The messy world of real experiments: Powder diffraction, Rietveld analysis and pdCIF

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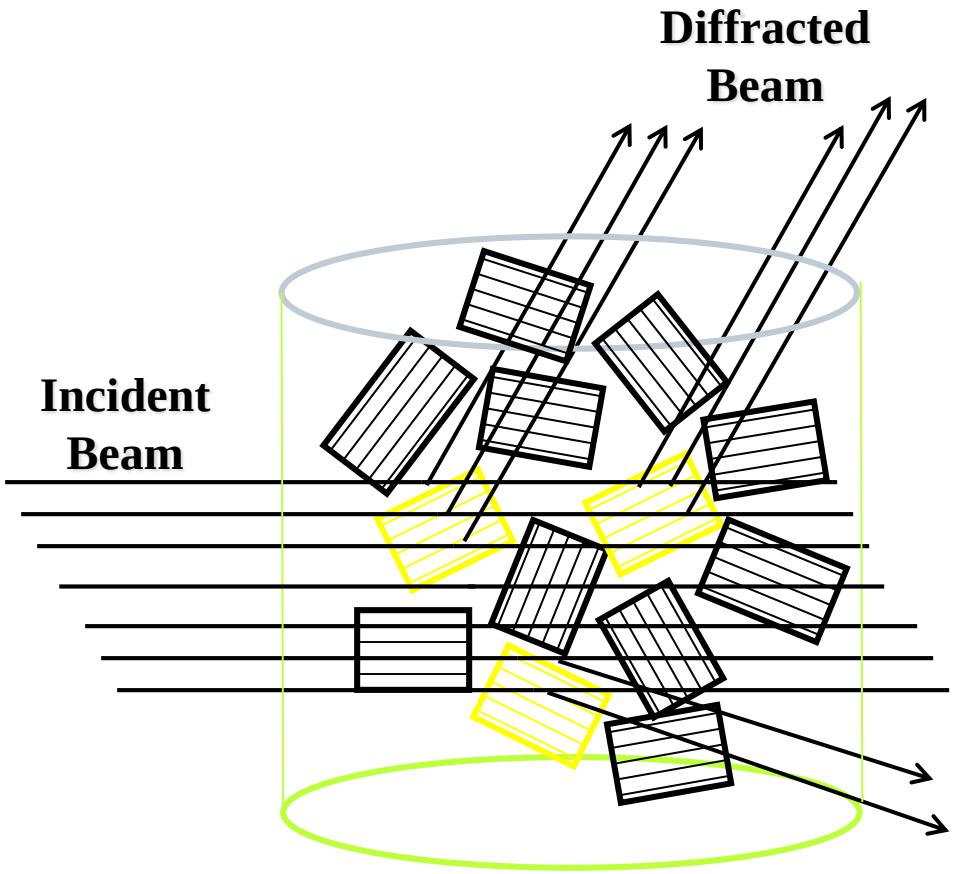
Diffraction from random polycrystalline material

In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder) contains a very large number of crystallites.

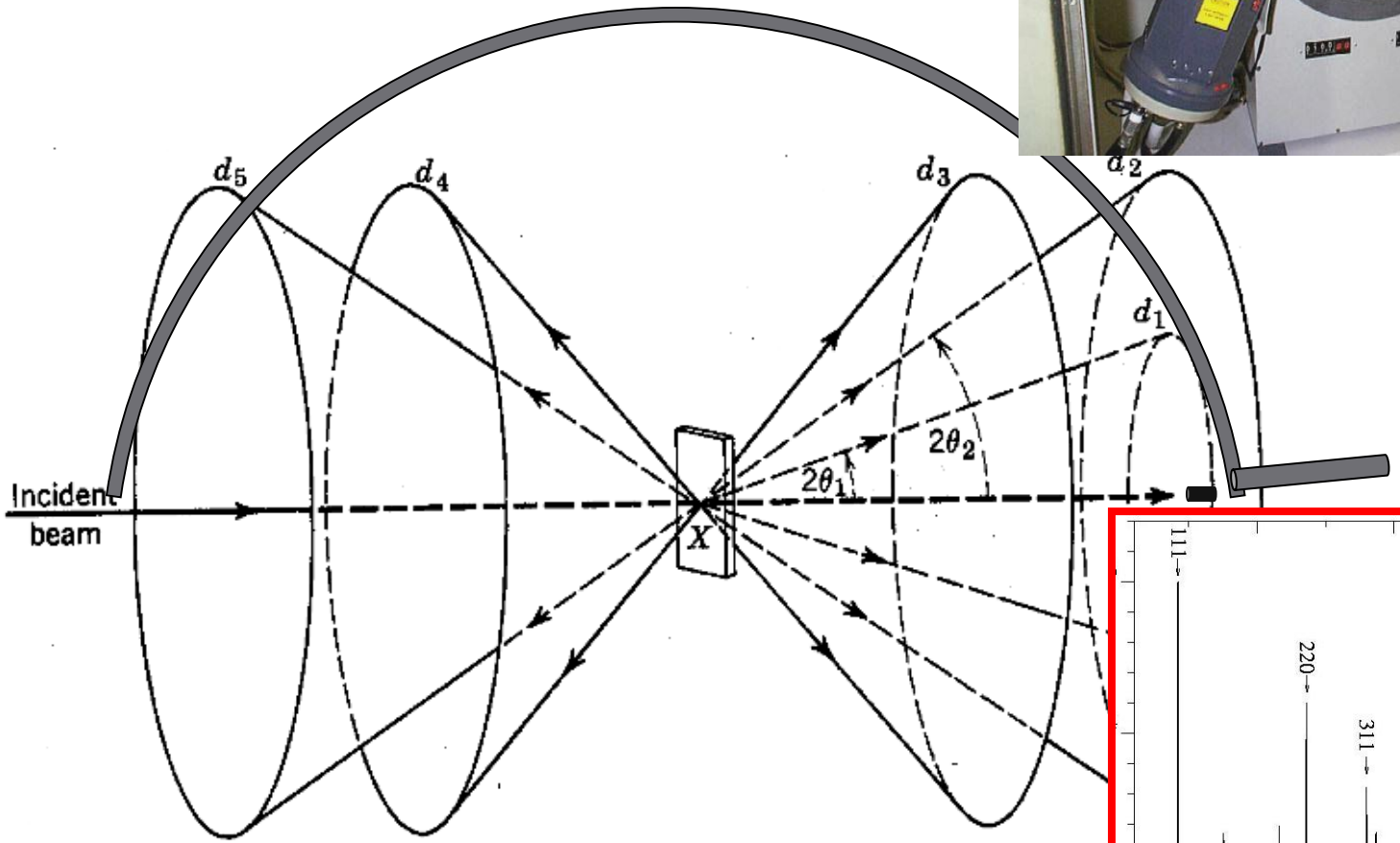
A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction

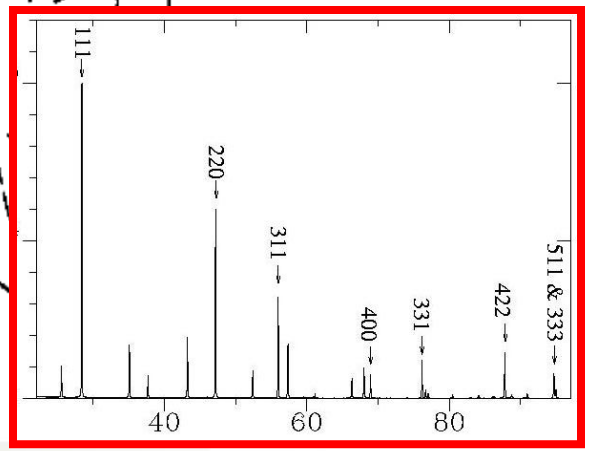
Diffraction occurs only at specific angles, those where Bragg's Law is satisfied.



Measuring powder diffraction

- Angular dispersion: a single detector is moved over a range of 2θ angles.
  - Sample irradiated with monochromatic radiation





Why is a universal format for Powder Diffraction data so valuable?

- Graphical examination of fits: viewing the observed and simulated data is the ultimate quality test

- Every instrument has its own format. There are serious difficulties encountered with bringing data from instrument X into program Y.

- Archival and reproduction of previous studies

This motivated an effort to develop a standardized format for powder diffraction data through the International Centre for Diffraction Data in the late 1980's.

Storage of Powder Diffraction Data and Results

The goal for recording powder diffraction is to record the raw data, provenance information, the intermediate analysis information and extracted results.

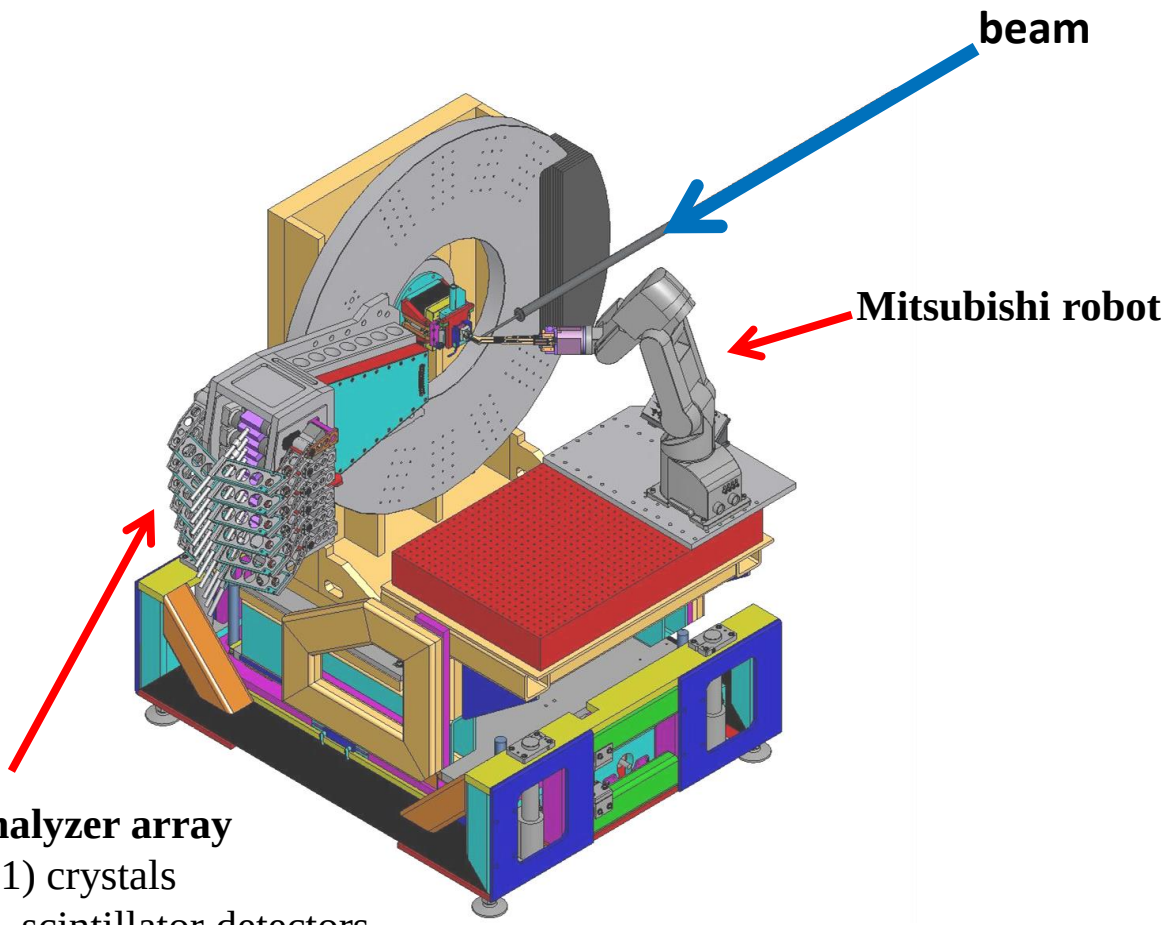
The hope would be that a standard format would be used for data collection and subsequent processing information would be added to the file.

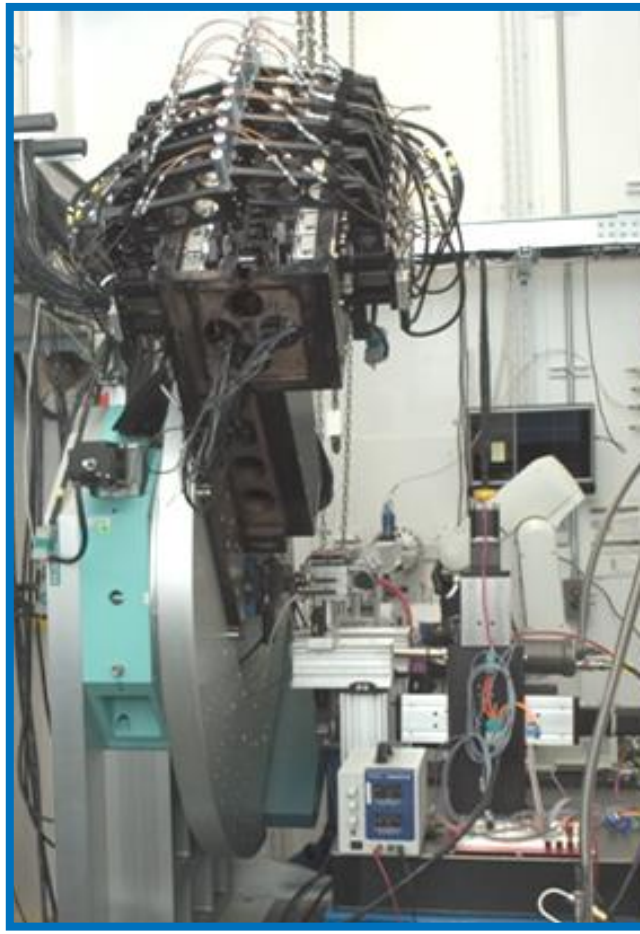
File sections

- Sample description, data collection metadata, other provenance,…
- Raw or minimally processed data
- Reduced, normalized and calibrated data
- Diffraction peaks (when lattice is not known)
- Structural model (coordinates)
- Structure factor tables (*N.B.* F_{obs} values are computed based on F_{calc} values – *depends on model*)

Challenge: There are many ways that powder diffraction data are measured, with very different file storage demands.

Highest resolution powder data requires a perfect crystal analyzer between the sample and detector: typically 8-40 such detectors are used.

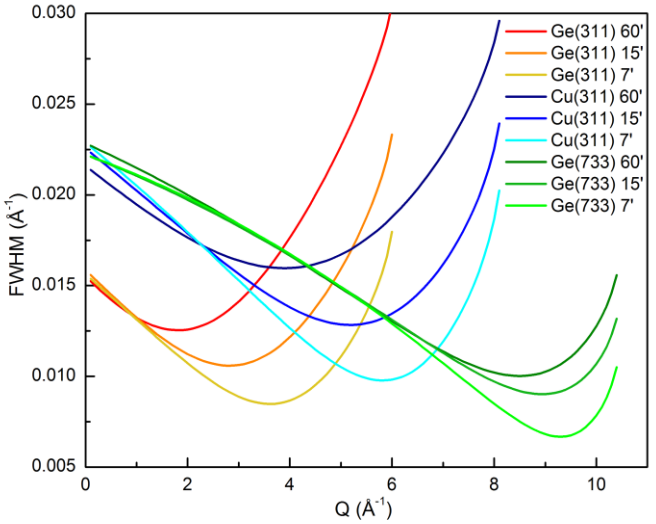




12 analyzer array
Si(111) crystals
$LaCl_3$ scintillator detectors
2° apart in 2Θ.

11-BM (@APS) collects twelve overlapping scans; each has a slightly different wavelength

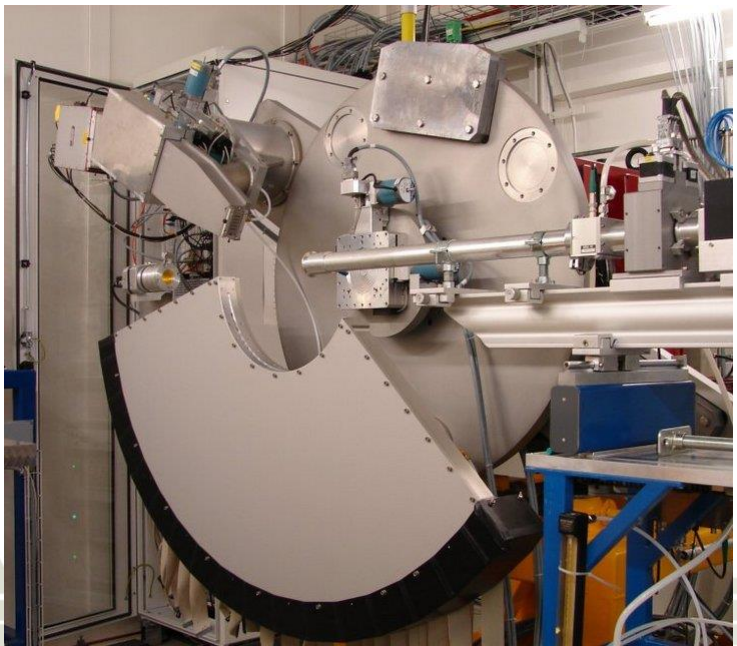
Reactor based Neutron Powder Instruments: Constant Wavelength, Angular Scans



beamline BT1 at NIST (NCNR)

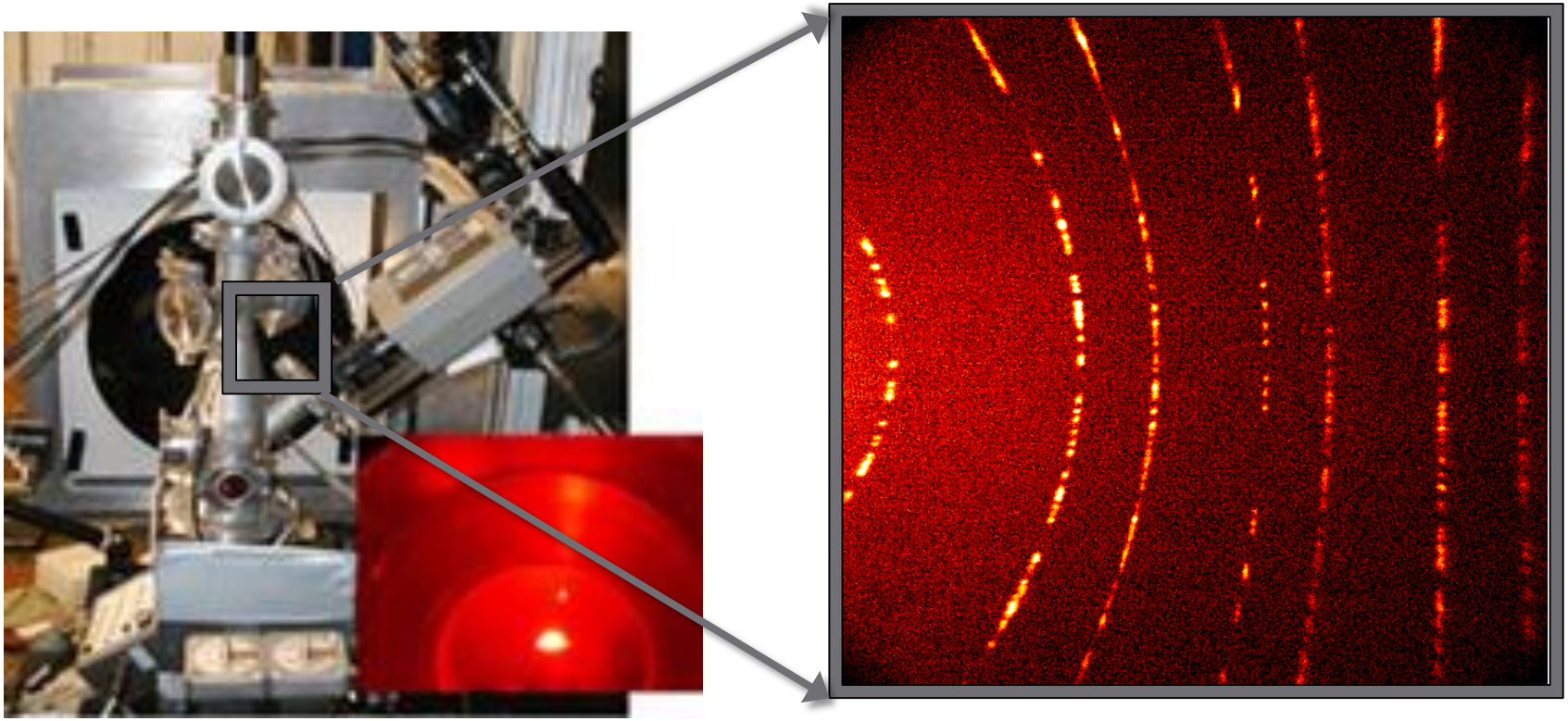
Linear detectors

- Linear detectors collect data very quickly, but usually need to be repositioned to increase the data range or compensate for gaps between detectors.
  - Data are typically similar to that from multiple discrete detection: multiple overlapping scans; except that number of scans and offsets between them may vary by measurement.
- Used in lab-based instruments, synchrotrons & neutron facilities



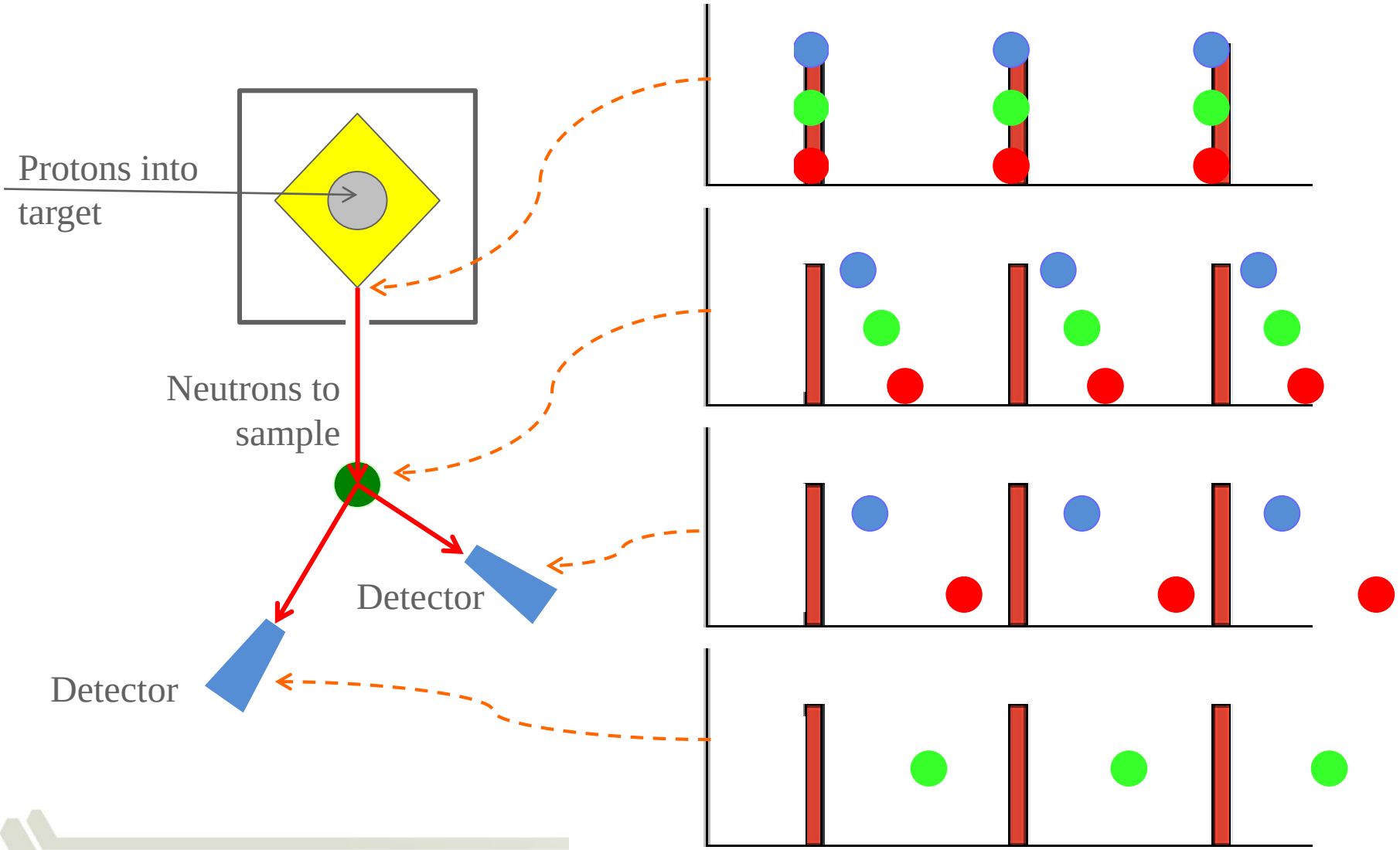
Area Detection

- With an area detector, a complete powder diffraction pattern can be collected in a fraction of a second.
  - Fast
  - Medium resolution
  - High background



Time of Flight Diffraction

Time of flight diffraction uses the fact that neutrons with different energies (velocities) have different wavelengths, $\lambda = h/mv$ (de Broglies relationship)



TOF diffraction

- Older instruments collect data in histograms: number of counts vs. time of neutron pulse generation for a given scattering angle.
  - Neutron wavelength can be calibrated in terms of this time of flight
  - Counts for each channel from 10^3 to 10^6 pulses are summed.
- Newer instruments tend to have linear or area detection so there is a histogram for each pixel.
- The SNS (and ESS?) collect data in event mode: a record is made for each detected neutron, noting the pixel location, time-of-flight and pulse number.
  - Postprocessing allows for different resolution etc by applying selection criteria to events

Summary of data requirements

Raw data

- Data may be recorded as counts or intensity vs. angle at fixed (or variable) wavelength
- Data may be recorded as counts vs. TOF at fixed angles
- Data may be recorded as counts vs. pixel (sometimes vs. TOF)
- Area detection produces large 2-D or ≥3-D datasets

Reduced data

- Since instrumental effects must be modeled, data should be minimally processed, but calibration corrections are applied to angles, pixel locations, TOF, etc. to put data in absolute units. Rebinning may change the number of data points.
- Reduced data are usually 1-D scans, but may have many scans vs. other variable(s), T, P, azimuth

Results from Powder Diffraction Extend Beyond Crystallography

Note that powder diffraction experiments are most frequently performed for reasons other that structure determination:

- Crystallographic phase identification or quantification (sometimes >10 phases)
- Texture
- Residual or applied stress
- Crystallite size

pdCIF progress

- Stage 0 (Negative progress): Drop initial JCAMP-DX standard to start pdCIF (~1991)
- Stage 1 (Useless): pdCIF dictionary largely complete (1995)
  - Convinced the ICDD to sign onto CIF in 1995
- Stage 2 (Write-only): export to pdCIF possible with GSAS2CIF (1995-2001)
  - First pdCIF submitted as supplementary material (D. Ramprasad, *et al.*, "Solid-State Lithium Cyanocobaltates with A High-Capacity for Reversible Dioxygen Binding - Synthesis, Reactivity, and Structures". *JACS*. **117**: 10694 **(1995)**, 91 citations].
- Stage 3 (some utility): first reader: pdCIFplot (2002)
  - Later used as input format for CMPR, EXPGUI, Jade,…
- Stage 4: (universal): pdCIF is routinely used for exchange of experimental data and analysis results (not yet)
  - ICDD releases a data deposition mechanism based on pdCIF (2012)
  - IUCr Journals integrate pdCIF into publication (2013)

Potentially Complex data block structure

Very common:

- Multiple (M) crystallographic phases are present in a single diffraction dataset

Somewhat less common:

- Different diffraction measurements (N datasets) may be employed in a single fit

CIF(1): multiple definition of core items requires multiple blocks

Simplest case: one dataset, one phase: one CIF block

With N > 1 or M > 1: must have >1 CIF blocks (best is N+M+1 IMHO)

pdCIF uses block pointers to describe the interrelationships between CIF blocks

- Still to be completely resolved: some parameters will have NxM values [peak profiles, $R(F^2)$,…]

Resulting pdCIF “schema” makes reading data complex

Ordinate one of: **_pd_meas_2theta_scan**, **_pd_meas_time_of_flight**, **_pd_proc_2theta_corrected**, **_pd_proc_d_spacing** or **_pd_proc_recip_len_Q**; **_pd_meas_2theta_range_[min,max,step]** or **_pd_proc_2theta_range_[min,max,step]**

Abcissa 1 (one of)**:_pd_meas_counts_total**, **_pd_meas_intensity_total**, **_pd_proc_intensity_total** or **_pd_proc_intensity_net**

Error bars from *2* (one of) **_pd_proc_ls_weight** or s.u. **of _pd_meas_counts_total**

Abcissa 2 (one of): **_pd_calc_intensity_net** or **_pd_calc_intensity_total**

Abcissa 3: **_pd_proc_intensity_bkg_calc**

Where are we now?

- The IUCr Journals are having difficulty with getting submission of complete CIFs that include powder diffraction data. Many Rietveld packages are quite old and do not offer CIF export.
  - There are still many widely used powder diffraction software suites that have poor (or no) support for CIF

- The International Centre for Diffraction Data (ICDD) has embraced CIF as a mechanism for submission of data for their database. They have created a tool that reviews pdCIFs for information they seek or alternately collects that data and builds and submits a the CIF.

- The IUCr has integrated a new web-based version of pdCIFplot into the review and publication process. Produces interactive and publication quality graphics.

New “killer” pdCIF application: powder data viewer
(thanks to IUCr’s Simon Westrip)

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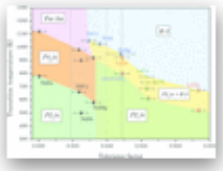
J. Appl. Cryst. (2013). **46**, 1085-1093 [doi:10.1107/S0021889813013253]



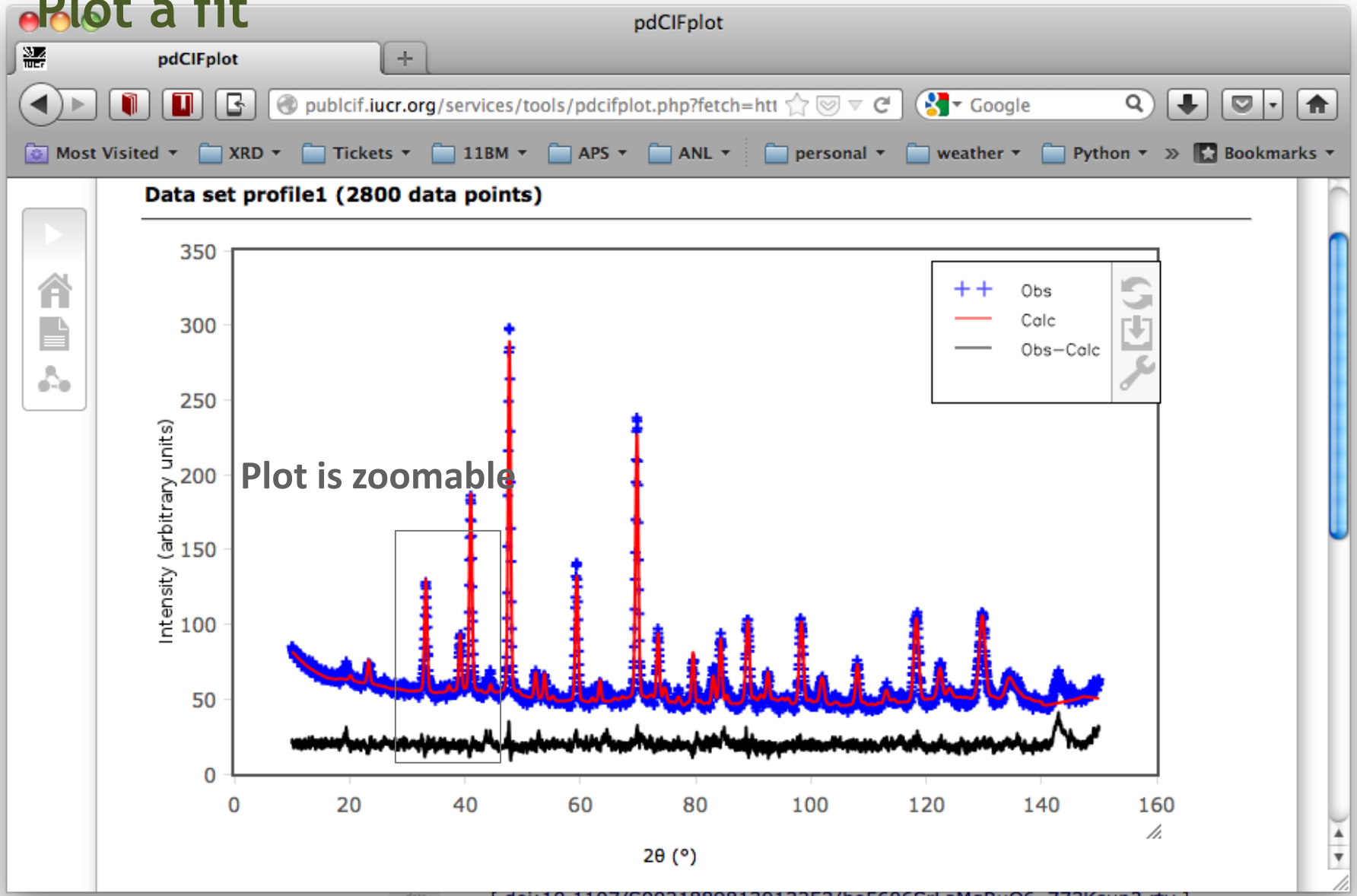
Symmetry-mode analysis of the phase transitions in $SrLaZnRuO_6$ and $SrLaMgRuO_6$ ordered double perovskites

E. Iturbe-Zabalo, J. M. Igartua and M. Gateshki

Synopsis: Structural investigations under temperature variation were carried out on $SrLaMRuO_6$ (M = Zn and Mg) double perovskites using diffraction techniques and a symmetry-mode analysis approach. The temperature *versus* tolerance factor phase diagram was completed for $SrLnMRuO_6$.

Online 22 June 2013

Plot a fit

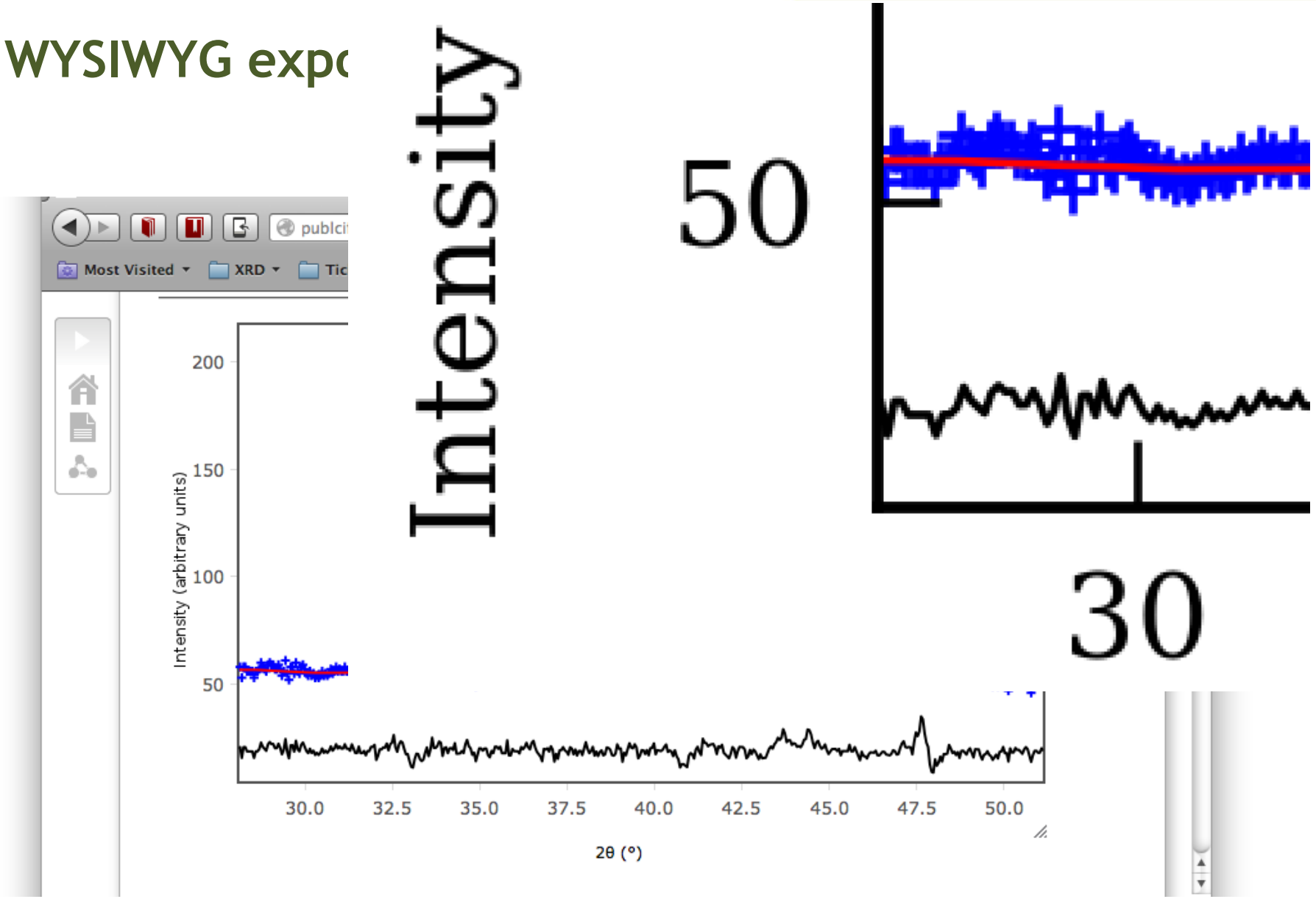


[doi:10.1107/S0021889813013253/he5606SrLaMgRuO6_773Ksup3.rtv]
Contains datablock profile1

display plot download

Rietveld powder data file (CIF format) (95.2 kbytes)

WYSIWYG expo



Conclusions

The community stands to gain from more widespread use of pdCIF through better review of refinements and through archival of the experimental record

Achieving adoption of any standard rests on three principles:

- The standard must be well designed and fill a need ✓
- Good software must smooth the use of the standard ←
- The user must gain something from adoption of the standard ✓