SINGLE-CRYSTAL DIFFUSE SCATTERING USING PULSED NEUTRON DIFFRACTION

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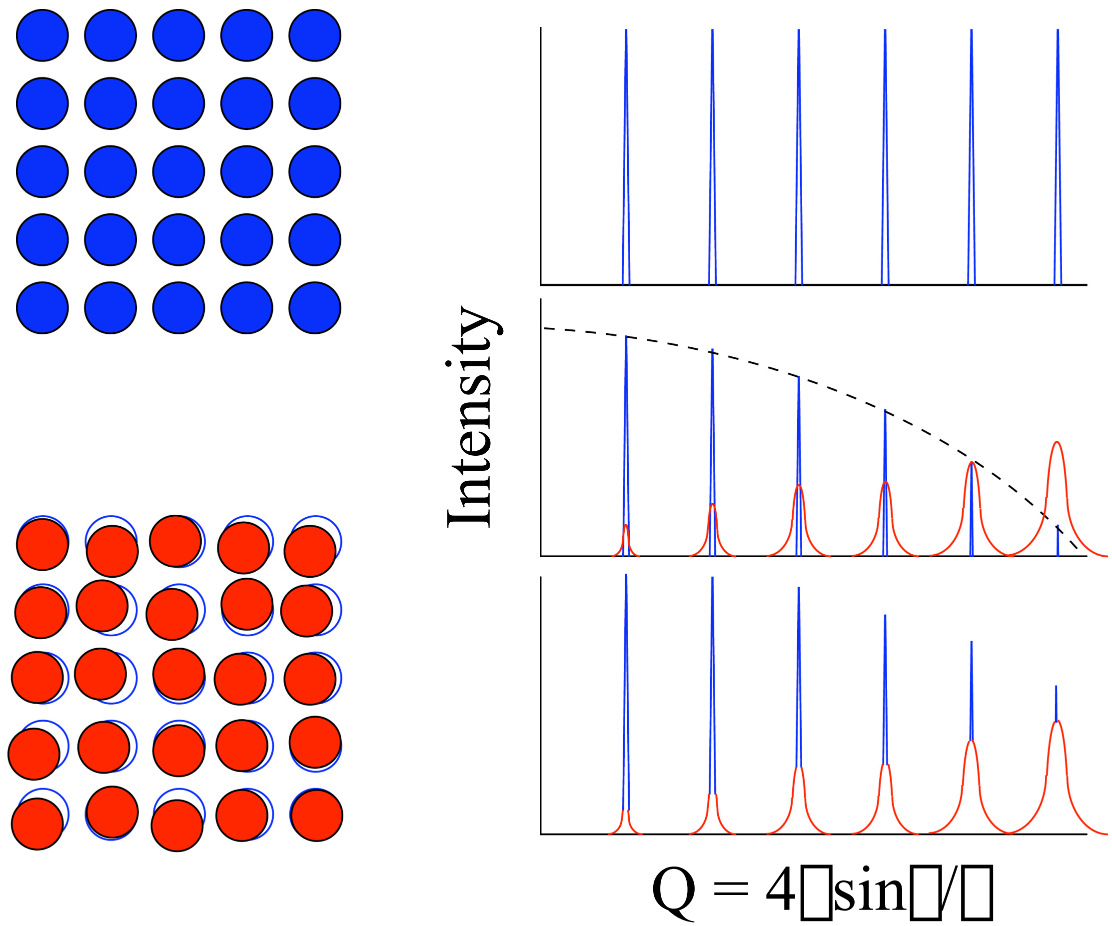
ACKNOWLEDGEMENTS

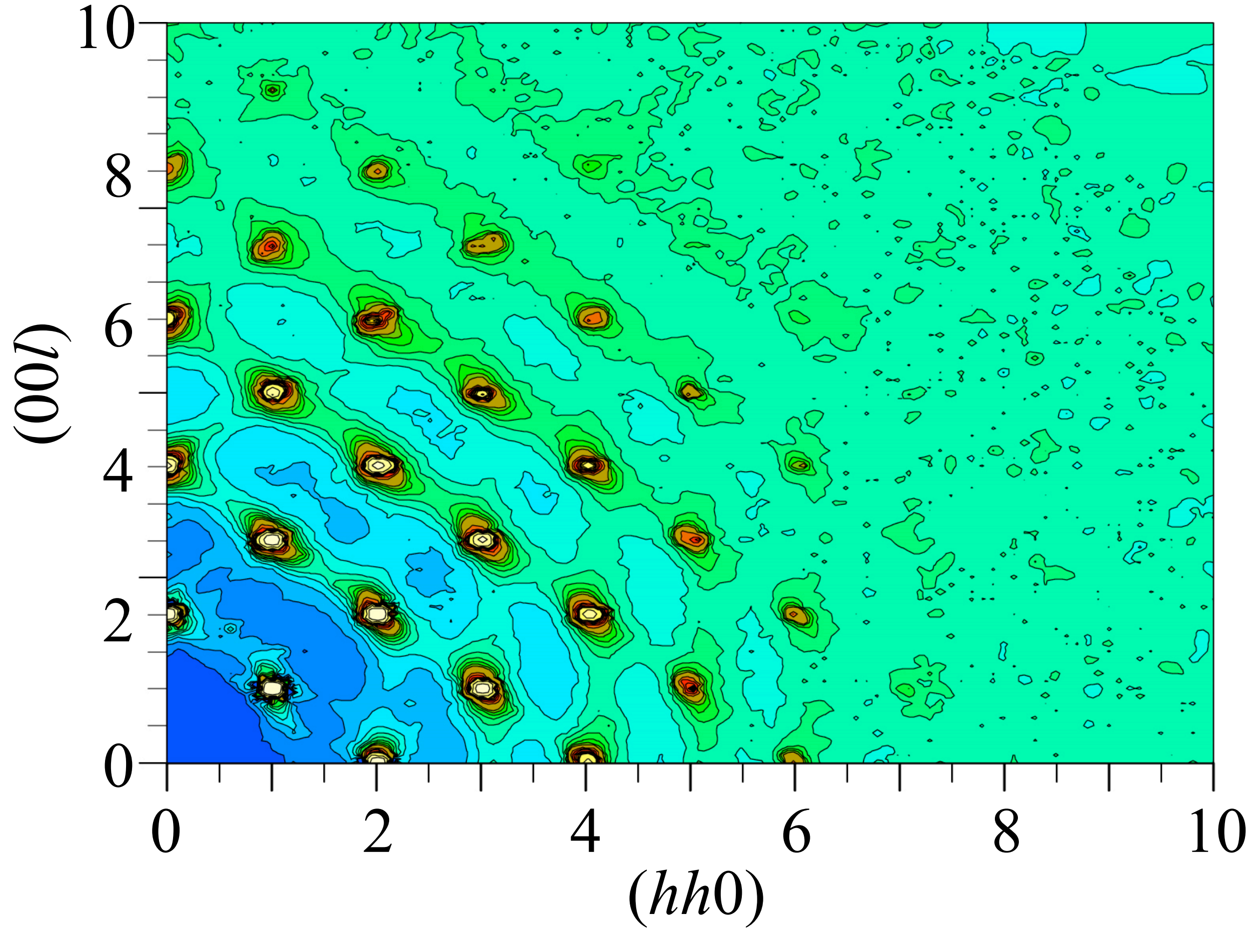
Richard Welberry, Royal School of Chemistry, ANU, Canberra

Matthias Gutmann, ISIS Facility, RAL

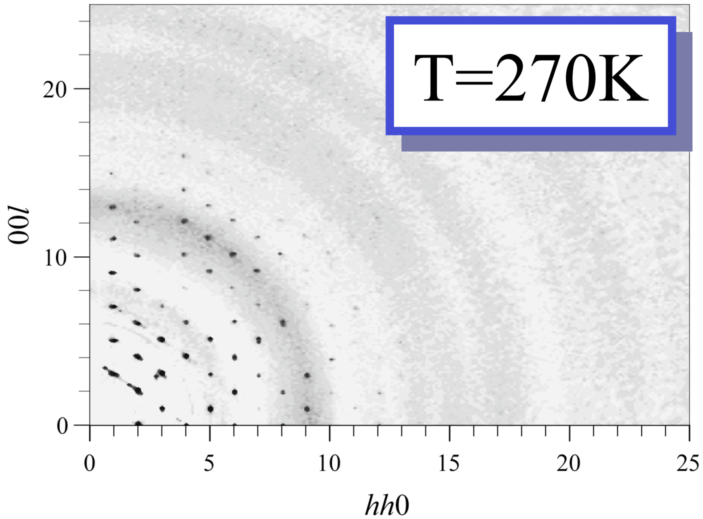
The Origin of Diffuse Scattering

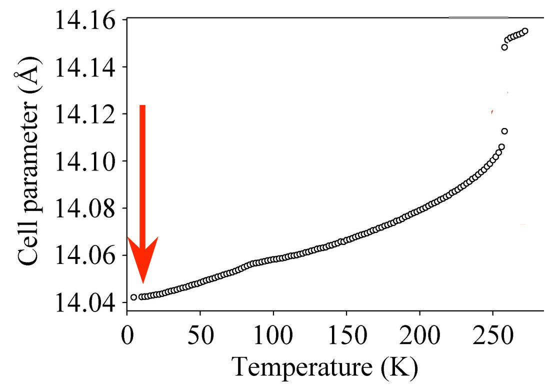


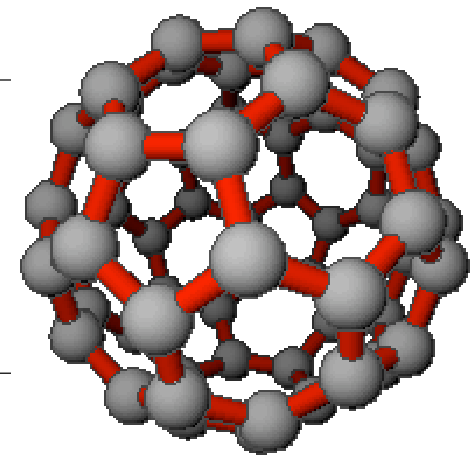
LEAD AT 373K

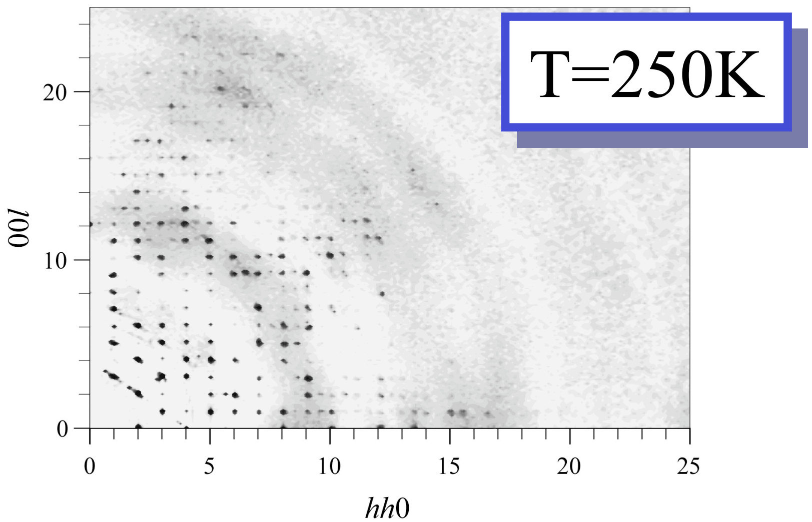


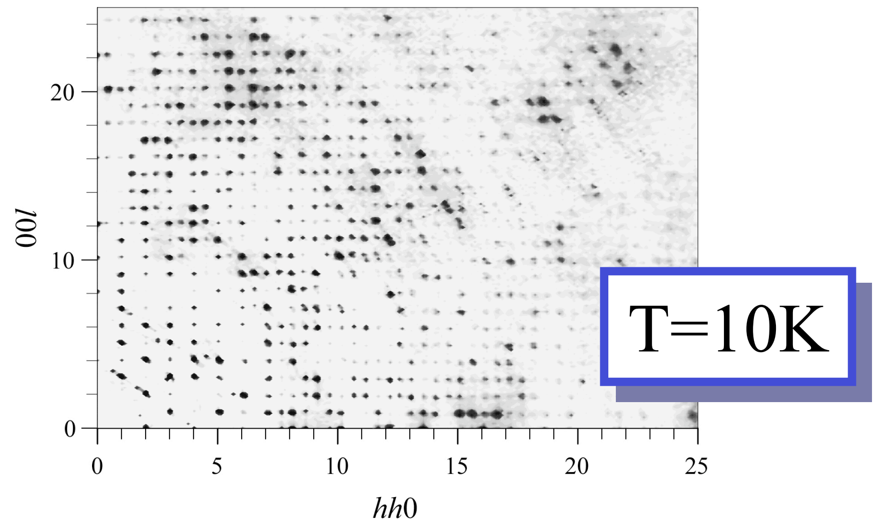
C_{60}


T=270K
00l
hh0
0
5
10
15
20
25
0
10
20

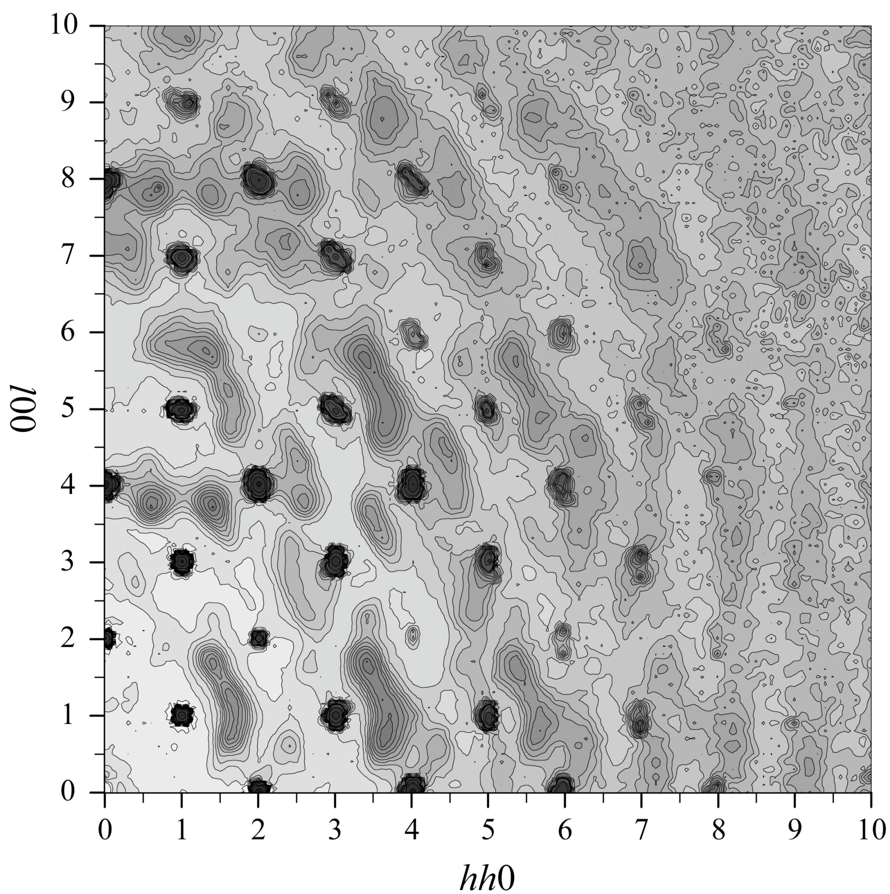

Cell parameter (Å)
Temperature (K)
14.16
14.14
14.12
14.10
14.08
14.06
14.04
0
50
100
150
200
250

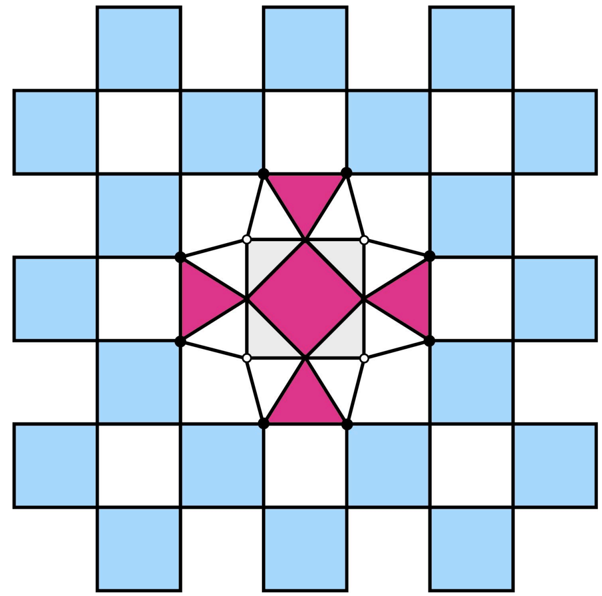



T=250K
00l
hh0
0
5
10
15
20
25
0
10
20


T=10K
00l
hh0
0
5
10
15
20
25
0
10
20

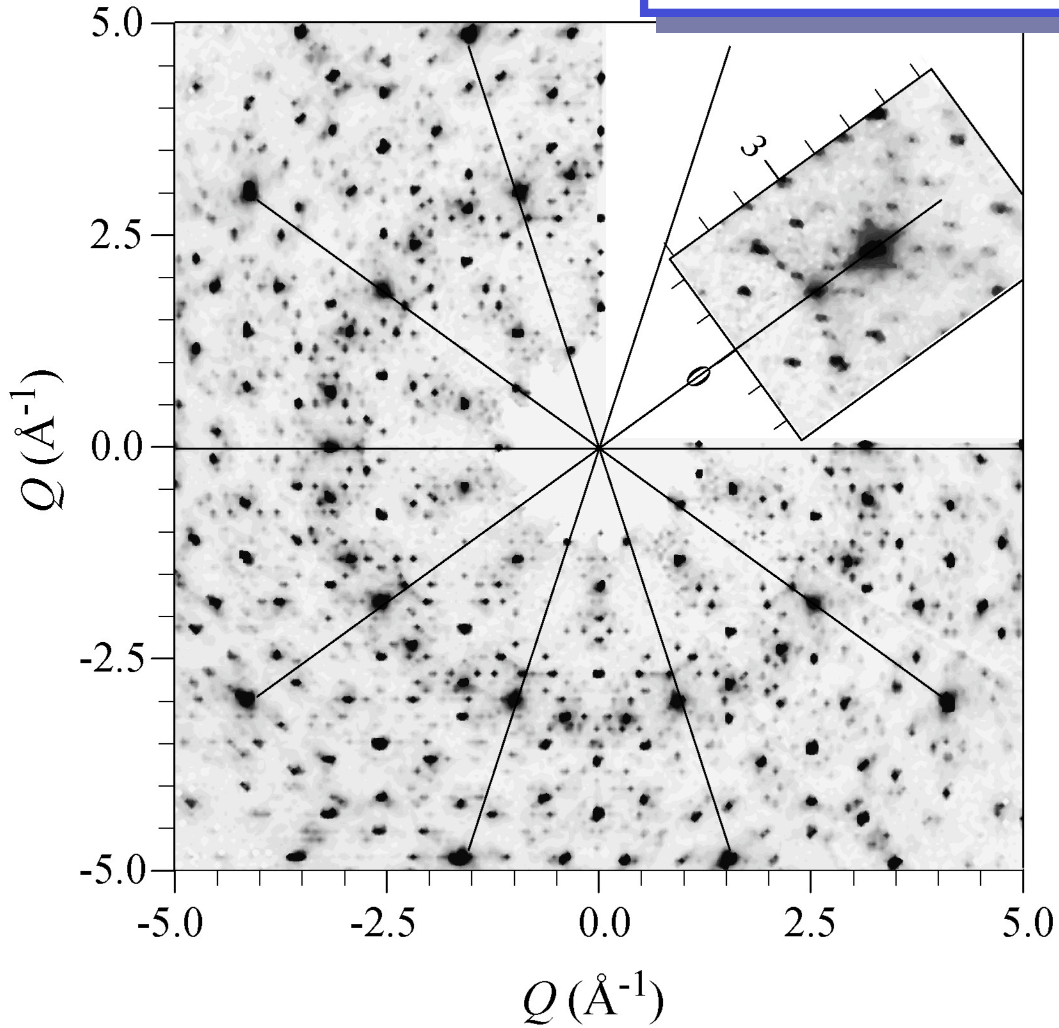
DOPED FLUORITES





Cubeoctahedral defects accommodate excess anions within the fluorite lattice

QUASICRYSTALS

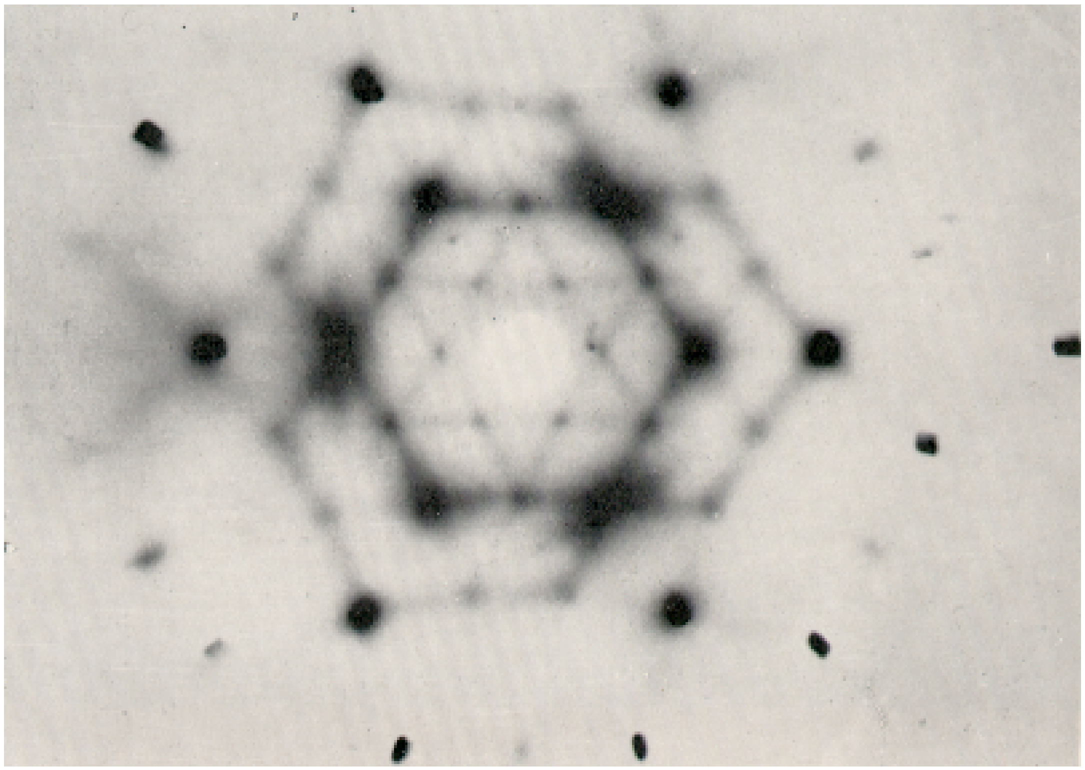


SUMMARY OF DIFFUSE SCATTERING INTRODUCTION

- Diffuse scattering arises when a structure does not have perfect long-range order.
- Diffuse scattering is often associated with structural deviations which are short-range.
- Diffuse scattering is especially pronounced in (amongst others)
  - molecular crystals (e.g. C_{60}, SF_6, Ice)
  - substitutional alloys (e.g. CuMn)
  - flexible systems (e.g. network silicates)
  - defective crystals (e.g. superionic fluorites and halides)
  - 'host-guest' lattices (e.g. urea inclusion compounds, MeH_x)
  - quasicrystals (e.g. AlPdMn)
  - amorphous materials (e.g. B_2O_3, GeO_2)
  - liquids.
- *Diffuse scattering data interpretation can be very complex.*

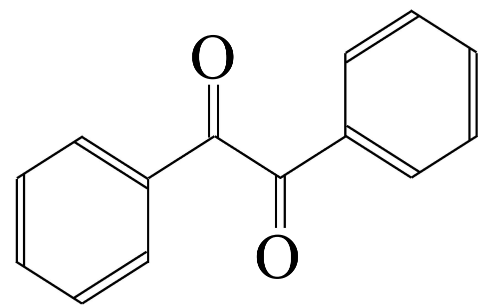
HISTORICAL PERSPECTIVE

Royal Society Discussion Meeting on Diffuse Scattering in London in 1941

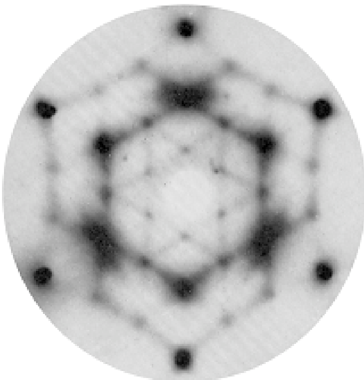


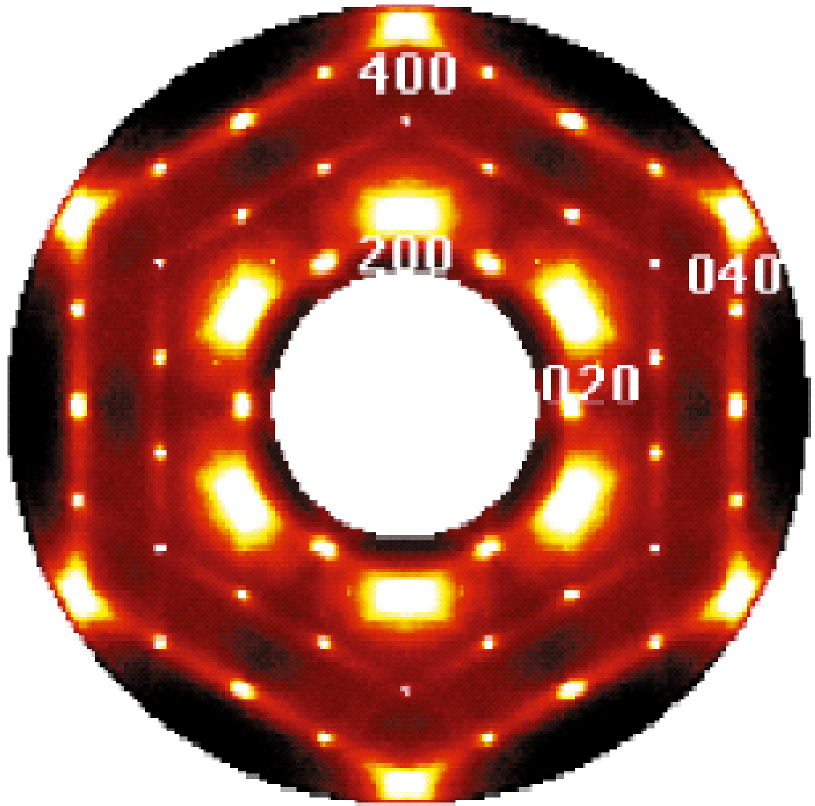
Lonsdale & Smith *Proc. Roy. Soc.* A **179** (1941).

BENZIL
110 vertical,
monochromatic Cu K_{α}
beam along 001.
2 hr exposure, 3.5 cm film to sample distance.



HISTORICAL PERSPECTIVE



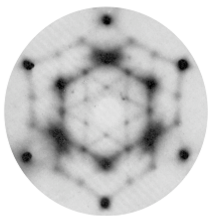


BENZIL
100 vertical, *hk*0 plane
monochromatic Co K_{α}.
Linear psd in
Weissenberg geometry.

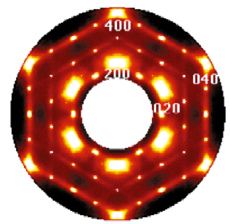
Welberry *et al Acta Cryst.* A **57** 101 (2001).

HISTORICAL PERSPECTIVE

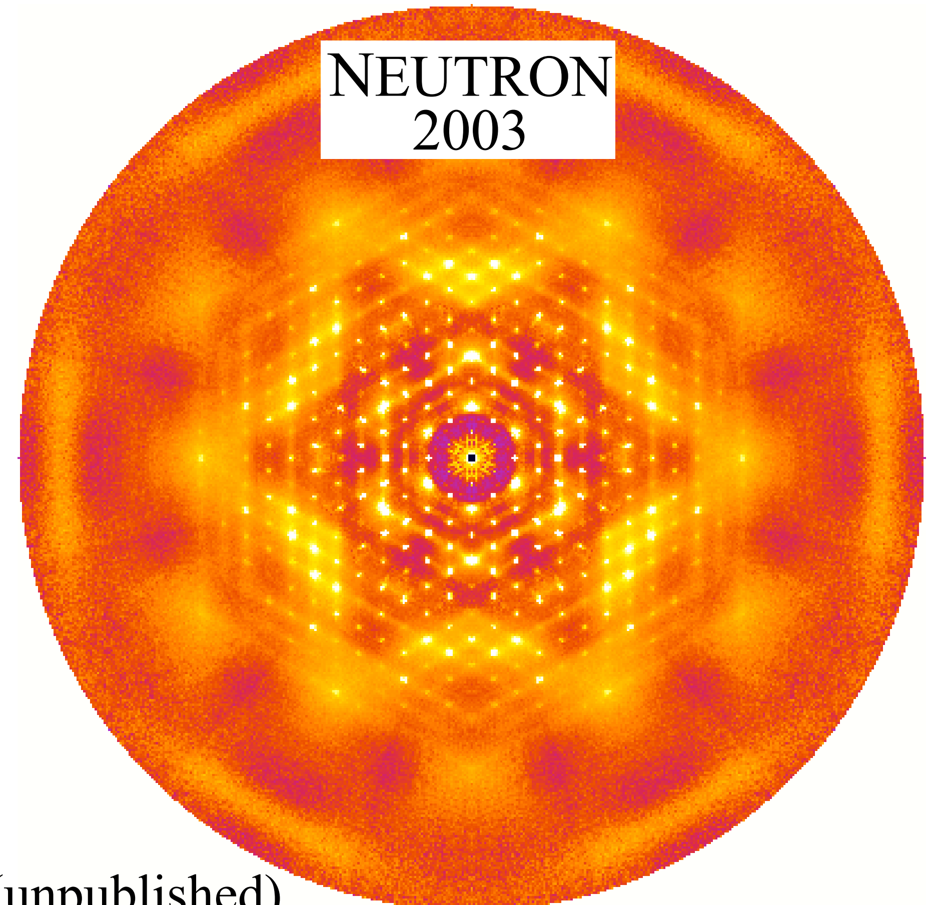
X-RAY



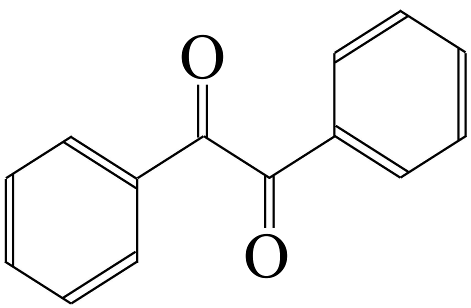
1941



2001



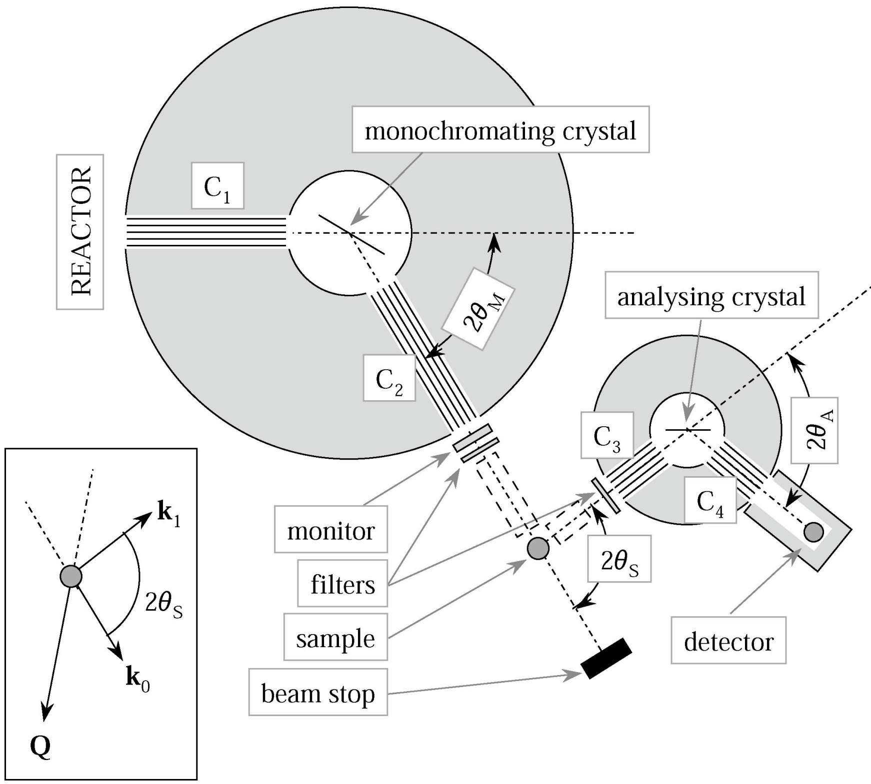
BENZIL
100 vertical, *hk*0 plane
polychromatic neutron
diffraction on SXD.



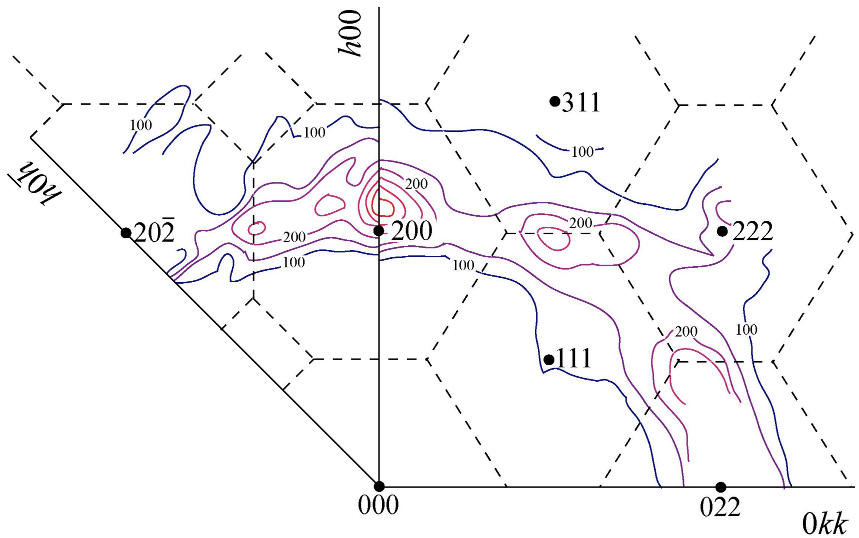
Welberry *et al* (unpublished)

NEUTRON SCATTERING SPECTROMETERS

TRIPLE-AXIS SPECTROMETERS



CaF$_2$ 1473K

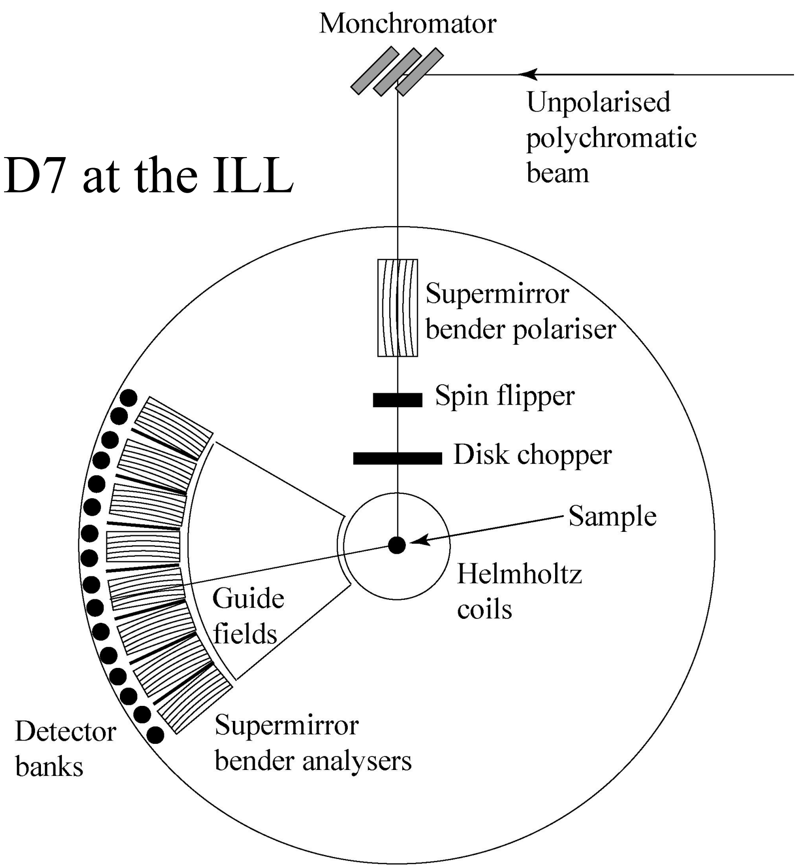


Hutchings *et al J. Phys.* C **17** 3903 (1984)

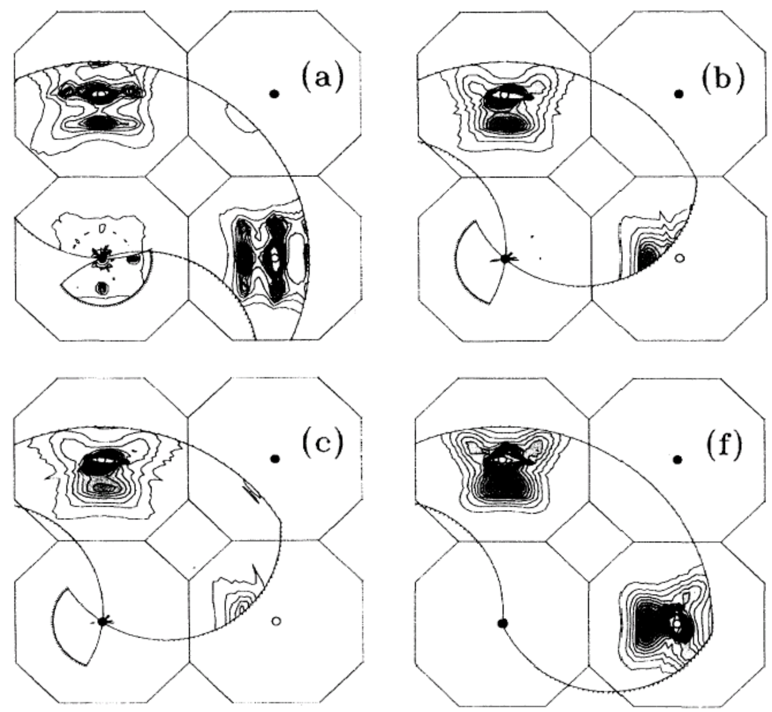
NEUTRON SCATTERING SPECTROMETERS

TIME-OF-FLIGHT SPECTROMETERS

D7 at the ILL



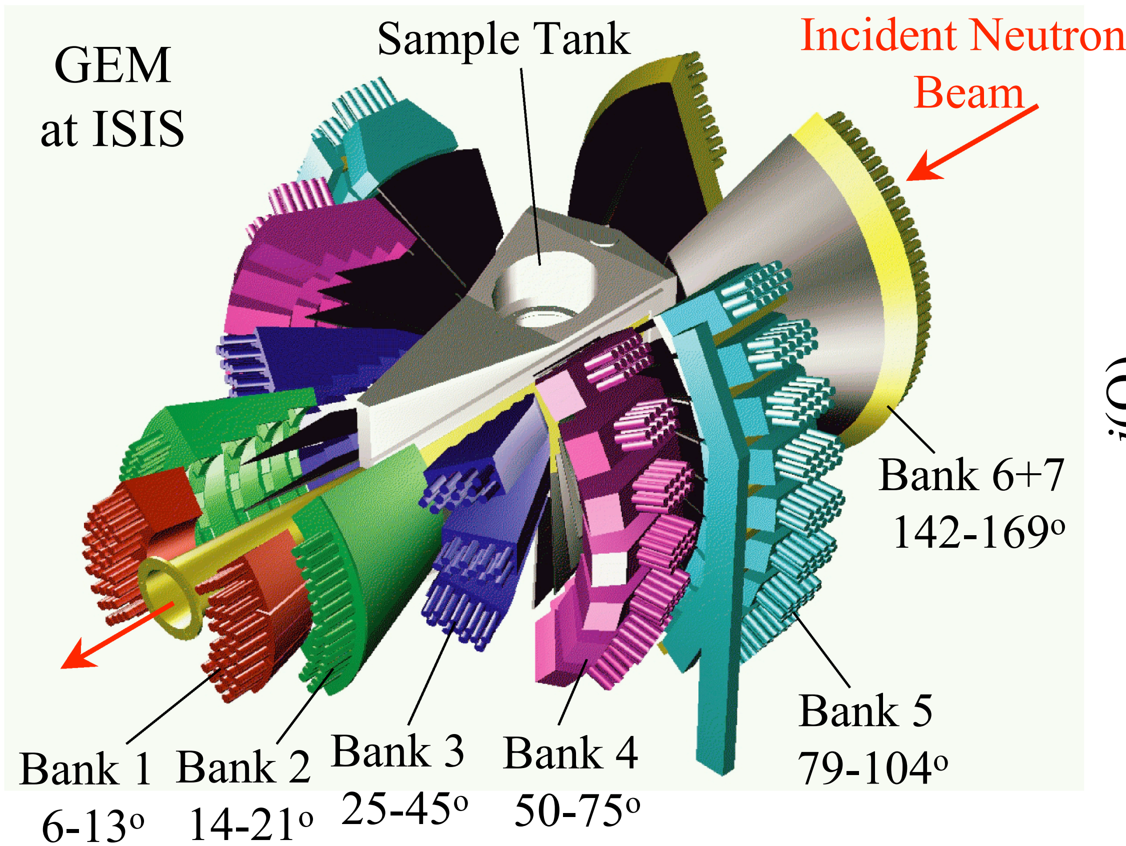
$Fe_{1-x}O$ (100) plane

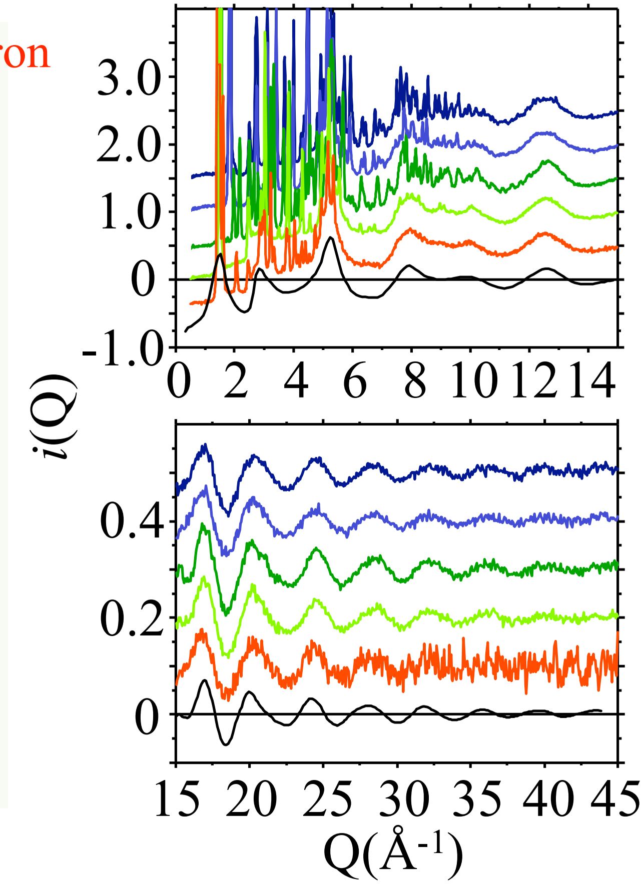


Schweika *et al Phys. Rev.* B **51** 15771 (1995)

NEUTRON SCATTERING SPECTROMETERS

TOTAL SCATTERING POWDER DIFFRACTOMETERS



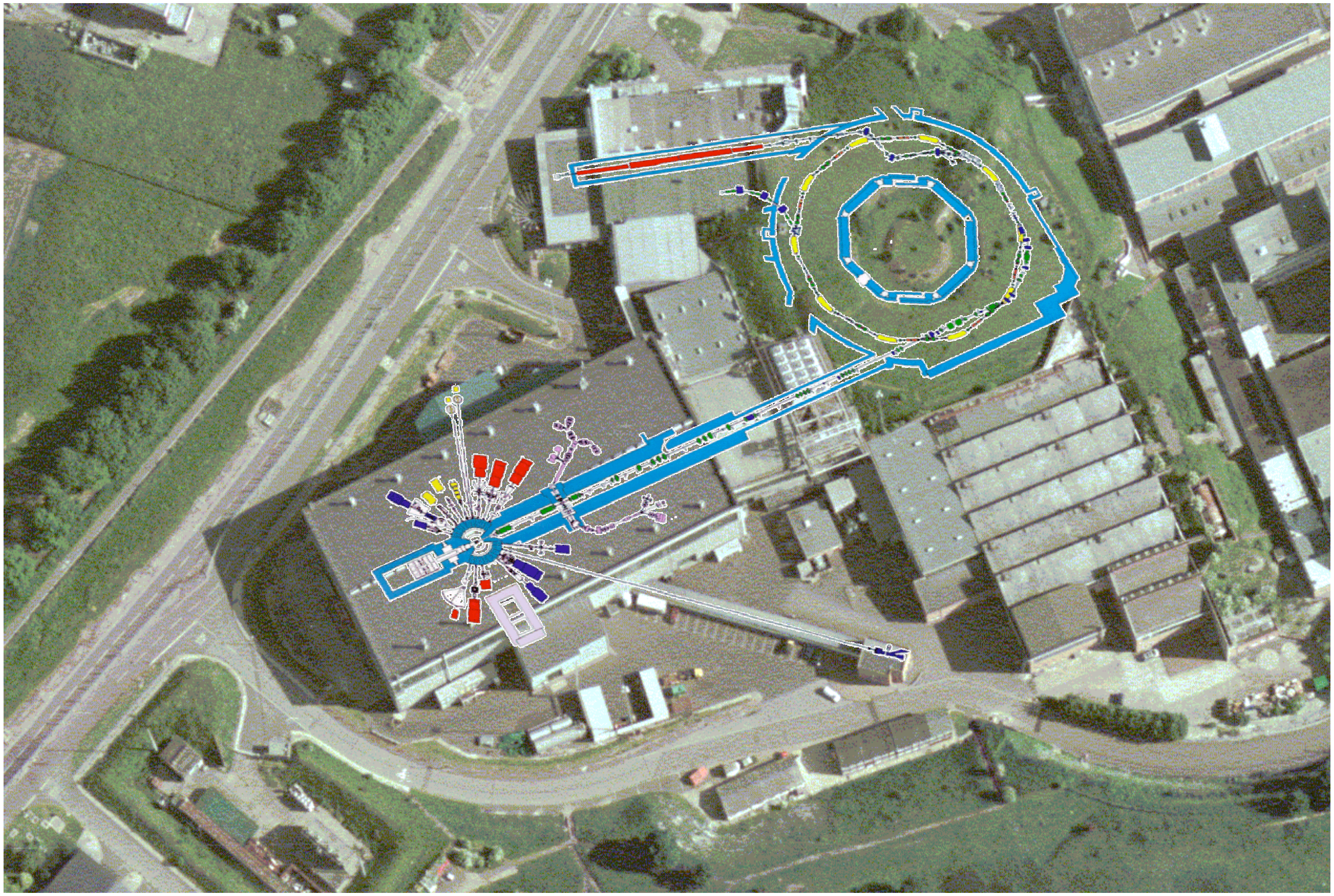


ELASTIC VERSUS TOTAL SCATTERING

Elastic scattering gives a *time-average* picture of the structure. Bragg scattering gives unit cell metric, average atom positions and symmetry; disorder is modelled via partially occupied sites and anisotropic temperature factors.
Elastic diffuse scattering gives information on static deviations from long-range order.

Total scattering (i.e. scattering integrated over all changes of neutron energy) gives a *snap-shot* picture of the structure.
This includes *all* the Bragg and diffuse scattering contributions.
Disorder is inherent in the snap-shot – the challenge is to interpret it!

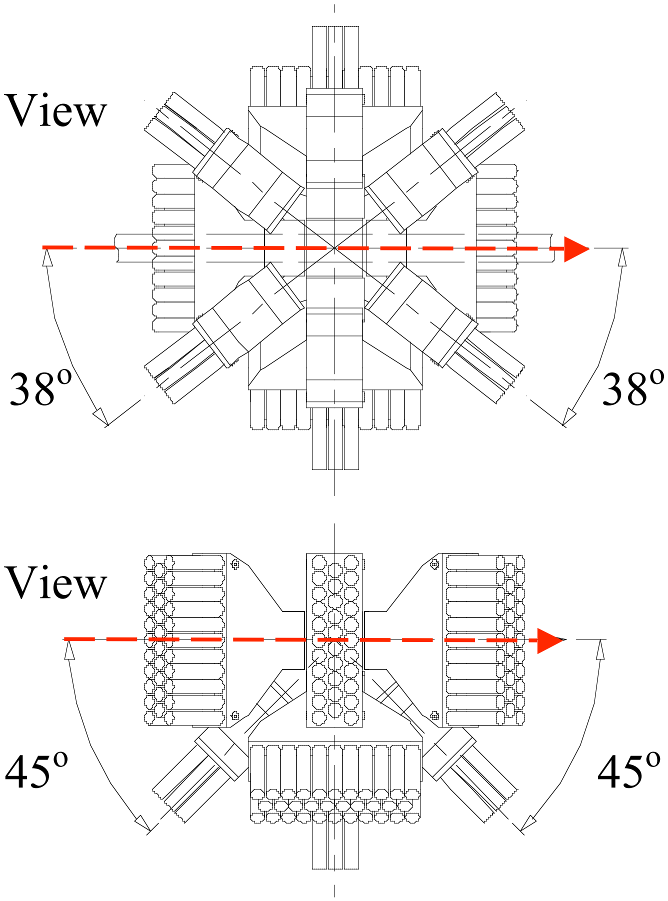
THE ISIS PULSED NEUTRON AND MUON FACILITY



DESIGN FOR SXD AT ISIS

Plan View

Side View

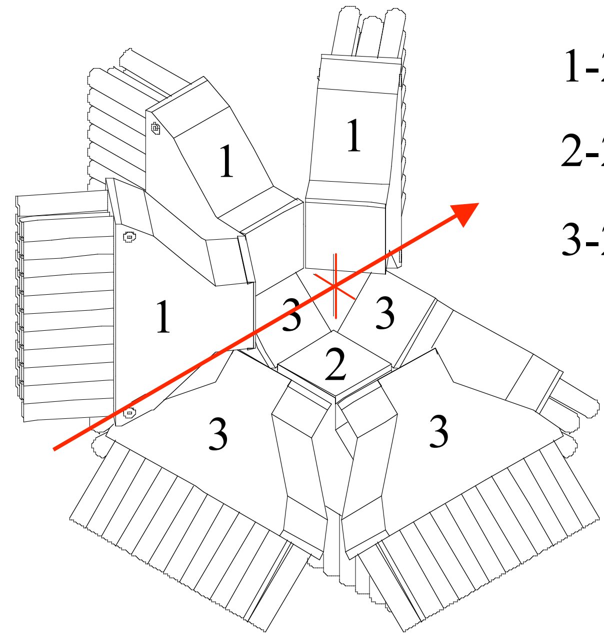


Sample to detector distances

1-225mm (6)

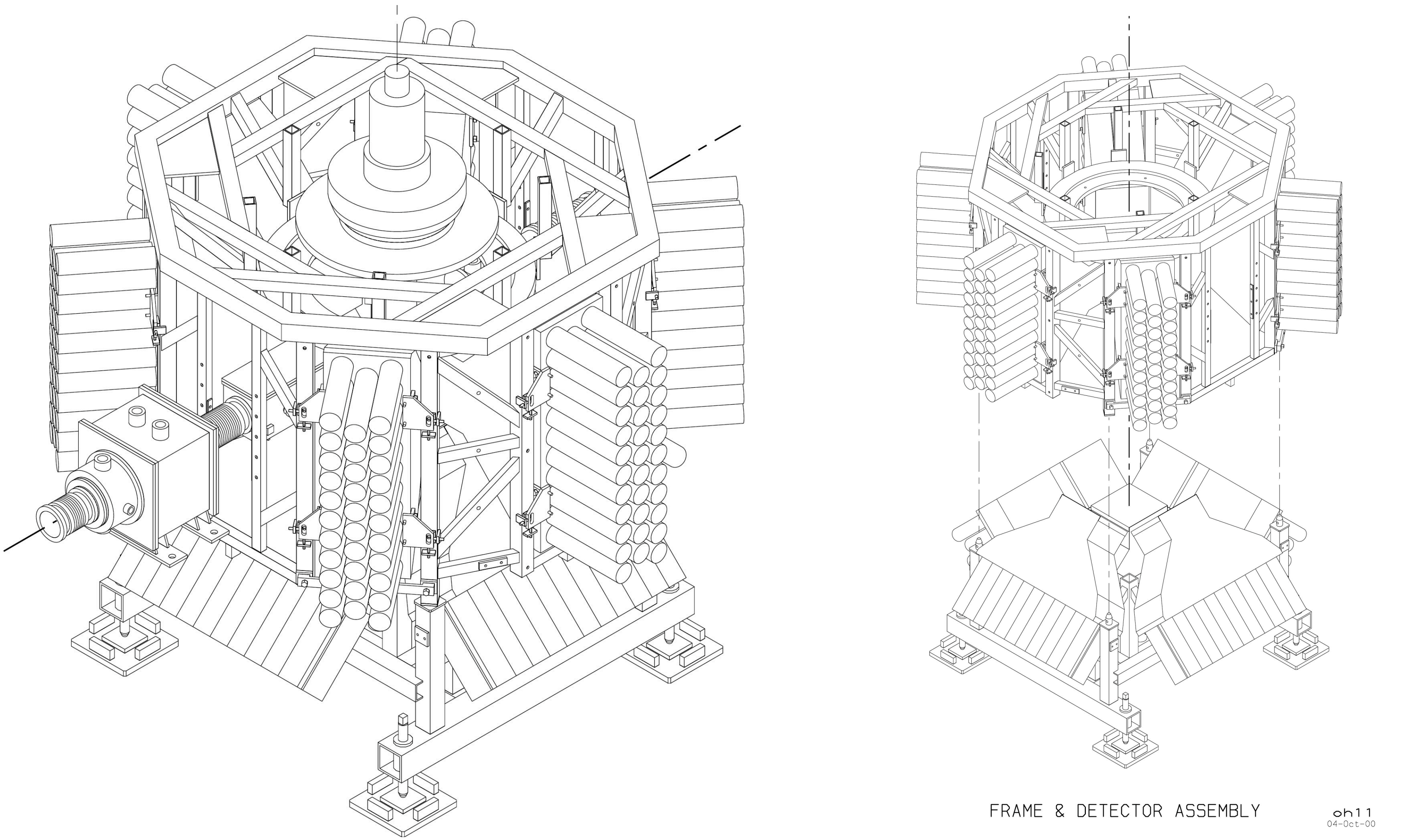
2-280mm (1)

3-270mm (4)

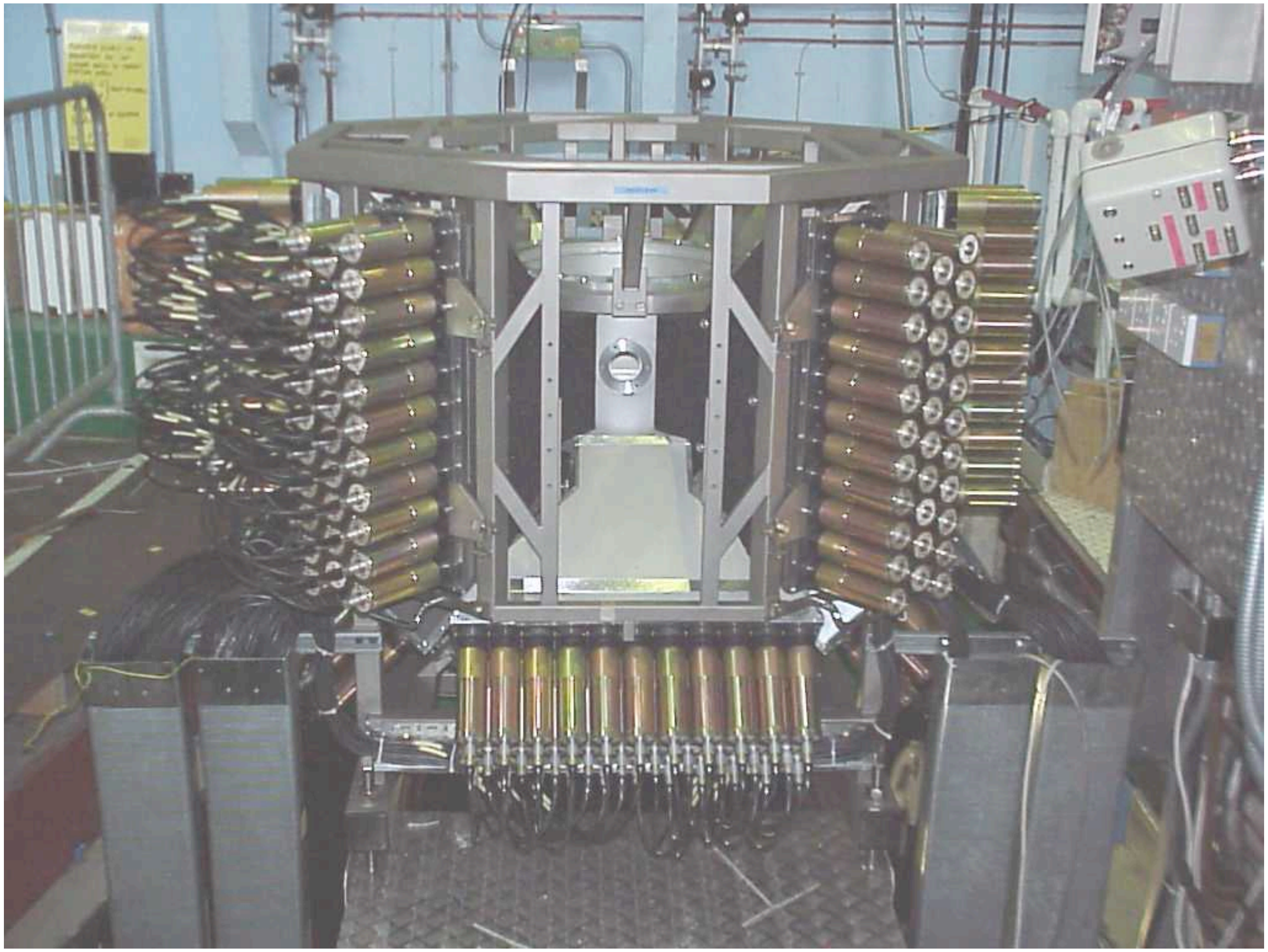


11 2D position-sensitive detectors, each with 4096 pixels. ~2π solid angle, arranged largely in the equatorial plane and around $2\theta \sim 90^{\circ}$

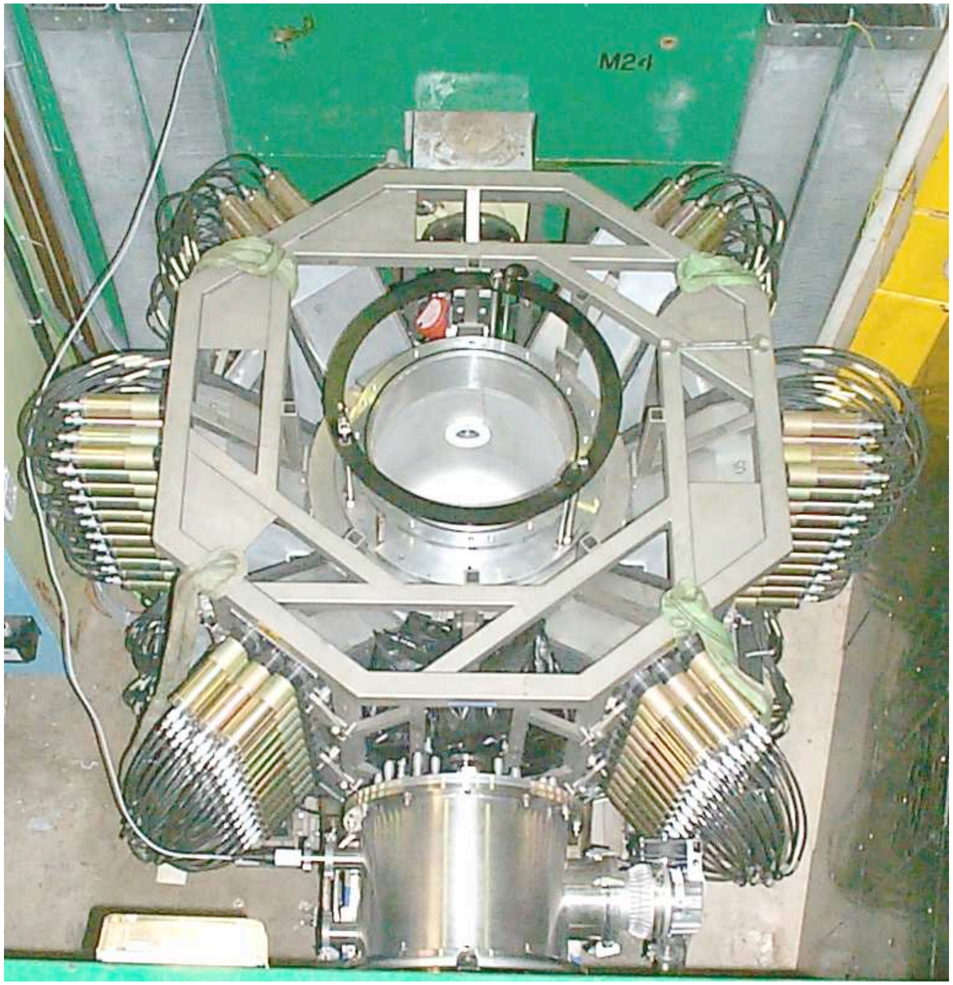
DRAWING OF SXD AT ISIS



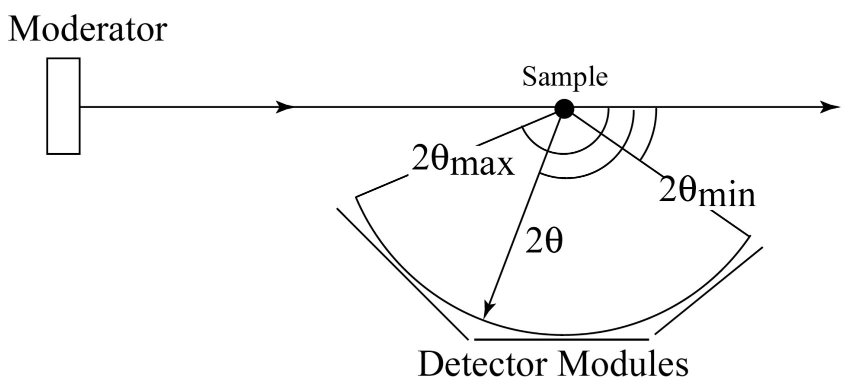
SXD at ISIS During Installation

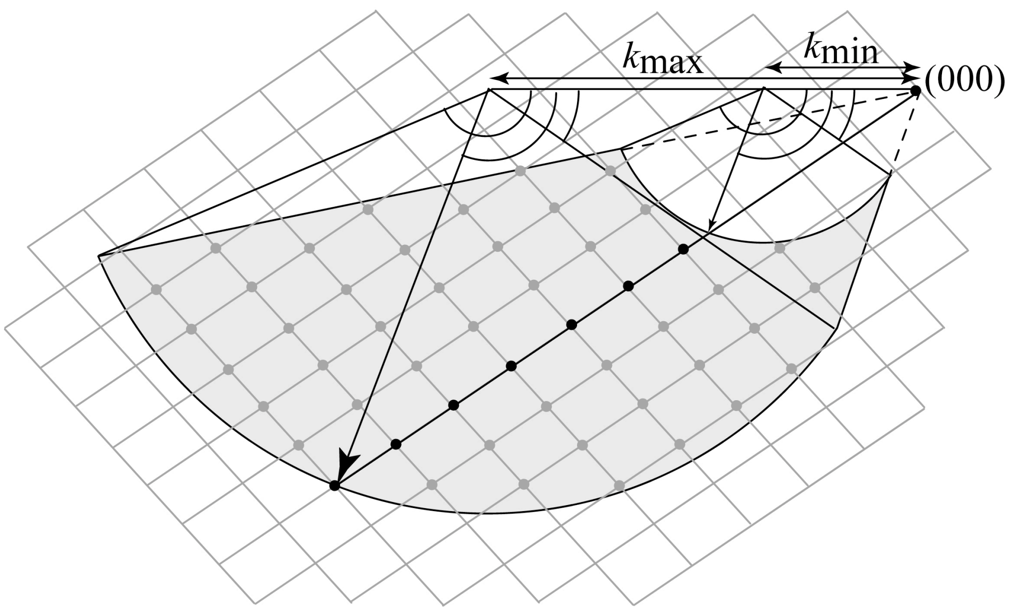


SXD AT ISIS DURING INSTALLATION



Reciprocal Space Covered by Neutron Time-of-Flight Single Crystal Diffraction

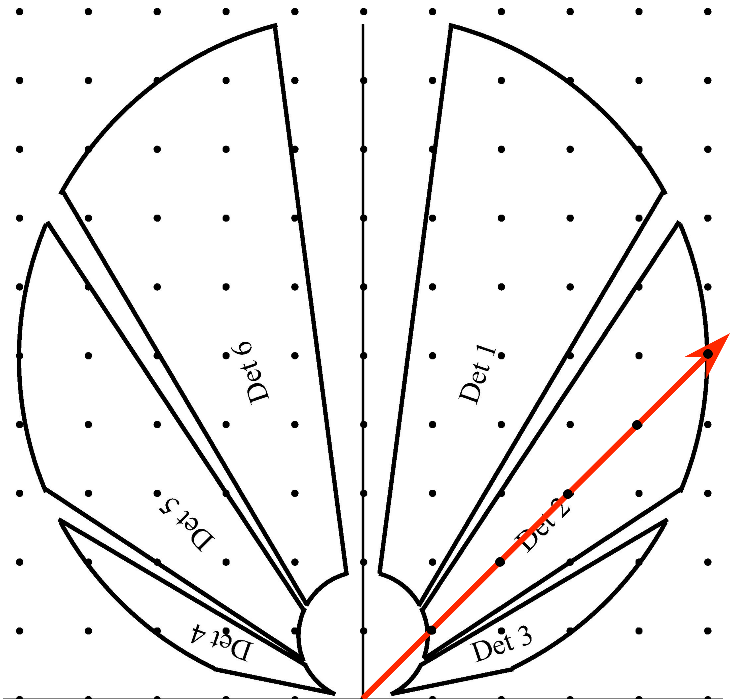


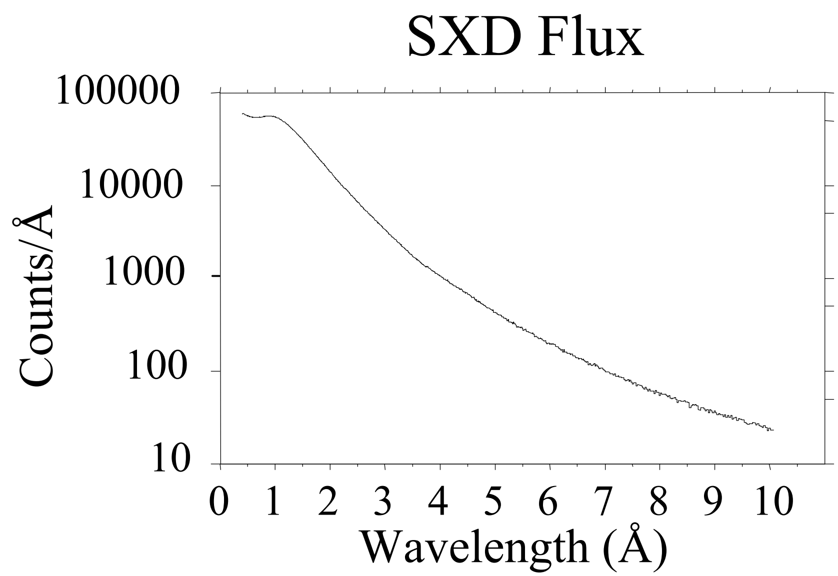


- Fixed crystal, equatorial section.
- Continuous data are collected between two Ewald spheres and the maximum and minimum scattering angles.
- The orders of a given reflection are separated in neutron time-of-flight.

Single Crystal Neutron Time-of-Flight Diffraction in Practice on SXD at ISIS

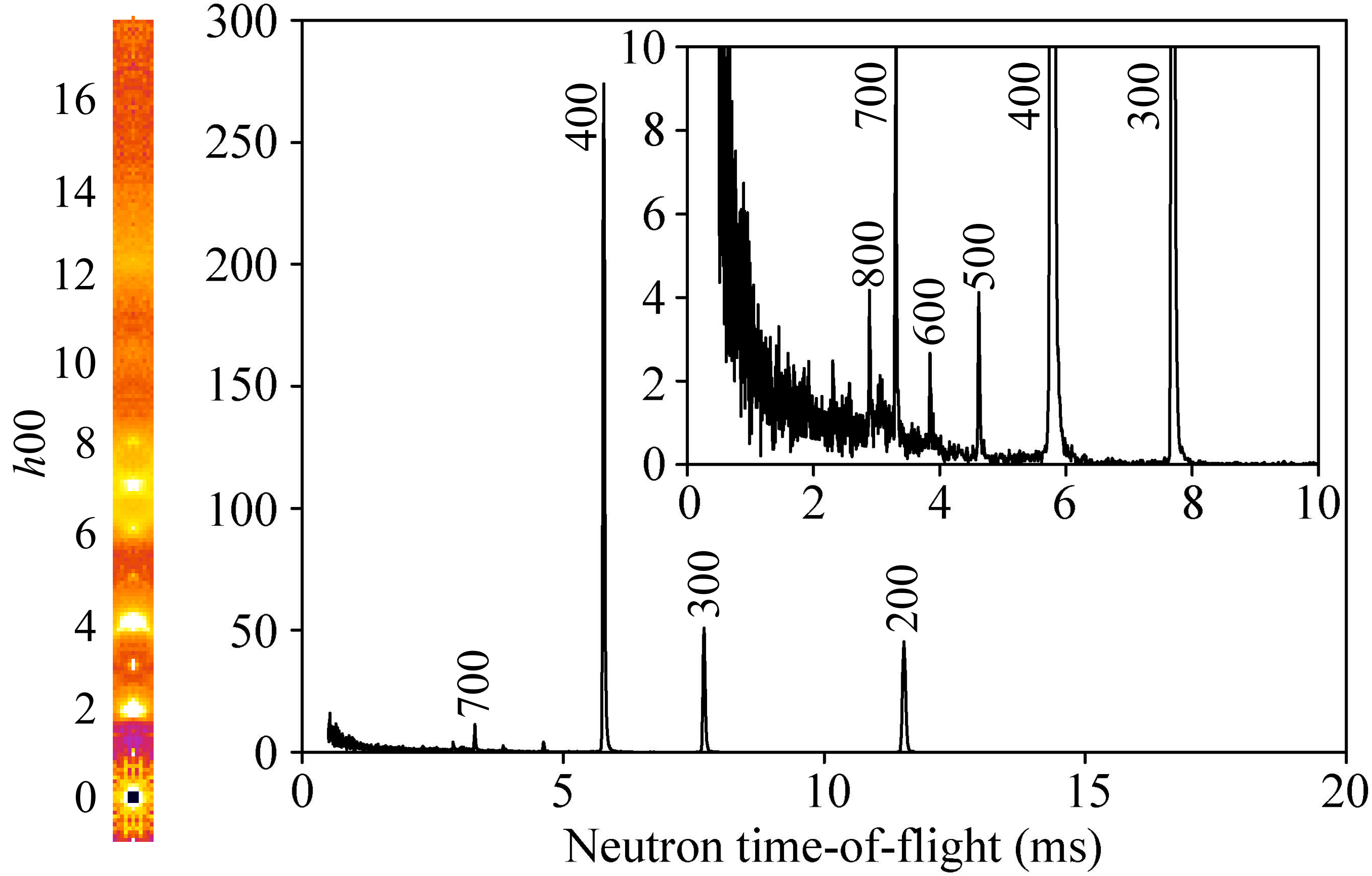
Typical values are: $15^o < 2\theta < 165^o$, $0.15Å < \lambda < 10Å$





A data collection consists of a small number of frames (fixed sample and detectors), with the sample rotated about one axis between each frame.

SINGLE CRYSTAL NEUTRON TIME-OF-FLIGHT DIFFRACTION IN PRACTICE ON SXD AT ISIS

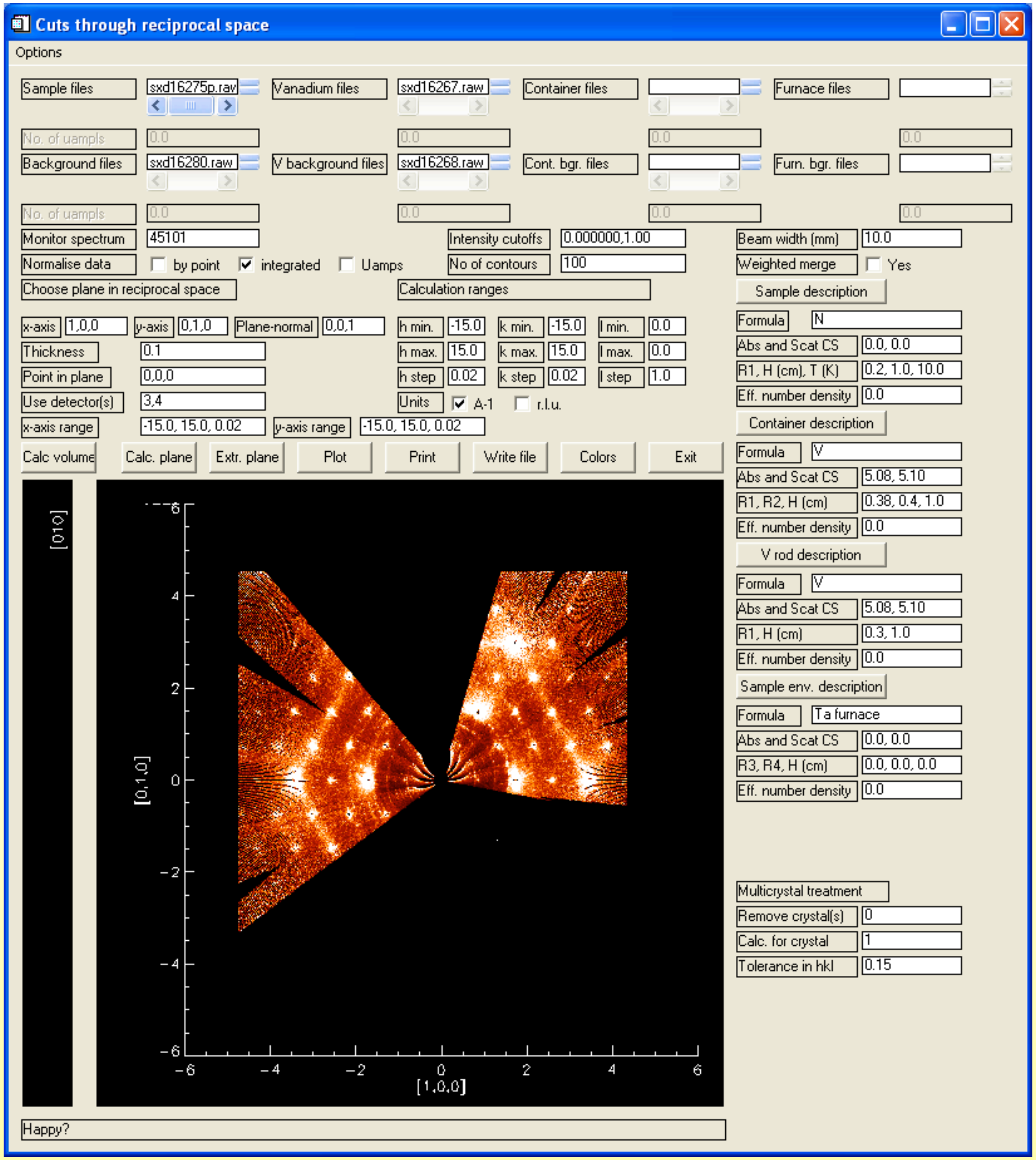


SXD Data Treatment

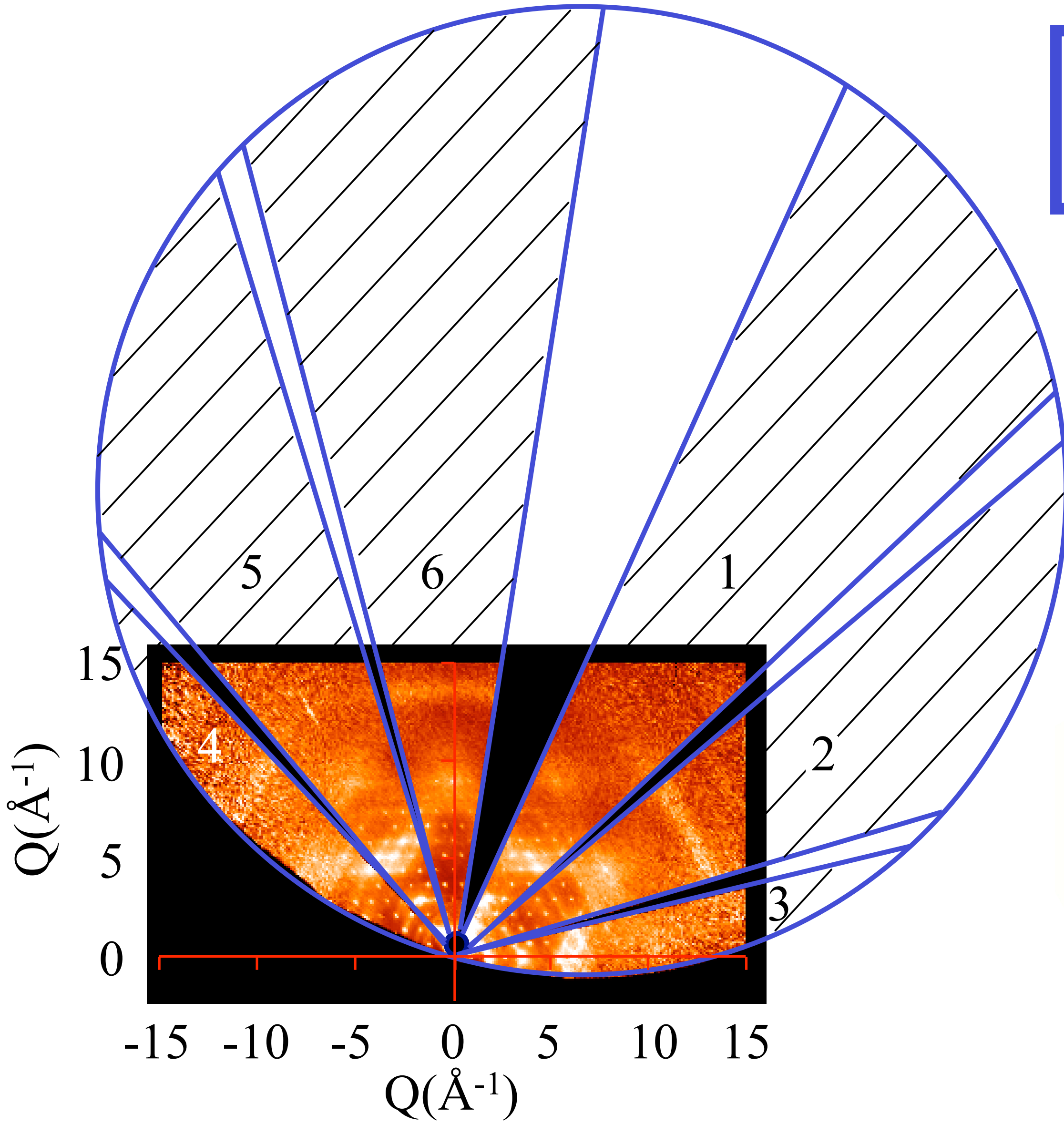
- Search the data for Bragg peaks.
- Determine UB orientation matrix/matrices.

(• Extract Bragg intensities for structure refinement.)

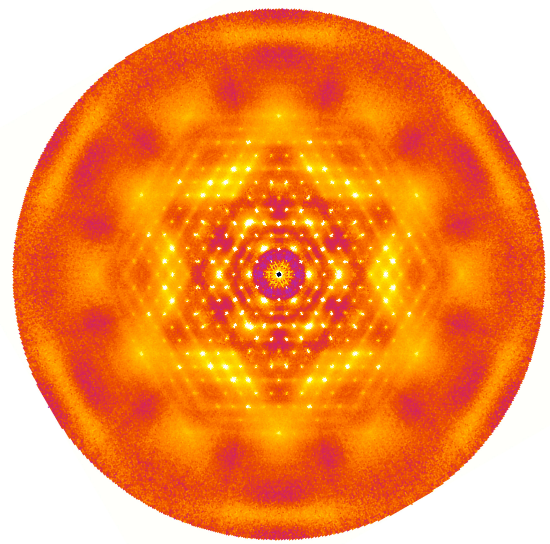
- Normalise each pixel in each detector of each frame of the experiment using vanadium and monitor data (~2000 × 4096 × 11 × 6 data).
- Convert (*t-o-f*, *spectra*) data to (q_h, q_k, q_l) or (q_x, q_y,q_z).
- Extract planes of interest using merged data.
- Plot and analyse the data.
- All within a PC-based IDL environment.


Cuts through reciprocal space
Options
Sample files
sxd16275p.raw
Vanadium files
sxd16267.raw
Container files
Furnace files
No. of uampls
0.0
Background files
sxd16280.raw
V background files
sxd16268.raw
Cont. bgr. files
Furn. bgr. files
Monitor spectrum
45101
Intensity cutoffs
0.000000,1.00
Beam width (mm)
10.0
Normalise data
by point
integrated
Uamps
No of contours
100
Weighted merge
Yes
Choose plane in reciprocal space
Calculation ranges
Sample description
x-axis
1,0,0
y-axis
0,1,0
Plane-normal
0,0,1
h min.
-15.0
k min.
-15.0
l min.
0.0
Formula
N
Thickness
0.1
h max.
15.0
k max.
15.0
l max.
0.0
Abs and Scat CS
0.0, 0.0
Point in plane
0,0,0
h step
0.02
k step
0.02
l step
1.0
R1, H (cm), T (K)
0.2, 1.0, 10.0
Use detector(s)
3,4
Units
A-1
r.l.u.
Eff. number density
0.0
x-axis range
-15.0, 15.0, 0.02
y-axis range
-15.0, 15.0, 0.02
Container description
Calc volume
Calc. plane
Extr. plane
Plot
Print
Write file
Colors
Exit
Formula
V
Abs and Scat CS
5.08, 5.10
R1, R2, H (cm)
0.38, 0.4, 1.0
Eff. number density
0.0
V rod description
Formula
V
Abs and Scat CS
5.08, 5.10
R1, H (cm)
0.3, 1.0
Eff. number density
0.0
Sample env. description
Formula
Ta furnace
Abs and Scat CS
0.0, 0.0
R3, R4, H (cm)
0.0, 0.0, 0.0
Eff. number density
0.0
Multicrystal treatment
Remove crystal(s)
0
Calc. for crystal
1
Tolerance in hkl
0.15
[010]
[0,1,0]
[1,0,0]
Happy?

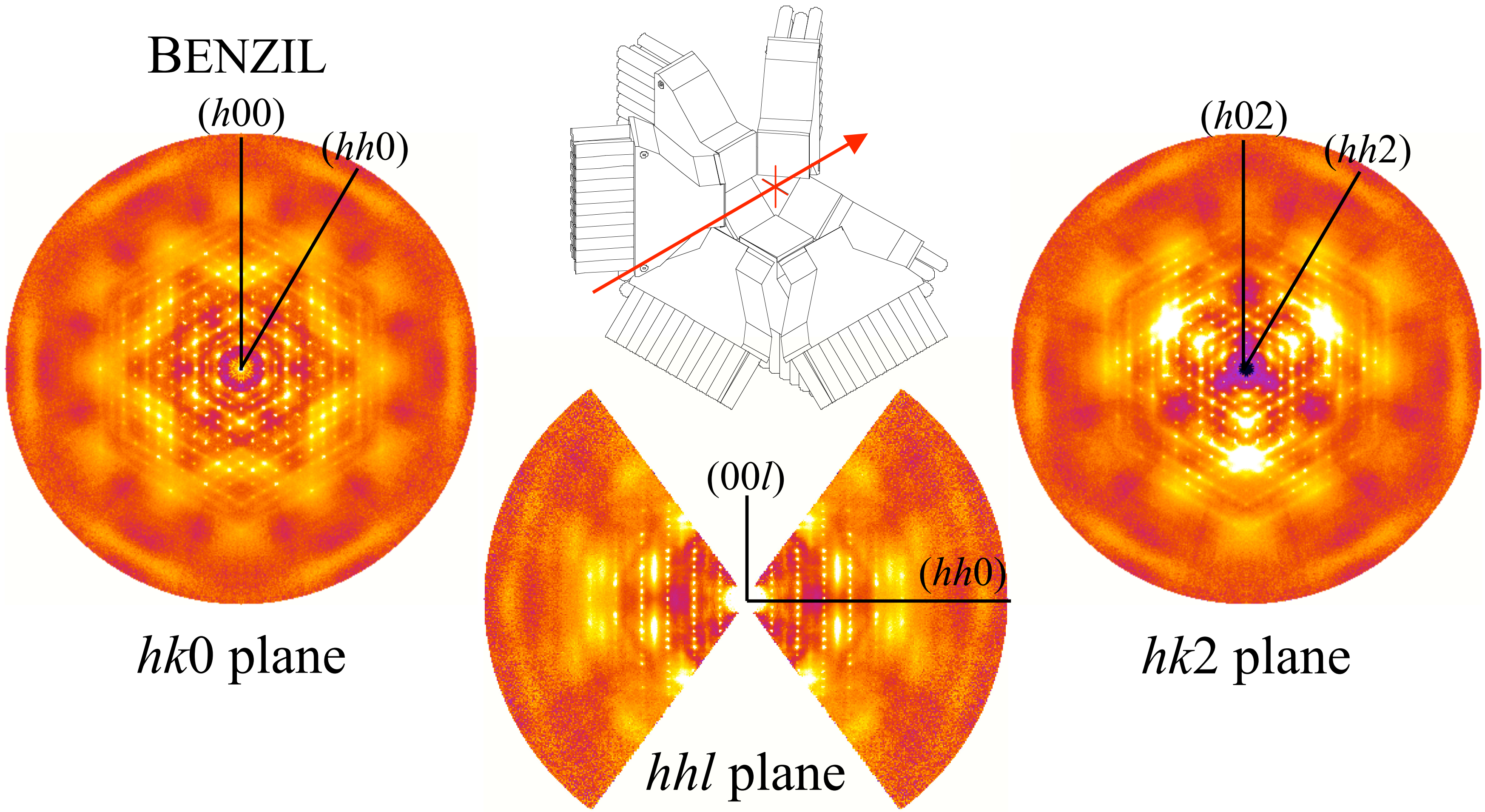
AN SXD DATA 'FRAME'



BENZIL on SXD
001 vertical, one crystal setting, six equatorial detectors.

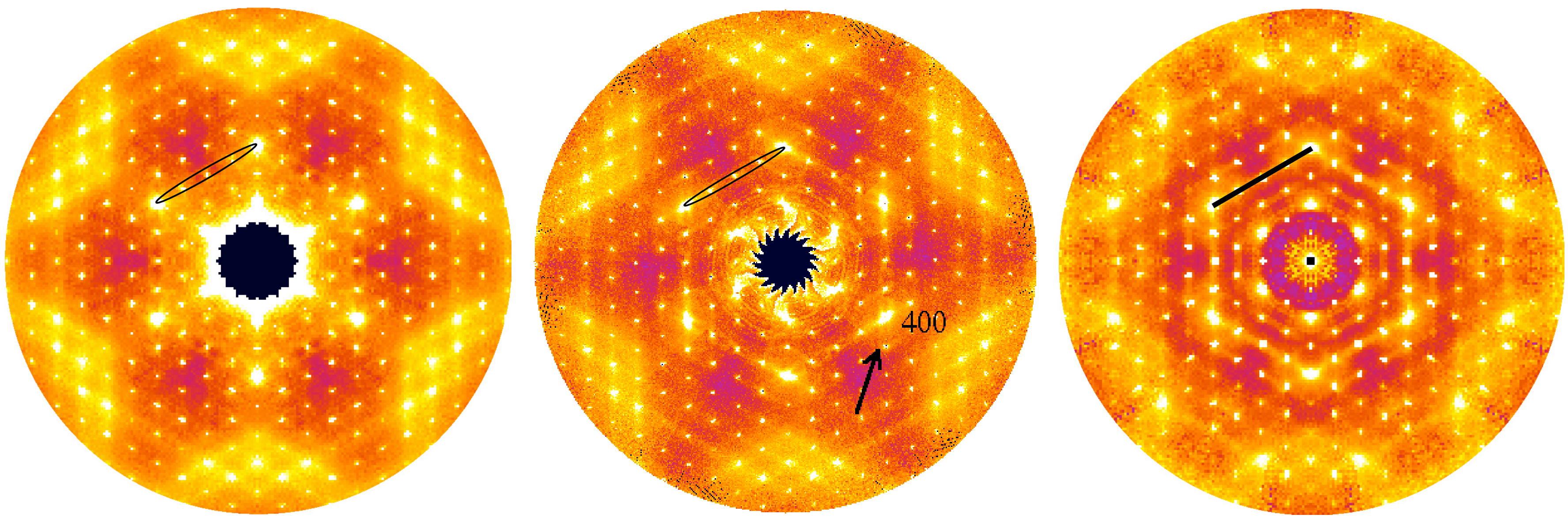


VOLUMES OF DATA FROM SXD



BALANCING *Q*-RESOLUTION AND □-INTEGRATION

BENZIL

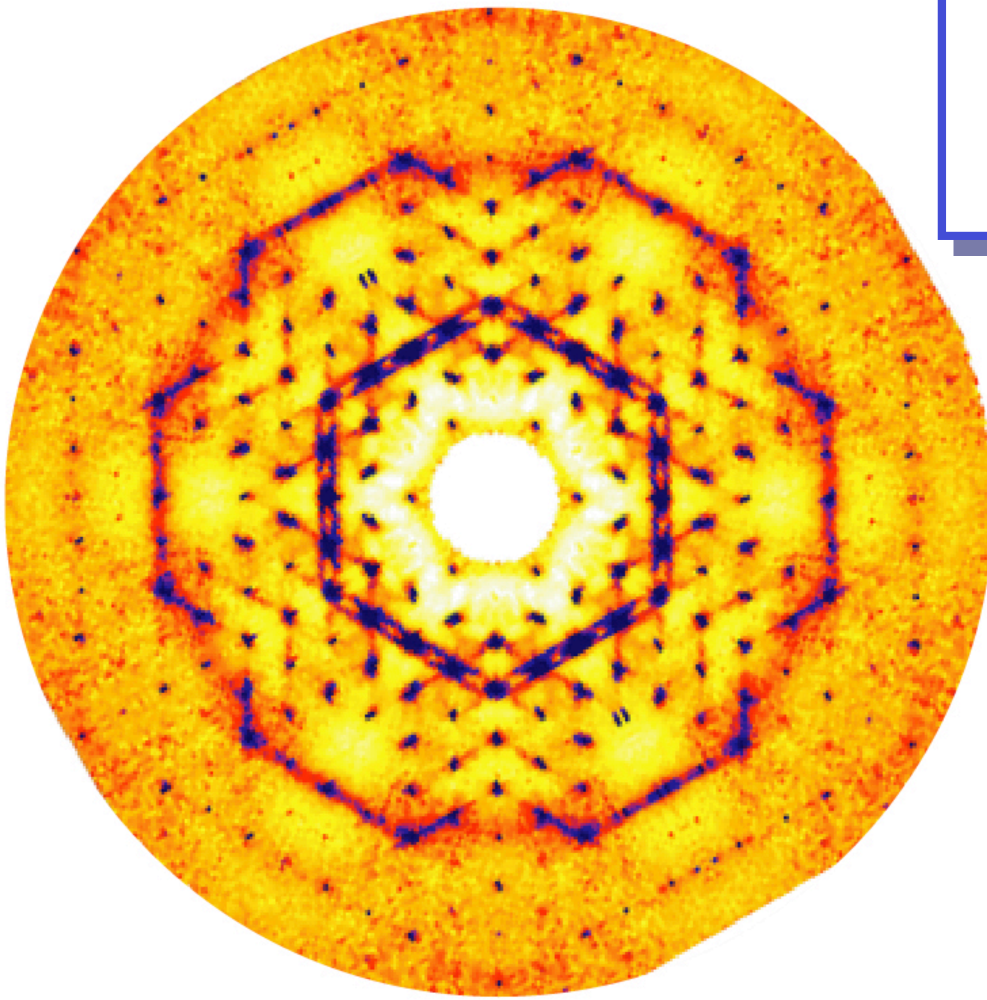


Detector 1
2□~142.5°

Detector 2
2□~90.0°

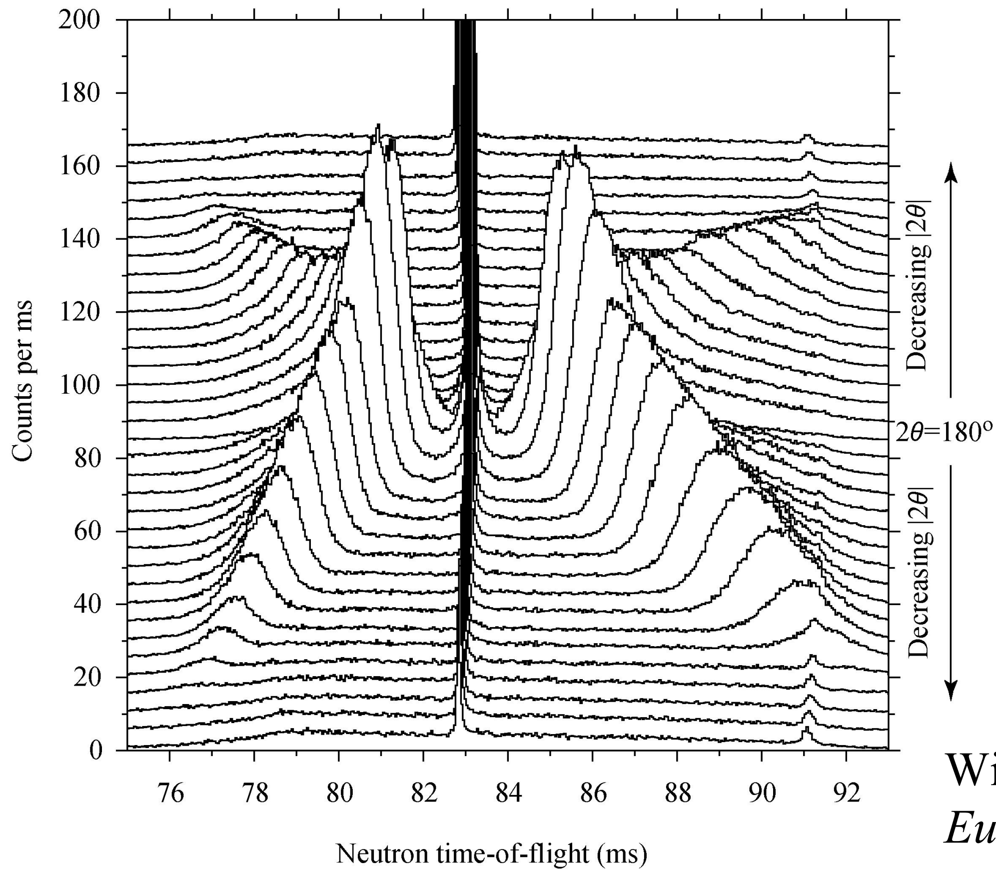
Detector 3
2□~37.5°

DIFFUSE SCATTERING FROM QUARTZ



EXTREME THERMAL DIFFUSE SCATTERING EFFECTS

PYROLYTIC GRAPHITE



HRPD Data

004 Bragg reflection scattering at $2\theta \sim 180^{o}$ such that $v_s > v_n > v_s \cos\theta$

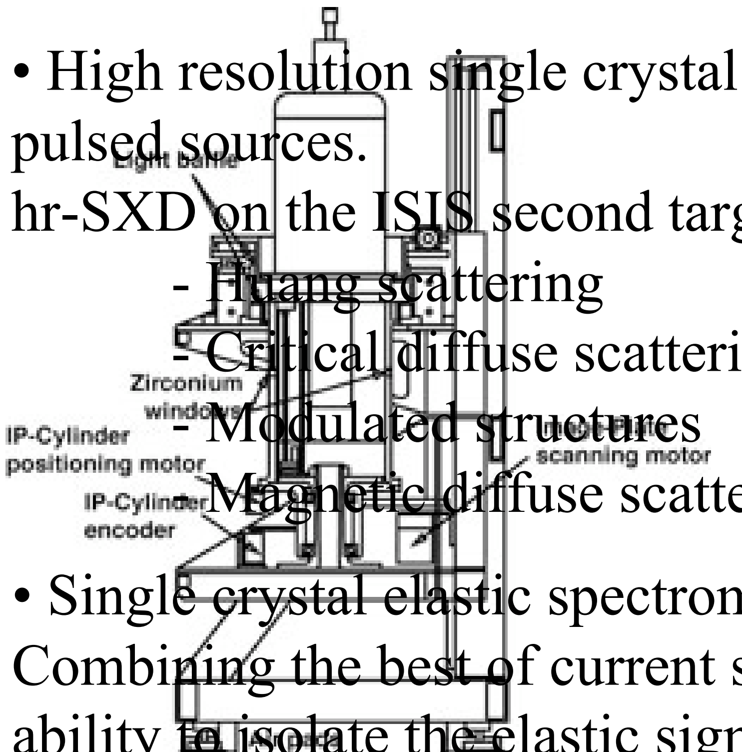
Willis *et al*
Europhys. Lett. **2** 767 (1986)

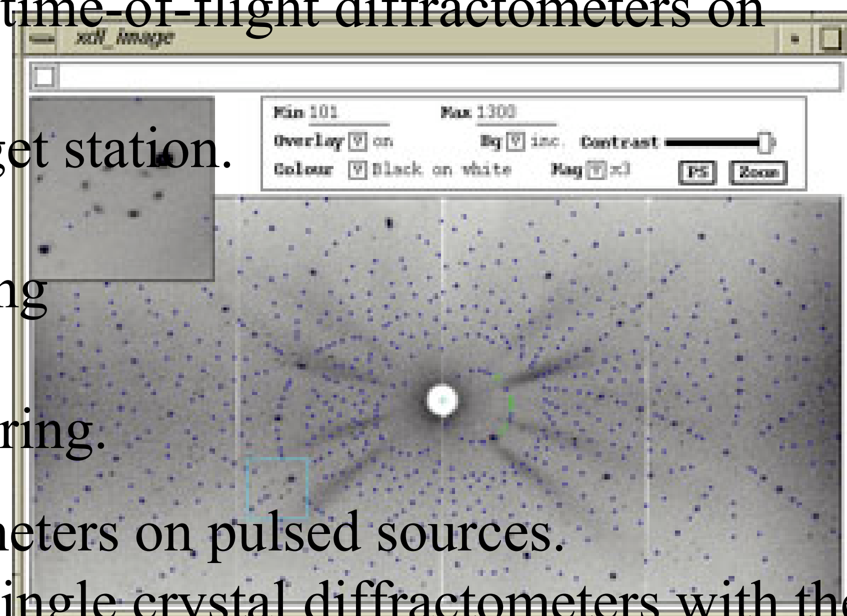
FUTURE DIFFUSE NEUTRON SCATTERING DEVELOPMENTS

• Image plate Laue and monochromatic diffractometers on reactor sources. VIVALDI (**V**ery-**I**ntense, **V**ertical-**A**xis **L**aue **Di**ffractometer)

• High resolution single crystal time-of-flight diffractometers on pulsed sources.
hr-SXD on the ISIS second target station.

- Huang scattering
- Critical diffuse scattering
- Modulated structures
- Magnetic diffuse scattering.





• Single crystal elastic spectrometers on pulsed sources.
Combining the best of current single crystal diffractometers with the ability to isolate the elastic signal…

SINGLE CRYSTAL ELASTIC DIFFUSE SCATTERING SPECTROMETERS ON PULSED SOURCES…