CSNS中子学校2024

CW和TOF数据分析

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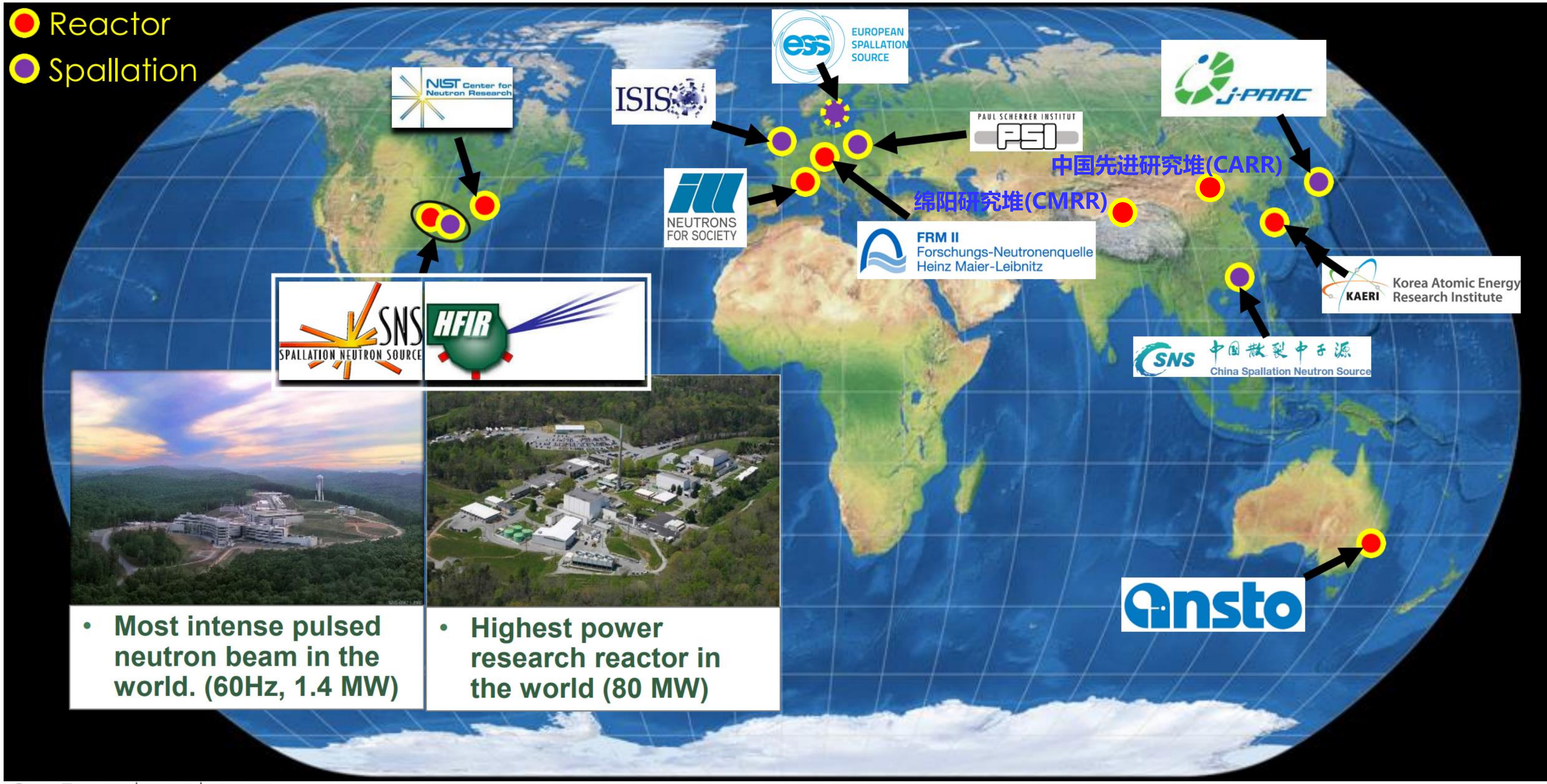
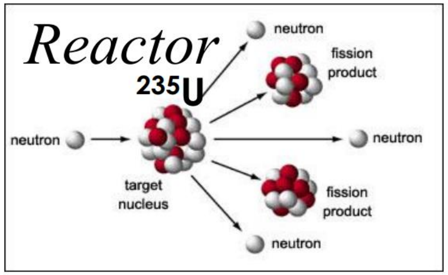
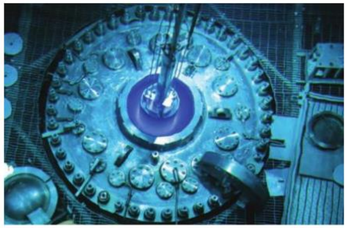
东莞 2024-11-23

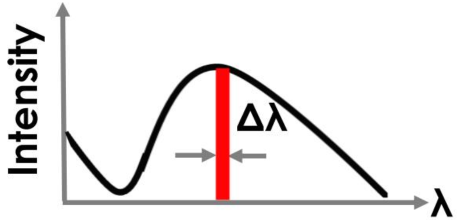
世界上主要的中子源

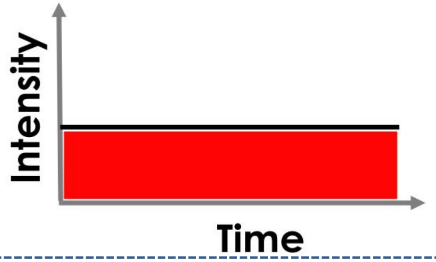

Reactor
Spallation
NIST Center for Neutron Research
ISIS
ess
EUROPEAN SPALLATION SOURCE
PAUL SCHERRER INSTITUT
PSI
J-PARC
中国先进研究堆(CARR)
绵阳研究堆(CMRR)
NEUTRONS FOR SOCIETY
FRM II
Forschungs-Neutronenquelle
Heinz Maier-Leibnitz
Korea Atomic Energy Research Institute
KAERI
CSNS 中国散裂中子源
China Spallation Neutron Source
ansto
SNS
SPALLATION NEUTRON SOURCE
HFIR
• Most intense pulsed neutron beam in the world. (60Hz, 1.4 MW)
• Highest power research reactor in the world (80 MW)

Constant-Wavelength (CW)和Time of Flight（TOF)

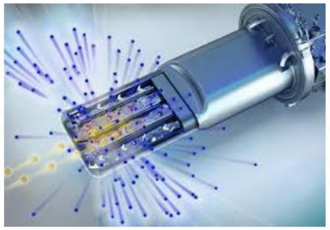


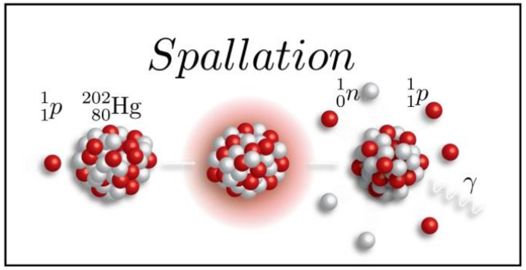




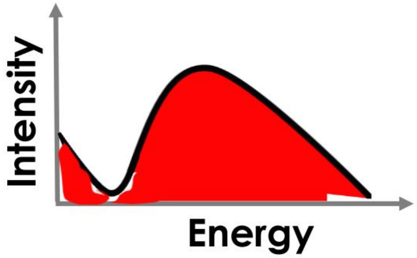


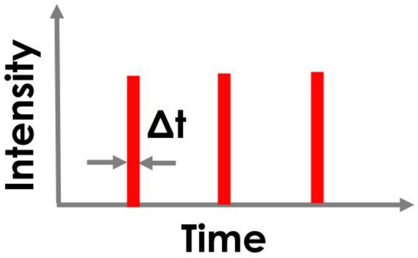
反应堆-波长变化非常小
持续的强度



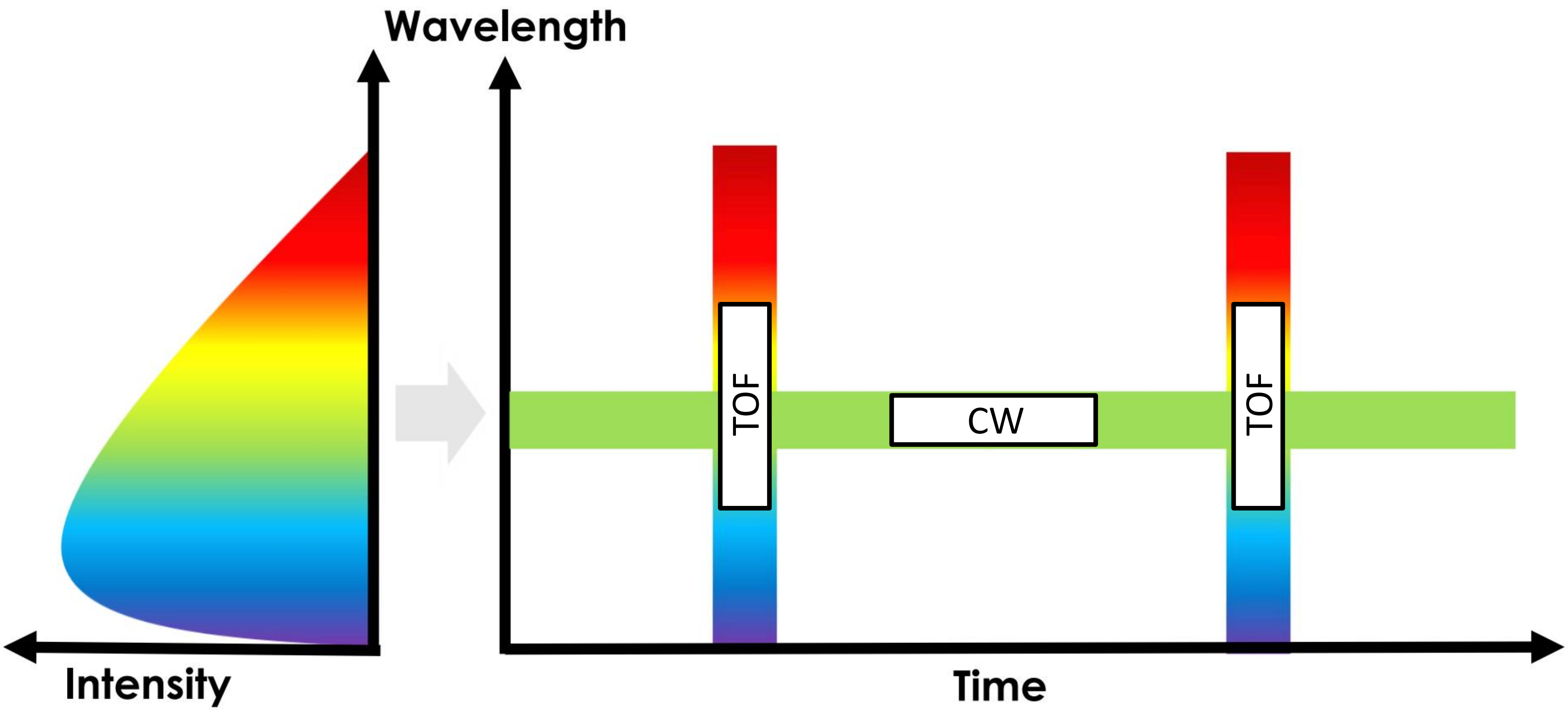


散裂源-宽范围的波长
脉冲





你喜欢用什么样的中子来做实验呢?



CW – 部分中子、所有的时间
TOF –所有的中子、脉冲

美国NIST的BT-1中子粉末衍射仪

$\lambda = 2d \sin \theta$

Monochromator (选择波长、单一波长)

⬇

2θ角度的探测器测量single d/Q

Q的限制为4π/λ

中国散裂中子源GPPD谱仪

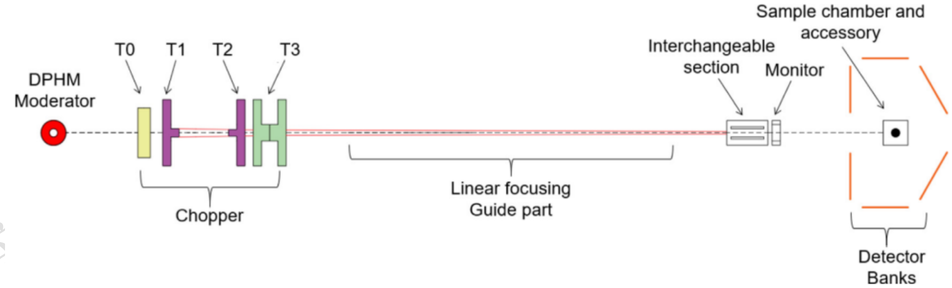


Fig. 1. Schematic drawing of the beamline layout of GPPD.

De Broglie wavelength: $\lambda = h/mv = ht/mL$

Bragg's law: $\lambda = 2d \sin\theta$

⬇

$t = d * 2mL\sin\theta/h$

分辨率 $$\frac{\Delta d}{d} = \sqrt{\left(\frac{\Delta L}{L}\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + (\cot\theta\,\Delta\theta)^2}.$$

2θ角度的探测器测量multiple d/Q

d/Q range determined by λ_{min}, λ_{max} and 2θ

Intensity

CW
- 更高的通量
- 强度调控 (monochromator, collimators)

TOF
- 更高的峰值亮度
- 仪器距离、带宽和覆盖范围的平衡

宽Q覆盖
- Qmax可以非常高（>100 Å^{-1}）
- 即使使用有限的探测器也能提供覆盖范围

d/Q-Resolution

CW
- 可调节的d/Q范围
- 简单、对称的峰形函数

TOF
- 高分辨率
- 与谱仪相关的复杂非对称峰形

d/Q-Range

CW
- d/Q范围有限，但可调
- 最高Q_{max}（约20 Å^{-1}）
- 需要宽/连续的探测器覆盖范围

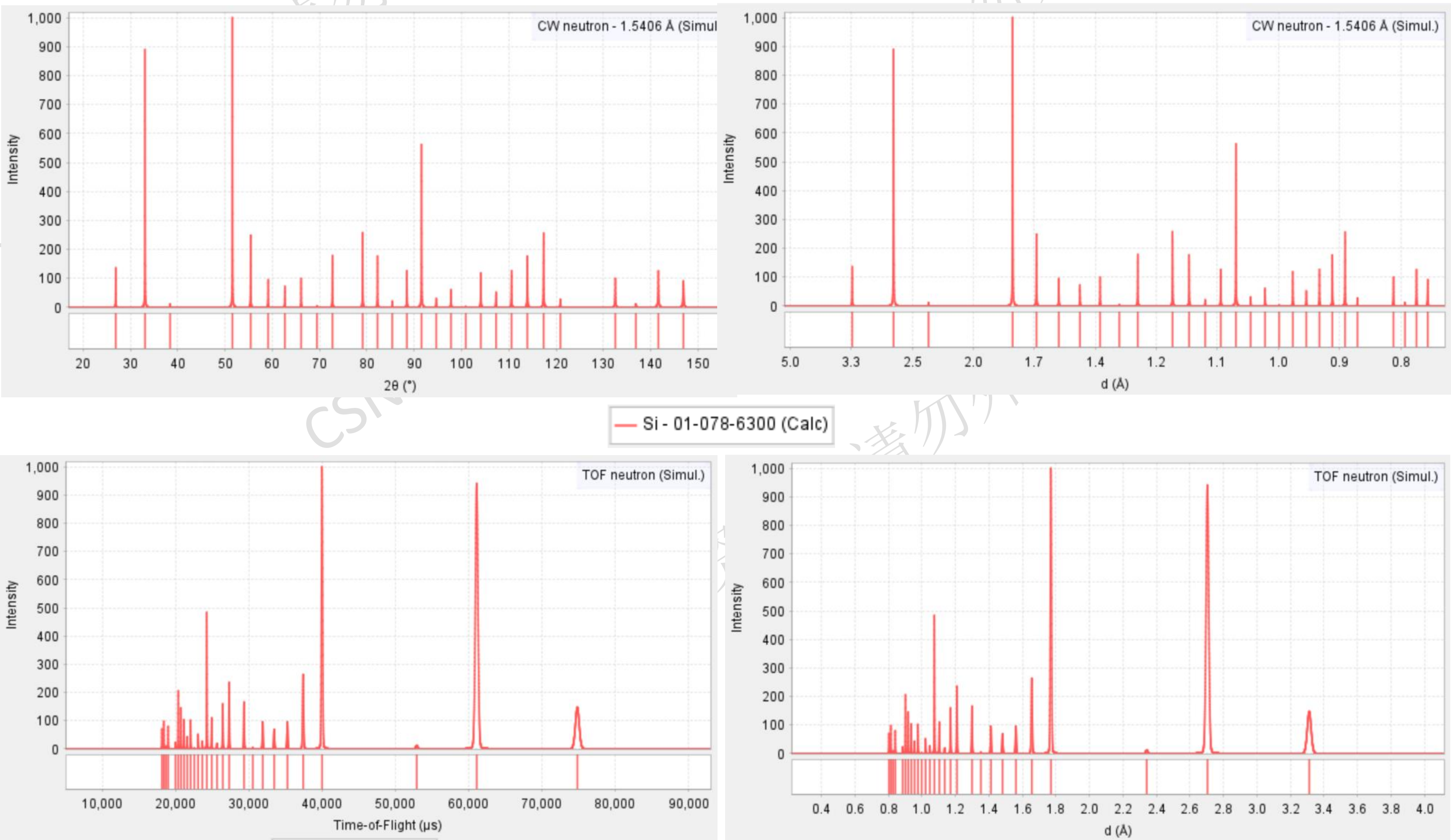
TOF
- 宽Q覆盖
- Q_{max}可以非常高（>100 Å^{-1}）
- 即使使用有限的探测器也能提供良好的覆盖范围

Table 2.3.5

Advantages of CW and TOF instruments (modified from Kisi & Howard, 2008)

CW	TOF
(1) Incident beam may be essentially monochromatic, in which case the spectrum is well characterized 入射中子基本单一波长，谱图特性好	(1) The whole incident spectrum is utilized, but it needs to be carefully characterized if intensity data are to be used 运用全入射谱，强度数据需仔细进行刻度校正。
(2) Large *d*-spacings are easily accessible for study of complex magnetic and large-unit-cell structures 能测量大d值晶面间距，有利于分析复杂磁结构和大晶胞晶体结构	(2) Data are collected to very large *Q* values (small *d*-spacings) 能测量非常大Q值数据 (小晶面间距*d*)
(3) Can fine tune the resolution during an experiment 在实验过程中能调整分辨率	(3) Few cold neutron instruments are available for study of complex magnetic and large-unit-cell structures 冷中子谱仪可用于研究磁结构和大晶胞结构。
(4) More common 更通用	(4) Resolution is constant across the whole pattern 整个谱图的分辨率不变
(5) Peak shapes are simpler to model 峰型简单更容易拟合	(5) Very high resolution is readily attained by using long flight paths 用长的飞行管道可达到非常高的分辨率
(6) Absorption and extinction corrections are relatively straightforward 吸收和消光校正相对简单	(6) Complex sample environments are very readily used if 90° detector banks are available 复杂的样品环境可用于90度的探测器组。
(7) Data storage and reduction is simpler 数据存储和简化简单	(7) Simpler to intersect a large proportion of the Debye–Scherrer cones with large detector banks 用大的探测器组对横切大比例Debye-Scherrer锥更为简单。
(8) Extremely rapid data collection and stroboscopic measurements are feasible 可进行极快的数据收集和频闪测量	(8) Very fast data collection is feasible 数据采集非常快捷。
(9) Engineering diffractometers are very well suited for strain scanning in complex objects 工程衍射仪非常适合复杂构件的应变扫描	(9) Engineering diffractometers use an extended diffraction pattern, ideal for *in situ* loading and/or heating 工程谱议适合原位加载和/或加热，连续采集衍射谱。
(10) Texture is straightforward to measure on engineering diffractometers 工程衍射仪对织构测量简单容易	(10) Texture can be measured on universal instruments 通用谱议可测织构。

CW – TOF 谱图 – Si标样



通用粉末谱仪(GPPD) - 用户实验数据

GPPD_BANK1_V2.0_RUN0005142	2020/1/6 16:14	DAT 文件	97 KB
GPPD_BANK1_V2.0_RUN0005142.gsa	2020/1/6 16:14	GSA 文件	154 KB
GPPD_BANK1_V2.0_RUN0005142.histogramIgor	2020/1/6 16:14	HISTOGRAMIGO...	84 KB
GPPD_BANK1_V2.0_RUN0005142_d	2020/1/6 16:14	DAT 文件	98 KB
GPPD_BANK2_V2.0_RUN0005142	2020/1/2 11:43	DAT 文件	76 KB
GPPD_BANK2_V2.0_RUN0005142.gsa	2020/1/2 11:43	GSA 文件	122 KB
GPPD_BANK2_V2.0_RUN0005142.histogramIgor	2020/1/2 11:43	HISTOGRAMIGO...	66 KB
GPPD_BANK2_V2.0_RUN0005142_d	2020/1/2 11:43	DAT 文件	77 KB
GPPD_BANK3_V2.0_RUN0005142	2020/1/2 12:56	DAT 文件	22 KB
GPPD_BANK3_V2.0_RUN0005142.gsa	2020/1/2 12:56	GSA 文件	36 KB
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GPPD_BANK3_V2.0_RUN0005142_d	2020/1/2 12:56	DAT 文件	23 KB

GPPD提供4种格式的数据:

Data File; HISTOGRAMIGOR; GSAS; _d Data File.

1. For Fullprof

- Data format: Date File

Format data for Fullprof, the first three lines are Title, and the Rexp factor is given; The data columns are TOF, INTENSITY, and ERROR respectively from left to right.

```
GPPD Diffraction Histogram for 180-degree bank, RUN0004075, Rexp is 2.15583782564
The original intensities and sigmas have been multiplied by 10000
TOF INT ERR
1473.43 2239.975327 400.351582
1474.61 2239.975327 400.191537
1475.79 2239.975327 400.031557
```

- Conversion (Instrument) parameter file

```
!   Zero     Code   Dtt1       Code   Dtt2    Code   2ThetaBank  -> Patt# 1
    13.370   61.00  14718.982  71.00  3.426   81.00  150.000
```

As shown above, the conversion (instrument) parameter parameters are given in the provided .pcr file.

2. For Z-Rietveld

- Data format: HISTOGRAMIGOR

Z-rietveld format data, the first three lines are Title. The data columns are TOF, INTENSITY, and ERROR respectively from left to right.

```
IGOR
WAVES/O tof yint yerr
BEGIN
2946.86 0.095522 0.007601
2949.21 0.095522 0.007598
```

- Conversion parameter file

```
[Conversion parameters]
    [Value] 1.86880621866503
    [ID] Vary
[Conversion parameters]
    [Value] 14742.188067213
    [ID] Vary
[Conversion parameters]
    [Value] -2.02522105963946
    [ID] Vary
```

As shown above, the instrument (transformation) parameters are shown in the provided ZDIFFRACTOMETER file.

3. For GSAS

- Data format: .gsa

The data for GSAS, the first two lines are Title. The data columns are TOF, INTENSITY, and ERROR respectively from left to right.

```
GPPD Diffraction Histogram for 180-degree bank, RUN0004075, Rexp is 2.15583782564
BANK 1 4073 4073 RALF 47136 37 47200 0.000800 FXYE
 1473.427592 0.2640352997 0.0471911225
```

- Conversion parameter file

```
HST 1 ICONS 14721.26 2.81 11.87
HST 2 ICONS 11478.56 -8.32 2.01
HST 3 ICONS 1478.65 2.15 9.63
```

As shown above, the instrument (transformation) parameters are shown in the provided .prm file.

4. _d Data File

Reference data (in *d* space), the first three lines are Title.

The data columns are *d*, Intensity, and Error respectively from left to right.

```
GPPD Diffraction Histogram for 180-degree bank, RUN0004075, Rexp is 2.15583782564
The original intensities and sigmas have been multiplied by 10000
d INT ERR
0.099243 2239.975327 400.351582
0.099323 2239.975327 400.191537
```

1. GPPD could provide **three sets of detector data**, including Bank1 (center of the diffraction angle range $\theta_c = 150^\circ$), Bank2 ($\theta_c = 90^\circ$) and Bank3 ($\theta_c = 30^\circ$). Bank1 is a Backward Bank with the **highest resolution** among the three banks, which is suitable for **high resolution research**. Bank2 is a Medium-Angle Bank, and its detector can avoid the observation of scattering from the container wall. Therefore, Bank2 shows **the advantages for the case where there is a container (such as under the environment of variable temperature, external magnetic field, etc.)**. Bank3 is a Low-Angle Bank, and its *d* space covers a wide range, which is suitable for determining the **crystal structure of large molecules or complex magnetic structures.** Users can perform single bank analysis or multiple bank joint analysis according to the experimental requirements.
2. An individual **format data** with the simple modification could still be available for relevant **commercial software**. For example, users could use the data file for **TOPAS software** by changing the .dat format file to .xye one, deleting the file title and using the conversion parameters provided for the other software.

通用粉末谱仪(GPPD) - 用户实验数据

GPPD Diffraction Histogram for 90-degree bank, RUN0004079

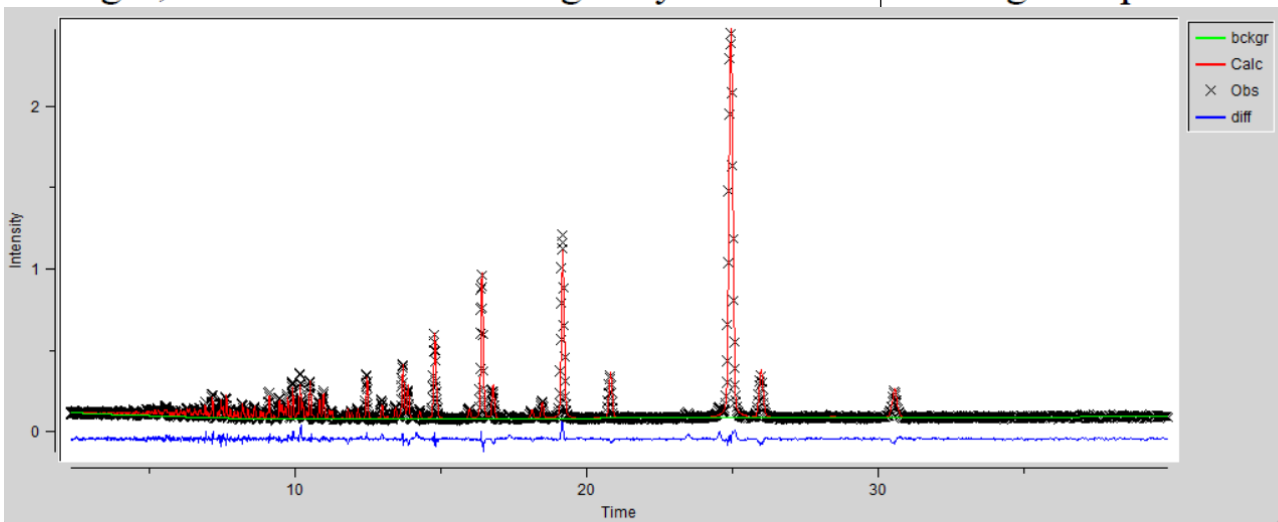
BANK 2 3575 3575 RALF 73344 58 73472 0.000800 FXYE

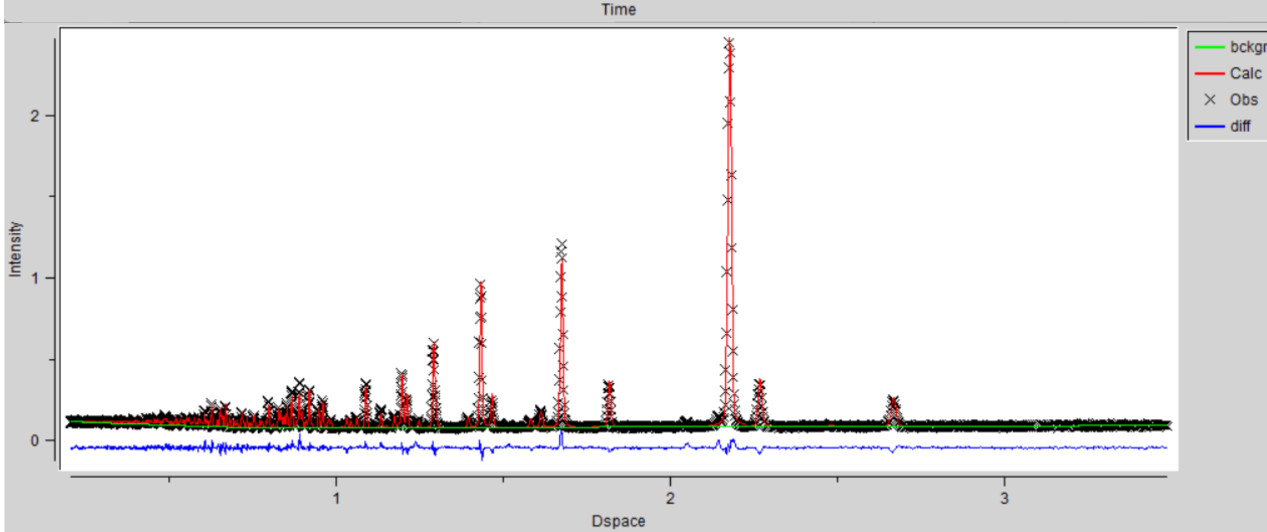
飞行时间	强度	误差
2292.435011	0.2183120195	0.0448170124
2293.351985	0.2184865311	0.0448349073
2295.186668	0.2186613999	0.0448528540
2297.022817	0.2188362686	0.0448707792
2298.860435	0.2190113754	0.0448887317
2300.699524	0.2191864823	0.0449066627
2302.540084	0.2193619462	0.0449246452
2304.382116	0.2195374101	0.0449426063
2306.225621	0.2322779301	0.0455929246
2308.070602	0.2384194654	0.0459029677
2309.917059	0.2386102325	0.0459213313
2311.764992	0.2388011286	0.0459396977
2313.614405	0.2389920248	0.0459580421
2315.465296	0.2391833081	0.0459764388
2317.317668	0.2393747206	0.0459948384
2319.171523	0.2395661330	0.0460132159
2321.026861	0.2397578035	0.0460316209
2322.883682	0.2389134814	0.0459736319
2324.741989	0.2112946381	0.0439155480
2326.601783	0.2114636249	0.0439331006
2328.463065	0.2116327253	0.0439506558
2330.325835	0.2118020528	0.0439682369
2332.190096	0.2119716075	0.0439858441
2334.055849	0.2121410486	0.0440034068
2335.923094	0.2123108304	0.0440210188
2337.791832	0.2124806122	0.0440386099
2339.662066	0.2126506211	0.0440562269
2341.533795	0.2131945089	0.0439725476

通用粉末谱仪(GPPD) - 用户实验数据 T – d转换

$T_{ph} = DIFC\ d_p + DIFA\ d^2_p + ZERO.$

The three parameters DIFC, DIFA and ZERO are characteristic of a given counter bank on a TOF powder diffractometer. The values of these constants as used in **GSAS** yield TOF in µsec. DIFC may be calculated with good precision from the flight paths, diffraction angle, and counter tube height by use of the de Broglie equation.



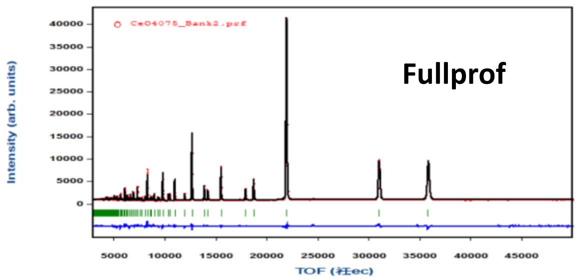


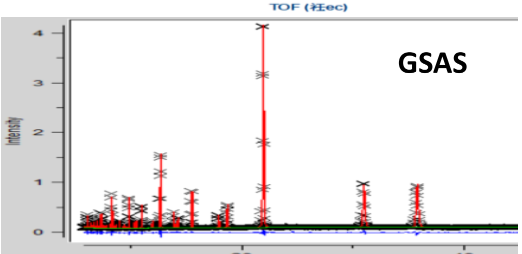
仪器参数文件 – 功率提升

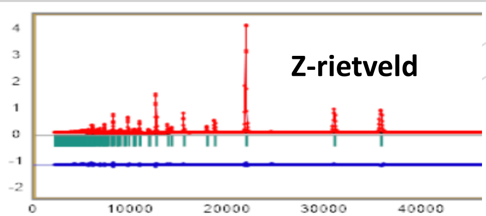
$$\mathrm{TOF} = \underline{\mathbf{Zero}} + \underline{\mathbf{Dtt1}}\, d + \underline{\mathbf{Dtt2}}\, d^2$$

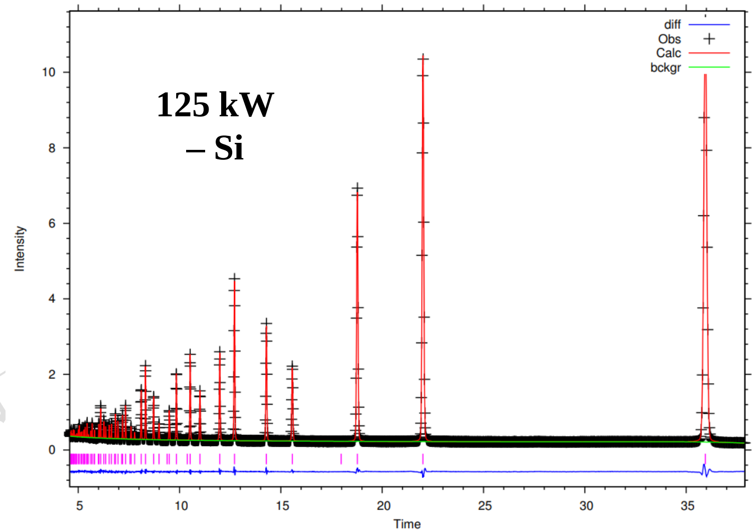
Profile Function

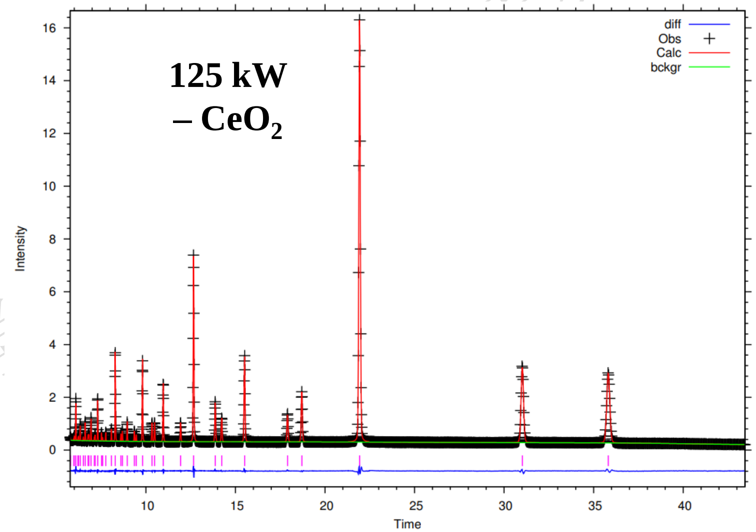
$$\alpha' = \frac{1}{c_1 + c_2 d}$$
$$\beta_1' = \beta_{1,0}\,(const.)$$
$$\beta_0' = \beta_{0,0} + \frac{\beta_{0,1}}{d}$$











- **Determination of diffractometer status**
- **Provide instrumental parameters to users**

通用粉末谱仪(GPPD) - 用户实验数据 Zero能修吗?

GSAS手册中指出了DIFC DIFA ZERO的由来，但是并没有明确在精修用户数据时，Zero是否要修？修了ZERO的χ^2值更小！

T(K)	Zero		Refine-Rwp		Zero	Fix-Rwp
5	-7.1033	0.5036	4.6		3.897	5.76
100	-7.7053	0.496	4.44			5.64
200	-9.1573	0.7216	6.63			9
300	-9.5563	0.5809	5.33			7.31
	精修Zero				固定zero	

一般认识:

1、仪器的零点原则上是仪器参数，但与样品的位置以及机械加工精度（固定波长有移动探测器）。

2、对我们的情况，样品的位置偏差应该会影响峰的位置。

3、仪器的设计、加工、安装和使用不可能达到理论值。校正后得到的仪器参数在环境等影响都可能有变化。我们的仪器也在不断地更新，完善，磨合，老化中，不可能有不变的。

用户处理数据时，Zero为转换参数，Zero不修！！！

更多的细节可以关注

Ron Smith, Crystallography Group, ISIS Facility, Rutherford Appleton Laboratory

H. E. Brand, *et al*. Phys. Chem Minerals 2009, 36: 29

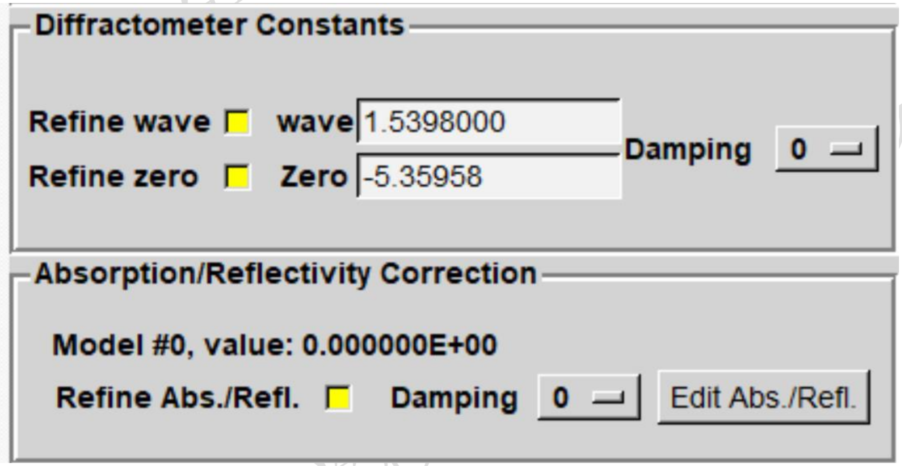
B. Hunter, http://www.ccp14.ac.uk

- CW – TOF 数据差异及其举例说明

1-仪器参数；

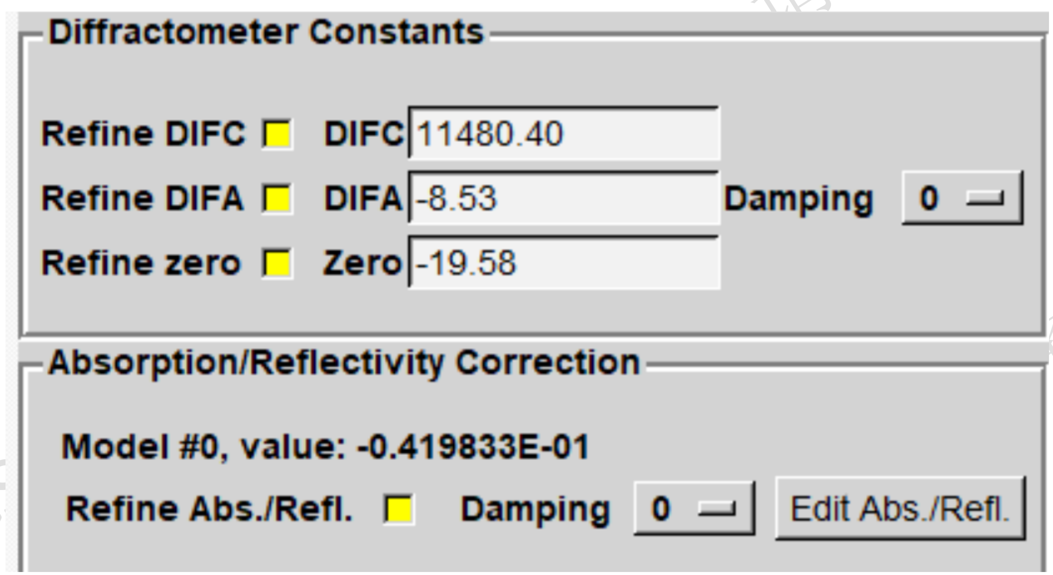
2-峰型函数

CW



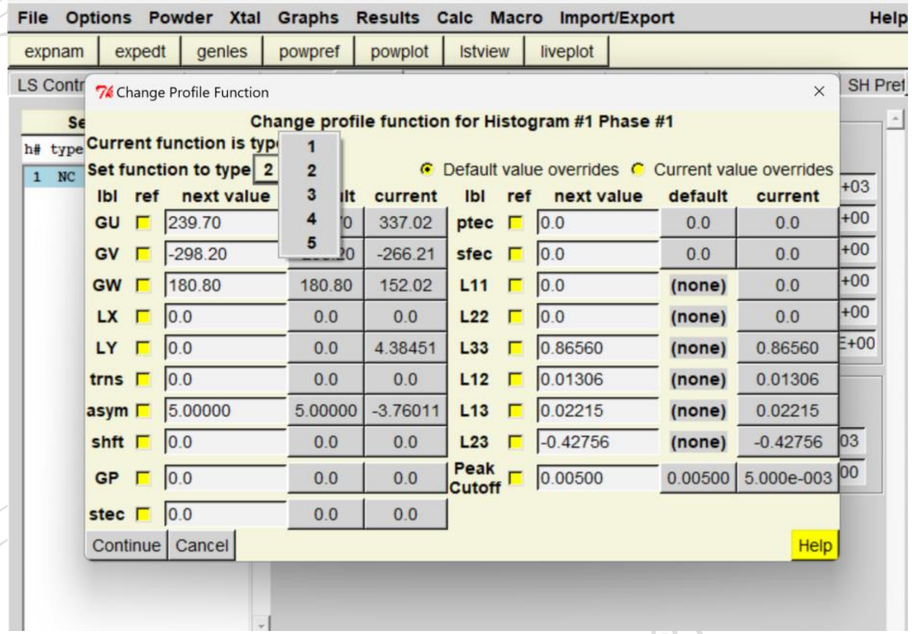
Diffractometer Constants
Refine wave
wave 1.5398000
Refine zero
Zero -5.35958
Damping 0
Absorption/Reflectivity Correction
Model #0, value: 0.000000E+00
Refine Abs./Refl.
Damping 0
Edit Abs./Refl.

TOF

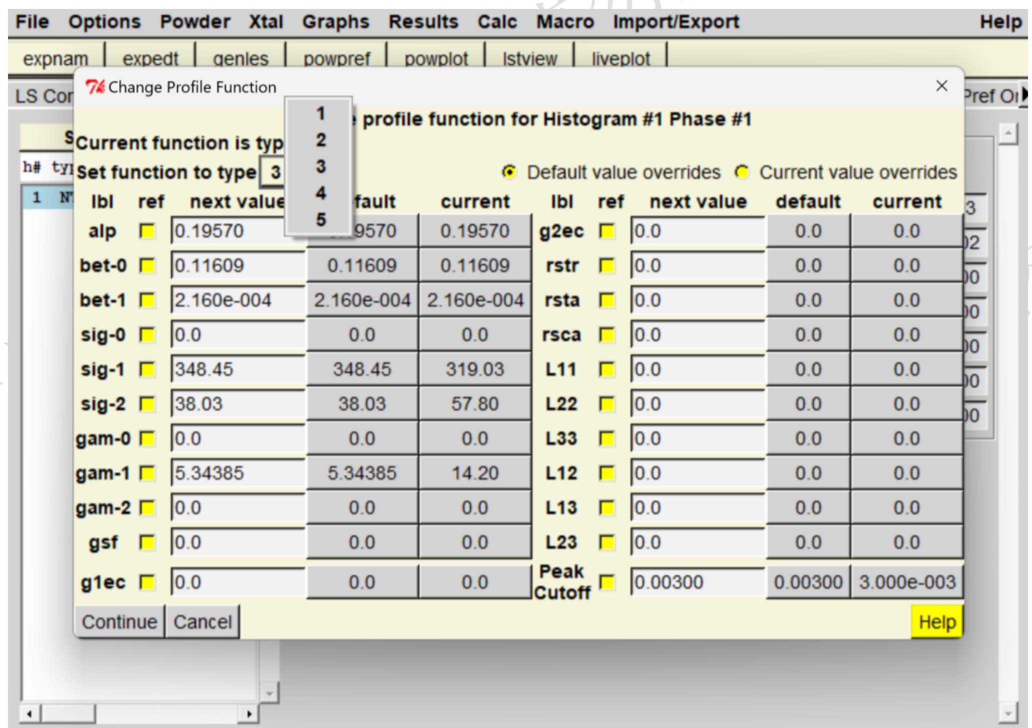


Diffractometer Constants
Refine DIFC
DIFC 11480.40
Refine DIFA
DIFA -8.53
Refine zero
Zero -19.58
Damping 0
Absorption/Reflectivity Correction
Model #0, value: -0.419833E-01
Refine Abs./Refl.
Damping 0
Edit Abs./Refl.

CW


File Options Powder Xtal Graphs Results Calc Macro Import/Export Help
expnam expedt genles powpref powplot lstview liveplot
Change Profile Function
Change profile function for Histogram #1 Phase #1
Current function is type
Set function to type 2
1 2 3 4 5
Default value overrides
Current value overrides
lbl ref next value default current lbl ref next value default current
GU 239.70 337.02
GV -298.20 -266.21
GW 180.80 180.80 152.02
LX 0.0 0.0 0.0
LY 0.0 0.0 4.38451
trns 0.0 0.0 0.0
asym 5.00000 5.00000 -3.76011
shft 0.0 0.0 0.0
GP 0.0 0.0 0.0
stec 0.0 0.0 0.0
ptec 0.0 0.0 0.0
sfec 0.0 0.0 0.0
L11 0.0 (none) 0.0
L22 0.0 (none) 0.0
L33 0.86560 (none) 0.86560
L12 0.01306 (none) 0.01306
L13 0.02215 (none) 0.02215
L23 -0.42756 (none) -0.42756
Peak Cutoff 0.00500 0.00500 5.000e-003
Continue Cancel Help

TOF


File Options Powder Xtal Graphs Results Calc Macro Import/Export Help
expnam expedt genles powpref powplot lstview liveplot
Change Profile Function
profile function for Histogram #1 Phase #1
Current function is typ
Set function to type 3
1 2 3 4 5
Default value overrides
Current value overrides
lbl ref next value default current lbl ref next value default current
alp 0.19570 0.19570
bet-0 0.11609 0.11609 0.11609
bet-1 2.160e-004 2.160e-004 2.160e-004
sig-0 0.0 0.0 0.0
sig-1 348.45 348.45 319.03
sig-2 38.03 38.03 57.80
gam-0 0.0 0.0 0.0
gam-1 5.34385 5.34385 14.20
gam-2 0.0 0.0 0.0
gsf 0.0 0.0 0.0
g1ec 0.0 0.0 0.0
g2ec 0.0 0.0 0.0
rstr 0.0 0.0 0.0
rsta 0.0 0.0 0.0
rsca 0.0 0.0 0.0
L11 0.0 0.0 0.0
L22 0.0 0.0 0.0
L33 0.0 0.0 0.0
L12 0.0 0.0 0.0
L13 0.0 0.0 0.0
L23 0.0 0.0 0.0
Peak Cutoff 0.00300 0.00300 3.000e-003
Continue Cancel Help

CW

Hist 1 -- Phase 1 (type 2)

Damping: 0 | Peak cutoff: 0.00500 | Change Type

GU	☑	0.337024E+03	GV	☑	-0.266211E+03	GW	☑	0.152021E+03
LX	☐	0.000000E+00	LY	☑	0.438451E+01	trns	☐	0.000000E+00
asym	☑	-0.376011E+01	shft	☐	0.000000E+00	GP	☐	0.000000E+00
stec	☐	0.000000E+00	ptec	☐	0.000000E+00	sfec	☐	0.000000E+00
L11	☐	0.000000E+00	L22	☐	0.000000E+00	L33	☑	0.865602E+00
L12	☑	0.130596E-01	L13	☑	0.221467E-01	L23	☑	-0.427561E+00

TOF

Hist 1 -- Phase 1 (type 3)

Damping: 0 | Peak cutoff: 0.00300 | Change Type

alp	☐	0.195695E+00	bet-0	☐	0.116092E+00	bet-1	☐	0.216000E-03
sig-0	☐	0.000000E+00	sig-1	☑	0.319028E+03	sig-2	☑	0.578003E+02
gam-0	☐	0.000000E+00	gam-1	☑	0.141973E+02	gam-2	☐	0.000000E+00
gsf	☐	0.000000E+00	g1ec	☐	0.000000E+00	g2ec	☐	0.000000E+00
rstr	☐	0.000000E+00	rsta	☐	0.000000E+00	rsca	☐	0.000000E+00
L11	☐	0.000000E+00	L22	☐	0.000000E+00	L33	☐	0.000000E+00
L12	☐	0.000000E+00	L13	☐	0.000000E+00	L23	☐	0.000000E+00

谢谢大家！