_Sample_Thickness_mm_Shape(u, uv, d, dv)
Description	Corrects the peak shape for absorption effects.
	[u, uv]: Parameter name, linear absorption coefficient in cm^{-1}.
	[d, dv]: Parameter name, sample thickness in [mm].

Absorption_With_Sample_Thickness_mm_Shape_Intensity

Syntax	Absorption_With_Sample_Thickness_mm_Shape_Intensity(u, uv, d, dv)
Description	Corrects the peak intensity for absorption effects.
	[u, uv]: Parameter name, absorption coefficient in cm^{-1}.
	[d, dv]: Parameter name, sample thickness in [mm].

Strain_G

Syntax	Strain_G(c, v)
Description	Applies a Gaussian convolution with a FWHM that varies according to the relation gauss_fwhm = c Tan(Th). [c, v]: Parameter name, strain.

LVol_FWHM_CS_G_L

Syntax	LVol_FWHM_CS_G_L(k, lvol, kf, lvolf, csgc, csgv, cslc, cslv)
Description	Calculates FWHM and IB (integral breadth) based volume-weighted column heights (LVol). For details refer to section 6.4. [k, lvol]: shape factor (fixed to 1), integral breadth based LVol. [kf, lvolf]: shape factor (defaults to 0.89), FWHM based LVol. [csgc, csgv]: Parameter name, Gaussian component. [cslc, cslv]: Parameter name, Lorentzian component.

9.3.5 Phase peak_type's

PV_Peak_Type, PVII_Peak_Type, TCHZ_Peak_Type

Syntax	PV_Peak_Type(ha, hav, hb, hbv, hc, hcv, lora, lorav, lorb, lorbv, lorc, lorcv), TCHZ_Peak_Type(u, uv, v, vv, w, wv, x, xv, y, yv, z, zv) PVII_Peak_Type(ha, hav, hb, hbv, hc, hcv, ma, mav, mb, mbv, mc, mcv)
Description	Pseudo-Voigt, TCHZ pseudo-Voigt and PearsonVII functions. For the definition of the functions and function parameters refer to section 6.2.

The following *peak_type*'s are available in TOPAS:

- fp : Fundamental Parameters
- pv : Pseudo-Voigt
- spvii : Split-PearsonVII
- spv : Split-PseudoVoigt

The definitions of these pseudo-Voigt and PearsonVII functions are provided in Table 6-2 (symmetric functions) and Table 6-3 (split functions). The following terms are used:

Symmetric functions:

- x : $(2\theta\text{-}2\theta_k)$ where $2\theta_k$ is the position of the kth reflection
- *fwhm* : full width at half maximum
- η : PV mixing parameter

Asymmetric functions:

- *fwhm*1, *fwhm*2 : fwhm for the left and right composite function
- *m*1, *m*2 : Exponents for the composite functions
- $\eta 1$, $\eta 2$: PV mixing parameters for the composite functions

Table 6-2: Unit area peak types for symmetric functions.

Profile Function:	Definition:
Gaussian, $G_{UA}(x)$	$G_{UA}(x)=\left(\frac{g_1}{fwhm}\right)Exp\left(\frac{-g_2x^2}{fwhm^2}\right)$
	where
	$g_1=2\sqrt{(Ln(2)/\pi)}$
	$g_2=4\,Ln(2)$
Lorentzian, $L_{UA}(x)$	$L_{UA}(x)=\left(\frac{l_1}{fwhm}\right)\Big/\left(\frac{1+l_2x^2}{fwhm^2}\right)$
	where
	$l_1=2/\pi$
	$l_2=4$
PseudoVoigt, $PV_{UA}(x)$	$PV=\eta L_{UA}(x)+(1-\eta)G_{UA}(x)$

Table 6-3: Unit area peak types for split functions.

Profile Function:	Definition:
Split PearsonVII, SPVII	$SPVII = PVII\_Left + PVII\_Right$ where $PVII\_Left = \left(1 + b_1 x^2\right)^{-m1} / a$ for $(-\infty < x < 0)$ $PVII\_Right = \left(1 + b_2 x^2\right)^{-m2} / a$ for $(0 < x < \infty)$ $a = (\tfrac{1}{2})\Gamma(\tfrac{1}{2})\left[\frac{\Gamma(m1 - \tfrac{1}{2})}{\Gamma(m1)\sqrt{b_1}} + \frac{\Gamma(m2 - \tfrac{1}{2})}{\Gamma(m2)\sqrt{b_2}}\right]$ $b_1 = \left(2^{-m1} - 1\right) / h1^2$ $b_2 = \left(2^{-m2} - 1\right) / h2^2$ $fwhm1 = 2\,h1$ $fwhm2 = 2\,h2$ $fwhm = h1 + h2$
Split PseudoVoigt, SPV	$SPV = 2\left(PV\_Left + a\,PV\_Right\right)/(1 + a)$ where $PV\_Left = PV(h1, \eta 1)$ for $(-\infty < x < 0)$ $PV\_Right = PV(h2, \eta 2)$ for $(0 < x < \infty)$ $a = (PV\_Left(x = 0)/(PV\_Right(x = 0)$ $fwhm1 = 2\,h1$ $fwhm2 = 2\,h2$ $fwhm = h1 + h2$

For classic analytical full pattern fitting the macros PV_Peak_Type, PVII_Peak_Type, TCHZ_Peak_Type can be used. These macros use the following relationships to describe profile width and shape as smooth functions of 2θ:

PV_Peak_Type:

$fwhm = ha + hb \tan\theta + hc/\cos\theta$

$\eta = lora + lorb \tan\theta + lorc/\cos\theta$

where

- *ha*, *hb*, *hc*, *lora*, *lorb*, *lorc* are refineable parameters

PVII_Peak_Type:

$fwhm1 = fwhm2 = ha + hb \tan\theta + hc/\cos\theta$

$m1 = m2 = 0.6 + ma + mb \tan\theta + mc/\cos\theta$

where

- *ha*, *hb*, *hc*, *ma*, *mb*, *mc* are refineable parameters

TCHZ_Peak_Type:

The modified Thompson-Cox-Hastings pseudo-Voigt "TCHZ" is defined as (e.g. Young, 1993)

$\eta = 1.36603\, q - 0.47719\, q^2 + 0.1116\, q^3$

where

- $q = \Gamma_L/\Gamma$
- $\Gamma = (\Gamma_G^5 + A\Gamma_G^4\Gamma_L + B\Gamma_G^3\Gamma_L^2 + C\Gamma_G^2\Gamma_L^3 + D\Gamma_G\Gamma_L^4 + \Gamma_L^5)^{0.2} = fwhm$
  $A = 2.69269,\ B = 2.42843,\ C = 4.47163,\ D = 0.07842$
- $\Gamma_G = (U \tan^2\theta + V \tan\theta + W + Z/\cos^2\theta)^{0.5}$
- $X \tan\theta + Y/\cos\theta$
- with *U, V, W, X, Y, Z* as refineable parameters.

Quantitative analysis

Apply_Brindley_Spherical_R_PD

Syntax	Apply_Brindley_Spherical_R_PD(R, PD)
Description	Applies the Brindley correction for quantitative analysis (Brindley, 1945).
	[R, PD]: Radius of the particle in [cm], packing density.

MVW

Syntax	MVW(m_v, v_v, w_v)
Description	Returns cell mass, cell volume, and relative phase amount.
	[m_v, v_v, w_v]: Mass, volume, and weight parameters.

scale

Syntax	[*scale* E]
Description	The Rietveld scale factor.

phase_MAC

Syntax	*phase_MAC* !E
Description	Calculates the mass absorption coefficient in cm^2/g for the current phase. See description for *mixture_MAC*.

phase_name

Syntax	[*phase_name* $phase_name]
Description	The name given to a phase, used for reporting purposes.

r_bragg

Syntax	[*r_bragg* #]
Description	Reports on the R-Bragg value encountered in the refinement.
Hint	Note, R-Bragg is independent of hkl's and thus can be calculated for all phase types that contain phase peaks.

str_mass, volume, weight_percent

Syntax [*str_mass* ! N] [*volume* ! N] [*weight_percent* !N]

Description Weight percent parameters.

[*str_mass* !N]: Unit cell mass.

[*volume* !N]: Unit cell volume.

[*weight_percent* !N]: Relative phase amount in a mixture.

The weight fraction w_p for phase "p" is calculated as follows:

$$w_p = \frac{Q_p}{\sum_{p=1}^{N_p} Q_p}$$

where

- N_p = Number of phases
- Q_p = $S_p M_p V_p / B_p$
- S_p = Rietveld scale factor for phase p.
- M_p = Unit cell mass for phase p.
- V_p = Unit cell volume for phase p.
- B_p = Brindley correction for phase p.

The Brindley correction is a function of *brindley_spherical_r_cm* and the phase and mixture linear absorption coefficients; the latter two are in turn functions of *phase_MAC* and *mixture_MAC* respectively, or,

B_p is function of : $(LAC_{phase} – MAC_{mixture})$ *brindley_spherical_r_cm*

where

- LAC_{phase} = linear absorption coefficients of phase p, packing density of 1.
- $MAC_{mixture}$ = linear absorption coefficients of the mixture, packing density of 1.

This makes B_p a function of the weight fractions w_p of all phases and thus w_p as written above cannot be solved analytically. Subsequently w_p is solved numerically through the use of iteration.

The keyword *space_group* is used to define the space group; here are some examples:

- `space_group "I a -3"`
- `space_group I_a_-3`
- `space_group P_63_M_C`
- `space_group I_41/A_M_D`
- `space_group I_41/A_M_D:2   ' defines second setting of I_41/A_M_D`
- `space_group 206`
- `space_group 222:2          ' defines second setting of 222`

*.inp

Phase_LAC_1_on_cm(725.41213)
Phase_Density_g_on_cm3(6.77698)
Cubic(@ 7.43973)
site Cu1 num_posns 6 occ Cu+2 1 beq 1 x 0 y 0.5 z 0.5
site O2 num_posns 24 occ O-2 1 beq 1 x 0 y @ 0.29393 z @ 0.22710
site Ti1 num_posns 8 occ Ti+4 0.5 beq 1 x 0.25 y 0.25 z 0.25
site ta2 num_posns 8 occ Ta+5 0.5 beq 1 x 0.25 y 0.25 z 0.25
xo_ls
xo @ 16.9550654
I @ 13.0775354
CS_L(@, 216.31479)

9.3.2 Lattice parameters

Cubic, Tetragonal, Hexagonal, Rhombohedral

Syntax	Cubic(a_cv) Tetragonal(a_cv, c_cv) Hexagonal(a_cv, c_cv) Rhombohedral(a_cv, al_cv)
Description	Simply the definition of lattice parameters. [a_cv]: Lattice parameter a. [c_cv]: Lattice parameter c. [al_cv]: Lattice parameter alpha.

a, *b*, *c*, *al*, *be*, *ga*

Syntax	[*a* E] [*b* E] [*c* E] [*al* E] [*be* E] [*ga* E]
Description	Lattice parameters in Angstroms and lattice angles in degrees.

site

Syntax

[*site* $site_name [*x* E] [*y* E] [*z* E]]...
[*occ* $atom E [*beq* E]]...
[*num_posns* #] [*rand_xyz* !E] [*inter* !N #]

Description

Defines a site where $site_name is a user-defined string used to identify the site.

[*x* E] [*y* E] [*z* E]: Fractional atomic coordinates.

[*occ* $atom E [*beq* E]]: Defines the site occupancy factor and the equivalent isotropic temperature factor Beq. $atom corresponds to a valid atom symbol or isotope the data of which is contained in the file ATMSCAT.CPP.

[*num_posns* #]: Corresponds to the number of unique equivalent position generated from the space group; *num_posns* is updated on termination of refinement.

[*rand_xyz* E!]: When *continue_after_convergence* is defined, *rand_xyz* processes are initiated after convergence. It introduces a random displacement to the site fractional coordinates (*x*, *y*, *z*) that are independent parameters. The size of the random displacement in Å is given by the current *temperature* multiplied by the value returned by *rand_xyz*.

[*inter* !N #]: Corresponds to the sum of all GRS interactions which are a function of the *site*. The value of *inter* can represent site electrostatic potentials depending on the type of GRS interactions defined.

Example

Definition of a site fully occupied by aluminum:

```
site Al1  x 0       y 0       z 0.3521  occ Al+3 1    beq 0.3
```

Definition of a site occupied by two different cations:

```
site Fe2  x 0.9283  y 0.25    z 0.9533  occ Fe+3 0.5  beq 0.25
                                         occ Al+3 0.5  beq 0.25
```

xo_ls

Syntax	[*xo_ls*]... [*lebail* #] [*xo* E *I* E]...
Description	Defines a phase type that uses 2θ values for generating peak positions. [*lebail* #]: The *lebail* keyword instructs TOPAS to extract intensities using the LeBail method. [*xo* E *I* E]: *xo* corresponds to the peak position and *I* is the intensity parameter before applying any *scale_pks* equations.
Hint	When there are a large number of parameters then sparse matrix methods can be invoked using the keywords *use CG*, *sparse A*, *auto sparse CG*.

d_ls

Syntax	[*d_ls*]... [*lebail* #] [*d* E *I* E]...
Description	Defines a phase type that uses d-spacing values for generating peak positions. [*lebail* #]: The *lebail* keyword instructs TOPAS to extract intensities using the Lebail method. [*d* E *I* E]: *d* corresponds to the peak position in d-space and *I* is the intensity parameter before applying any *scale_pks* equations.
Hint	When there are a large number of parameters then sparse matrix methods can be invoked using the keywords *use_CG, sparse_A, auto_sparse_CG*.

hkl_ls

Syntax

[*hkl_ls*]...
[*space_group* $symbol]
[*lebail* #]
[*hkl_m_d_th2* # # # # # # *I* E]...

Description

Defines a phase type that uses hkls for generating peak positions.

[*space_group* $symbol]: $symbol can be any space group symbol occurring in the ICSD, it can also be a space group number.

[*lebail* #]: The *lebail* keyword instructs TOPAS to extract intensities using the Lebail method. When there are a large number of parameters then sparse matrix methods can be invoked using the keywords *use_CG, sparse_A, auto_sparse_CG*.

[*hkl_m_d_th2* # # # # # # *I* E]: The numbers after the keyword *hkl_m_d_th2* define h k l m d and 2θ values, where

h, k, l	: Miller indicies
m	: multiplicity.
d and th2	: d and 2θ values (not used by TOPAS).
I	: Peak intensity parameter before applying any *scale_pks*.

If no *hkl_m_d_th2* keywords are defined then the hkls are generated using the space group; the generated *hkl_m_d_th2* details are appended at the end of the *space_group* keyword at the end of refinement. Intensity parameters are given an initial starting value of 1. If the Le Bail keyword is not defined then the intensity parameters are given the unique code of @ .

Example

For example, the following input segment:

```
xdd quartz.inp
      ...
      hkl_Is
         Hexagonal(4.91459, 5.40603)
         space_group P_31_2_1
```

will generate the following OUT file:

```
xdd quartz.inp
      ...
      hkl_Is
         Hexagonal(4.91459, 5.40603)
         space_group P_31_2_1
         load hkl_m_d_th2_I
         {
            1   0   0   6    4.25635   20.85324 @ 3147.83321
            1   0   1   6    3.34470   26.62997 @ 8559.23955
            1   0  -1   6    3.34470   26.62997 @ 8559.23955
            ...
         }
```

Hint

After the hkl intensity file has been created it can then be used as input for the *hkl_Is* phase. Even though the structure would have no sites, the *weight_percent* keyword can still be used; it will use whatever value is defined by *str_mass* in order to calculate *weight_percent*.

space_group is also used by the *str* construct.

关于单晶数据

xdd_scr

Syntax

[*xdd_scr* $file_name] …
[*dont_merge_equivalent_reflections*]
[*dont_merge_Friedel_pairs*]
[*ignore_differences_in_Friedel_pairs*]
[*str*]
[*auto_scale* !N]
[*i_on_error_ratio_tolerance* #]
[*num_highest_I_values_to_keep* #num]
[*out_single_crystal_details* $file_name]

Description

xdd_scr defines single crystal data from the file $file_name. The file can have extensions of *.HKL for ShelX HKL4 format or *.SCR for SCR format.

[*dont_merge_equivalent_reflections*]: Unmerges equivalent reflections, see also section 4.3.

[*dont_merge_Friedel_pairs*]: Prevents the merging of Friedel pairs, see also section 4.3.

Example

An example input segment for single crystal data refinement is as follows:

```
xdd_scr ylidm.hkl

MoKa2(0.001)
finish_X 35

weighting = 1 / Sin(X Deg / 2);

STR(P212121)
   a  5.9636
   b  9.0390
   c 18.3955
   scale @ 1.6039731906

   i_on_error_ratio_tolerance 4

   site S1  x @ 0.8090  y @ 0.1805  z @ 0.7402  occ S 1  beq 2
   site O1  x @ 0.0901  y @ 0.8151  z @ 0.2234  occ O 1  beq 2
   ...
```

Hint

Note the user-defined weighting function.

The SCR format is white space delimited and consists of any number of entries comprising h, k, l, m, d, 2θ, Fo which is the format outputted by the Create_hklm_d_Th2_Ip_file macro.

hkl_Is_from_hkl4

Syntax

[*xdd* $file_name.hkl]...
[*hkl_Is_from_hkl4*]
[*i_on_error_ratio_tolerance* #]
[*num_highest_I_values_to_keep* #num]

Description

hkl_Is_from_hkl4 is used for generating a powder pattern from single crystal data.

Example

The following example input file calculates a powder pattern for a specific instrument from single crystal data read from a file in ShelX HKL4 format:

```
xdd ylidm.hkl

MoKa2(0.001)
LP_Factor(26.4)
Full_Axial_Model(12, 15, 12, 2.3, 2.3)
Divergence(1)
Slit_Width(0.1)

bkg 100

hkl_Is_from_hkl4
      space_group P212121
      a  5.9636
      b  9.0390
      c 18.3955
      CS_L(500)
```

Shelxl, Shelxs

7.1 Site identifying strings

Keywords such as *operate_on_points* requires a site identifying string; this string can contain the wild card character '*' and a negation character '!'. The wild card character '*' used in "O*" means that sites with names starting with 'O' are considered. In addition to using the wild card character, the site names can be explicitly written within double quotation marks. For example, consider the following segment:

```
str
   site Pb1...
   site S1 ...
   site O1 ...
   site O2 ...
   site O31 ...
   site O32 ...
   site O4 ...
```

site O1 num_posns 2 occ O-2 1 beq 1
x 0.0000 y 0.000 z 0.000

Table 7-1 shows some *operate_on_points* strings and the corresponding sites identified for this particular example.

Table 7-1: Example *operate_on_points* strings and the corresponding sites identified.

***operate_on_points* $sites:**	**Sites identified:**
*	Pb1, S1, O1, O2, O31, O32, O4
Pb*	Pb1
"Pb1 S*"	Pb1, S1
O*	O1, O2, O31, O32, O4
"O* !O3*"	O1, O2, O4
"O* !O1 !O2"	O31, O32, O4

Rigid bodies and bond length restraints

Rigid bodies comprise points in space defined using either the *z_matrix* or *point_for_site* keywords or both simultaneously. All or some of these points can then be operated on using the *rotate* and *translate* keywords.

Successful use of rigid bodies entail:

- Translating a rigid body or part of a rigid body.
- Rotating a rigid body or part of a rigid body around a point.
- Rotating a rigid body or part of a rigid body around a line.
- Recognizing the fact that *ux*, *uy*, and *uz* of the *point_for_site* keyword, *ta*, *tb* and *tc* of the *translate* keyword, *qa*, *qb* and *qc* of the *rotate* keyword and the parameters of the *z_matrix* keyword are all refineable parameters which in turn means that parameter attributes such as *min/max* can be defined.

The following Web address further describe the use of Z-matrices:

- http://www.chemistry.mcmaster.ca/help/yaehmop/bind_manual/node92.html
- http://www.cchem.berkeley.edu/~mhggrp/class295/zmat.html
- http://theo1.theochem.tu-muenchen.de/qcl/help/zmatrix_e.html

7.2 Space groups, hkls and symmetry operator generation

The keyword *space_group* is used to define the space group; here are some examples:

- `space_group "I a -3"`
- `space_group I_a_-3`
- `space_group P_63_M_C`
- `space_group I_41/A_M_D`
- `space_group I_41/A_M_D:2   ' defines second setting of I_41/A_M_D`
- `space_group 206`
- `space_group 222:2          ' defines second setting of 222`

7.3 Occupancies and symmetry operators

Only unique positions are generated from symmetry operators. Fully occupied sites therefore require site occupancy values of 1. A comparison of atomic positions is performed in the generation of the unique positions with a tolerance in fractional coordinates of 10^{-15}. It is therefore necessary to enter fractions in the form of equations when entering fractional atomic coordinates that have recurring values such as 0.33333..., 0.666666... etc., for example, use

```
x = 1/3; y = 1/3; z = 2/3;
```

instead of

```
x 0.33333 y 0.33333 z 0.66666
```

7.5 Simulated annealing and structure determination

Keywords and processes typically used in structure determination are as follows:

```
chi2_convergence_criteria #
continue_after_convergence
dont_walk
file_name_for_best_solutions
line_min
penalty...
penalties_weighting_K1 #
seed
swap_sites...
swap_with_closest_sites
temperature #...
   move_to_the_next_temperature_regardless_of_the_change_in_rwp
   save_values_as_best_after_randomization
   use_best_values
   do_processes
try_site_patterns
```

```
try_site_patterns...

use_extrapolation

xdd... or xdd_scr...
   str...
      site ... rand_xyz...
      break_if_comming_back
      break_if_been_there
         been_there_buffer
```

For detailed descriptions see section 8.2.

Penalties used in structure determination

For powder data the default weighting scheme

```
weighting = If(Yobs <= 1, 1, 1 / Yobs);
```

for single crystal data

```
weighting = 1 / Sin(X Deg / 2);
```

```
weighting = ( Abs(Yobs-Ycalc) / Abs(Yobs+Ycalc) +1) / Sin(X Deg / 2);
```

Two penalty functions that have shown to facilitate the determination of structures are the anti-bumping (AB) penalty and the potential energy penalty U. The anti-bumping penalty is written as:

$$AB_i = \begin{cases} \sum (r_{ij} - r_\circ)^2, & \text{for } r_{ij} < r_\circ \text{ and } i \neq j \\ 0, & \text{for } r_{ij} \geq r_\circ \end{cases} \qquad (7\text{-}1)$$

where r_0 is a bond length distance, r_{ij} the distance between atoms i and j including symmetry equivalent positions and the summation is over all atoms of type j. The *box_interaction* is used to implement the penalty of equation 7-2, see the Anti_Bump macro.

TOPAS uses the *grs_interaction* to either calculate the Lennard-Jones or Born-Mayer potentials and it is suited to ionic atomic models; for a particular site i they comprise a Coulomb term C_i and a repulsive term R_i and is written as:

$$U_i = C_i + R_i \qquad (7\text{-}2)$$

where

- $C_i = A \sum Q_i Q_j / r_{ij}$, i≠j
- $R_i = \sum B_{ij} / r_{ij}^n$, for Lennard Jones and i≠j
- $R_i = \sum c_{ij} \exp(-d\, r_{ij})$, for Born-Mayer and i≠j

where $A = e^2/(4\pi\varepsilon_0)$ and ε_0 is the permittivity of free space, Q_i and Q_j are the ionic valences of atoms i and j, r_{ij} is the distance between atoms i and j and the summation is over all atoms to infinity. The repulsive constants B_{ij}, n, c_{ij} and d are are characteristic of the atomic species and their potential surrounds. The equation part of the *grs_interaction* is typically used to describe the repulsive terms.

The following processes are invoked after the last temperature in a particular temperature refinement cycle has converged and when *continue_after_convergence* is defined:

```
[swap_with_closest_sites $sites_1 $sites_2  #num_closest]
[try_site_patterns $site [num_patterns_at_a_time #]]...
[swap_sites $sites_1 $sites_2]...
```

拟合因子

Criteria of fit:	Definition:	
"R-pattern", R_p	$R_p = \sqrt{\frac{\sum \lvert Y_{o,m} - Y_{c,m} \rvert}{\sum Y_{o,m}}}$	$R_p' = \sqrt{\frac{\sum \lvert Y_{o,m} - Y_{c,m} \rvert}{\sum \lvert Y_{o,m} - Bkg_m \rvert}}$
"R-pattern", R_p' (background corrected)		
"R-weighted pattern", R_{wp}	$R_{wp} = \sqrt{\frac{\sum w_m \left(Y_{o,m} - Y_{c,m}\right)^2}{\sum w_m {Y_{o,m}}^2}}$	$R_{wp}' = \sqrt{\frac{\sum w_m \left(Y_{o,m} - Y_{c,m}\right)^2}{\sum w_m \left(Y_{o,m} - Bkg_m\right)^2}}$
"R-weighted pattern", R_{wp}' (background corrected)		
"R-expected", R_{exp}	$R_{exp} = \sqrt{\frac{\sum M - P}{\sum w_m Y_{o,m}^2}}$	$R_{exp}' = \sqrt{\frac{\sum M - P}{\sum w_m \left(Y_{o,m} - Bkg_m\right)^2}}$
"R-expected", R_{exp}' (background corrected)		

"Goodness of fit", GOF

$$GOF = chi^2 = \frac{R_{wp}}{R_{\exp}} = \sqrt{\frac{\sum w_m \left(Y_{o,m} - Y_{c,m}\right)^2}{M - P}}$$

"R-Bragg", R_B

$$R_B = \frac{\sum \left| I_{"o",k} - I_{c,k} \right|}{\sum I_{"o",k}}$$

"Durbin-Watson statistic", d

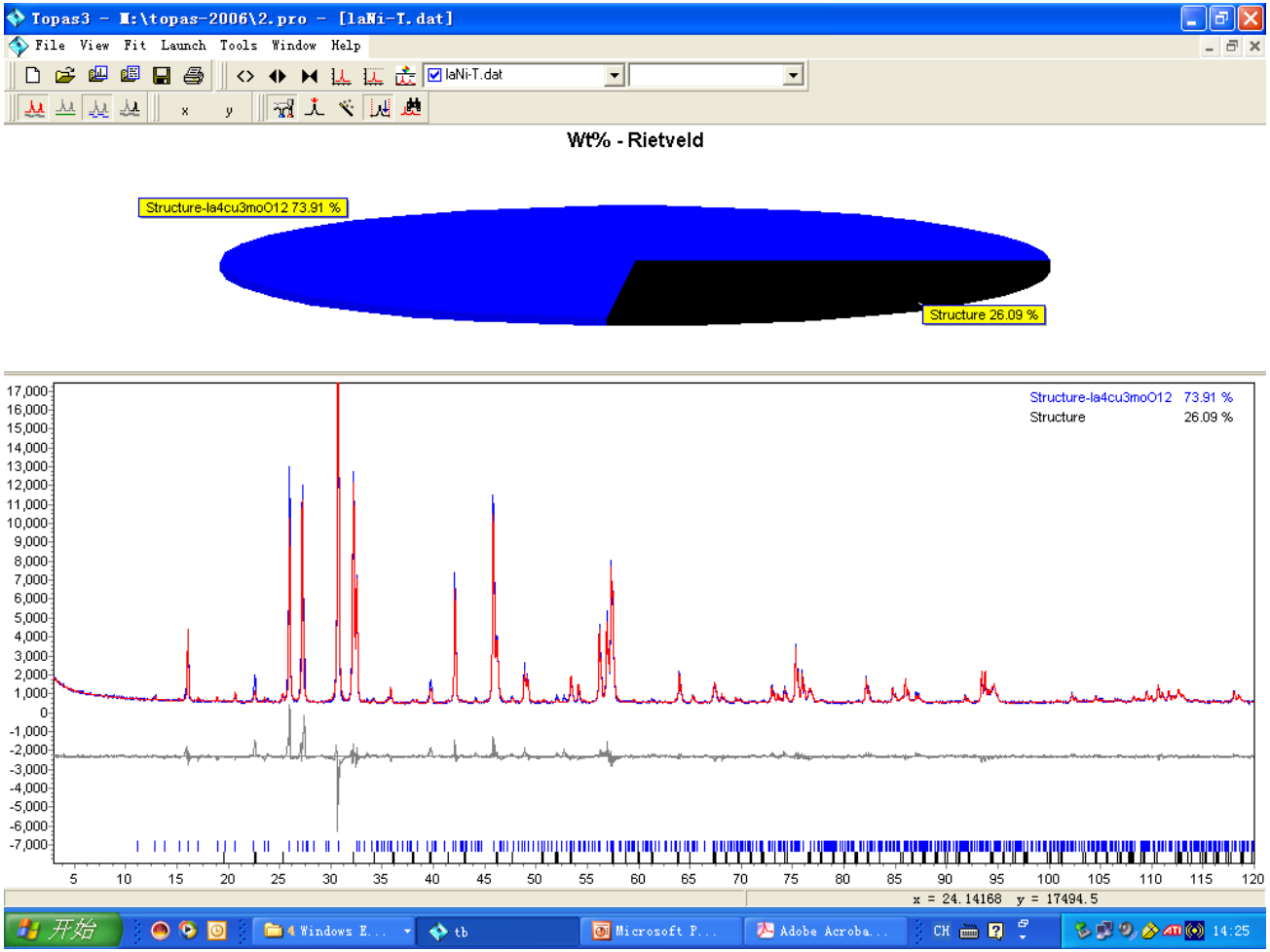
Durbin & Watson, 1971;
Hill & Flack, 1987

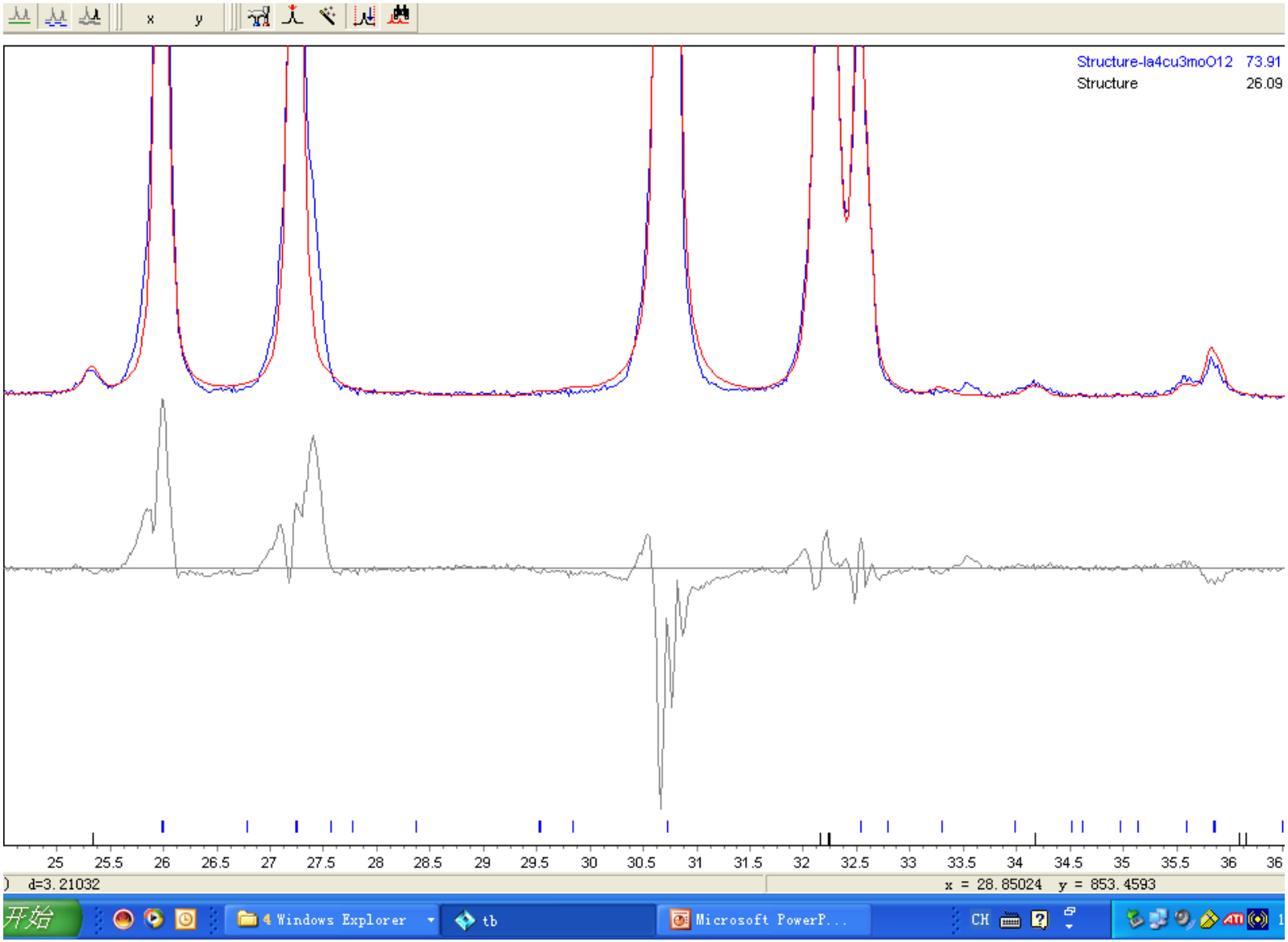
$$d = \frac{\sum_{m=2}^{M} \left(\Delta Y_m - \Delta Y_{m-1}\right)}{\sum_{m=1}^{M} \left(\Delta Y_m\right)^2}; \qquad \Delta Y_m = Y_{o,m} - Y_{c,m}$$

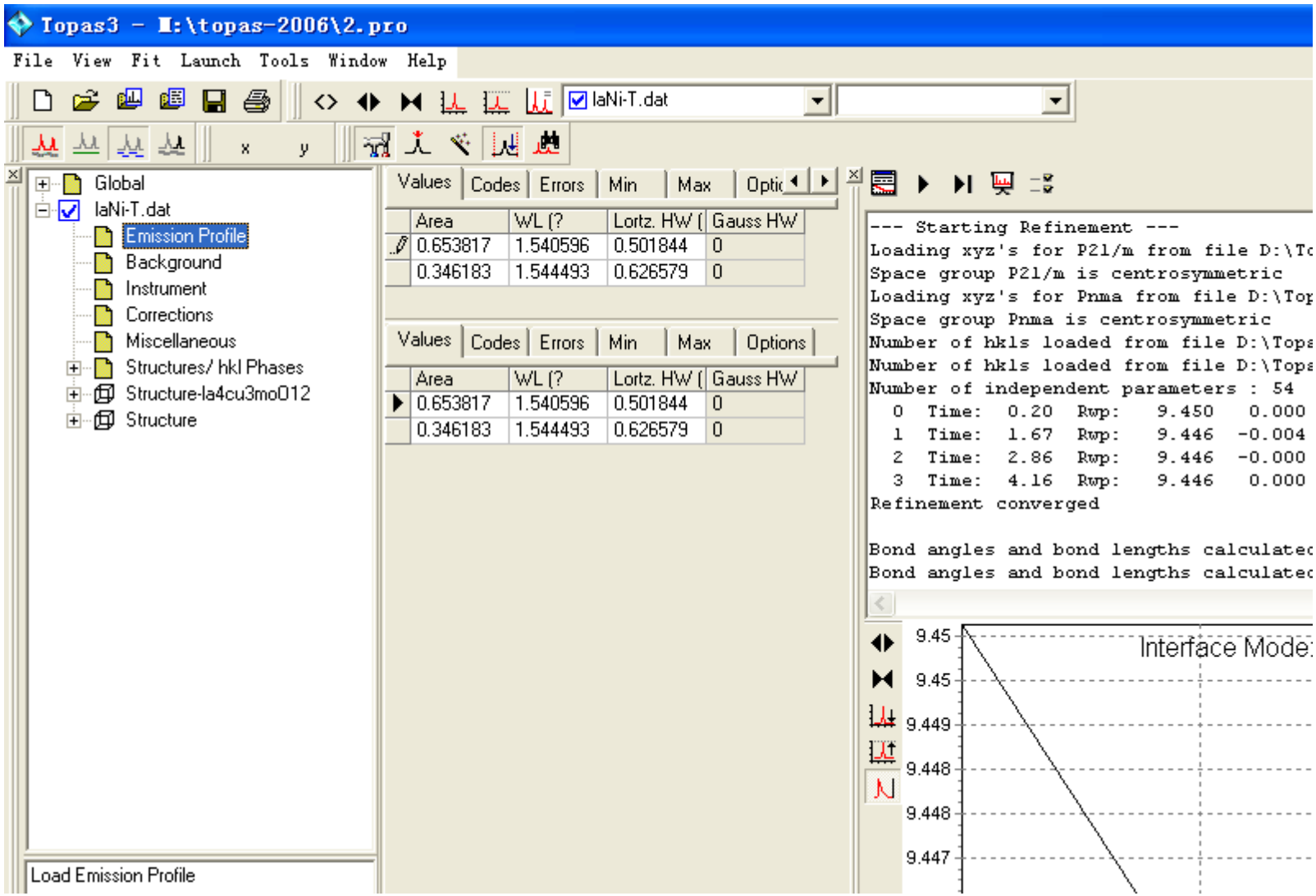
Table 5-2: Criteria of fit used in TOPAS. $Y_{o,m}$ and $Y_{c,m}$ are the observed and calculated data respectively at data point m, Bkg_m the background at data point m, M the number of data points, P the number of parameters, w_m the weighting given to data point m which for counting statistics is given by $w_m = 1/\sigma(Y_{o,m})^2$ where $\sigma(Y_{o,m})$ is the error in $Y_{o,m}$, and $I_{"o",k}$ and $I_{c,k}$ the "observed" and calculated intensities of the kth reflection.

结构精修

两相的精修


Topas3 - I:\topas-2006\2.pro - [laNi-T.dat]
File View Fit Launch Tools Window Help
laNi-T.dat
Wt% - Rietveld
Structure-la4cu3moO12 73.91 %
Structure 26.09 %
Structure-la4cu3moO12 73.91 %
Structure 26.09 %
x = 24.14168 y = 17494.5
开始
Windows E...
tb
Microsoft P...
Adobe Acroba...
CH
14:25


x
y
Structure-la4cu3moO12 73.91
Structure 26.09
25
25.5
26
26.5
27
27.5
28
28.5
29
29.5
30
30.5
31
31.5
32
32.5
33
33.5
34
34.5
35
35.5
36
d=3.21032
x = 28.85024 y = 853.4593
开始
4 Windows Explorer
tb
Microsoft PowerP...
CH


Topas3 - I:\topas-2006\2.pro
File View Fit Launch Tools Window Help
laNi-T.dat
x y
Global
laNi-T.dat
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
Structure-la4cu3mo012
Structure
Values Codes Errors Min Max Optic
Area WL (? Lortz. HW (Gauss HW
0.653817 1.540596 0.501844 0
0.346183 1.544493 0.626579 0
Values Codes Errors Min Max Options
Area WL (? Lortz. HW (Gauss HW
0.653817 1.540596 0.501844 0
0.346183 1.544493 0.626579 0
--- Starting Refinement ---
Loading xyz's for P21/m from file D:\To
Space group P21/m is centrosymmetric
Loading xyz's for Pnma from file D:\Top
Space group Pnma is centrosymmetric
Number of hkls loaded from file D:\Tops
Number of hkls loaded from file D:\Tops
Number of independent parameters : 54
0 Time: 0.20 Rwp: 9.450 0.000
1 Time: 1.67 Rwp: 9.446 -0.004
2 Time: 2.86 Rwp: 9.446 -0.000
3 Time: 4.16 Rwp: 9.446 0.000
Refinement converged
Bond angles and bond lengths calculated
Bond angles and bond lengths calculated
9.45
9.45
9.449
9.448
9.448
9.447
Interface Mode
Load Emission Profile

物相鉴定

寻峰

数据库的使用

结构解析(二)

- **真实结构与结构的可表征性**
- 有关物理性质与结构的相关性
- 电子衍射等电镜技术
- 中子衍射

有关物理性质与结构的相关性

- 对称中心

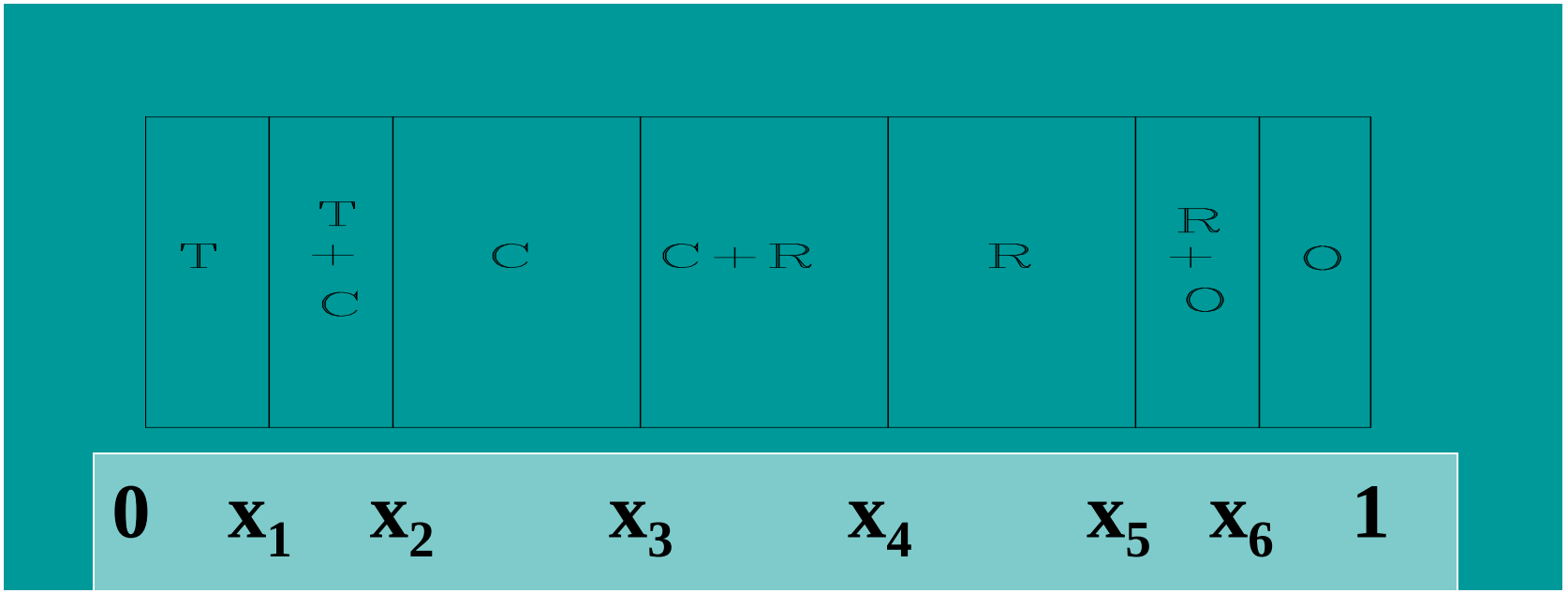
二阶非线性光学系数

铁电性

压电系数

发光

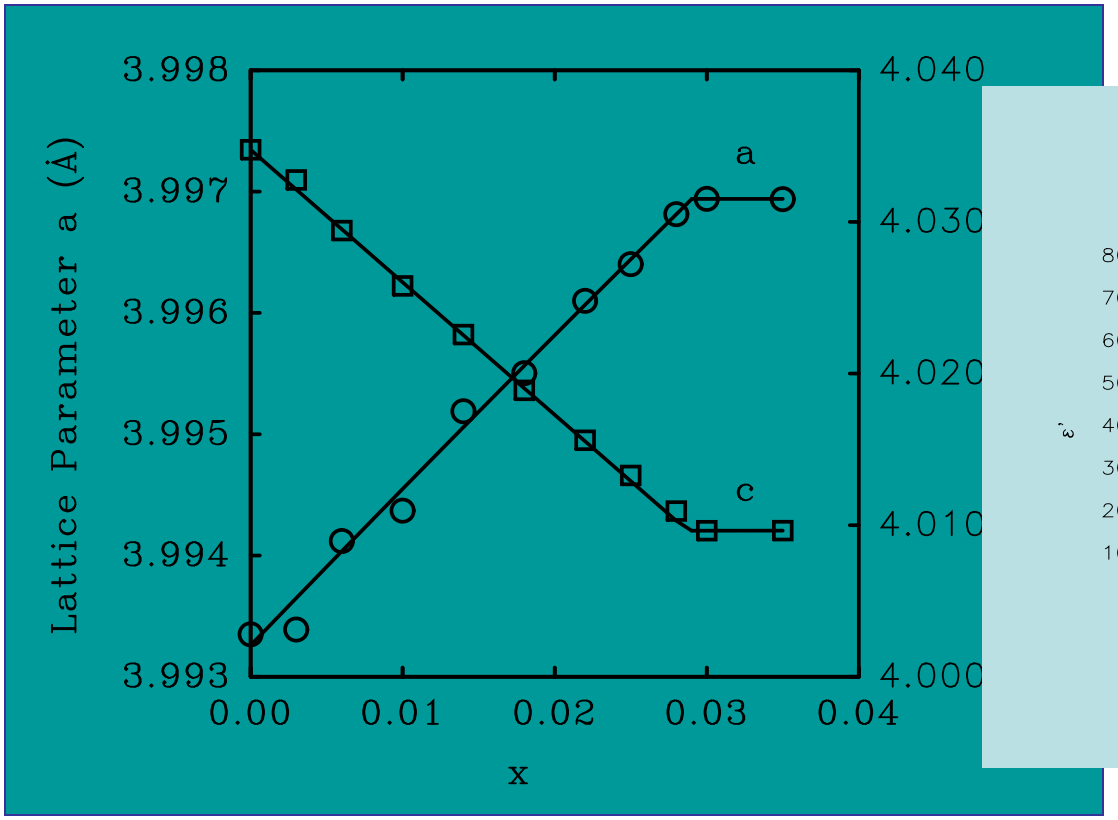
利用铁电性确定对称中心的不存在

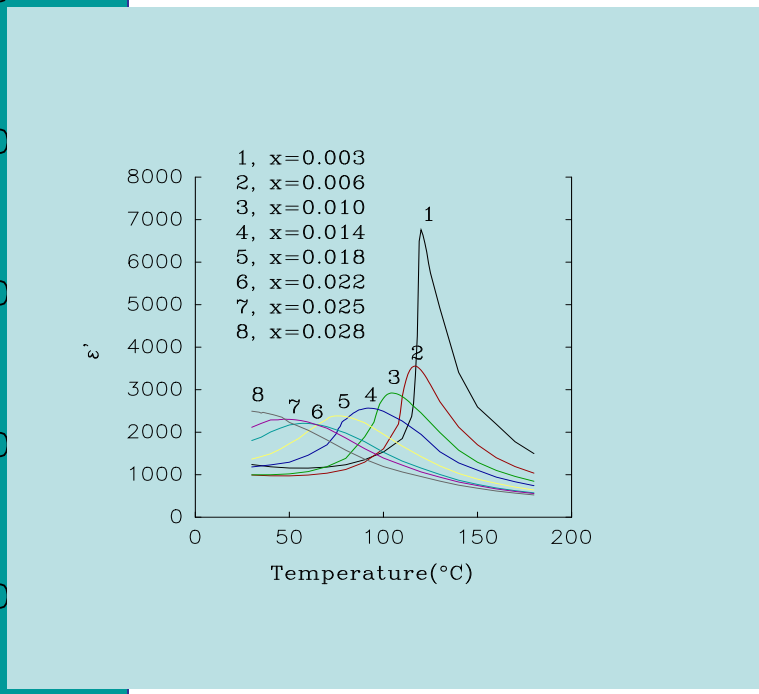


T, Tetragonal; C, Cubic; R, Rhombohedral; O, Orthorhombic.
X_1=0.029, X_2=0.0365, X_3=0.600, X_4=0.700, X_5=0.873, X_6=0.956.

$Ba_{1-x}La_xTi_{1-x}Cr_xO_3$ 的相关系示意图

四方固熔体$Ba_{1-x}La_xTi_{1-x}Cr_xO_3$的结构参数

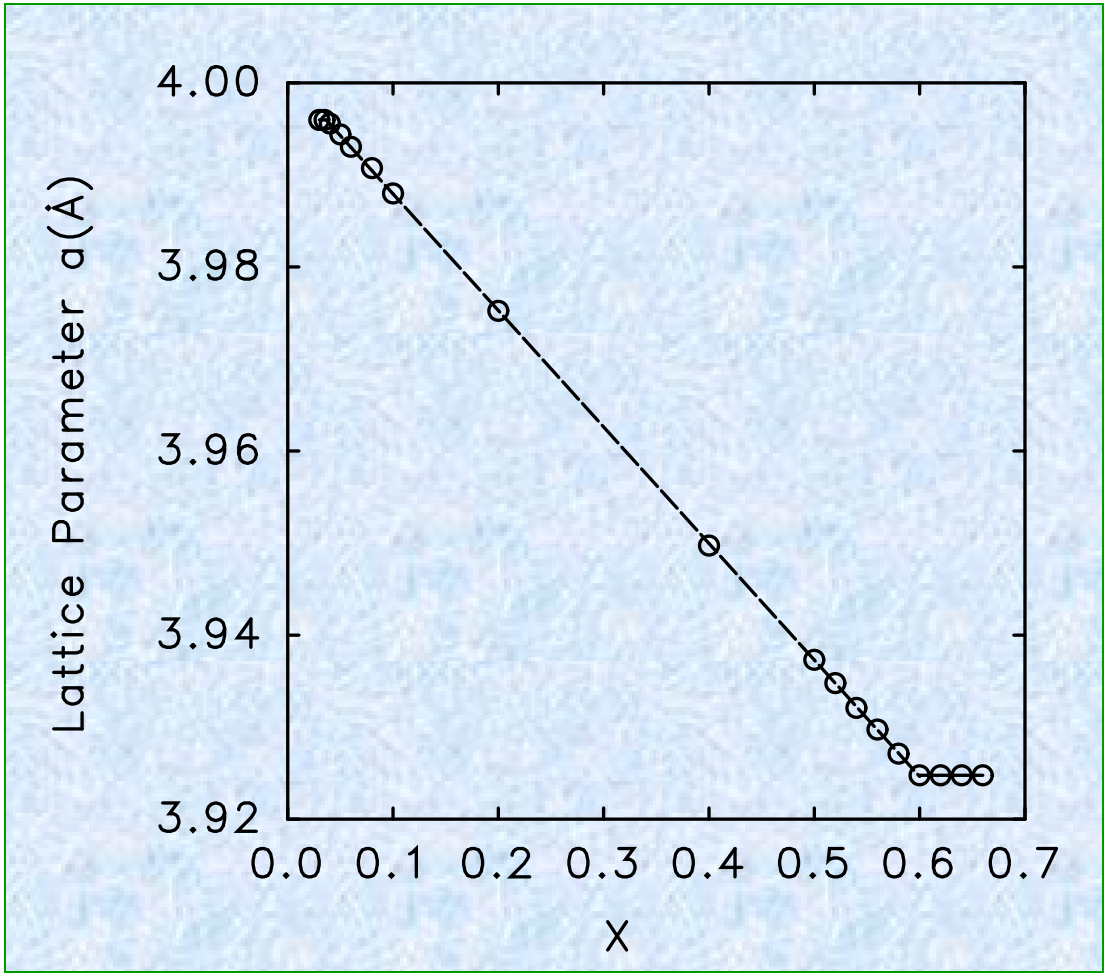




$0 \leqslant x \leqslant 0.029$

P4mm

立方固熔体$Ba_{1-x}La_xTi_{1-x}Cr_xO_3$的结构参数



$0.0365 \leqslant x \leqslant 0.600$

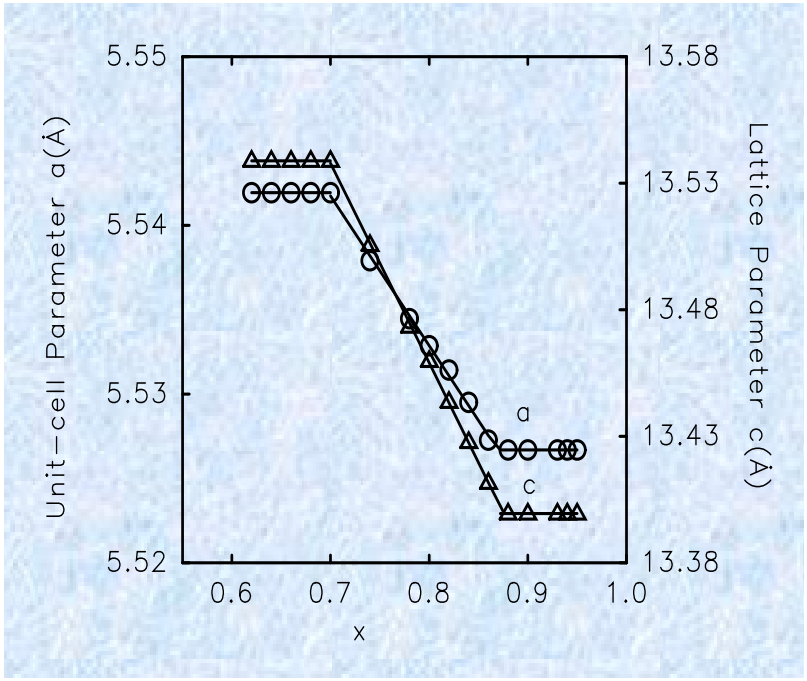
$Pm\bar{3}m$

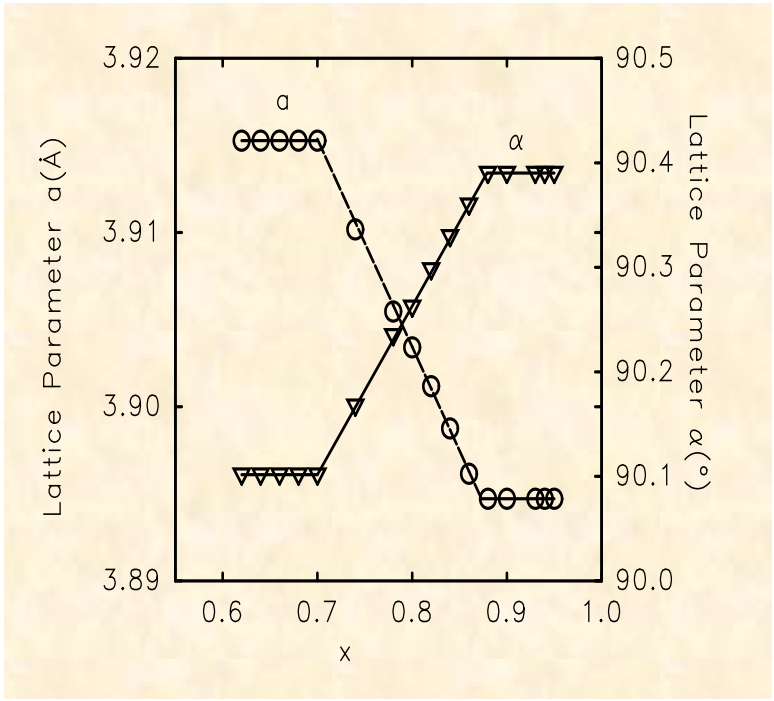
$R_{wp}<5.0\%$

$R_p<4.5\%$

三方固熔体$Ba_{1-x}La_xTi_{1-x}Cr_xO_3$的结构参数

$0.700 \leqslant x \leqslant 0.873$

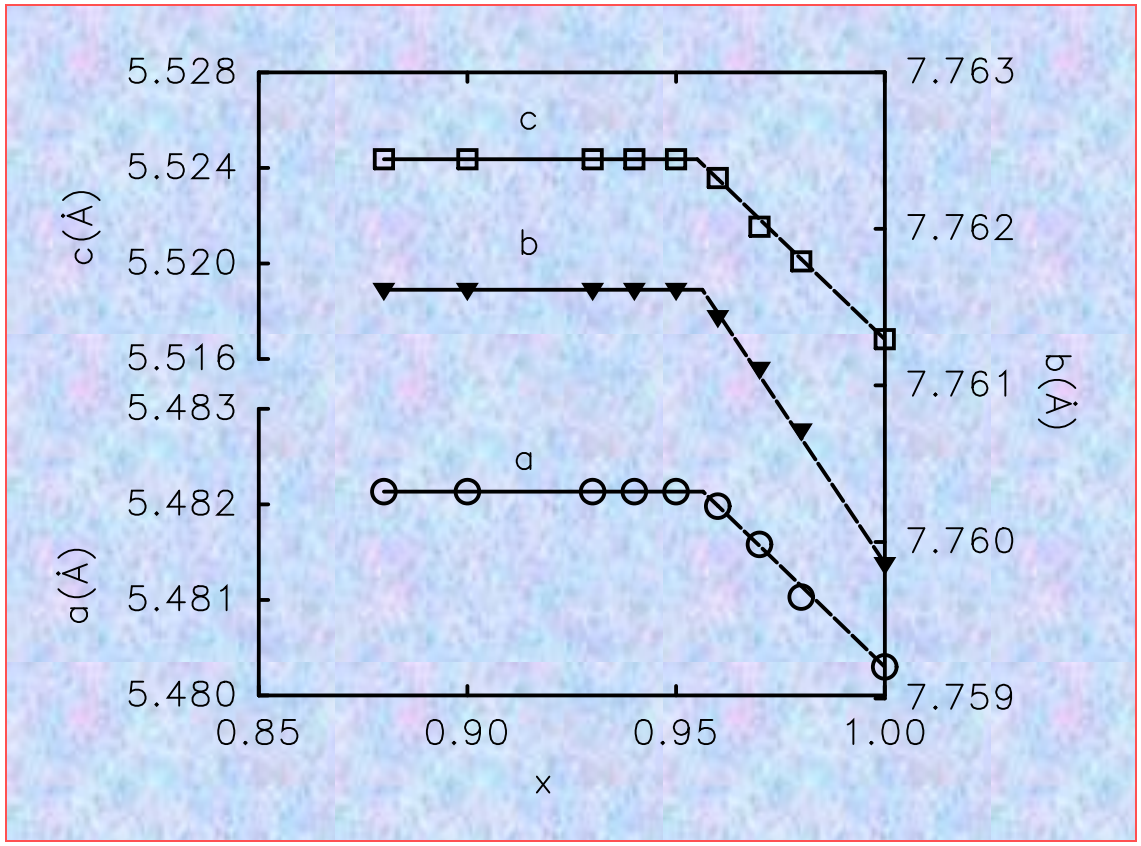




$R\bar{3}c$

$R_{wp}<2.5\%, R_p<2.2\%$

正交固熔体$Ba_{1-x}La_xTi_{1-x}Cr_xO_3$的结构参数



0. 956≤x≤1

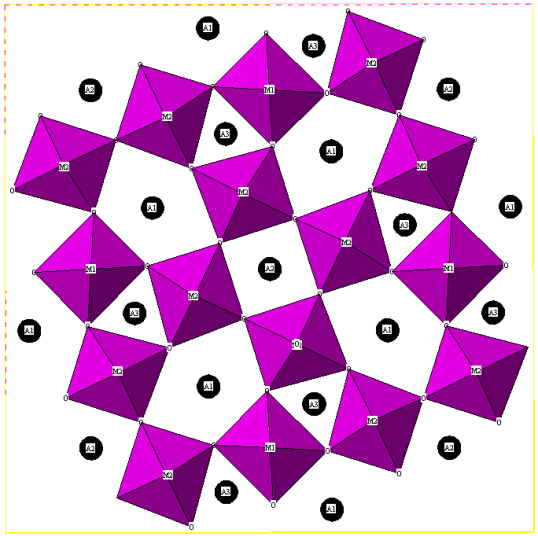
Pnma

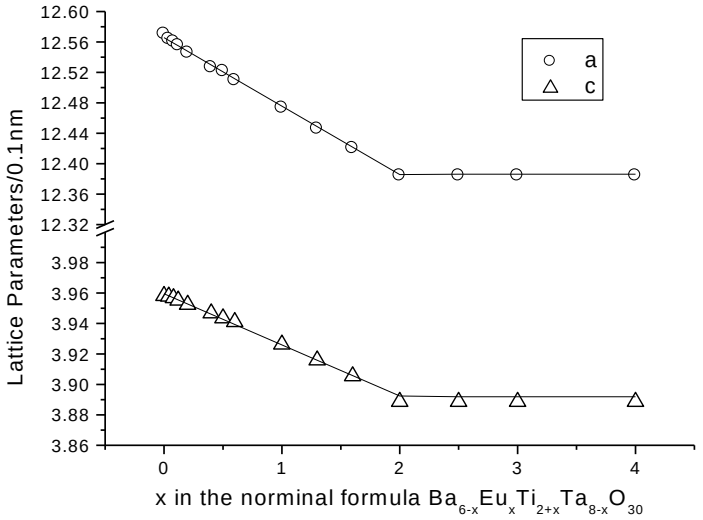
R_{wp}<2.4%

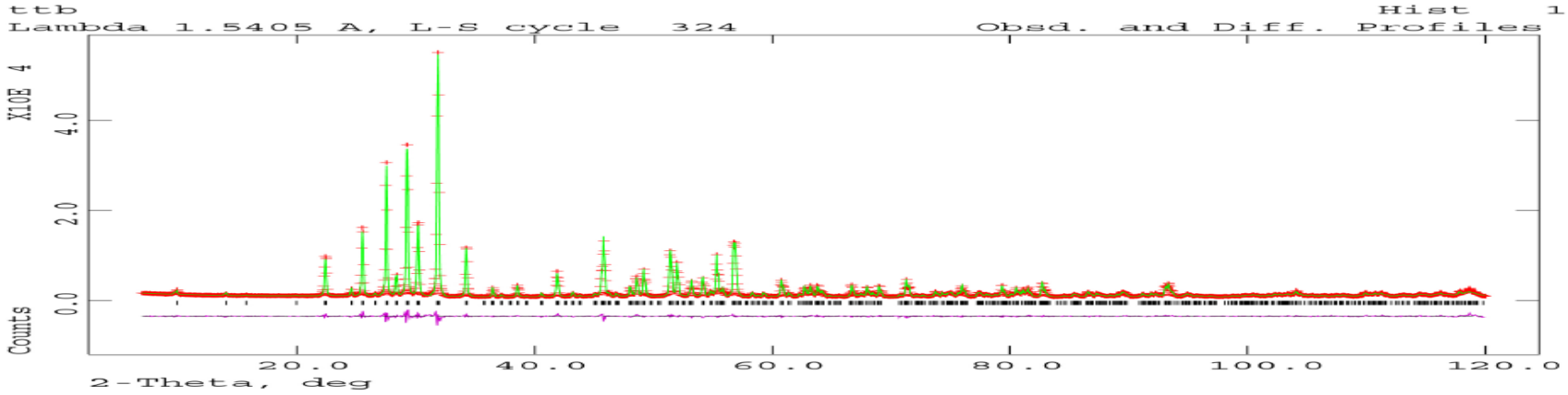
R_p<2.1%

利用发光特性确定对称中心的存在

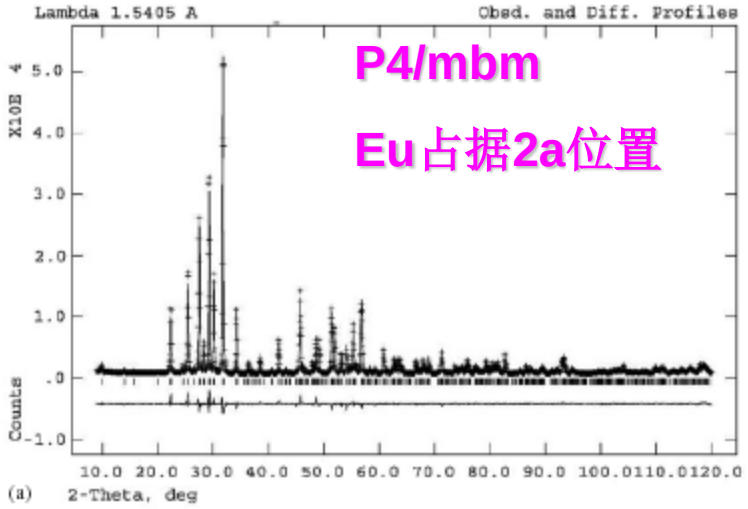
$Ba_{6-x}Eu_xTi_{2+x}Ta_{8-x}O_{30}$的结构问题 （对称性和占位问题）

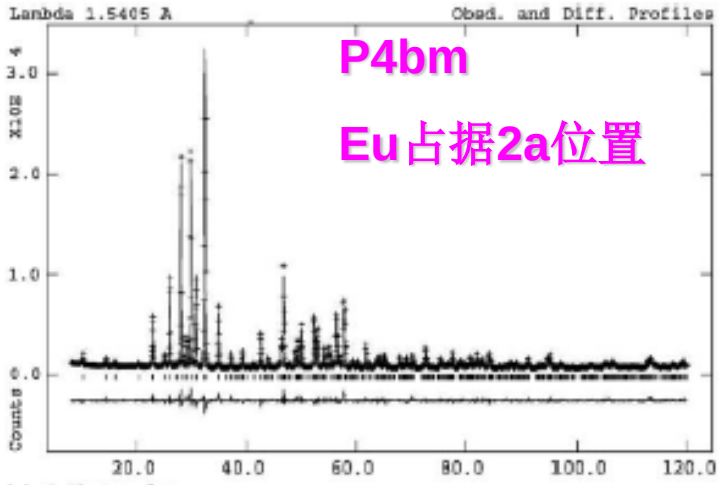


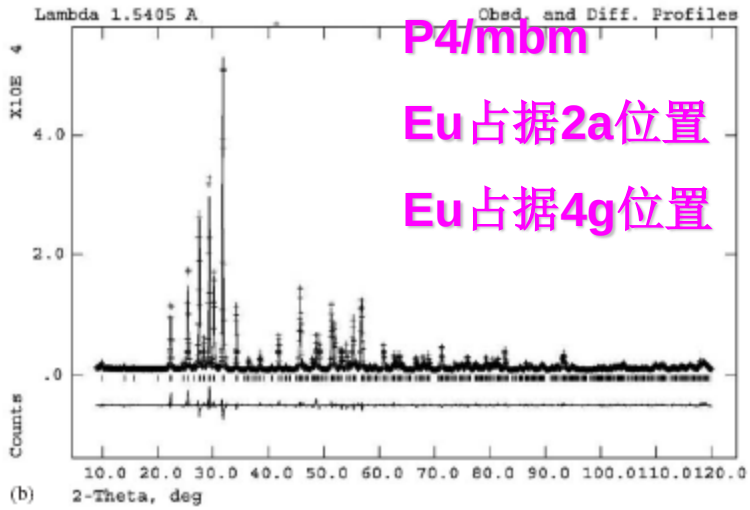


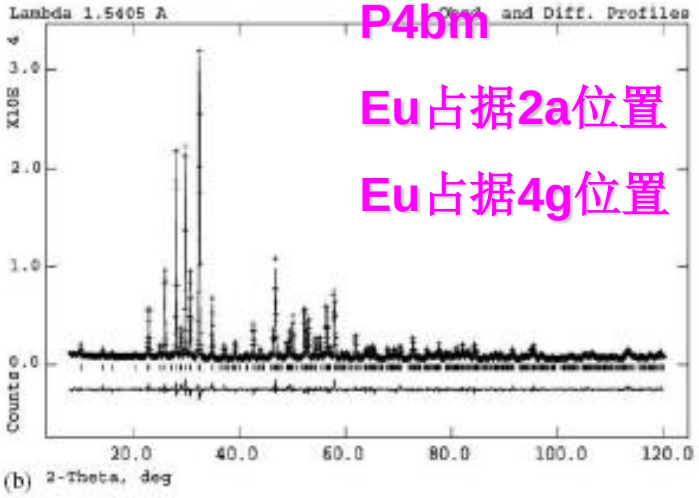


对称性和占位问题

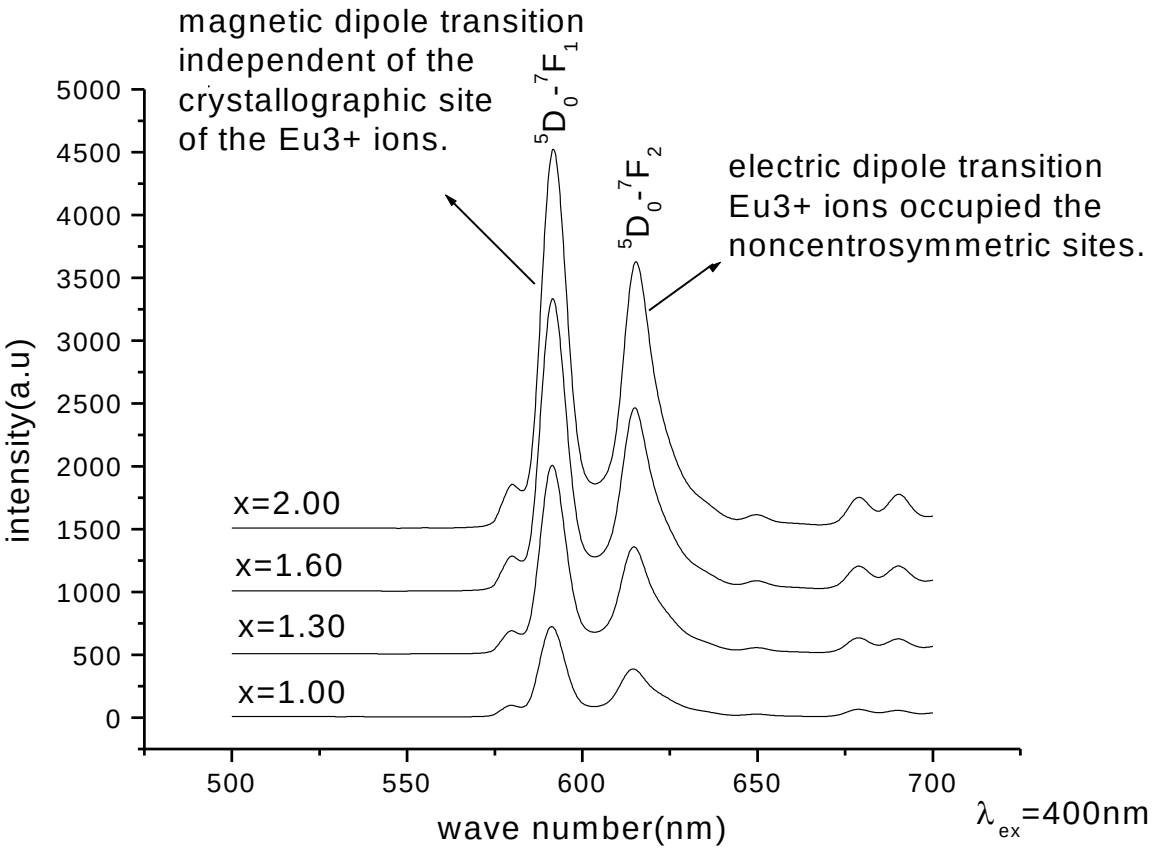

Lambda 1.5405 A
Obsd. and Diff. Profiles
X10E 4
Counts
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0110.0120.0
(a) 2-Theta, deg
P4/mbm
Eu占据2a位置


Lambda 1.5405 A
Obsd. and Diff. Profiles
X10E 4
Counts
20.0 40.0 60.0 80.0 100.0 120.0
P4bm
Eu占据2a位置


Lambda 1.5405 A
Obsd. and Diff. Profiles
X10E 4
Counts
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0110.0120.0
(b) 2-Theta, deg
P4/mbm
Eu占据2a位置
Eu占据4g位置

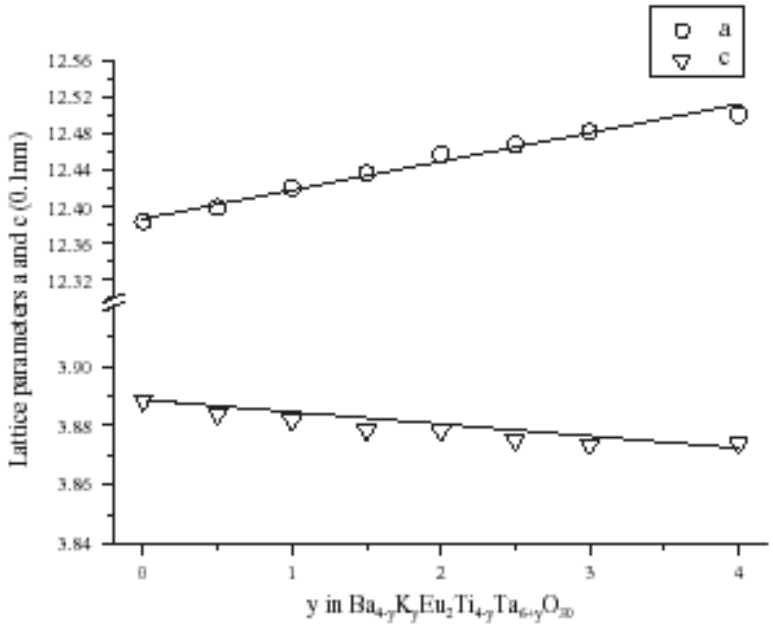

Lambda 1.5405 A
X10E 4
Counts
20.0 40.0 60.0 80.0 100.0 120.0
(b) 2-Theta, deg
P4bm
Eu占据2a位置
Eu占据4g位置

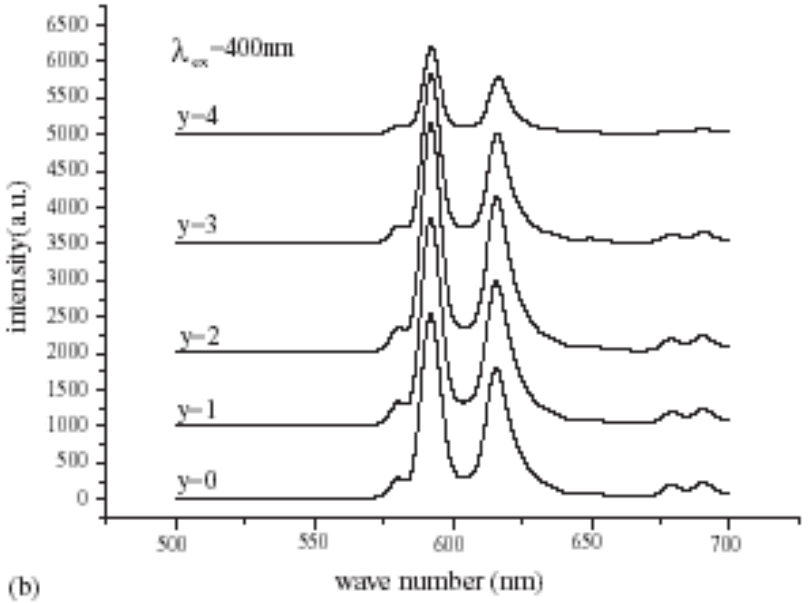
解决方案



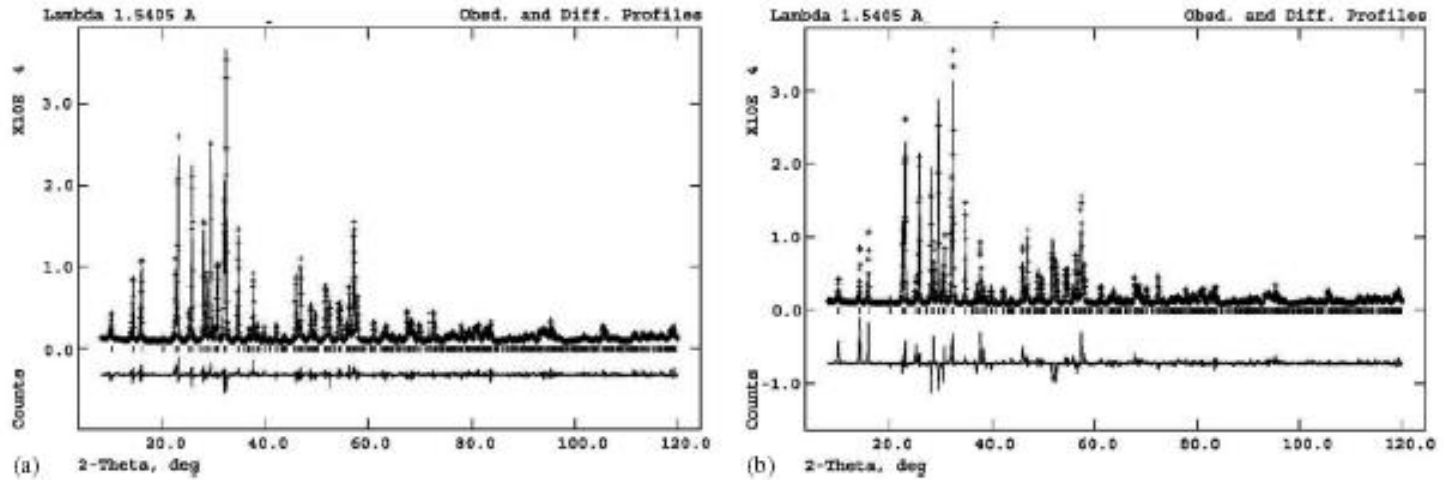
Emission spectra of the series $Ba_{6-x}Eu_xTi_{2+x}Ta_{8-x}O_{30}$

解决方案


a
c
Lattice parameters a and c (0.1nm)
12.56
12.52
12.48
12.44
12.40
12.36
12.32
3.90
3.88
3.86
3.84
0
1
2
3
4
y in $Ba_{4-y}K_yEu_2Ti_{4-y}Ta_{6+y}O_{30}$


λ_{ex}=400nm
y=4
y=3
y=2
y=1
y=0
intensity(a.u.)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
500
550
600
650
700
wave number (nm)
(b)

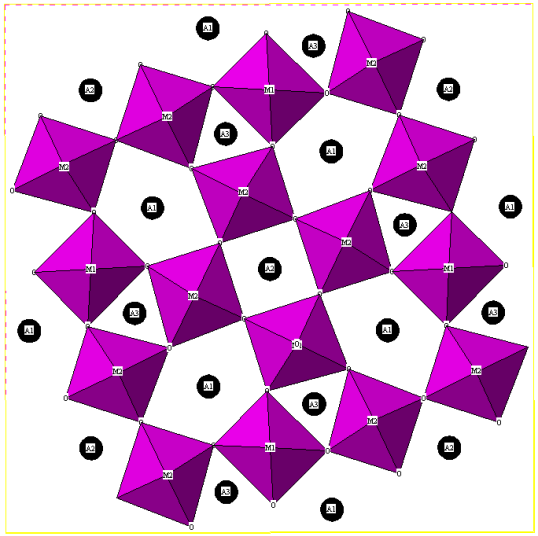
解决方案

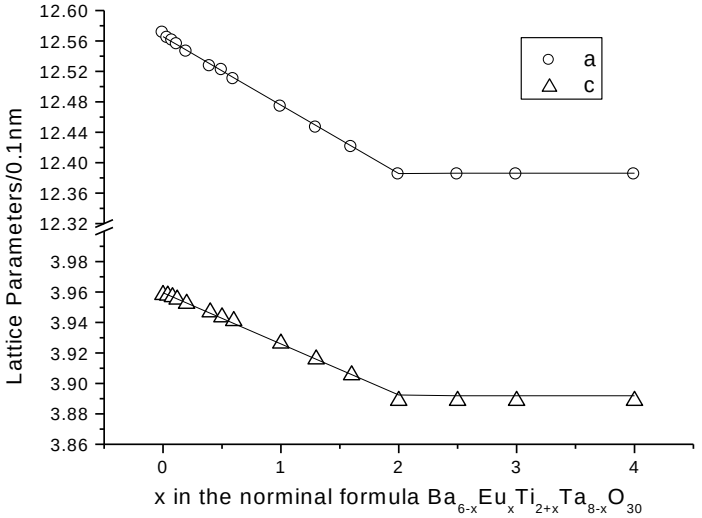


Atom	Coordination	Occupation	
		Model a	Model b
K/Eu1 2a	0, 0, 0	0.00/1.00	0.666/0.333
K/Eu2 4g	0.1698(1), 0.6698(1), 0	1.00/0.00	0.666/0.333
Ta1	0, 1/2, 1/2	1.00	1.00
Ta2	0.0758(1), 0.2140(1), 1/2	1.00	1.00
O1	0, 1/2, 0	1.00	1.00
O2	0.2808(1), 0.7808(1), 1/2	1.00	1.00
O3	0.0735(1), 0.1979(1), 0	1.00	1.00
O4	0.3463(1), 0.0051(1), 1/2	1.00	1.00
O5	0.1395(1), 0.0633(1), 1/2	1.00	1.00
R-values		$R_{wp} = 8.0\%$, $R_p = 6.0\%$	$R_{wp} = 16.7\%$, $R_p = 11.8\%$
Reduced CHI**2		11.9	52.2

[a] The basic crystallography parameters are the same: space group $P4/mbm$ with $a = 12.5006(1)$ (Å), $c = 3.8742(1)$ (Å).

结论：$Ba_{6-x}Eu_xTi_{2+x}Ta_{8-x}O_{30}$的结构





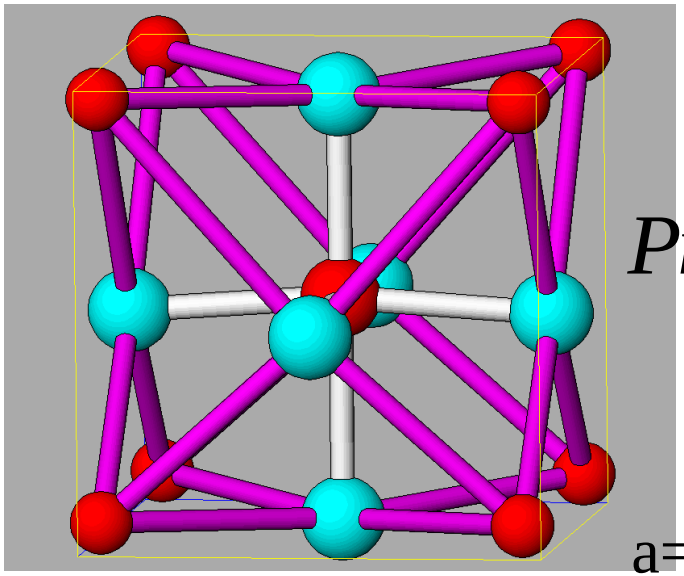
空间群: P4/mbm

Eu占据2a位置

X最大值为2.0

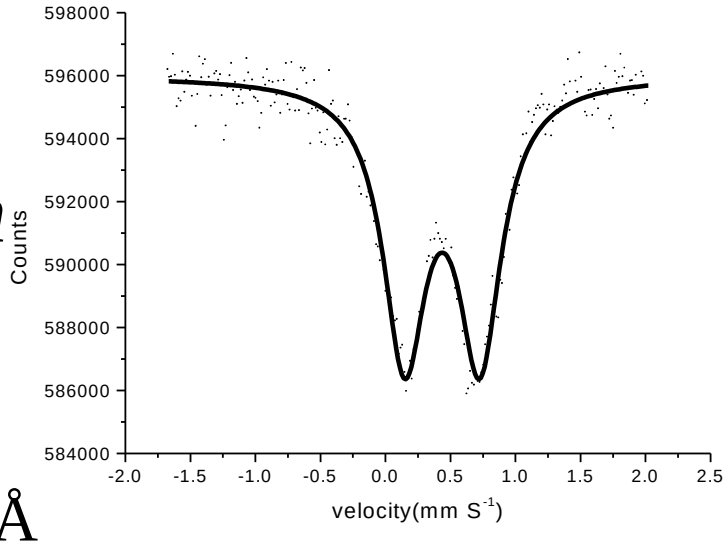
$Ba(Fe_{1/2}Ta_{1/2})O_3$ 的结构与问题

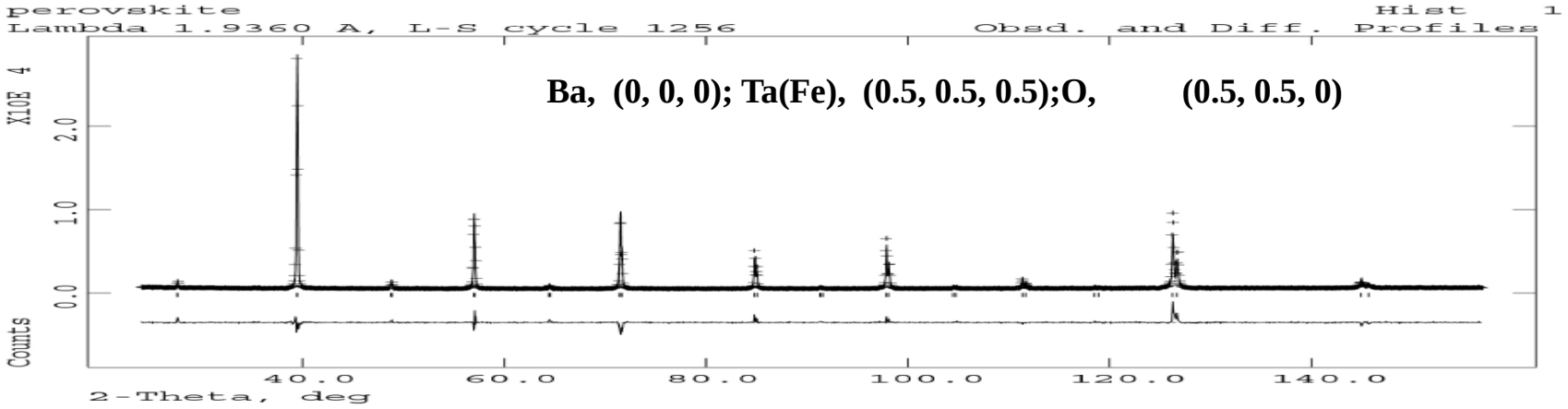
(汇聚束)电子衍射



$Pm\bar{3}m$

a=4.065Å

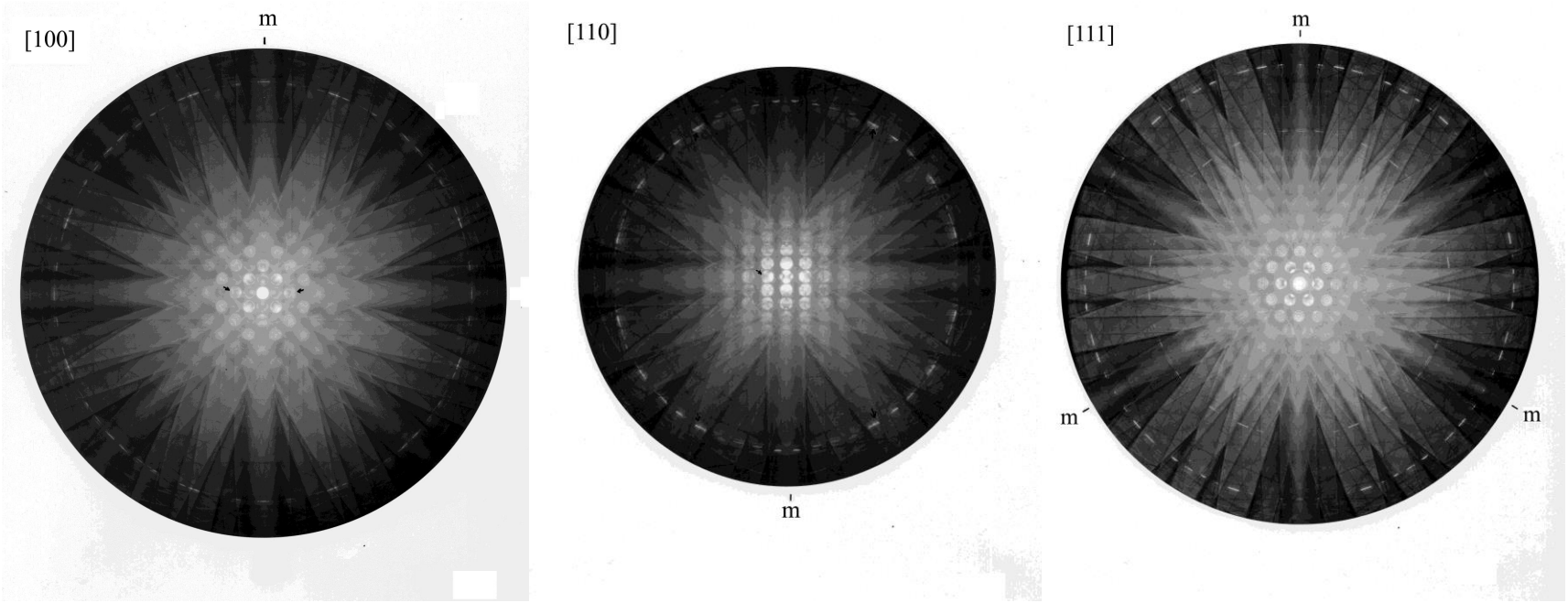




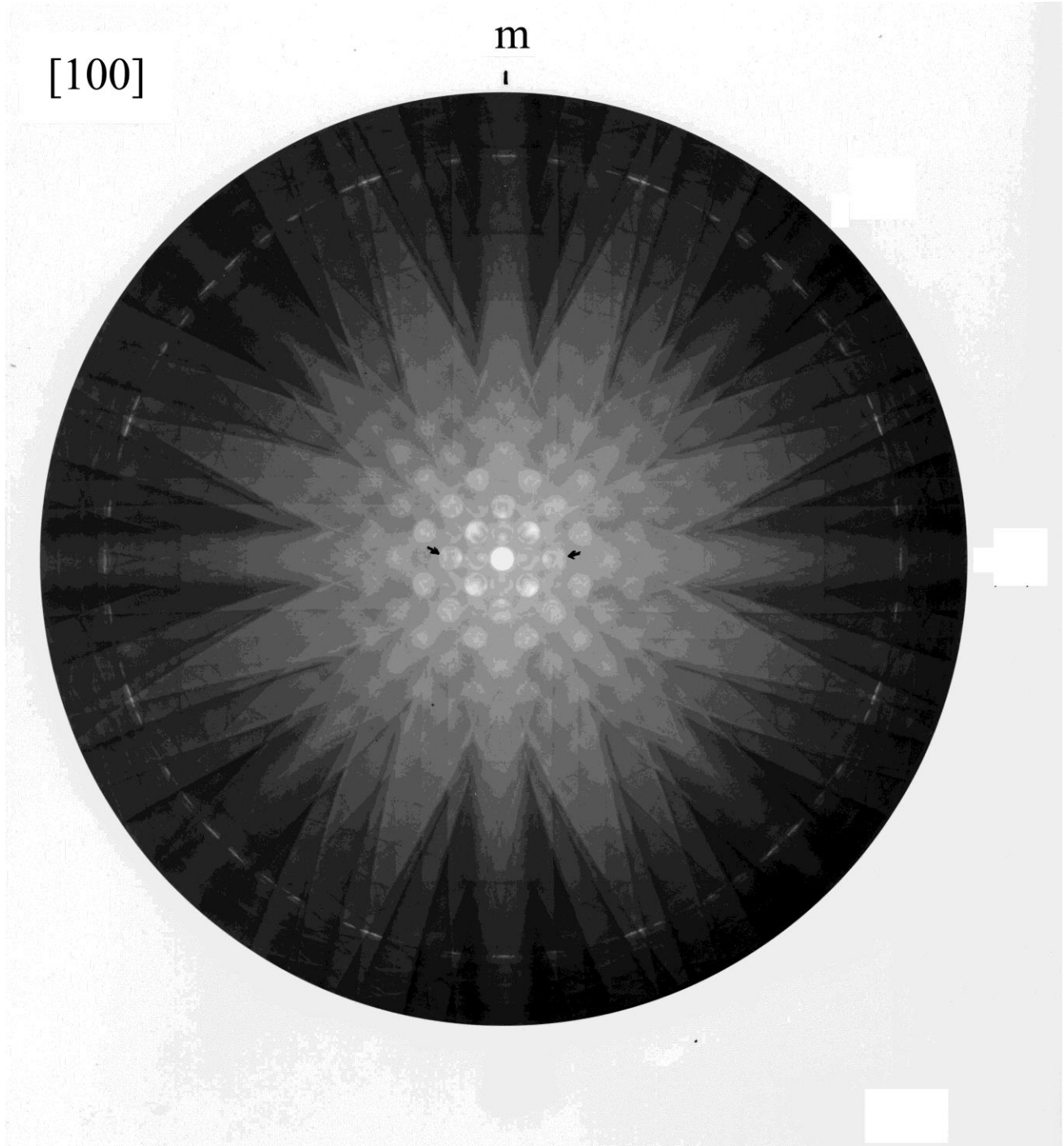
$Ba(Fe_{1/2}Ta_{1/2})O_3$ 的可能结构

Space Group	Pm-3m	R3m	P4mm	Cm	P1
R factor	R_p=4.37%, R_{wp}=5.99%	R_p=4.38%, R_{wp}=5.92%	R_p=4.37%, R_{wp}=5.89%	R_p=4.28%, R_{wp}=5.66%	R_p=4.37%, R_{wp}=5.84%
Lattice Parameter	a=4.0609(1) Å	a=5.7414(1) Å c=7.0317(1) Å	a=4.0611(1) Å c=4.0594(1) Å	a=5.7426(1)Å b=5.7418(1)Å c=4.0590(1) Å β=89.995(1)	a=4.0623(1) Å b=5.7416(1) Å c=4.0611(1) Å α=90.023(1) β=89.993(1) γ=135.012(1)
Ba	0, 0, 0*	0, 0,0*	0, 0, 0*	0, 0, 0*	0, 0, 0*
Ta (Fe)	0.5, 0.5, 0.5	0, 0, 0.5208(1)	0.5, 0.5, 0.5252(1)	0.4831(1), 0, 0.4763(1)	-0.0180(1), 0.4813(1), 0.4744(1)
O1	0.5, 0, 0.5	0.3400(1), 0.1700(1), 0.6876(1)	0.5, 0, 0.4913	0.4762(1), 0, 0.0019(1)	0.0108(1), 0.4737(1), 0.0115(1)
O2			0.5, 0.5, 0.0042(1)	0.2239(1), 0.2474(1), 0.4684(1)	0.4763(1), 0.5081(1), 0.4830(1)
O3					0.5667(1), 0.0171(1), 0.4854(1)

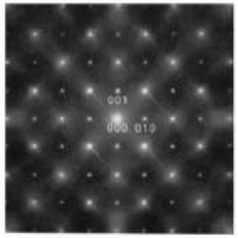
汇聚束电子衍射[CBED]



R3m　　P3m1


[100]
m

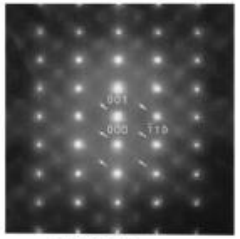
电子衍射



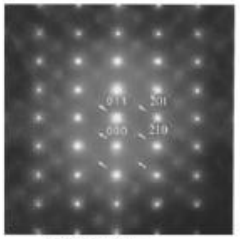
[100] R3m
a=b=c=4.061Å
α=β=γ=90

[211] R3m
a=b=5.741Å, c=7.032Å
α=β=90, γ=120

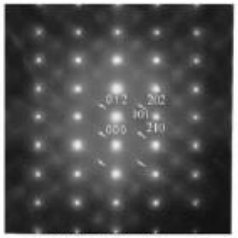
[421] P3m1
a=b=5.741Å, c=7.032Å
α=β=90, γ=120



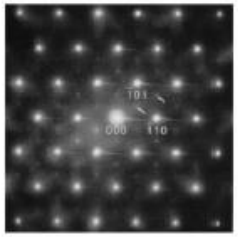
[110] R3m
a=b=c=4.061Å
α=β=γ=90



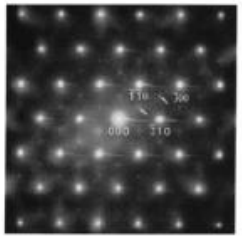
[122] R3m
a=b=5.741Å, c=7.032Å
α=β=90, γ=120



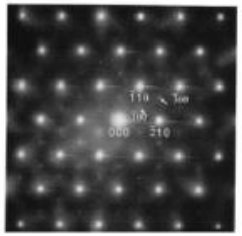
[242] P3m1
a=b=5.741Å, c=14.064Å
α=β=90, γ=120



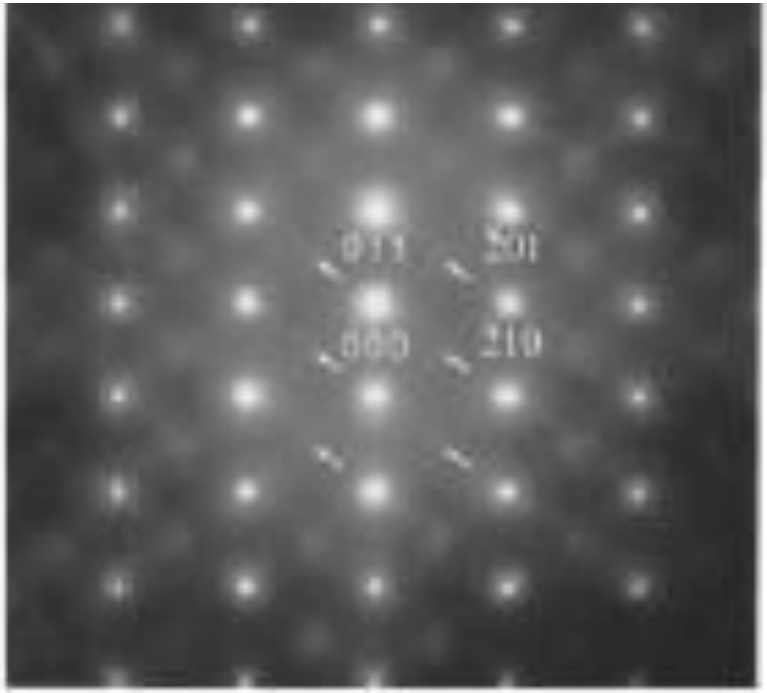
[111] R3m
a=b=c=4.061Å
α=β=γ=90



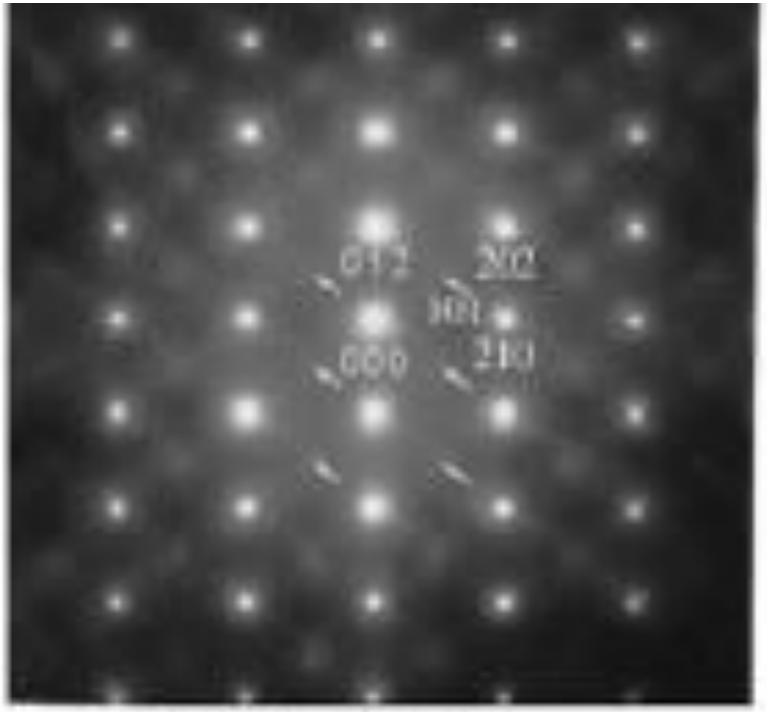
[001] R3m
a=b=5.741Å, c=7.032Å
α=β=90, γ=120



[001] P3m1
a=b=5.741Å, c=14.064Å
α=β=90, γ=120



[122] R3m
a=b=5.741Å, c=7.032Å



[242] P3m1
a=b=5.741Å, c=14.064Å

$Ba(Fe_{1/2}Ta_{1/2})O_3$ 的结构最终结论

Space group	$P3m1$
Lattice parameter (Å)	$a = 5.7414(1)$, $c = 14.0634(1)$
Cell volume (Å^3)	401.473(7)
Ba1[a]	0, 0, 0
Ba2	0, 0, 0.4999(1)
Ba3	1/3, 2/3, 0.8331(1)
Ba4	1/3, 2/3, 0.3331(1)
Ba5	2/3, 1/3, 0.6663(1)
Ba6	2/3, 1/3, 0.1663(1)
Ta/Fe1	0, 0, 0.7594(1)
Ta/Fe2	0, 0, 0.2595(1)
Ta/Fe3	1/3, 2/3, 0.5929(1)
Ta/Fe4	1/3, 2/3, 0.0930(1)
Ta/Fe5	2/3, 1/3, 0.9265(1)
Ta/Fe6	2/3, 1/3, 0.4267(1)
O1	0.1633(1), 0.8367(1), 0.6767(1)
O2	0.1633(1), 0.8367(1), 0.1767(1)
O3	0.4967(1), 0.5033(1), 0.0101(1)
O4	0.4967(1), 0.5033(1), 0.5101(1)
O5	0.8300(1), 0.1700(1), 0.8434(1)
O6	0.8200(1), 0.1700(1), 0.3434(1)
R factor	$R_{wp} = 0.061$, $R_p = 0.045$

[a] The Ba1 atom has been chosen as origin.

$La_4Cu_{3-x}Zn_xMoO_{12}$

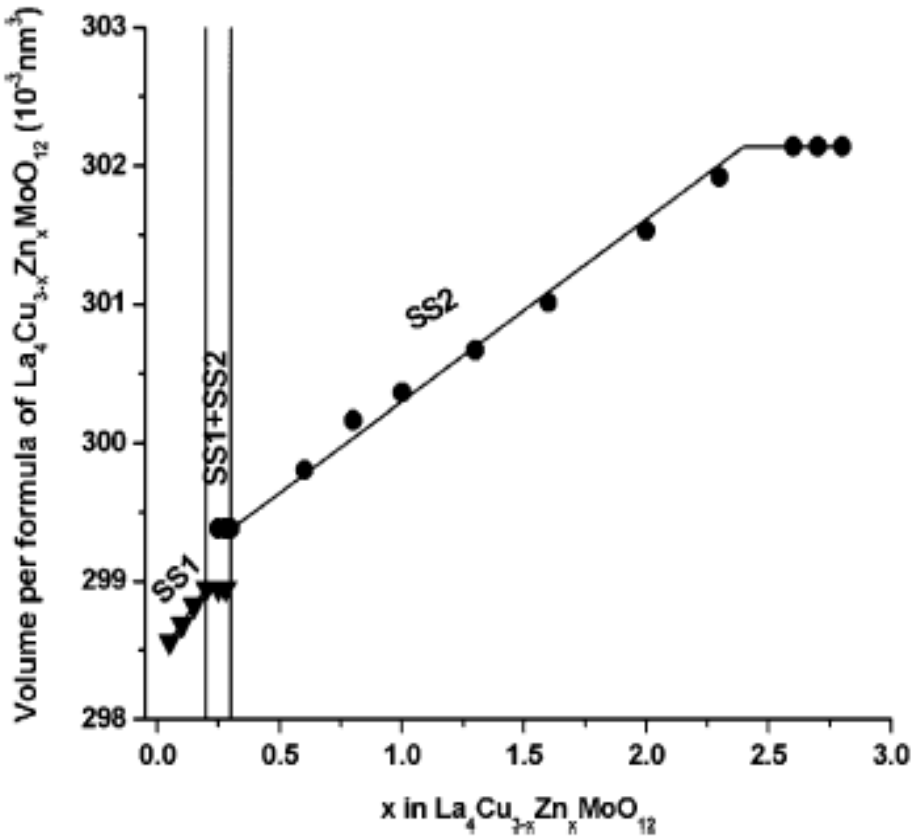


Figure 1. Unit cell volume as a function of the composition of $La_4Cu_{3-x}Zn_xMoO_{12}$; the solid solution SS1 is in the range of $0.05 \leq x \leq 0.20$, SS2 is in the range of $0.30 \leq x \leq 2.40$, and between consists of a two-phase region.

Pmnm, $P2_1/m$

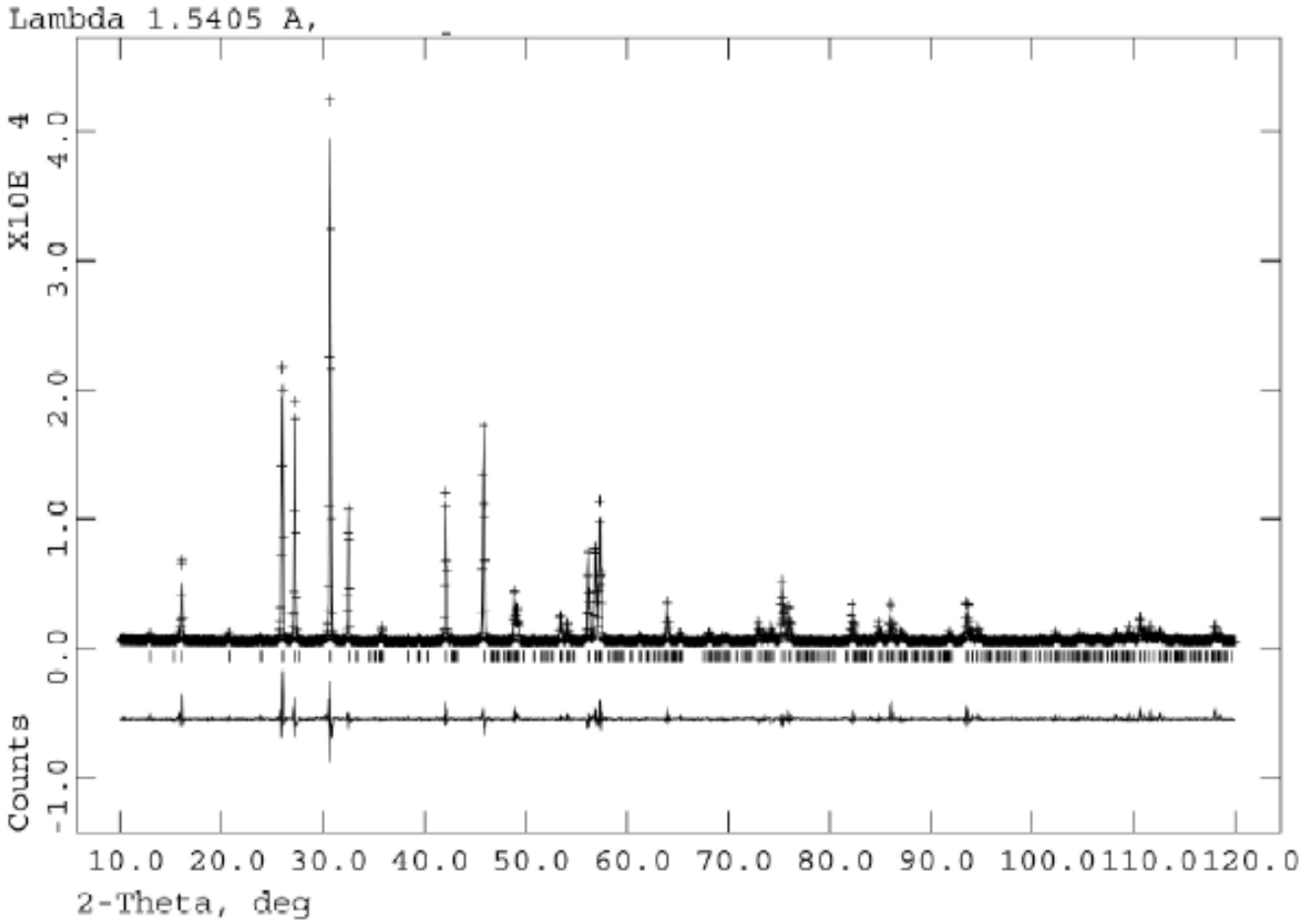


Figure S2 Rietveld plot of the X-ray powder diffraction pattern for $La_4Cu_{2.90}Zn_{0.10}MoO_{12}$.

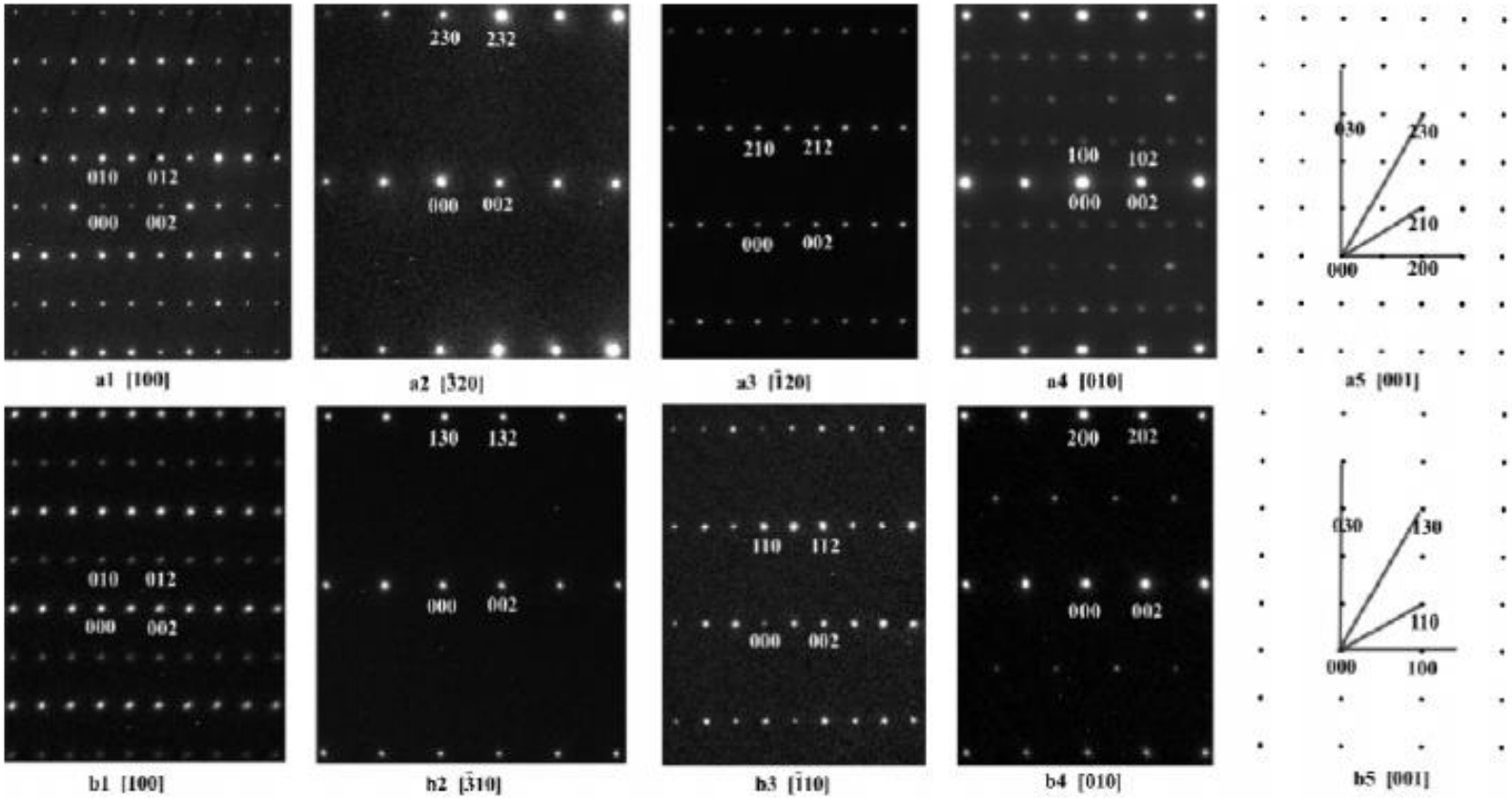
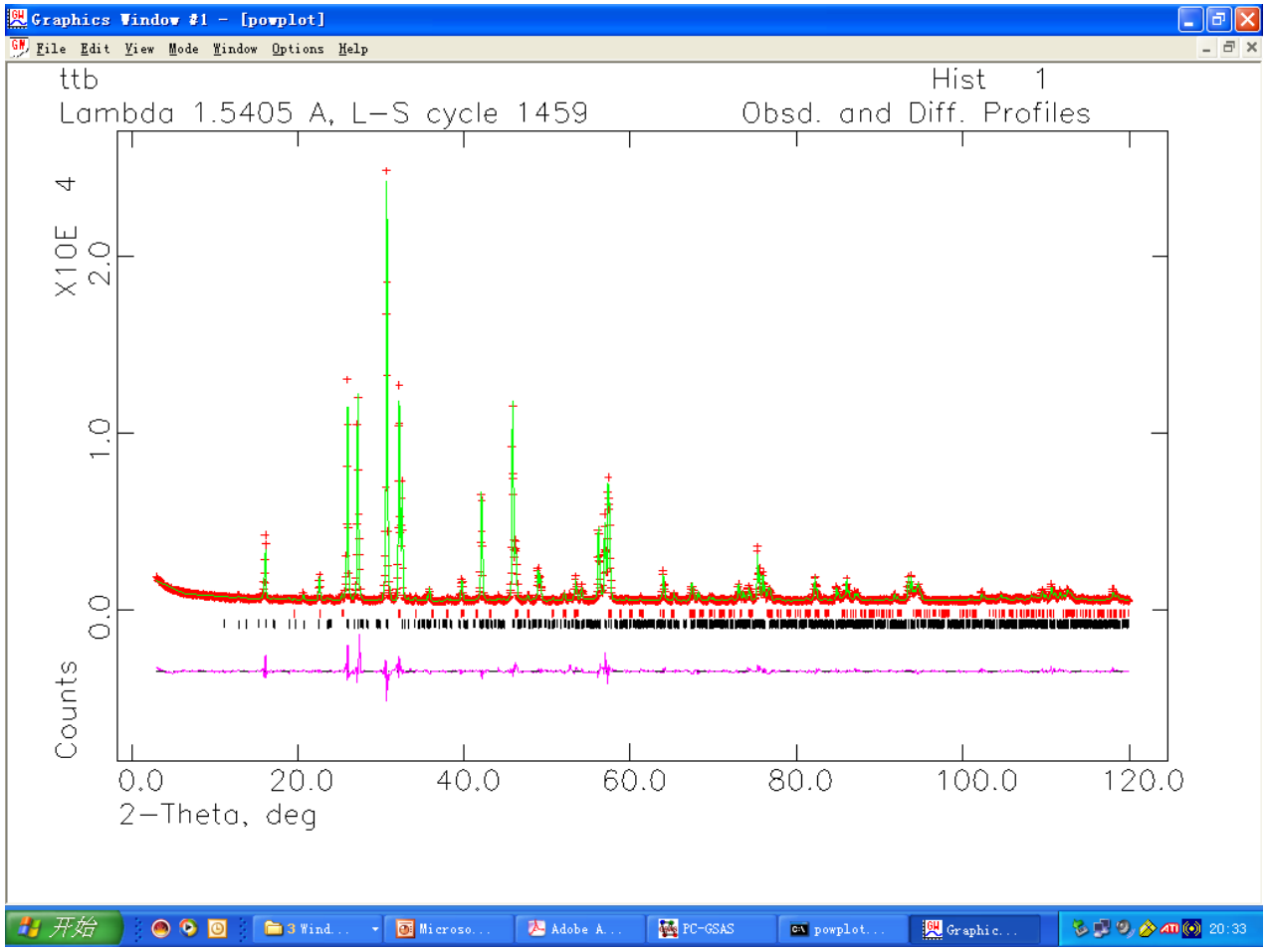


Figure 2. SAED patterns of $La_4Cu_3MoO_{12}$ (*a*1, *a*2, *a*3, *a*4, *a*5) and $La_4Cu_{2.9}Zn_{0.1}MoO_{12}$ (*b*1, *b*2, *b*3, *b*4, *b*5). *a*1, *a*2; *a*3, *a*4; *b*1, *b*2; and *b*3, *b*4, are the pair patterns when the samples rotate about the *c*-axis in 30° steps. *a*5 and *b*5 are the calculated patterns from *a*1, *a*2, *a*3, *a*4 and *b*1, *b*2, *b*3, *b*4, respectively, to show the difference of the two phases.

一般性问题

- 单一相的确定
- 杂相峰、超结构峰、非公度峰
- ……

杂相峰

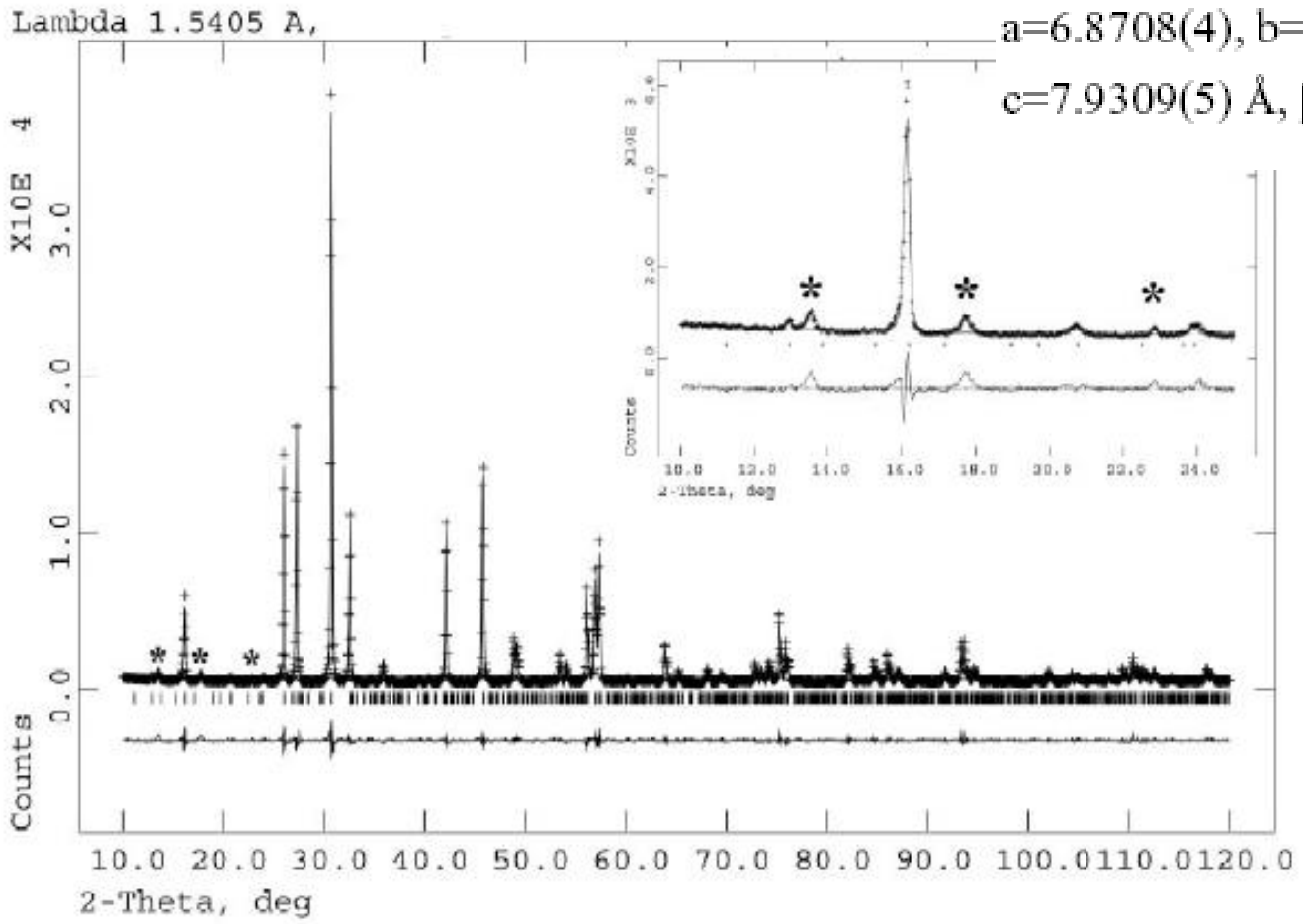

Graphics Window #1 - [powplot]
File Edit View Mode Window Options Help
ttb
Hist 1
Lambda 1.5405 A, L-S cycle 1459
Obsd. and Diff. Profiles
X10E 4
2.0
1.0
0.0
Counts
0.0
20.0
40.0
60.0
80.0
100.0
120.0
2-Theta, deg
开始
20:33

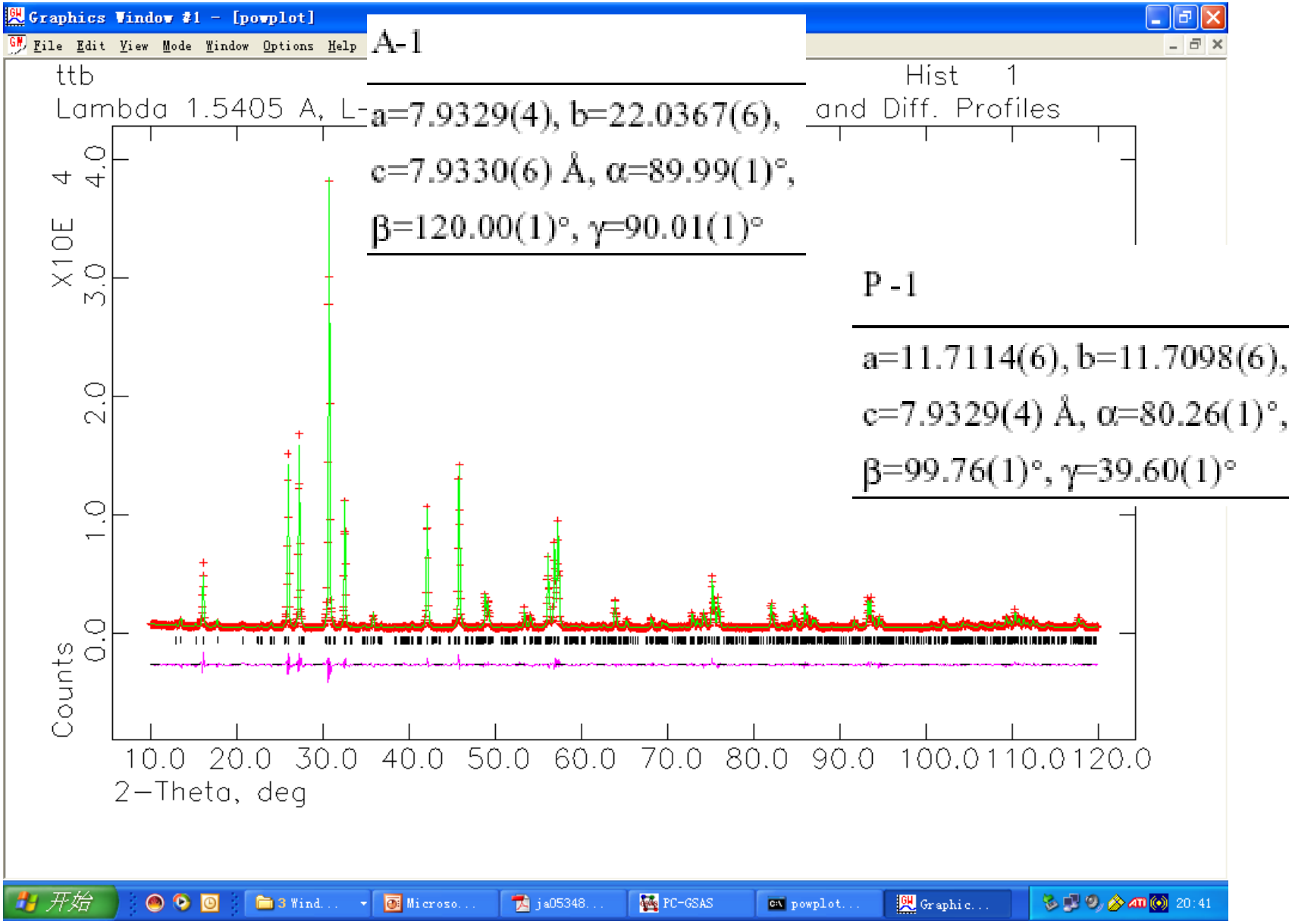
超结构峰

P21/m

a=6.8708(4), b=11.0180(2),

c=7.9309(5) Å, β=90.00(1)°




Graphics Window #1 - [powplot]
File Edit View Mode Window Options Help
ttb
Hist 1
Lambda 1.5405 A, L-
and Diff. Profiles
A-1
a=7.9329(4), b=22.0367(6),
c=7.9330(6) Å, α=89.99(1)°,
β=120.00(1)°, γ=90.01(1)°
P -1
a=11.7114(6), b=11.7098(6),
c=7.9329(4) Å, α=80.26(1)°,
β=99.76(1)°, γ=39.60(1)°
X10E 4
4.0
3.0
2.0
1.0
0.0
Counts
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0
2-Theta, deg
开始
3 Wind...
Microso...
ja05348...
PC-GSAS
powplot...
Graphic...
20:41

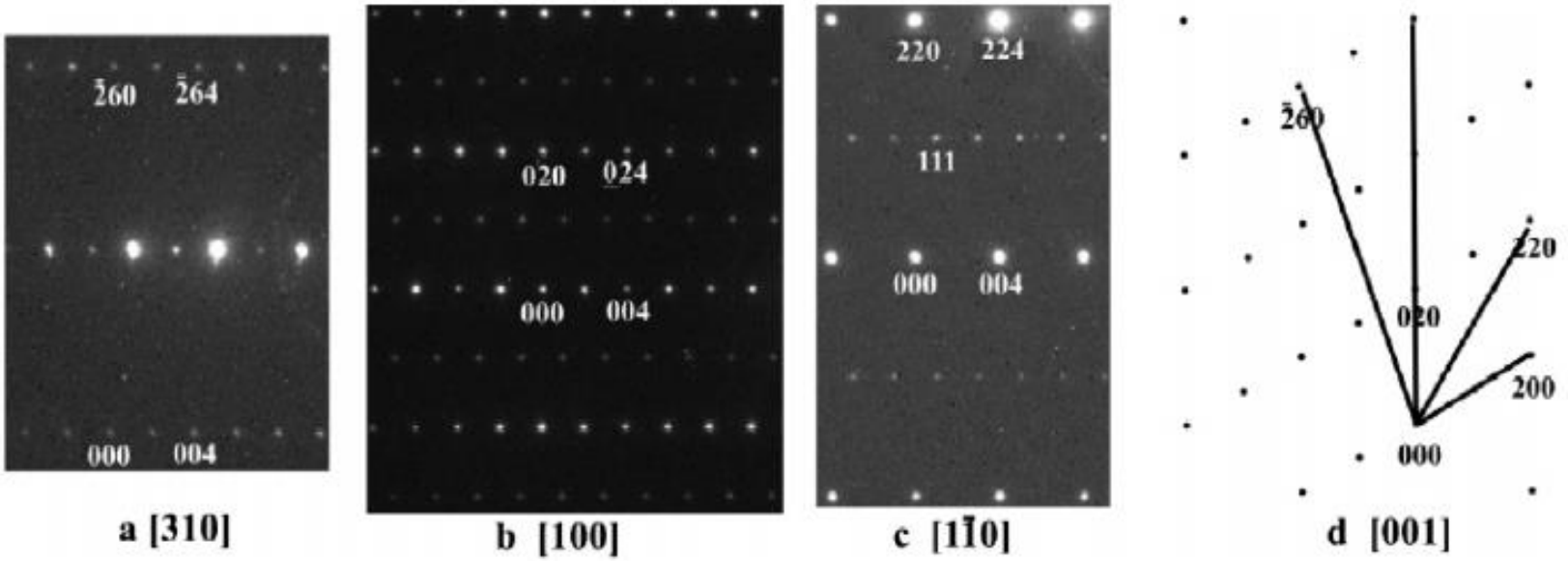


Figure 3. SAED patterns for $La_4Cu_2ZnMoO_{12}$ in the (310) (a), (100) (b), and (1$\bar{1}$0) (c) zones; (d) shows the orientation of the diffraction patterns. (The diffraction patterns were indexed using the A-centered pseudohexagonal cell, $a = 7.9$ Å and $c = 22$ Å.)

非公度峰

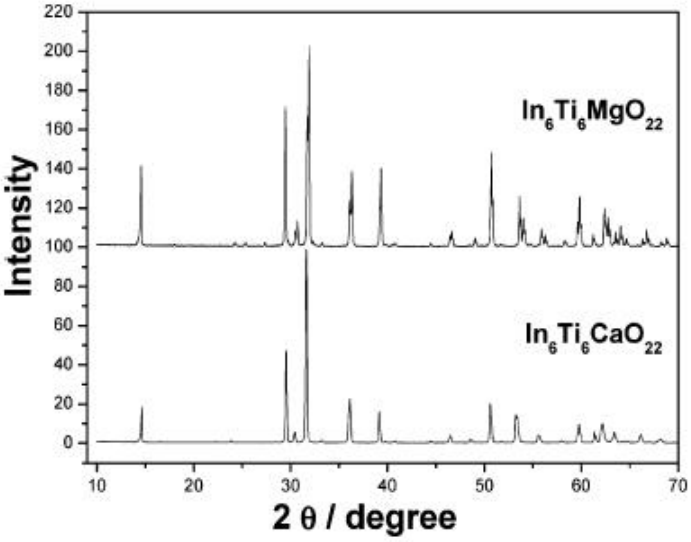


Figure 3. X-ray diffraction patterns of In_6 Ti_6CaO_{22} and $In_6Ti_6MgO_{22}$.

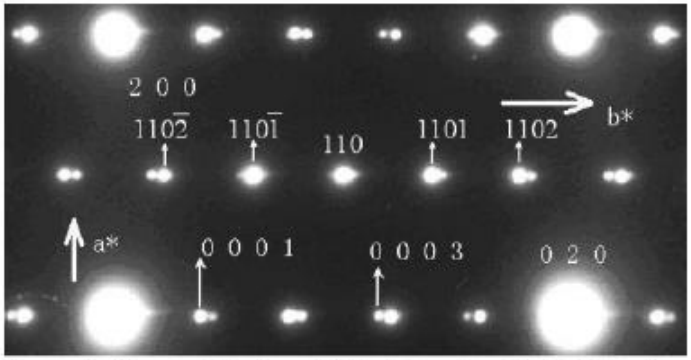


Figure 4. Electron diffraction of $Ti_6In_6CaO_{22}$ along the [001] direction.

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欢迎讨论！

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