High-pressure single-crystal x-ray diffraction data

processing with XDS

Andrzej Grzechnik, Karen Friese & Jose Maria Posse

Condensed Matter Physics, University of the Basque Country, Bilbao

andrzej.grzechnik@ehu.es

Acknowledgements: Wolfgang Morgenroth (Crystallography Group, Institute of Geosciences, Goethe University, Frankfurt am Main, Germany)

X-ray **D**iffraction **S**oftware: XDS, XSCALE, XDSCONV

W. Kabsch, *Acta Cryst*. D**66**, 125-132 (2010)

W. Kabsch, *Acta Cryst*. D**66**, 133-144 (2010)

http://xds.mpimf-heidelberg.mpg.de

Originally written for biological crystallography that most of the times deals with bad data due to ice rings, radiation damages, metastable phases, coexisting phases, poorly crystalline materials, etc. Bad data is exactly what a high-pressure crystallographer has to work with.

XDS: data indexing, integration, and correction from area-sensitive detectors

XSCALE: combining the data from different runs and correcting them for absorption and radiation damage

XDSCONV: hkl data conversion to different formats

XDS.INP file templates for various detectors

http://xds.mpimf-heidelberg.mpg.de/html_doc/xds_prepare.html

file name	detector
XDS-PILATUS.INP	PILATUS 6M pixel detector designed at PSI/SLS (Broennimann et al.)
XDS-ADSC.INP	ADSC detectors Quantum Q4, Q4r, Q105, Q210, Q210r, Q315r & Q315
XDS-NOIR.INP	Ed Westbrook's NOIR-1 lens focused CCD detector at ALS 4.2.2
XDS-MAR555.INP	Selenium based flat panel detector
XDS-MAR345.INP	MAR345 detector
XDS-MAR.INP	old MAR-detector
XDS-MARCCD.INP	MAR CCD-detector and (1k X 1k)-CCD used at CHESS
XDS-RAXIS2.INP	R-AXIS II IMAGING PLATE DETECTOR
XDS-RAXIS4.INP	R-AXIS IV IMAGING PLATE DETECTOR
XDS-RAXIS4++.INP	R-AXIS IV++ IMAGING PLATE DETECTOR
XDS-RAXIS5.INP	R-AXIS V IMAGING PLATE DETECTOR
XDS-SATURN.INP	Rigaku/MSC CCD detector
XDS-CRYSALIS.INP	Oxford Diffraction CCD detector
XDS-CCDBRANDEIS.INP	(2080 X 2072)-CCD Detector used at BNL X12c; (1k X 1k)-CCD Detector (Walter Phillips) used at BNL
XDS-BRANDEIS_B4.INP	(2k X 2k)-CCD Detector used at Brookhaven beamline B4
XDS-STOE.INP	STOE IMAGING PLATE DETECTOR
XDS-SIEMENS.INP	X100A SIEMENS Multiwire detector

Features of XDS to consider while working with the high-pressure single-crystal x-ray data

Pros:

1. Free software to process the data from several detectors on laboratory diffractometers and at synchrotron facilities.
2. Learned reflection profiles.
3. Gasket rings (or any Debye-Scherrer rings) could be treated like ice rings in the standard use of XDS.

Cons:

1. No reciprocal space reconstruction.
2. Does not handle incommensurate phases.
3. Kind of a “black box” with some cryptic actions (especially in CORRECT) – it is too automatic, tends to get wild, and tries to do too much for the “high-pressure” user.
4. Poor graphics and visualization of the data and results.

XDS: 8 subroutines

XYCORR performs spatial corrections at each pixel of a detector

INIT classifies pixels as background or strong (diffraction) spots

COLSPOT locates strong diffraction spots and finds their centroids

IDXREF finds and refines the orientation matrix

DEFPIX defines the obscured regions of the detector by intruding hardware, e.g., a cryostat (not useful for masking the shadowed areas of the detector by a diamond anvil cell)

XPLAN supports the planning of data collection (a run optimizer)

INTEGRATE determines the intensities

CORRECT applies various corrections to the intensities, determines the space group if unknown, and refines the unit-cell parameters

An example of XDS.INP for high-pressure data (marCCD165) from the beamline D3 at HASYLAB

```
!*****************************************************************************
!  Andrzej Grzechnik, Karen Friese & Jose Maria Posse (U. Basque Country, Bilbao).
!*****************************************************************************


! JOB= XDS
! JOB= COLSPOT IDXREF DEFPIX XPLAN INTEGRATE CORRECT
! JOB= IDXREF DEFPIX XPLAN INTEGRATE CORRECT
! JOB= INTEGRATE CORRECT
! JOB= DEFPIX INTEGRATE CORRECT
  JOB= CORRECT


 NAME_TEMPLATE_OF_DATA_FRAMES=../frames/BiMn2O5_P2_05_????.tif                ! INIT, COLSPOT, IDXREF, INTEGRATE
 DATA_RANGE=       1 60  !Numbers of first and last data frame collected      ! COLSPOT, INTEGRATE, CORRECT
 BACKGROUND_RANGE= 41 42  !Numbers of first and last data frame for background  ! INIT
 SPOT_RANGE=       30 40  !First and last data frame number for finding spots   ! COLSPOT, IDXREF


 INCLUDE_RESOLUTION_RANGE= 15.0 0.0                                            ! DEFPIX, CORRECT
 VALUE_RANGE_FOR_TRUSTED_DETECTOR_PIXELS= 4000 30000                           ! DEFPIX
! SILICON=                          ! fraction of intensity loss per mm      ! XYCORR, CORRECT
! SENSOR_THICKNESS=  0.0                                                      ! XYCORR, CORRECT

!ORGX=1058.0 ORGY=1030.0  ! calibration          !Origin on detector (pixels)                    ! IDXREF
!ORGX=1060.0 ORGY=1031.0            !Origin on detector (pixels)                    ! IDXREF
ORGX=1069.4 ORGY=1020.6   !fayalit        !Origin on detector (pixels)                    ! IDXREF
                                                                                ! IDXREF
 DIRECTION_OF_DETECTOR_X-AXIS=  0 0 1
 DIRECTION_OF_DETECTOR_Y-AXIS=  0 1 0
 INCIDENT_BEAM_DIRECTION=      -1 0 0
 ROTATION_AXIS=  0.086824089 0.866025404 -0.492403877 ! direction cosines with respect to the laboratory system


 DETECTOR_DISTANCE=  81.38          !Distance of detector from crystal-mm       ! IDXREF
 OSCILLATION_RANGE=   1.0           !Of each data frame in degrees (must be >0) ! IDXREF
 STARTING_ANGLE=    238.1           !Of spindle at beginning of data frame #1.  ! IDXREF
 X-RAY_WAVELENGTH=    0.4           !X-ray wavelength in Angstroem units
```

```
 SPACE_GROUP_NUMBER=     1                                  ! IDXREF, CORRECT
 UNIT_CELL_CONSTANTS=    7.5 8.5 5.7 90.0 90.0 90.0       ! IDXREF, CORRECT
! UNIT_CELL_A-AXIS=
! UNIT_CELL_B-AXIS=
! UNIT_CELL_C-AXIS=

!REIDX= -1 0 0 0  0 1 0 0  0 0 -1 0  ! CORRECT
 FRIEDEL'S_LAW=FALSE       ! XPLAN, CORRECT

 INDEX_ORIGIN= 0 0 0    ! IDXREF

 BEAM_DIVERGENCE=          0.50  !arctan(spot diameter/DETECTOR_DISTANCE)        ! INTEGRATE
 BEAM_DIVERGENCE_E.S.D.=   0.05  !half-width (Sigma) of BEAM_DIVERGENCE=         ! INTEGRATE
 REFLECTING_RANGE=         0.30  !for crossing the Ewald sphere on shortest route   ! COLSPOT, IDXREF, INTEGRATE
 REFLECTING_RANGE_E.S.D.=  0.04  !half-width (mosaicity) of REFLECTING_RANGE=       ! INTEGRATE

 DELPHI= 10.0  ! INTEGRATE

!*****************************************************************************
!   The transformed spot can roughly be described as a Gaussian. Four parameters are used for this purpose:
!
!   1. BEAM_DIVERGENCE= is twice the opening angle of a cone with the diffracted beam wave vector as cone axis.
!   The interception of the cone with the data image traces the boundary of the spot and includes some
!   neighbouring background pixels. The parameter value can be estimated as
!      BEAM_DIVERGENCE= arctan(spot_diameter/detector_distance).
!
!   2.  BEAM_DIVERGENCE_E.S.D.=  characterizes the Gaussian spot shape by its standard deviation.
!
!   3. REFLECTING_RANGE= is the approximate rotation angle required for a strong spot recorded perpendicular
!   to the rotation axis to pass completely through the Ewald sphere.
!
!   4. REFLECTING_RANGE_E.S.D.= is the standard deviation of the Gaussian intensity distribution when
!   the reflection is rotated through the Ewald sphere on shortest route. This is also defined as the mosaicity
!   of the crystal.
!
!   All of the four parameters describing shape and extension of the spots can be determined automatically
!   from the data images.
!*****************************************************************************




!*****************************************************************************
```

```
 MAXIMUM_NUMBER_OF_PROCESSORS=  2   ! COLSPOT, IDXREF, INTEGRATE, CORRECT
 MINUTE=   1      !Maximum number of minutes to wait until data frame must appear ! XYCORR, INIT, COLSPOT, INTEGRATE
 TEST=   1           !Test flag. 1,2 additional diagnostics and images  ! XYCORR, INIT, COLSPOT, INTEGRATE


! Detector description MARCCD 165
 DETECTOR=     CCDCHESS      ! XYCORR, INTEGRATE
 NX=2048       NY=2048       ! XYCORR, INIT, COLSPOT, IDXREF
 QX=0.079076   QY=0.079076   ! XYCORR, IDXREF

 OVERLOAD=50000              ! XYCORR, INIT, COLSPOT, INTEGRATE, CORRECT
! MINIMUM_VALID_PIXEL_VALUE= 0  ! INIT, COLSPOT, INTEGRATE

 TRUSTED_REGION= 0.0 1.0     ! INIT, IDXREF

 UNTRUSTED_RECTANGLE= 1010 1110 0 1000  ! INIT

! ROFF TOFF   ! XYCORR


! EXCLUDE_RESOLUTION_RANGE= 3.93 3.87 ! ice-ring at 3.897 ï¿½  ! DEFPIX, CORRECT
! MINIMUM_ZETA= 0.15                  ! default = 0.15        ! XPLAN, INTEGRATE, CORRECT

 FRACTION_OF_POLARIZATION=0.950      !0.90 at DESY; 0.5 for unpolarized beam.   ! CORRECT
 POLARIZATION_PLANE_NORMAL= 0.0 0.0 1.0  ! war 0 1 0  ! CORRECT
! AIR  ! CORRECT

 MAX_CELL_AXIS_ERROR=    0.03  ! 0.03                ! IDXREF, CORRECT
 MAX_CELL_ANGLE_ERROR=   2.0  ! 2.0            ! IDXREF, CORRECT


! INDEX_QUALITY= 0.6


 TEST_RESOLUTION_RANGE=  10.0  2.0             ! CORRECT
 MIN_RFL_Rmeas=          25  ! default = 50          ! CORRECT
 MAX_FAC_Rmeas=          2.0                   ! CORRECT

! REFINE(IDXREF)=BEAM AXIS ORIENTATION DISTANCE CELL ! ALL         ! IDXREF
! REFINE(INTEGRATE)=BEAM AXIS ORIENTATION DISTANCE CELL ! ALL    ! INTEGRATE
! REFINE(CORRECT)=BEAM AXIS ORIENTATION DISTANCE CELL ! ALL   ! CORRECT
```

```
! NUMBER_OF_PROFILE_GRID_POINTS_ALONG_ALPHA/BETA= 9           ! INTEGRATE
! NUMBER_OF_PROFILE_GRID_POINTS_ALONG_GAMMA= 9             ! INTEGRATE

WFAC1= 50.0

! STRICT_ABSORPTION_CORRECTION= FALSE ! default = FALSE   ! CORRECT

 CORRECTIONS=!  ALL MODULATION DECAY ABSORPTION    ! CORRECT
! MINIMUM_I/SIGMA=3.0  ! default = 3.0     ! CORRECT

! REFLECTIONS/CORRECTION_FACTOR= 50   !default approx. 50  ! CORRECT
```

Important input parameters (apart from the specific "hardware", distortion, noise, detector position, and incident beam parameters for the specific detector and format)

DATA_RANGE – the first and last data image

BACKGROUND_RANGE – the first and last data image to determine the background

SPOT_RANGE – the first and last data image to identify and locate strong spots

ROTATION_AXIS – direction cosines of the rotation axis with respect to the laboratory system. The direction of the axis is chosen to describe a right-handed rotation.

STARTING_ANGLE – the phi angle of the first data image in SPOT-RANGE

SPACE_GROUP_NUMBER – while using XDS for the high-pressure data in always has to be 1

EXCLUDE_RESOLUTION_RANGE – used for any ice/gasket rings

Important output files

IDXREF.LP – the results and data diagnostics of IDXREF

XPARM.XDS – the initial orientation matrix and parameters determined by IDXREF subsequently used in INTEGRATE

INTEGRATE.HKL – the hkl file from INTEGRATE (not processed by CORRECT)

INTEGRATE.LP – the results and data diagnostics of INTEGRATE

GXPARM.XDS – the final orientation matrix and parameters determined by CORRECT

CORRECT.LP – the results and data diagnostics of CORRECT

XDS_ASCII.HKL - the final hkl data processed by CORRECT

XDS procedure for high-pressure data

1. make a new directory (each run requires a separate directory)
2. copy the appropriate template and rename it XDS.INP
3. put the correct parameters in XDS.INP: ROTATION_AXIS, BACKGROUND_RANGE, SPOT_RANGE, STARTING_ANGLE. Check all the “hardware”, distortion, noise, detector position, and incident beam parameters to make sure they are correct.
4. execute xds
5. check IDXREF.LP
6. run XDS with the commands DEFPIX INTEGRATE CORRECT. In case of problems with indexing, use the commands COLSPOT IDXREF DEFPIX XPLAN INTEGRATE CORRECT. If this does not work, change the SPOT_RANGE
7. cp GXPARM.XDS XPARM.XDS
8. run XDS for your DATA_RANGE using the commands INTEGRATE CORRECT.
9. check the peak shape in INTEGRATE.LP
10. go to the point No. 7.

Things to be careful about to run XDS efficiently with high-pressure data

1. Try to find 2 or 3 background frames (BACKGROUND_RANGE) with no diamond reflections. Do not have to change them afterwards for integration, etc..

2. SPOT_RANGE is used to index the data only and NOT for integrating them. Do not have to change it once the cell is found.

3. STARTING_ANGLE corresponds to the first frame in SPOT_RANGE and NOT to the first frame in your run. **NEVER** change it after indexing!!!!

4. Once the data are ready for integration, only change the DATA_RANGE expanding it by a few frames on both ends. The most effective total number of frames added is lower than the DELPHI parameter providing that OSCILLATION_RANGE= 1.0. This will make sure that the orientation matrix is not messed up when the integration goes awry.

5. Good integration requires several xds runs and checking the peak shape in INTEGRATE.LP each time.

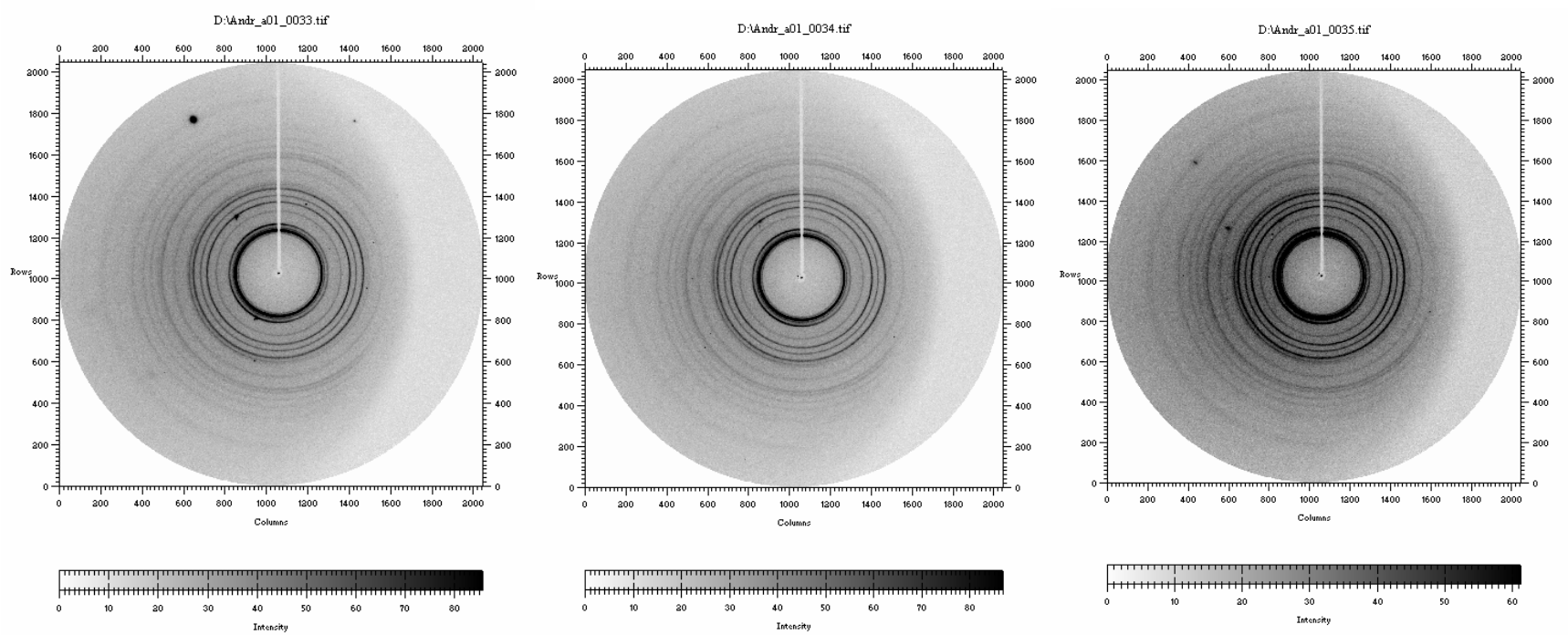
6. Always run CORRECT with space group no. 1 for the high-pressure data even though you are absolutely sure of the exact symmetry. Check your XDS.INP file and put it back to 1 when higher symmetry is found! Otherwise, CORRECT will perform corrections and data averaging that depend on the space group symmetry and will yield disastrous intensities.

Some issues to know about:

- Background
- Indexing
- Integration
- Corrections

Background

Our experience with the high-pressure data from marCCD165 tells us that the best way to determine the background is to use the data images without strong diamond reflections:



When using XDS, the most difficult task is to index the high-pressure data. Once the cell is found, the rest is easy!

The most common reasons for failing to index the high-pressure data in the default run of XDS are wrong input parameters, crystal misalignment, and/or the presence of *alien* strong spots arising from diamond reflections and gasket rings. Providing the input parameters are correct and the crystal is well aligned, the error message at the end of the run in the file IDXREF.LP nearly always is: INSUFFICIENT PERCENTAGE (<50%) OF INDEXED REFLECTIONS. The program just complains that less than 50% of spots could be indexed, although the cell is correct. If you get any other error message, it means that something must be wrong with the input parameters, diffractometer, and/or crystal.

The orientation matrix is in the direct space. It refers to the spindle position at the start of the first data image (STARTING_ANGLE) and *not to the true spindle dial setting* (see the files XPARM.XDS and GXPARM.XDS).

If it happens that your material has undergone a phase transition and you have no idea about the lattice, you could use the following entries in the file XDS.INP (please note the ! exclamation signs, the numbers for the second parameter do not matter):

```
!SPACE_GROUP_NUMBER=     1                          ! IDXREF, CORRECT
!UNIT_CELL_CONSTANTS=    7.5 8.5 5.7 90.0 90.0 90.0      ! IDXREF, CORRECT
```

This procedure is equivalent to the parameter:

SPACE_GROUP_NUMBER= 0 ! IDXREF, CORRECT

In this case, the line with UNIT_CELL_CONSTANTS is ignored.

If you know the lattice, you use these parameters without the "!" exclamation signs and a set of approximate lattice parameters. Remember that the space group has to be always No. 1 for high-pressure studies:

SPACE_GROUP_NUMBER= 1 ! IDXREF, CORRECT

Another trick is to use the (approximate) components of the unit-cell basis vectors with respect to the laboratory coordinate system for the unrotated crystal specified by the parameters UNIT_CELL-A-AXIS, UNIT_CELL_B-AXIS, and UNIT_CELL_C-AXIS.

Integration

The spots are described as Gaussians with four parameters BEAM_DIVERGENCE, BEAM_DIVERGENCE_E.S.D., REFLECTING_RANGE, and REFLECTING_RANGE_E.S.D. If any of them is unspecified, its value is determined automatically from the data images (the learned reflection profiles). These parameters are optimized during each integration.

The INTEGRATE subroutine generates various profile templates for the reflections within the DATA_RANGE and DELPHI parameters (the profile templates are explained in the XDS manual http://xds.mpimf-heidelberg.mpg.de and in the XDS publications in Acta Cryst. D). They are in the diagnostics file INTEGRATE.LP and should look more or less like this:

```
 0  0  0  0  0  1  0  0  0     0  0  0  0  1  1  0  0  0     0  0 -1 -1  0  0  0  0  0
 0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  1  0  0
 0  0  0  0  0  0  0  0  0     1  0  0  1  0  0  0  0  0     0  0  0  1  2  1  1  0  0
 0  0  0  0  0  0  0  0  0     0  0  0  1  2  0  0  0  0     0  0  1  5 12  5  1  0  0
 0  0  0  0  0  0  0  0  0     0  0  0  2  4  2  0  0  0     0  0  1 10 26 10  1  0  0
 0  0  0  0  0  0  0  0  0     0  0  0  1  2  1  0  0  1     0  0  1  5 12  5  1  0  0
 0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0  0  0     0  0  0  1  2  1  0  0  0
 0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0  0  0     0  0  0  0  1  0  0  0  0
 0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0  0  0


 0  0 -1  0  0  1  1  0  0     0  0 -1  0  1  1  2  0  0     0  0 -1  0  1  0  1  0  0
 0  0 -1  0  1  1  1  0  0     0  0 -1  0  2  1  1  1  0     0  0 -1  0  1  0  1  0  0
 1  0  1  4  6  3  1  0 -1     1  0  1  5  8  4  1  0 -1     1  0  1  3  6  3  1  0 -1
 0  0  3 15 32 14  2  0 -1     1  1  3 20 46 20  3  0 -1     1  1  2 14 32 14  2  0 -1
 0  0  4 26 70 28  3  0  0     0  0  5 37100 40  4  0  0     0  0  4 26 70 28  2  0  0
-1  0  2 13 32 14  2  0  0    -1  0  3 18 45 20  2  0  0     0  0  2 13 32 14  2  0  0
-1 -1  1  3  4  2  0  0  0    -1 -1  2  4  6  3  0  0  0    -1  0  1  3  4  2  0  0  0
 0 -1 -1  1  1  0  1 -1  0     0 -1 -1  1  1  0  1 -1  0     0  0  0  1  1  0  1 -1  0
 0  0  0  0  0 -1  0  0  0     0  0  0  0 -1 -1  0  0  0     0  0  0  0 -1 -1  0  0  0


 0  0  0  0  0  0  0  0  0     0  0 -1  0  0  0  0  0  0     0  0 -1  0  0  0  0  0  0
 0  0  0  0  0  0  0  2  0     0 -1  0  0  0  0  0  1  0     0 -1  0  0  0  0  0  0  0
 0  0  0  1  2  1  0  0 -1     0  0  0  0  0  0  0  0  0     1  0 -1  0  0  0  0  0  0
 0  1  1  5 12  5  0  0 -1     0  0  0  1  2  1  0  0  0     1  0  0  0  1  0  0  0  1
 0  0  1  9 25 10  1  0  0     0  1  1  2  4  2  0  0  0     1  0  0  0  1  0  0  0  0
 0  0  1  4 12  5  0  0  0     0  0  1  1  2  1  0  0  0     1  0  1  1  0  1  0  0  0
 0  0  1  1  2  1  0  0  1     0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0 -1  0
 0  0  0  0  0  0  1  0  0     0  0  0  0  0  0  0  0  0     0  0  0  0  0 -1  0 -1  0
 0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0  0  0     0  0  0  0  0  0  0  0  0
```

The off-centered profiles (e.g., the number 100 is not exactly in the middle) indicate the unrefined or wrong orientation matrix, misindexing, crystal decentering, etc. The profiles extending to the borders of the box indicate

wrong BEAM_DIVERGENCE, BEAM_DIVERGENCE_E.S.D., REFLECTING_RANGE, and REFLECTING_RANGE_E.S.D. parameters. Their optimized values are given in the file INTEGRATE.LP (in this file they are called “SUGGESTED VALUES FOR INPUT PARAMETERS”).

To get the profiles right, you need to run INTEGRATE several times. Also important is the refinement of the lattice parameters within the data image range specified by the DELPHI parameter. If it does not converge, you have a problem similar to the profiles being off-centered.

Corrections

The errors in the lattice parameters are given in the file CORRECT.LP.

XDS does not give you the orientation matrix in the ABSORB form (UB). To run ABSORB, the XDS_ASCII.HKL file has to be converted into the shelx format with direction cosines using XDSCONV in the XDS package.