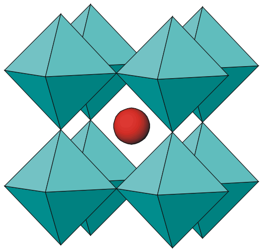
2D Detectors for Powder X-ray Diffraction: Data Reduction and Rietveld Refinements

Anthony Arulraj
Ramanujan Fellow
MSG, IGCAR

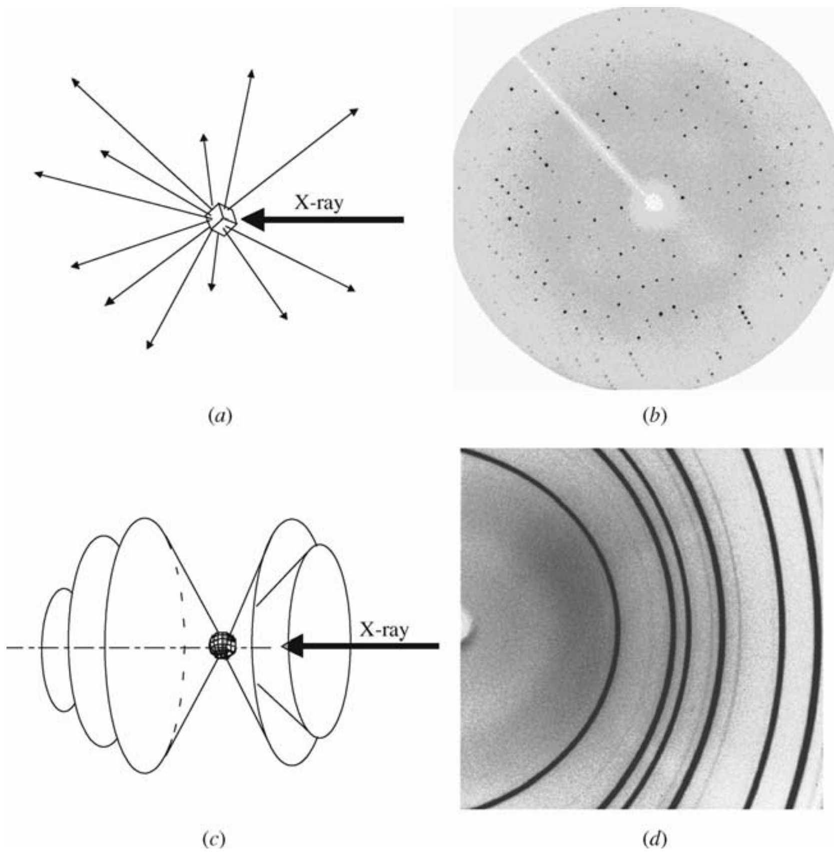


25 JANUARY 2012
RRCAT, INDUS II MEETING

Outline

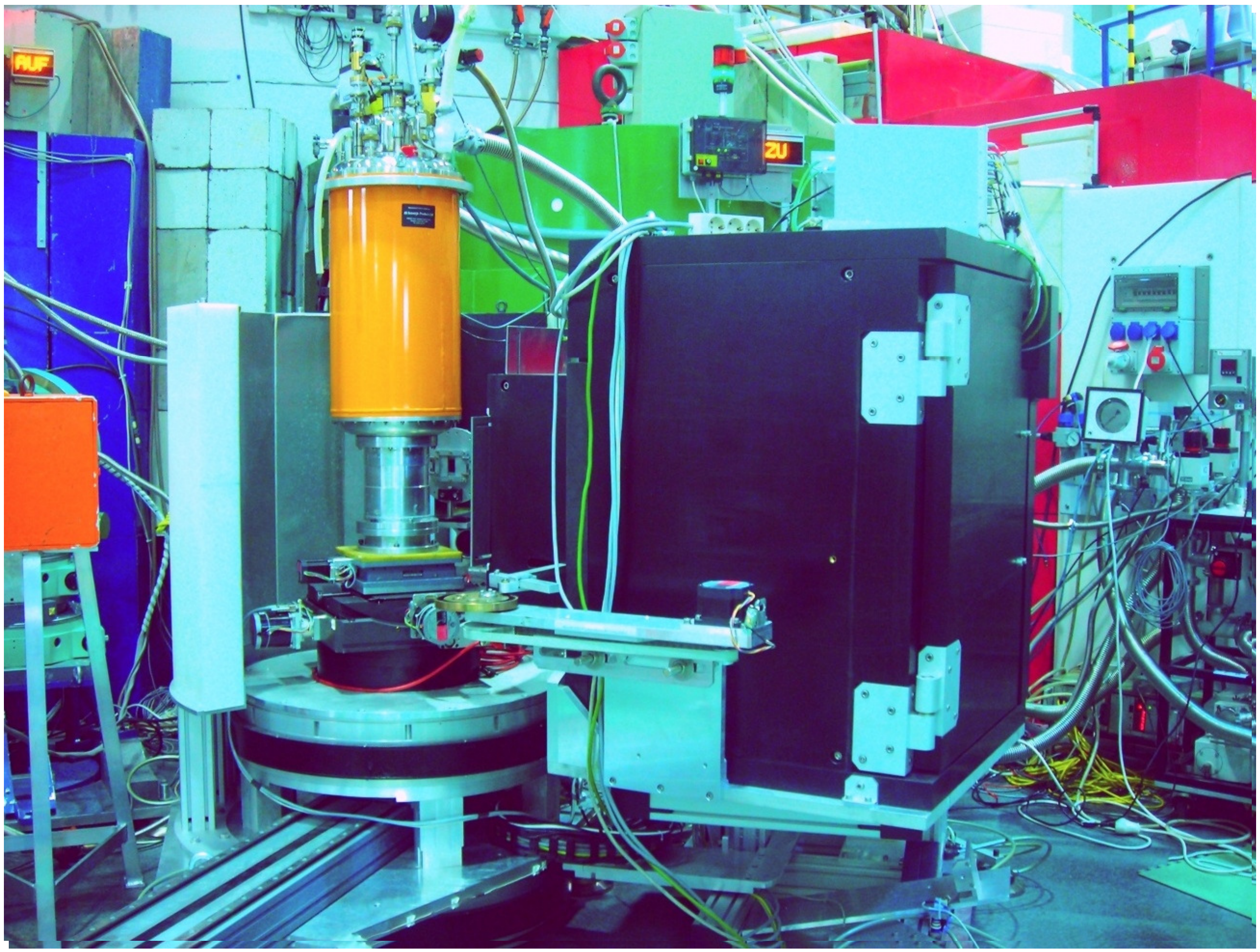
- Introduction : 2D diffraction , Area detectors
- Data Reduction Procedures as implemented in FIT2D Program
- Rietveld Refinements: examples from own Research

2D diffraction

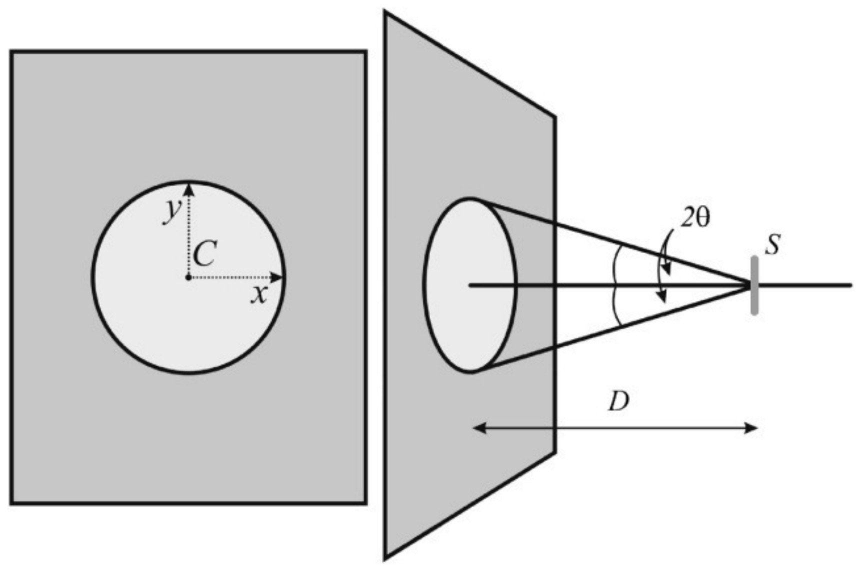


(a) (b) (c) (d)

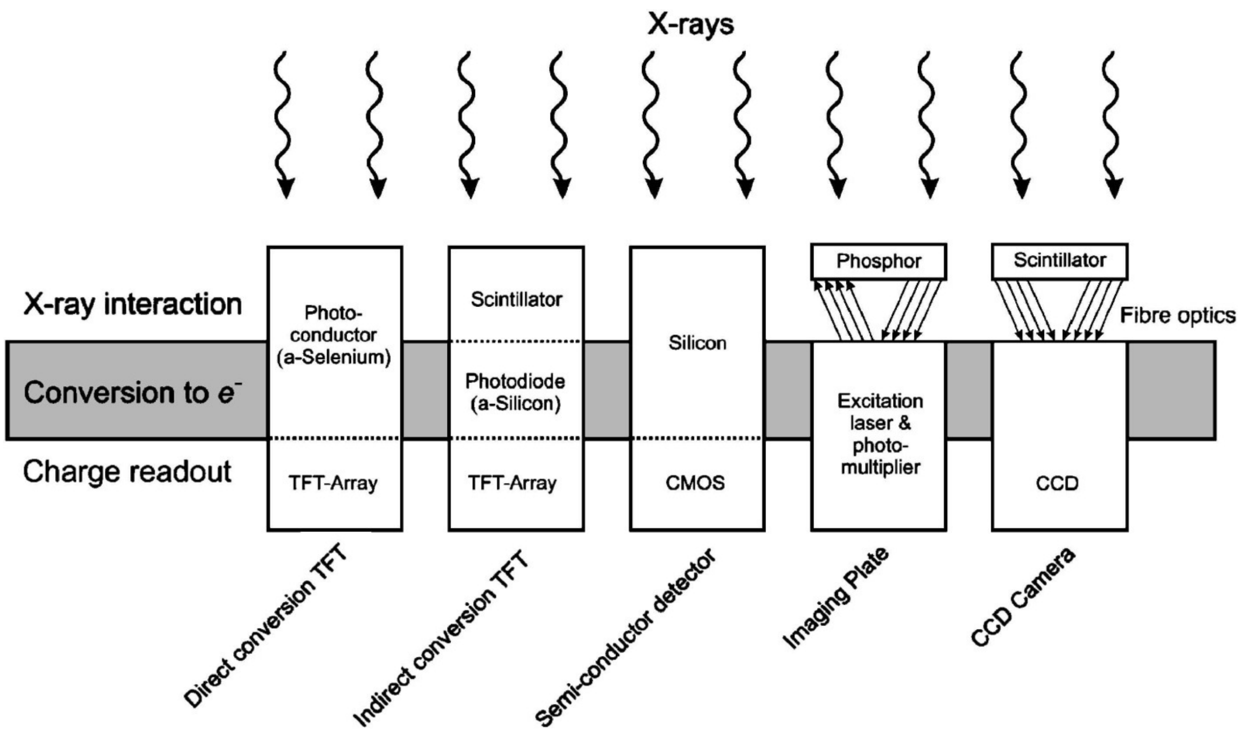
E6 Focusing diffractometer at BENSC



Cartoon of an IP detector perpendicular to the X-ray beam



Types of Area Detectors

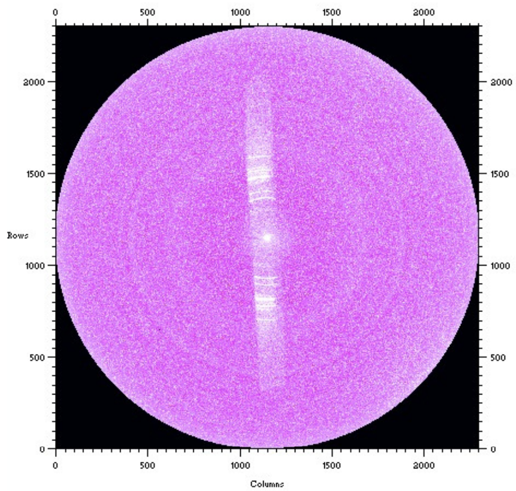


Detector types

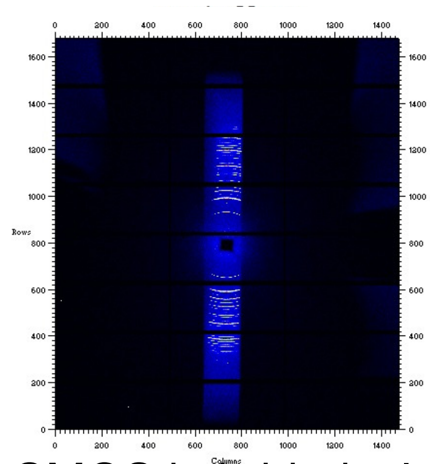
Comparison can be made using the following technical details: Detective Quantum Effciency (DQE), Point spread function, size, speed, dynamic range

Ref. Powder Diffraction: Theory and Practice

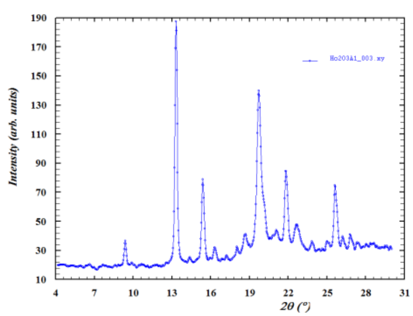
Types of Area Detectors

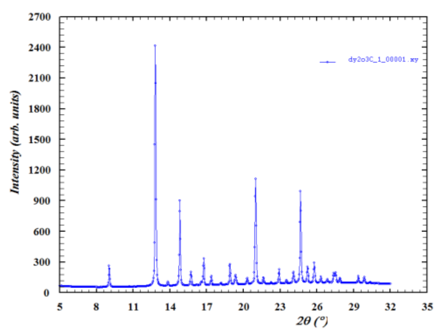


Mar345 IP detector



CMOS hybrid-pixel technology Pilatus 2M detector



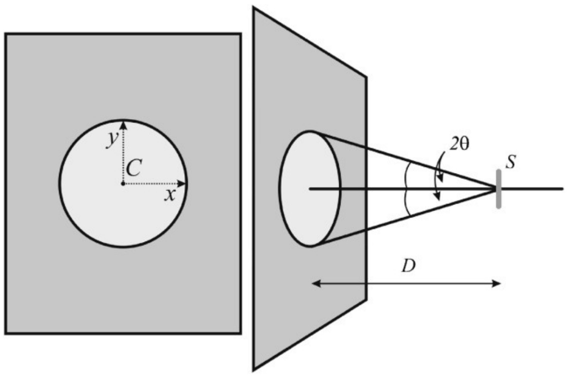


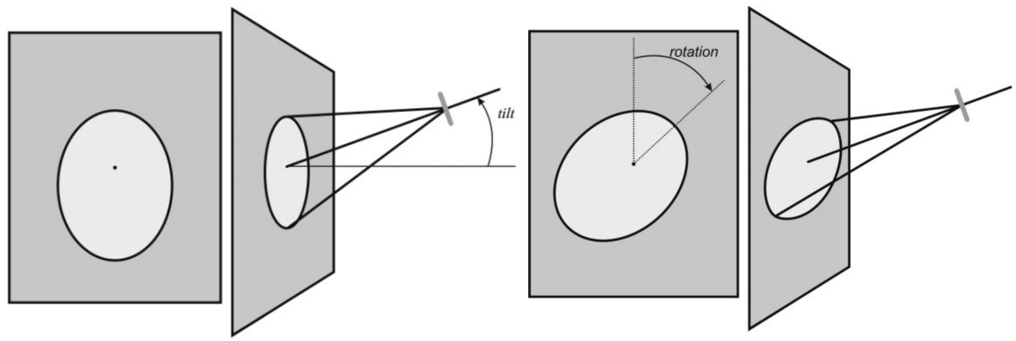
Detector types Comparison

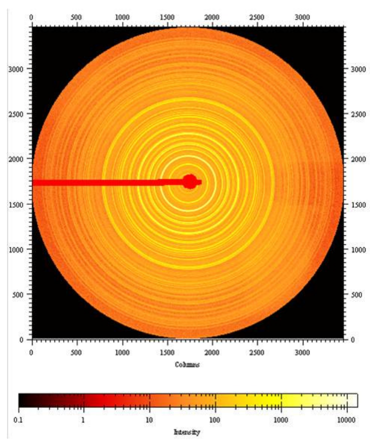
Technical specifications

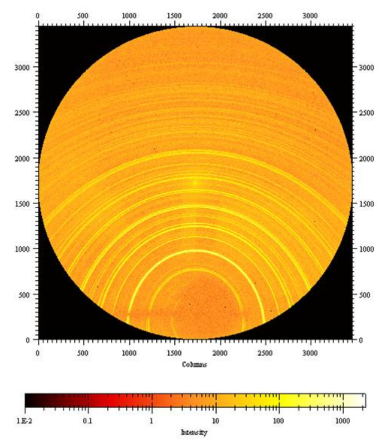
Number of modules 3 × 8 = 24
Sensor Reverse-biased silicon diode array
Sensor thickness 320 µm
Pixel size 172 × 172 µm2
Format 1475 × 1679 = 2,476,525 pixels
Area 254 × 289 mm2
Intermodule gap x: 7 pixels, y: 17 pixels, 8.0 % of total area
Dynamic range 20 bits (1:1,048,576)
Counting rate per pixel > 2 x 10^6 X-ray/s
Energy range 3 – 30 keV
Quantum efficiency 3 keV: 80 %
(calculated) 8 keV: 99 %
15 keV: 55 %
Energy resolution 500 eV
Adjustable threshold range 2 – 20 keV
Threshold dispersion 50 eV
Readout time 2.2 ms
Framing rate 30 Hz
Point-spread function 1 pixel

Diffraction Geometry









Perpendicular and tilted detector geometries

Ref. Powder Diffraction: Theory and Practice

Data Analysis

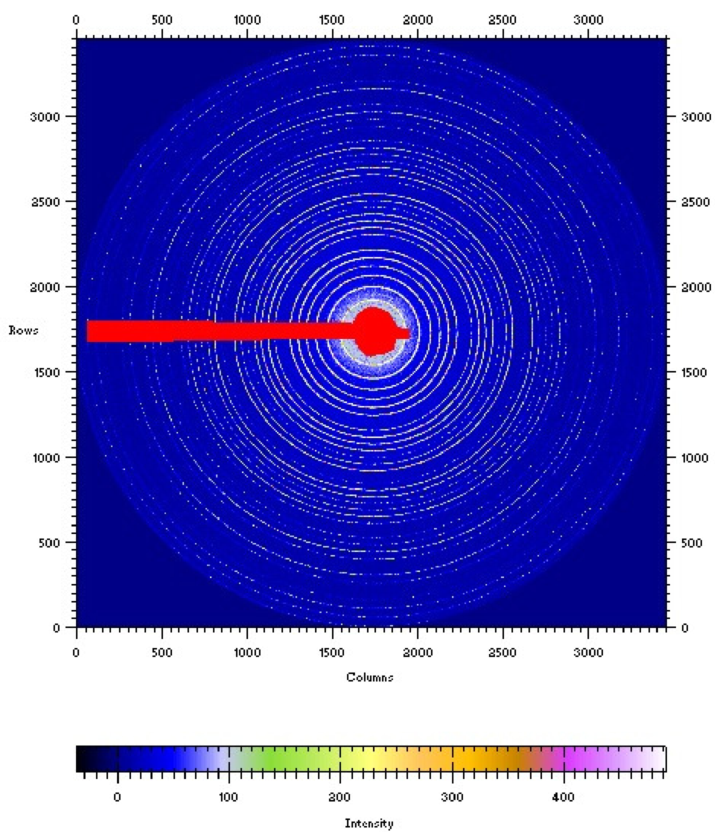
- Calibration and determination of the Detector Characteristic
- Determination of the experimental geometry (Beam Center, tilt)
- Application of the data reduction procedure
- Application of the diffraction geometry related corrections

Data Reduction using Fit2d

- Determination of the experimental geometry (Beam Center, tilt)

- Application of the diffraction geometry related corrections

Data Reduction using Fit2d

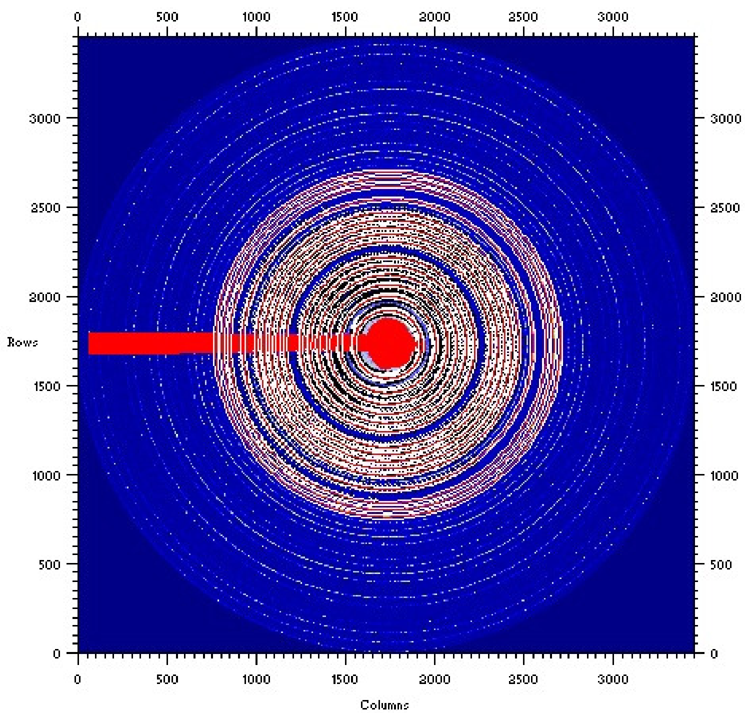


O.K. | CANCEL | ? | HELP | INFO

DESCRIPTIONS	VALUES	CHANGE
SAMPLE TO DETECTOR DISTANCE (MM) (STARTING)	120.0000	DISTANCE
WAVELENGTH (ANGSTROMS) (STARTING)	0.652863	WAVELENGTH
SIZE OF HORIZONTAL PIXELS (MICRONS)	100.0000	X-PIXEL SIZE
SIZE OF VERTICAL PIXELS (MICRONS)	100.0000	Y-PIXEL SIZE
NUMBER OF AZIMUTHAL SECTIONS	180	ANGULAR SECTIONS
REJECT OUT-LYING POSITIONS AND RE-REFINE	YES	REJECT OUTLIERS
REJECT LIMIT FROM IDEAL (STANDARD DEVIATIONS)	2.000000	REJECT LIMIT
OUTPUT FULL INFORMATION	YES	FULL INFO
REFINE X/Y BEAM CENTRE	YES	REFINE BEAM X/Y
REFINE SAMPLE TO DETECTOR DISTANCE	YES	REFINE DISTANCE
REFINE X-RAY WAVELENGTH	YES	REFINE WAVELENGTH
REFINE DETECTOR NON-ORTHOGONALITY	YES	REFINE TILT
FIT INTERMEDIATE NUMBER OF RINGS	NO	EXTRA ITERATIONS

LaB_6 for sample-detector distance, tilt etc.

Data Reduction using Fit2d

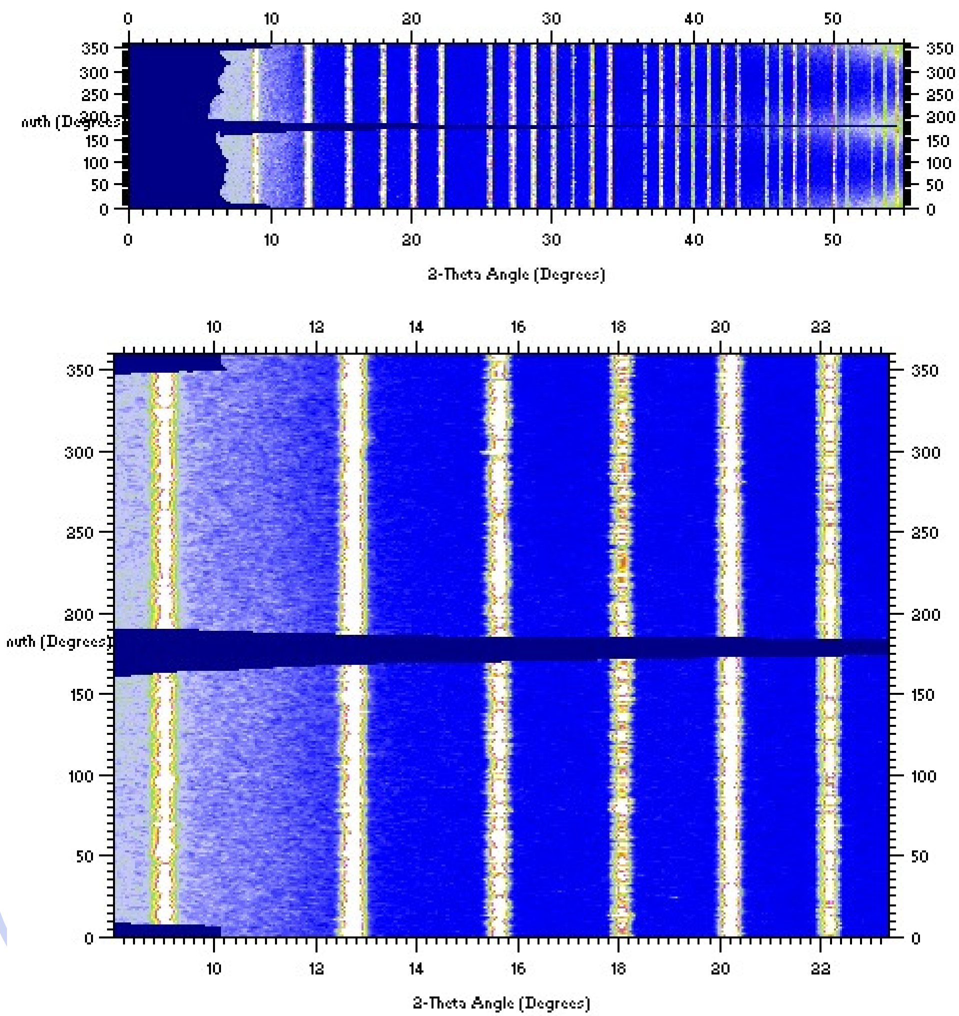


O.K. | CANCEL | ? | HELP | INFO

DESCRIPTIONS	VALUES	CHANGE
SIZE OF HORIZONTAL PIXELS (MICRONS)	100.0000	X-PIXEL SIZE
SIZE OF VERTICAL PIXELS (MICRONS)	100.0000	Y-PIXEL SIZE
SAMPLE TO DETECTOR DISTANCE (MM)	119.7349	DISTANCE
WAVELENGTH (ANGSTROMS)	0.652721	WAVELENGTH
X-PIXEL COORDINATE OF DIRECT BEAM	1734.759	X-BEAM CENTRE
Y-PIXEL COORDINATE OF DIRECT BEAM	1727.645	Y-BEAM CENTRE
ROTATION ANGLE OF TILTING PLANE (DEGREES)	33.93871	TILT ROTATION
ANGLE OF DETECTOR TILT IN PLANE (DEGREES)	0.284901	ANGLE OF TILT

LaB_6 for sample-detector distance: Refined Value

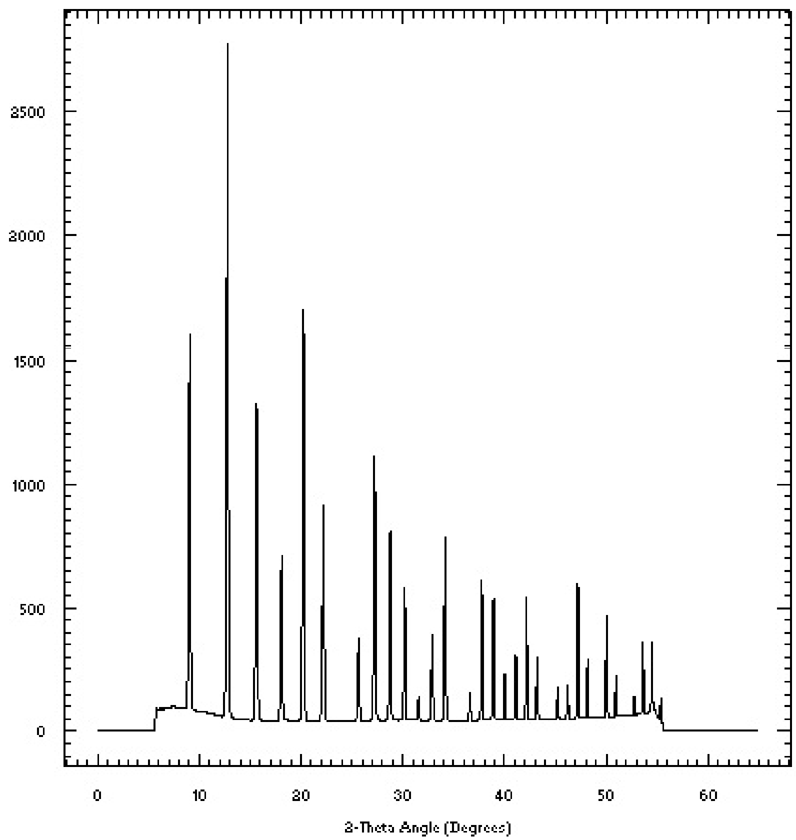
Data Reduction using Fit2d



O.K. | CANCEL | ? | HELP | INFO

DESCRIPTIONS	VALUES	CHANGE
STARTING AZIMUTH ANGLE (DEGREES)	0.0	START AZIMUTH
END AZIMUTH ANGLE (DEGREES)	360.0000	END AZIMUTH
INNER RADIAL LIMIT (PIXELS)	0.0	INNER RADIUS
OUTER RADIAL LIMIT (PIXELS)	1712.064	OUTER RADIUS
SCAN TYPE (RADIAL, 2-THETA, Q-SPACE)	2-THETA	SCAN TYPE
DEFAULT TO APPROX. 1 DEGREE SIZE AZIMUTHAL BINS	NO	1 DEGREE AZ
NUMBER OF AZIMUTHAL BINS	360	AZIMUTH BINS
NUMBER OF RADIAL/2-THETA BINS	1712	RADIAL BINS
INTENSITY CONSERVATION	NO	CONSERVE INT.
APPLY POLARISATION CORRECTION	YES	POLARISATION
POLARISATION FACTOR	0.990000	FACTOR
MAXIMUM FOR D-SPACINGS SCANS (ANGSTROMS)	20.00000	MAX. D-SPACING
GEOMETRICAL CORRECTION TO INTENSITIES	YES	GEOMETRY COR.

Data Reduction using Fit2d



O.K.	CANCEL	?	HELP	INFO

DESCRIPTIONS	VALUES	CHANGE
SCAN TYPE (D, RADIAL, 2-THETA, Q-SPACE)	2-THETA	SCAN TYPE
INTENSITY CONSERVATION	NO	CONSERVE INT.
APPLY POLARISATION CORRECTION	YES	POLARISATION
POLARISATION FACTOR	0.990000	FACTOR
GEOMETRICAL CORRECTION TO INTENSITIES	YES	GEOMETRY COR.
MAXIMUM 2-THETA ANGLE OF SCAN (DEGREES)	65.00000	MAX. ANGLE
NUMBER OF BINS IN OUTPUT SCAN	3450	SCAN BINS
MAXIMUM FOR D-SPACINGS SCANS (ANGSTROMS)	20.00000	MAX. D-SPACING

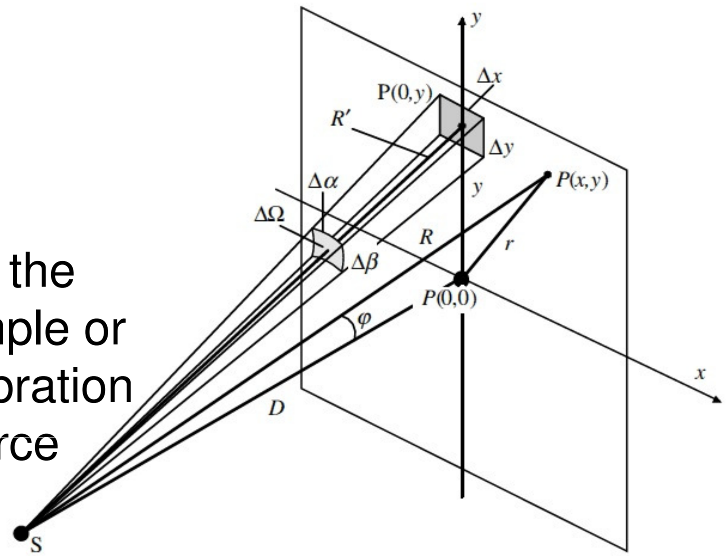
Data Reduction using Fit2d

- Polarization Corrections
- Lorenze correction
- Absorption correction

Polarization correction(Fit2D)= (I_h - I_v)/(I_h+I_v)
I_h----> horizontal component (direction of X-rays)
T_v-----> Vertical component

Data Reduction using Fit2d

Relationship between a pixel position and the solid angle covered by it.



S is the sample or calibration source

Angular range covered by the pixel in y and x directions

$$\Delta\beta = \frac{D}{D^2 + y^2}\Delta y = \frac{D}{R'^2}\Delta y \qquad \Delta\alpha = \frac{\Delta x}{R'}$$

Solid Angle covered by the pixel

$$\Delta\Omega = \Delta\alpha \cdot \Delta\beta = \frac{D}{R'^3}\Delta y \cdot \Delta x = \frac{D}{R'^3}\Delta A$$

For a pixel at arbitrary position P(x,y)

$$R = \sqrt{D^2 + x^2 + y^2} = \sqrt{D^2 + r^2}$$

Flux at P(x,y)

$$F(x,\, y) = \Delta\Omega B = \frac{\Delta ADB}{R^3} = \frac{\Delta ADB}{(D^2 + x^2 + y^2)^{3/2}}$$

Flux in photons/s and brightness of S in photons/s per $mrad^2$

Geometrical corrections to Intensities

$$\frac{F(x,\, y)}{F(0,\, 0)} = \frac{D^3}{R^3} = \frac{D^3}{(D^2 + x^2 + y^2)^{3/2}} = \cos^3\varphi$$

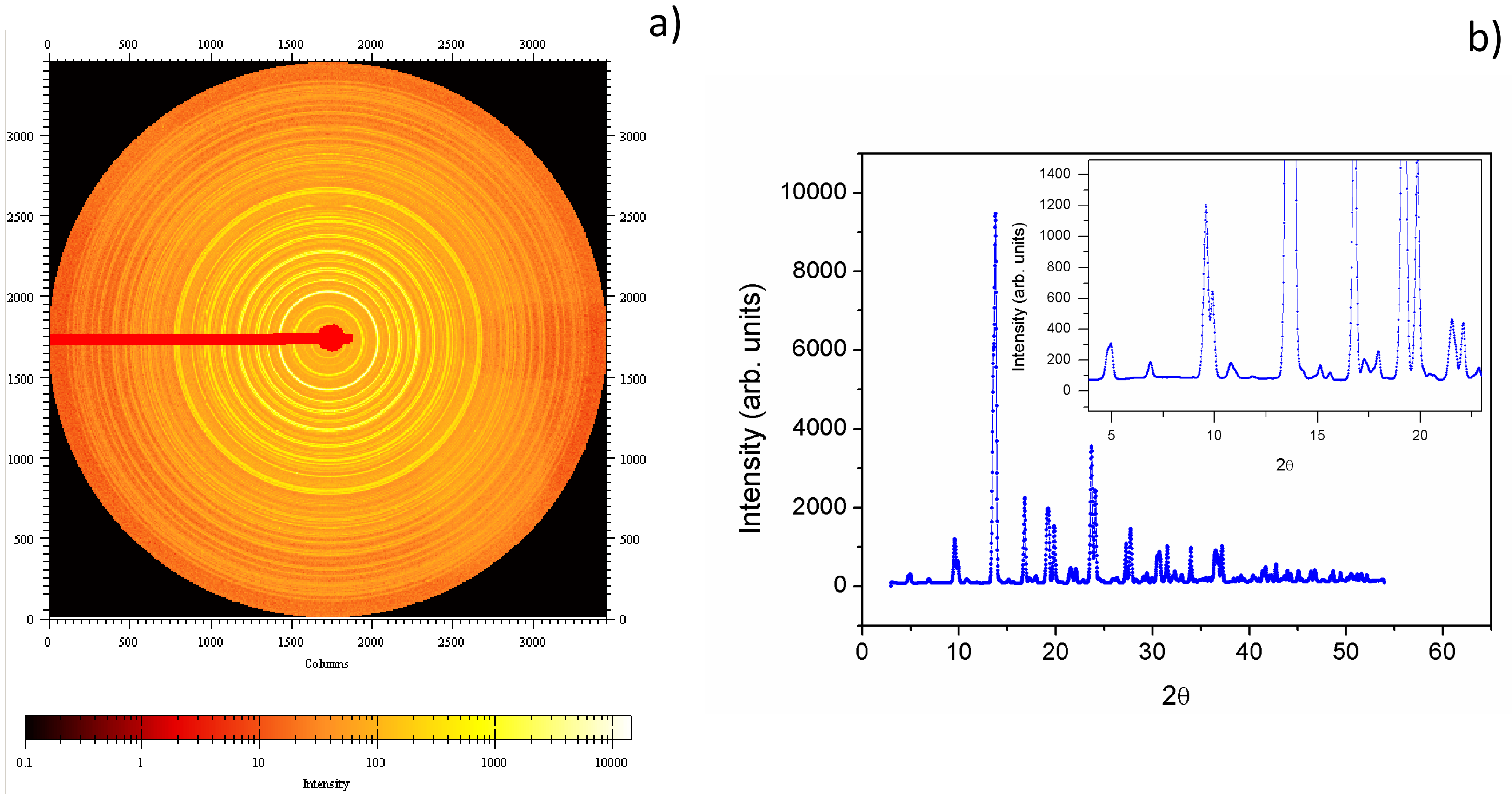


Figure 1. a) 2D image from the Mar345 Image Plate detector set perpendicular to the incident X-ray beam. b) Intensity versus 2θ plot obtained from the 2D image after various data reduction procedures as implemented in the program FIT2D. In the inset an expanded region of the plot is shown (λ=0.6519 Å; sample to detector distance=125.22 mm.)

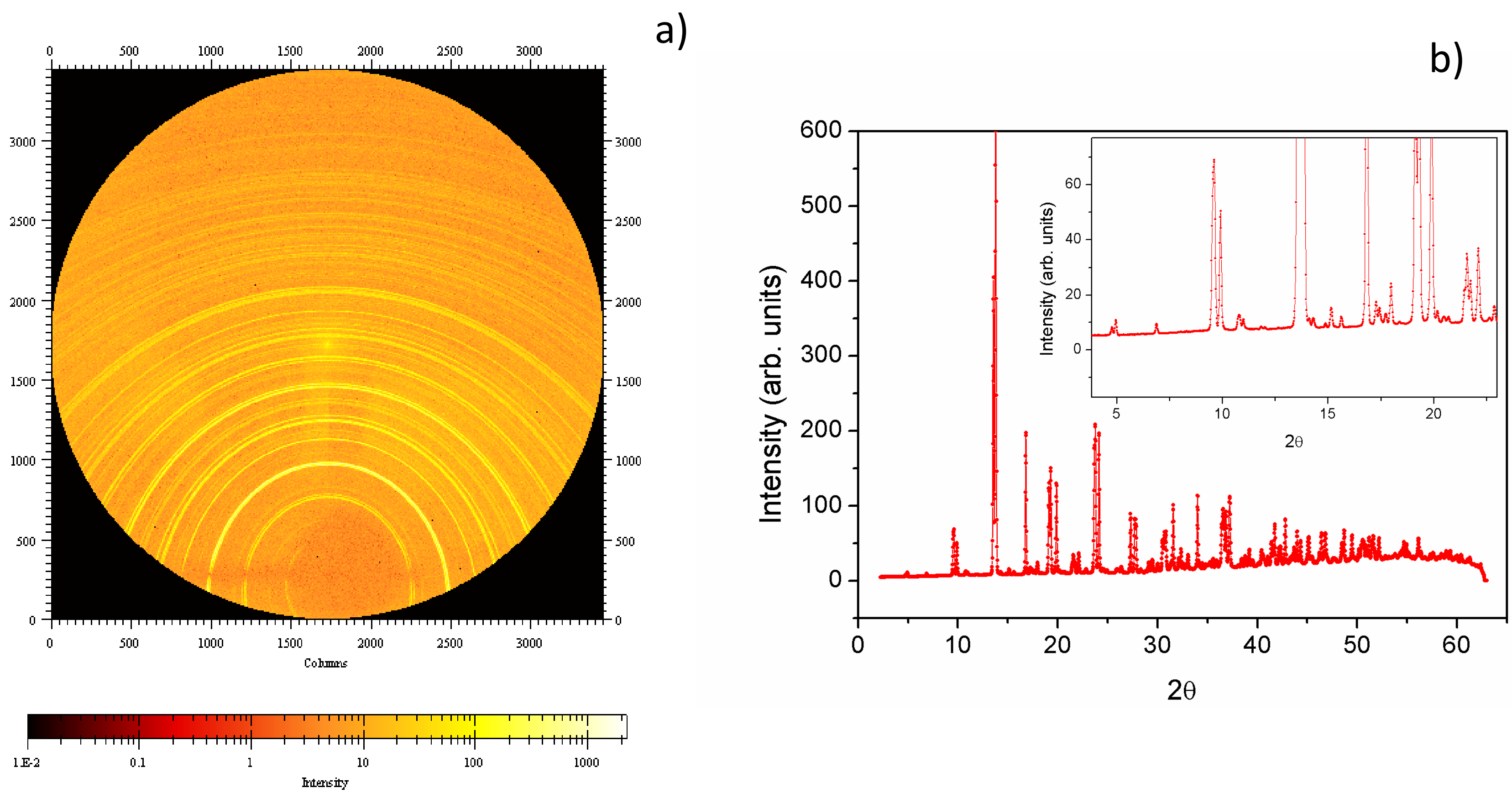


Figure 2. a) 2D image from the Mar345 Image Plate detector tilted w.r.t. the incident X-ray beam (angle of tilt = 30 deg). b) Intensity versus 2θ plot obtained from the 2D image using the program FIT2D. In the inset an expanded region of the plot is shown (λ=0.6519 Å; sample to detector distance=305 mm.)

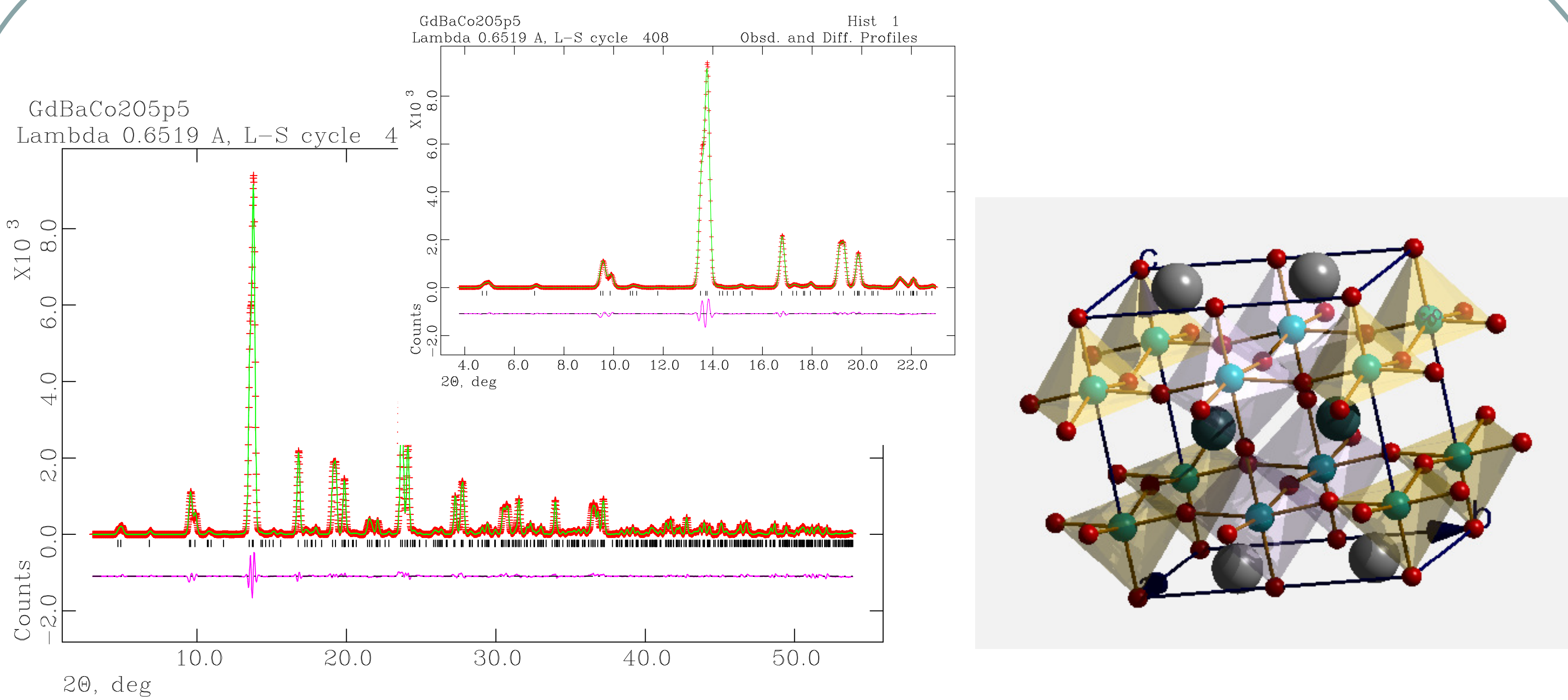


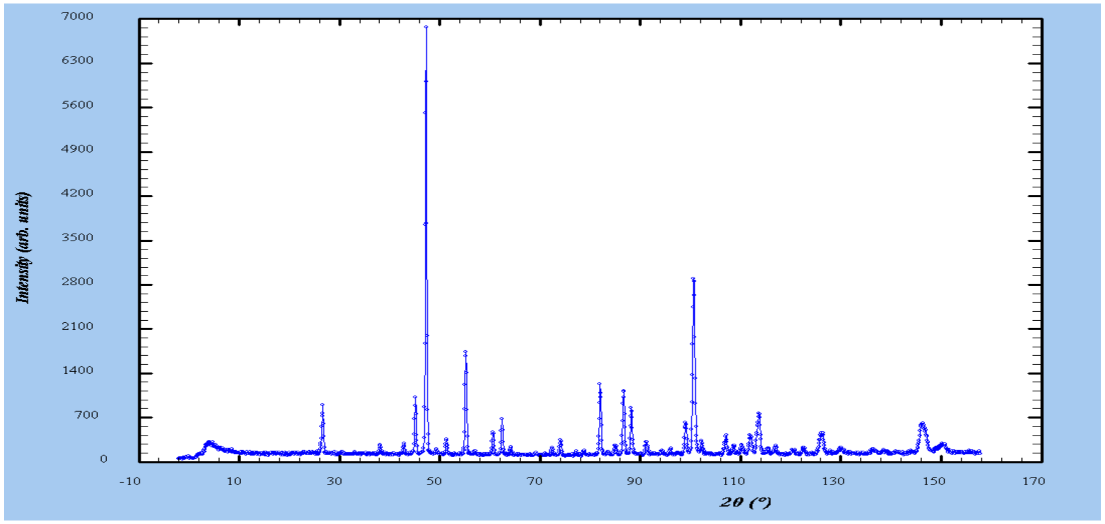
Figure 3. a) Rietveld refinement data for the $GdBaCo_2O_{5.5}$ system. The plot shows the observed and calculated Intensity versus 2θ values. The difference plot is also shown. In the inset an expanded region of the plot is shown. b) The crystal structure of $GdBaCo_2O_{5.5}$ from the refined values of lattice and structural parameters obtained from the Rietveld refinement.

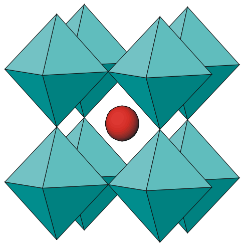
Neutron Powder Diffraction

(Ti, yi), i= 1, ….n

$T_i \rightarrow$ scattering variable ; 2θ, TOF, Energy

$y_i \rightarrow$ intensity





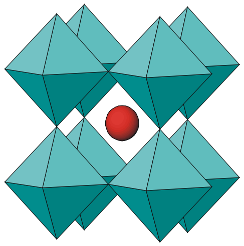
Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

The Rietveld Method

The Rietveld method is a structure refinement method that consists of refining a crystal (and/or magnetic) structure by minimizing the weighted squared difference between the observed and calculated pattern.

$$s_y = \sum_i^n w_i \left(y_i - y_{ci}\right)^2$$

$$w_i = \frac{1}{y_i}$$



y_i = observed intensity at the ith step,

y_{ci} = calculated intensity at the ith step,

n = total number of steps.

Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

The Rietveld Method

$$y_{ci} = s\sum_{K} L_K |F_K|^2 \varphi(2\Theta_i - 2\Theta_K) P_K A + y_{bi}$$

s → Scale factor

K → miller indices h, k, l

F_K → structure factor

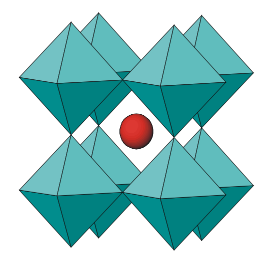
L_K → includes Lorentz factor, multiplicity

φ → profile shape function

P_K → preferred orientation

A → Absorption correction

y_{bi} → background intensity



Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

Structure Factors

$$F_{hkl} = \sum f_i \exp\left(-B_i\left(\frac{\sin\theta}{\lambda}\right)^2\right)\exp[2\pi i(hx_i + ky_i + lz_i)]$$

$$F_{mag} = \sum q_i p_i \exp[2\pi i(hx_i + ky_i + lz_i)]$$

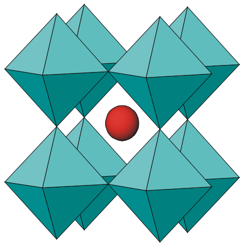
$p_i \rightarrow$ magnitude of magnetic cross section

$p = 0.54 S f_m \times 10^{-12}$ cm

$S \rightarrow$ magnetic moment

$f_m \rightarrow$ magnetic form factor

$q_i \rightarrow$ magnetic interaction vector $q_j = \varepsilon(\varepsilon . K_j) - K_j$



magnetic interaction vector for the jth atom depends on the unit vector (ε) for the scattering vector (**h**) and the unit vector for the magnetic moment on that atom(**K**j)

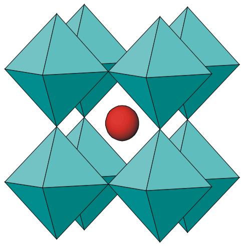
Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

Numerical criteria of the fit

$$R_{wp} = \left[\frac{\sum_i w_i (y_i - y_{ci})^2}{\sum_i w_i (y_i)^2} \right]$$

$$R_{\exp} = \left[\frac{n - P}{\sum_i w_i (y_i)^2} \right]$$

$$\chi^2 = \left[\frac{R_{wp}}{R_{\exp}} \right]$$



Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

Two sets of refinable parameters

Profile parameters:

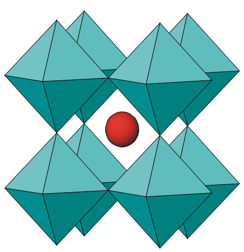
- Peak positions: A, B, C….; Zero shift

$$\frac{1}{d^2} = A.h^2 + B.k^2 + C.l^2 + D.k.l + E.h.l + F.h.k$$

- Profile: U, V, W etc…

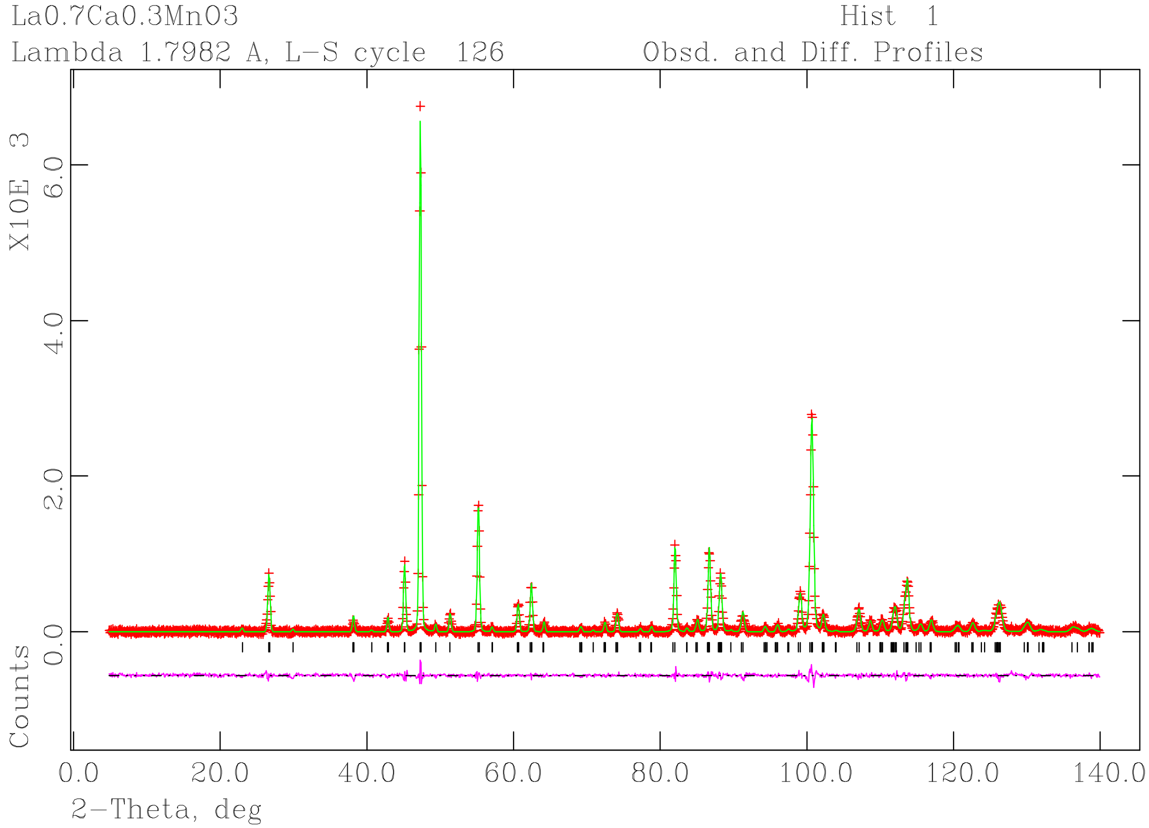
Structural parameters:

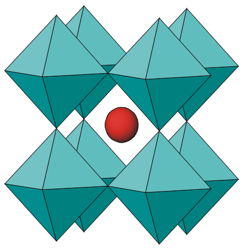
- Scale factor
- Atomic coordinates: x_i, y_i, z_i
- Temperature parameter: B_i
- Components of the magnetic moment vector: K_i



Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

LeBail fit

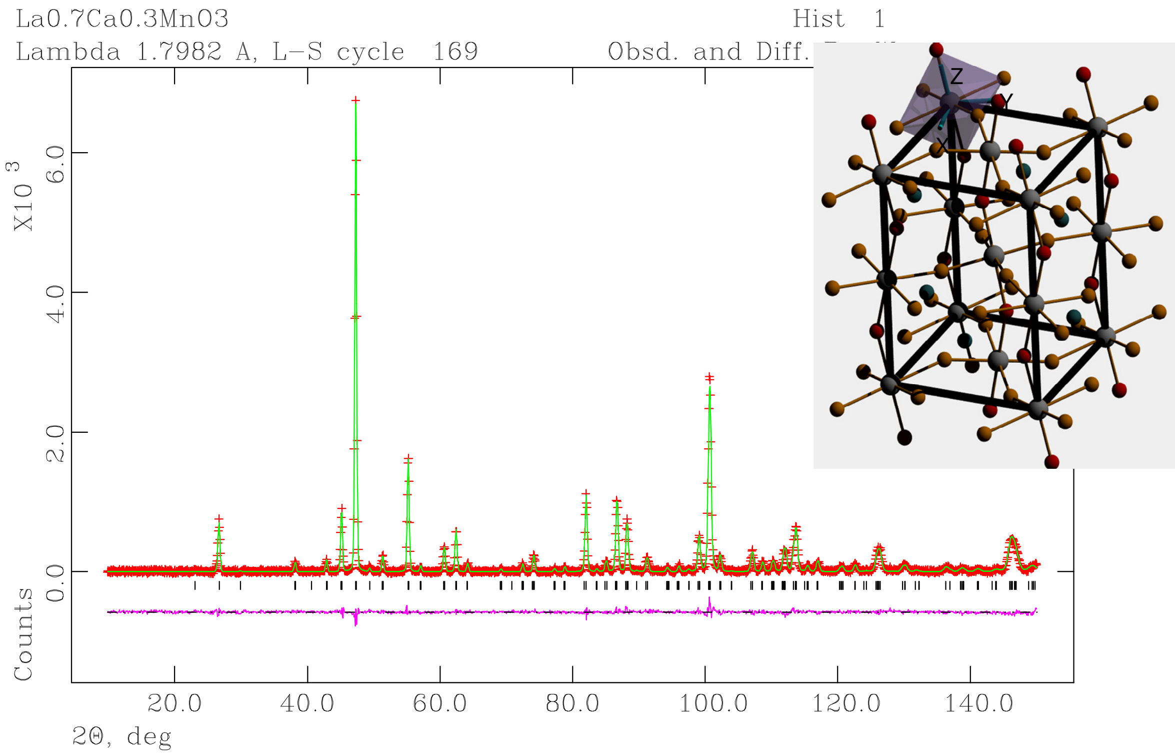


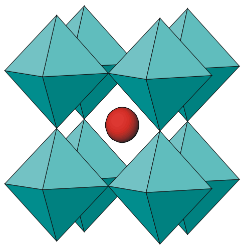


03 April 2009

Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

Rietveld refinement





Anthony Arulraj
Tel.: 030 8062-2793 | Fax: 030 8062-2999
anthony.arulraj@helmholtz-berlin.de

THANK YOU