Post-refinement data handling

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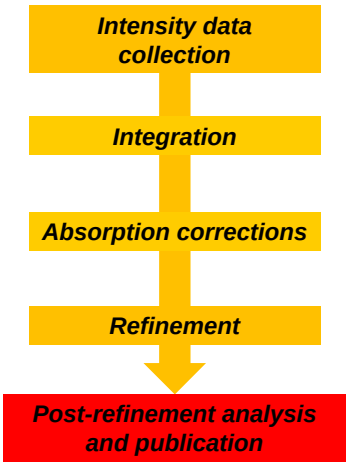
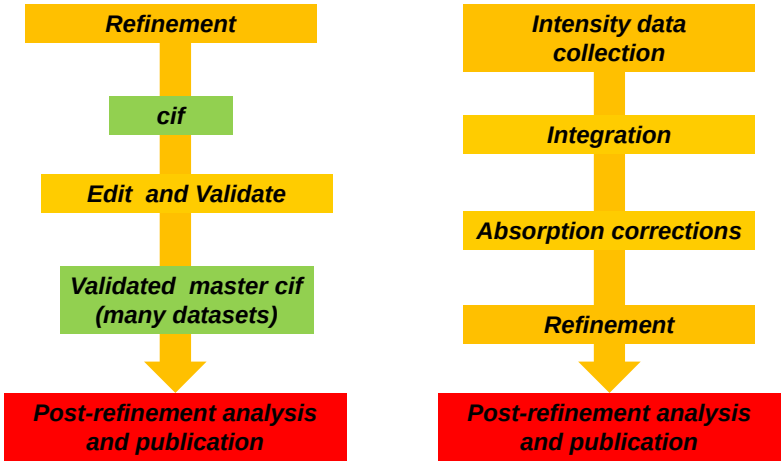
- Crystallographic Information Files (cif's)
  - High-pressure features
  - Response to cif-checker
  - Parametric data handling
- Post-refinement analysis tools
  - Mostly for inorganic structures

Post-refinement analysis

- Structure validation
  - Getting past the cif-checker
- Parametric data:
  - Challenges
  - Opportunities to exploit self-consistency



Post-refinement analysis



Parametric data, so report P,T

- In each data block:
- _cell_measurement_pressure
  - pressure in kilopascals at which unit cell parameters were measured
- _diffrn_ambient_pressure
  - mean hydrostatic pressure in kilopascals at which diffraction intensities were measured
- UNITS!!!
  - 1 GPa = 10 kbar = 1,000,000 kPa

Parametric data, so report P,T

- Don't forget the temperatures:

- _cell_measurement_temperature
  - temperature in Kelvin at which unit cell parameters were measured

- _diffrn_ambient_temperature
  - mean temperature in Kelvin at which diffraction intensities were measured

Some optional items

- _diffrn_ambient_pressure_gt
- _diffrn_ambient_pressure_lt
  - mean hydrostatic pressure in kilopascals above which (*_gt) or below which (*_lt) the intensities were measured

- _exptl_crystal_pressure history
  - relevant details concerning the pressure history of a sample

- _pd_prep_pressure
  - preparation pressure of the sample in kilopascals
  - (from powder cif dictionary)

- _cell_wave_vectors_pressure_max
- _cell_wave_vectors_pressure_min
  - maximum and minimum values of the pressure in kilopascals between which the modulation wave vector(s) were measured

From macromolecular cif dictionary

- _cell_measurement.pressure
- _diffrn.ambient_pressure
- _diffrn.ambient_pressure_gt
- _diffrn.ambient_pressure_lt

- _cell_measurement.pressure_esd
  - standard deviation of _cell_measurement.pressure
- _diffrn.ambient_pressure_esd
  - standard deviation of diffrn.ambient_pressure

- _exptl_crystal_grow.pressure
  - ambient pressure in kilopascals at which the crystal was grown
- _exptl_crystal_grow.pressure_esd
  - standard deviation of exptl_crystal_grow.pressure

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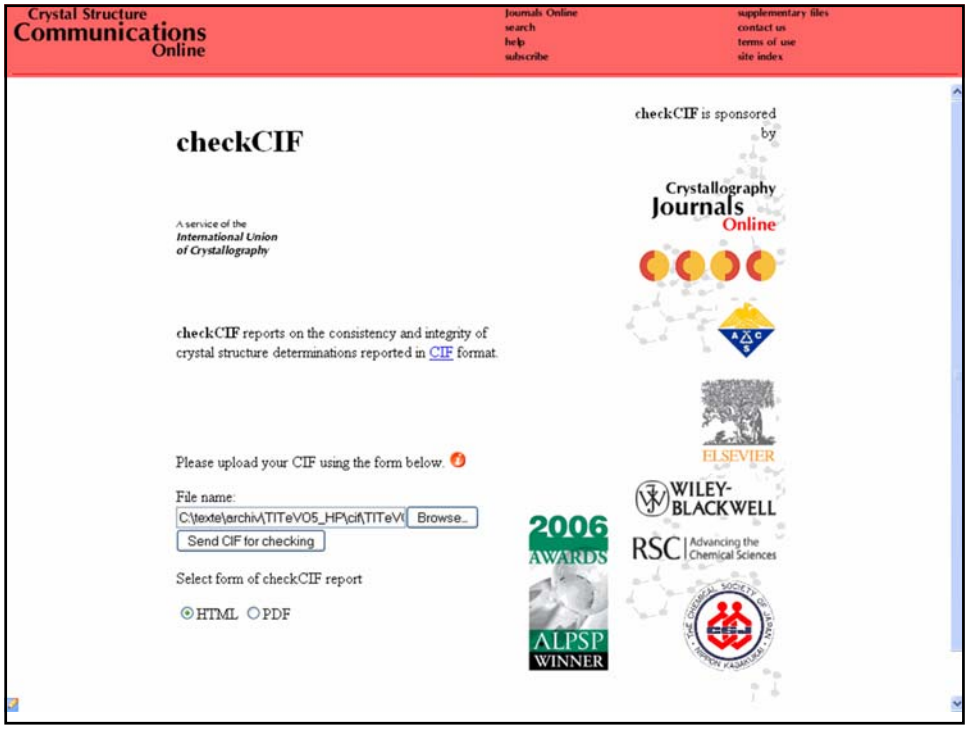


Alerts of level A

- These must be answered!

- PROBLEM: _diffrn_reflns_theta_full (too) Low ..... 12.64 Deg.
  RESPONSE: Due to limited opening angle of the diamond anvil cell.

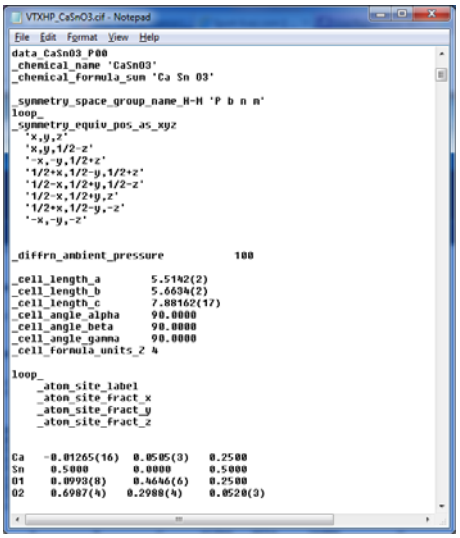
- PROBLEM: _diffrn_measured_fraction_theta_full Low 0.43
  RESPONSE: Due to limited opening angle of the diamond anvil cell.

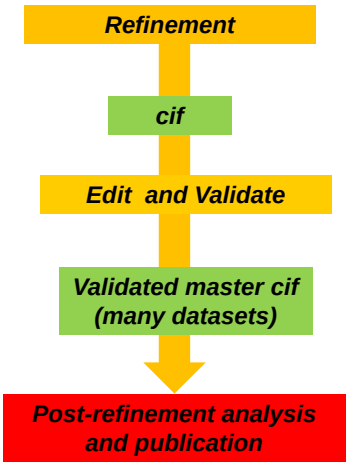
Cif-checker warnings

- The value of R(int) is greater than 0.12
  - R(int) given 0.131
  - RESPONSE: Data quality lower than normal because data collected from crystal in diamond-anvil pressure cell

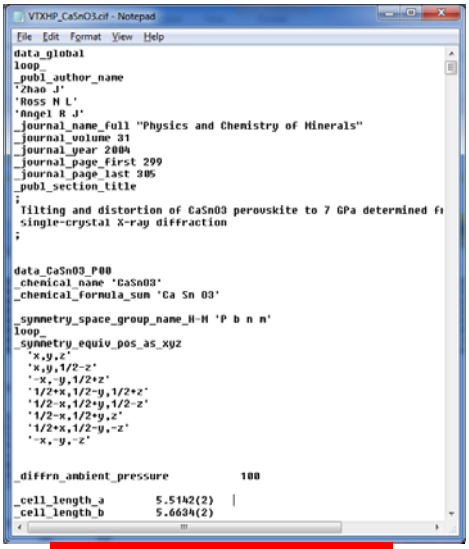
- Expected hkl max differ from CIF values
  - From the CIF: _diffrn_reflns_theta_max 28.29
  - From the CIF: _reflns_number_total 461
  - From the CIF: _diffrn_reflns_limit_ max hkl 6. 9. 9.
  - From the CIF: _diffrn_reflns_limit_ min hkl -7. -9. -9.
  - TEST1: Expected hkl limits for theta max
  - Calculated maximum hkl 9. 11. 9.
  - Calculated minimum hkl -9. -11. -9.
  - RESPONSE: Data restricted because data collected from crystal in diamond-anvil pressure cell

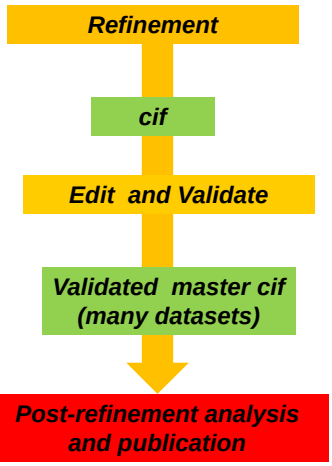
Validate cifs separately





Build a master cif





And lock it against editing!

Use your master cif for everything!

Validated master cif (many datasets)

- Generate tables for publication:
  - Cell parameters
  - Positional parameters
  - Bond lengths and angles

cifReader

- Geometrical parameters
  - Polyhedral distortions
  - Polyhedral tilts

IVTON

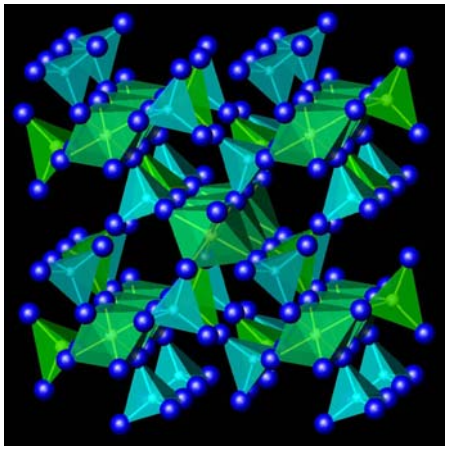
Isodisplace

cifReader

- Reads 1 cif at a time
  - Containing multiple datablocks
  - Research tool and badly written
  - But available at www.rossangel.net
  - And produces tables (e.g. bond lengths etc) and basic calculations, without any cutting and pasting!
- Command line driven
  - But undocumented

The concept of polyhedra

- In inorganic structures it is usual to group all chemical bonds reaching an atom and to define its coordination polyhedron
- Structures are considered as built from these strongly-bonded polyhedra
- Structural evolution:
  - Polyhedral internal changes
  - Tilts of the polyhedra



cifReader and polyhedra

DoS_cif.exe - Shortcut

```
19-JUL-12:14:40:Dataplotter>list bonds
Enter central atom name (or ALL):Sn


    BONDS FROM CENTRAL ATOM SN        BETWEEN  2.00 AND  2.50 ANGSTROM
 Pressure Temperature O1      O1      O2      O2      O2      O2      N AVERAGE    QE       AV      VOLUME
    0.000  298.000  2.0549  2.0549  2.0572  2.0572  2.0559  2.0559  6  2.0560  1.0007   2.466   11.576
    0.074  298.000  2.0537  2.0537  2.0488  2.0488  2.0571  2.0571  6  2.0532  1.0006   2.254   11.530
    1.500  298.000  2.0511  2.0511  2.0487  2.0487  2.0538  2.0538  6  2.0512  1.0007   2.472   11.495
    2.610  298.000  2.0460  2.0460  2.0430  2.0430  2.0519  2.0519  6  2.0469  1.0008   2.635   11.423
    3.940  298.000  2.0412  2.0412  2.0405  2.0405  2.0462  2.0462  6  2.0426  1.0006   2.008   11.354
    5.180  298.000  2.0358  2.0358  2.0392  2.0392  2.0431  2.0431  6  2.0393  1.0006   2.128   11.298
    5.980  298.000  2.0351  2.0351  2.0315  2.0315  2.0452  2.0452  6  2.0373  1.0007   2.303   11.263
    6.730  298.000  2.0320  2.0320  2.0268  2.0268  2.0411  2.0411  6  2.0333  1.0006   1.974   11.199

LIST BONDS> Enter central atom name:_
```

Quadratic elongation: $\langle\lambda\rangle = \frac{1}{n}\sum_i (l/l_0)^2$

Bond angle variance: $= \frac{1}{n-1}\sum_i (\theta_i - \theta_0)^2$

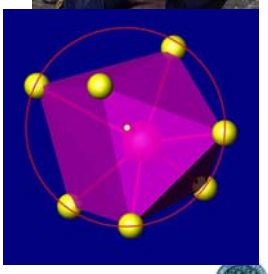
(Robinson et al., Science 172 (1971) 567-570)

For some alternative approaches see Porai-Koshits & Aslanov, J.Struct.Chem. 13 (1972) 244; Muetterties & Guggenberger, J.Am.Chem.Soc. 96 (1974) 1748-1756; Dollase, Acta Cryst. A30 (1974) 513-517; Drew, Coord.Chem.Rev. 24 (1977) 179-275

IVTON

- Developed by Tonci Balic-Zunic
  - Balic-Zunic & Vickovic, J.Appl.Cryst. (1996) 29, 305
  - Available from TonciB@snm.ku.dk

- Calculates new polyhedral parameters
  - Based on centroid
  - The centre of the best sphere fitted to the vertices of the polyhedron.
  - Can describe displacement of atom from centre
  - Can describe distortion of coordination atoms independent of central atom position.



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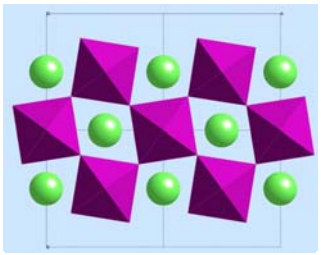
Isodisplace

- Analyses structural evolution in terms of symmetry-adapted modes
  - 'Frozen phonons'
  - Use when structure approximates a higher symmetry
  - For perovskites and octahedral frameworks can obtain tilt angles (Acta Cryst. B67: 302 (2011))
  - Unambiguous separation of tilts and distortions



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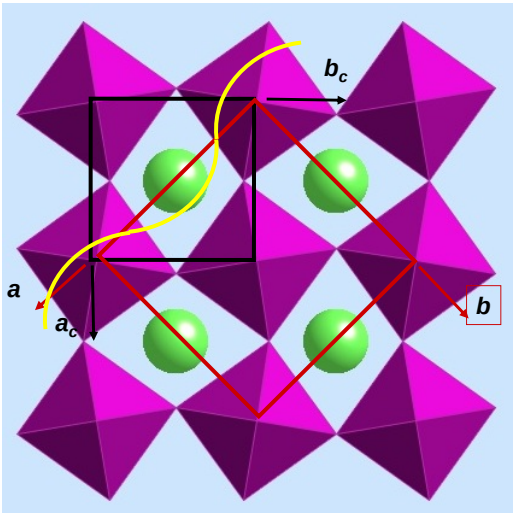
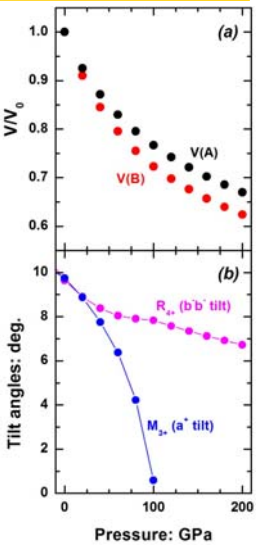
One tilt as a stationary plane wave



Isodisplace

- http://stokes.byu.edu/iso/isodistort.html
- Work on one refined structure at a time
- Decomposes the distortions from higher symmetry
  - Need a model of the high-symmetry structure
  - Load both to Isodisplace (Mode 4)
  - Obtain 'mode amplitudes'
  - Convert to tilt angles (Acta Cryst. B67: 302 (2011))



Summary

- Validate each structure
- Create Master cif
  - Lock it
  - Validate it
  - Avoid cut and paste errors!
- Generate tables for publication from it
- Do all post-refinement analysis from it!
- Avoid cut and paste errors!