WISH : experiences and lessons in moving towards solving magnetic structures from single crystal

Pascal Manuel and Fabio Orlandi

ISIS Pulsed Neutron and Muon Facility,

STFC Rutherford Appleton Laboratory,

United Kingdom

Science & Technology Facilities Council
ISIS

IKON15, 12/09/2018

Outline

- Quick Review of WISH
  - Stats
  - Science
  - Design
- Towards structure refinement
  - Lessons learned
  - Plan

Some stats

> 150 publications (since 2009 start):

From 3 papers in 2010 to about 30 per year

H-index = 24

25 papers in “high impact” journals.

15 papers with >50 citations

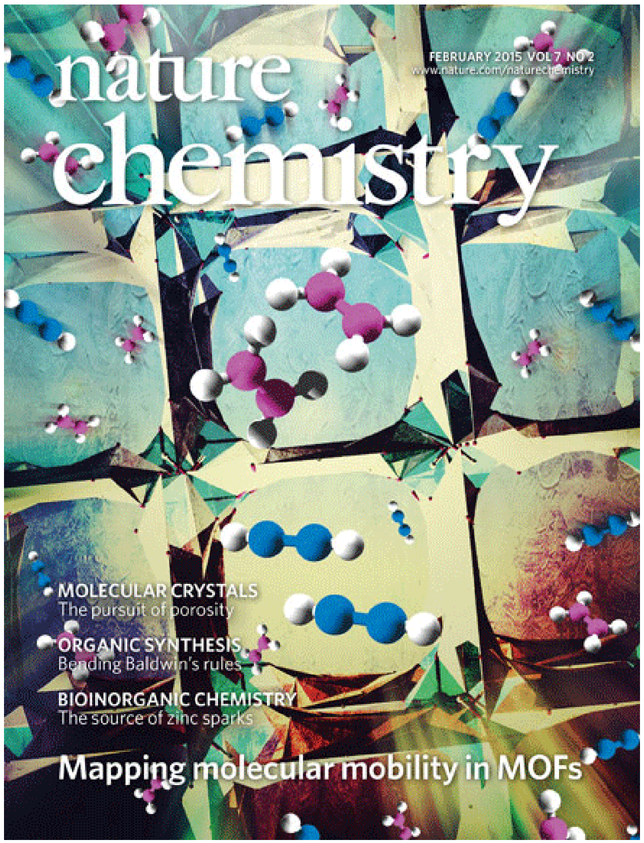
Oversubscription rate : typically 2-3 (peaked at 5 due to beam issues last year)

Nb of Experiments : ~80% powder / 20 % SX

corresponding to ~ 60% and 40% in beamtime

Science

~**85 % magnetism**, but also very successful programme on locating binding sites of gases in MOF



nature chemistry ARTICLES
PUBLISHED ONLINE: 1 DECEMBER 2014 | DOI: 10.1038/NCHEM.2114

Supramolecular binding and separation of hydrocarbons within a functionalized porous metal–organic framework

Sihai Yang[1]*, Anibal J. Ramirez-Cuesta[2], Ruth Newby[1], Victoria Garcia-Sakai[3], Pascal Manuel[3], Samantha K. Callear[3], Stuart I. Campbell[4], Chiu C. Tang[5] and Martin Schröder[1]*

Nott-300 large unit cell
$I4_122$, $a = b$ ~ 15-16, c ~ 12-13 Angstroms
Combination inelastic & neutron diffraction
Synchrotron(I11 @ DLS) . Modelling
Now a very successful programme :
Nat Commun 8 (2017) 14085
J Am Chem Soc 138, no. 29 (2016): 9119-9127
Nat Commun 8 (2017): 14212
J Am Chem Soc 138, no. 45 (2016): 14828-14831
…

Science & Technology Facilities Council ISIS

Requirements for magnetism beamline

- Magnetism shows up a low q. Need good resolution to solve structures (esp incommensurate ones) ie cannot just rely on low angles ie need long wavelength neutrons.

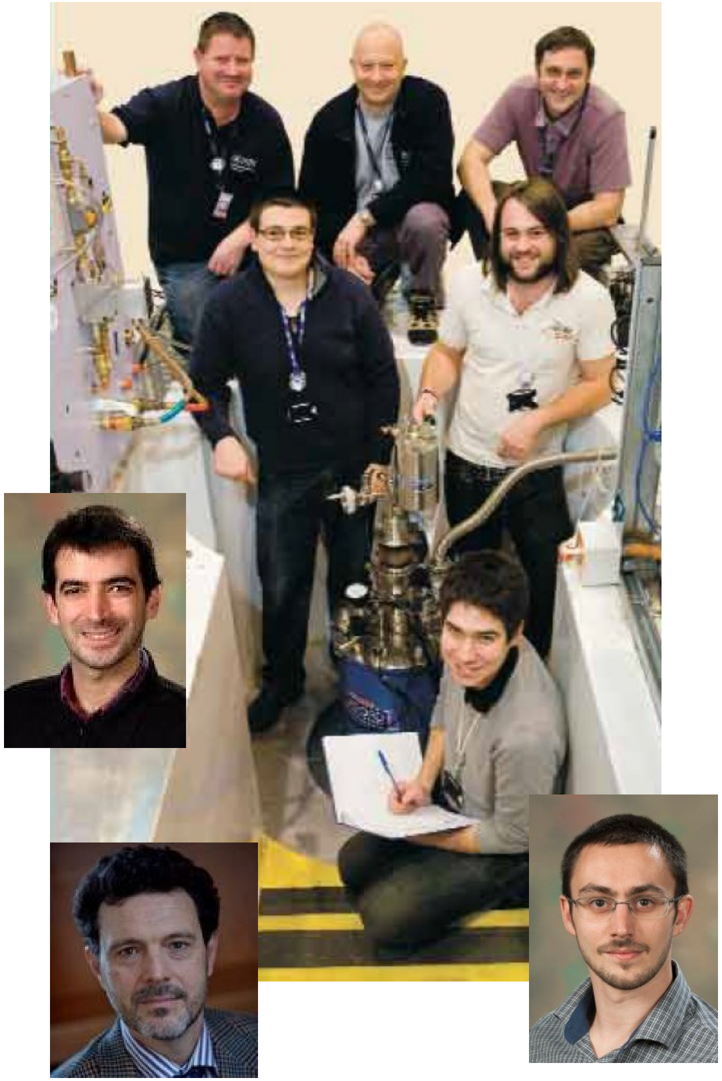
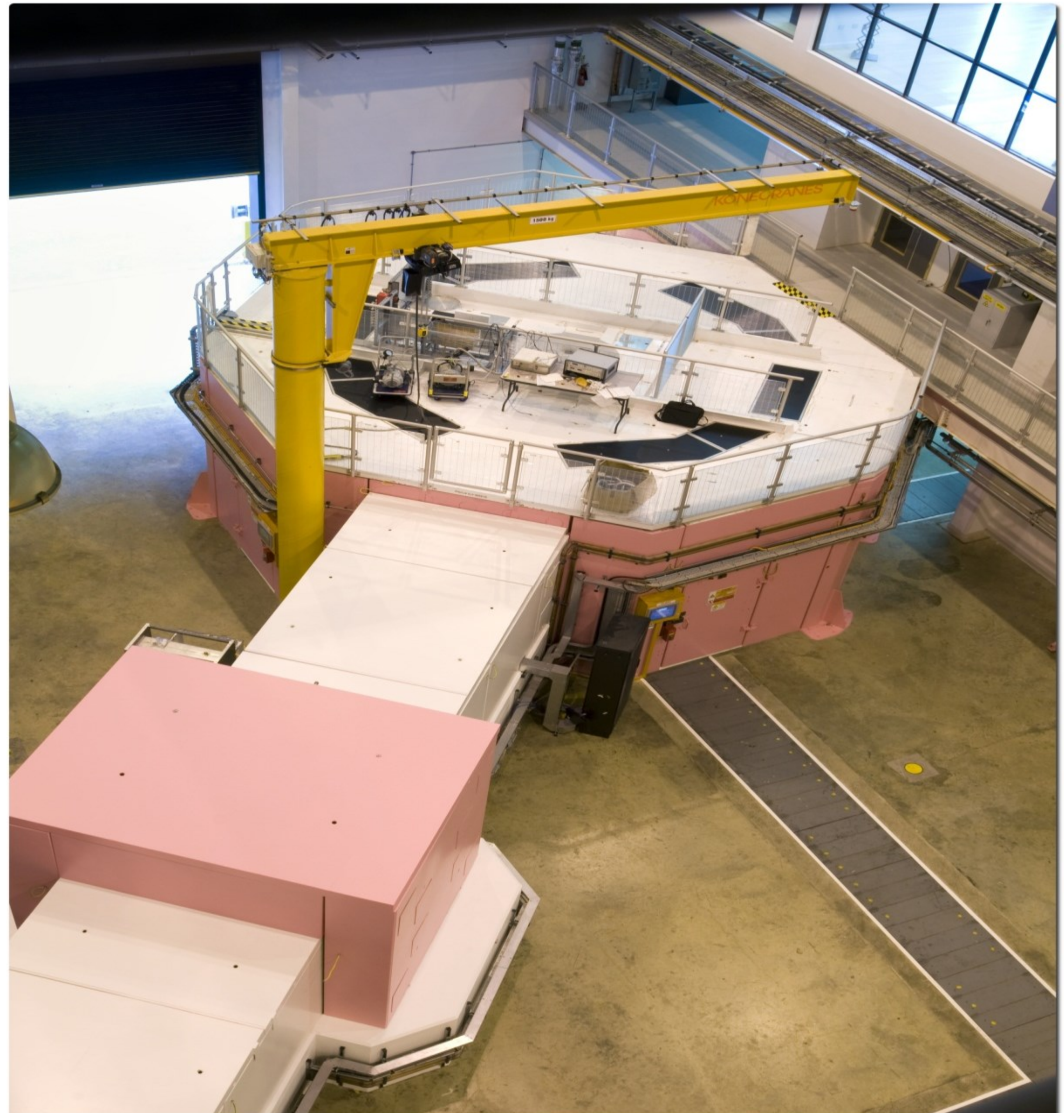
- Problem with complex SE: Absorption from gaskets, magnet rings… more pronounced at long wavelengths

- Therefore need very high flux at long wavelengths.

- Low background (small moments and/or samples) and good collimation.

- Optimize coverage wrt S.E.

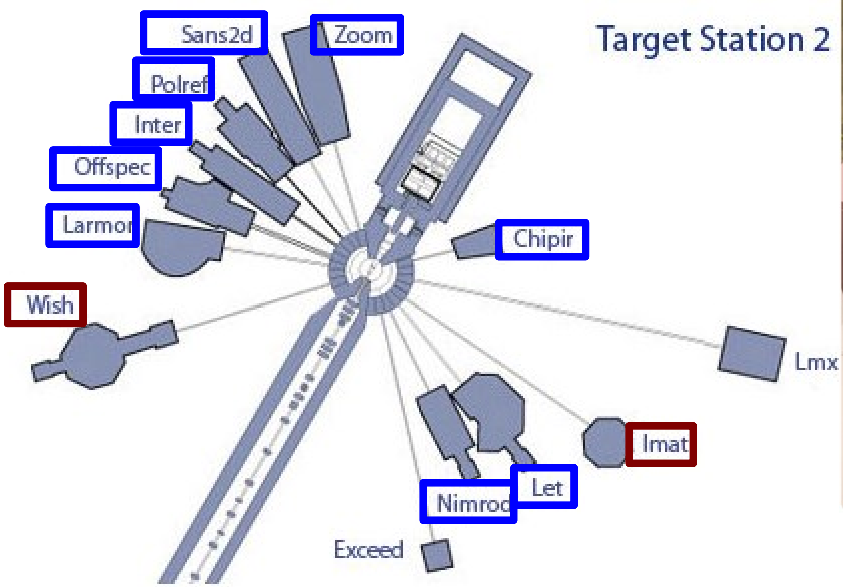
WISH beamline

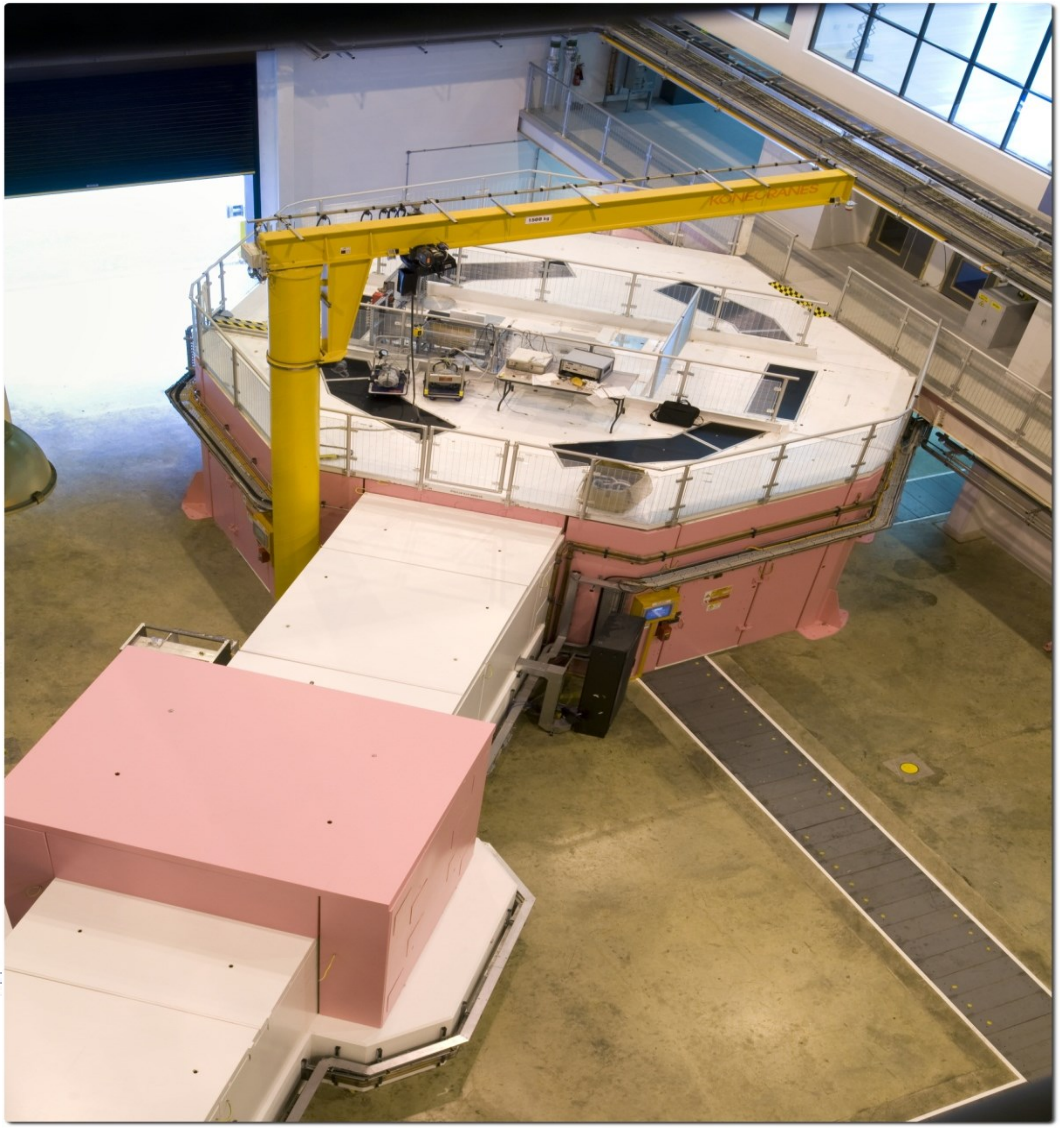



WISH beamline

Primary aim :
High resolution cold-neutron powder diffractometer to tackle eg. complex magnetic structures

Single crystal capabilities





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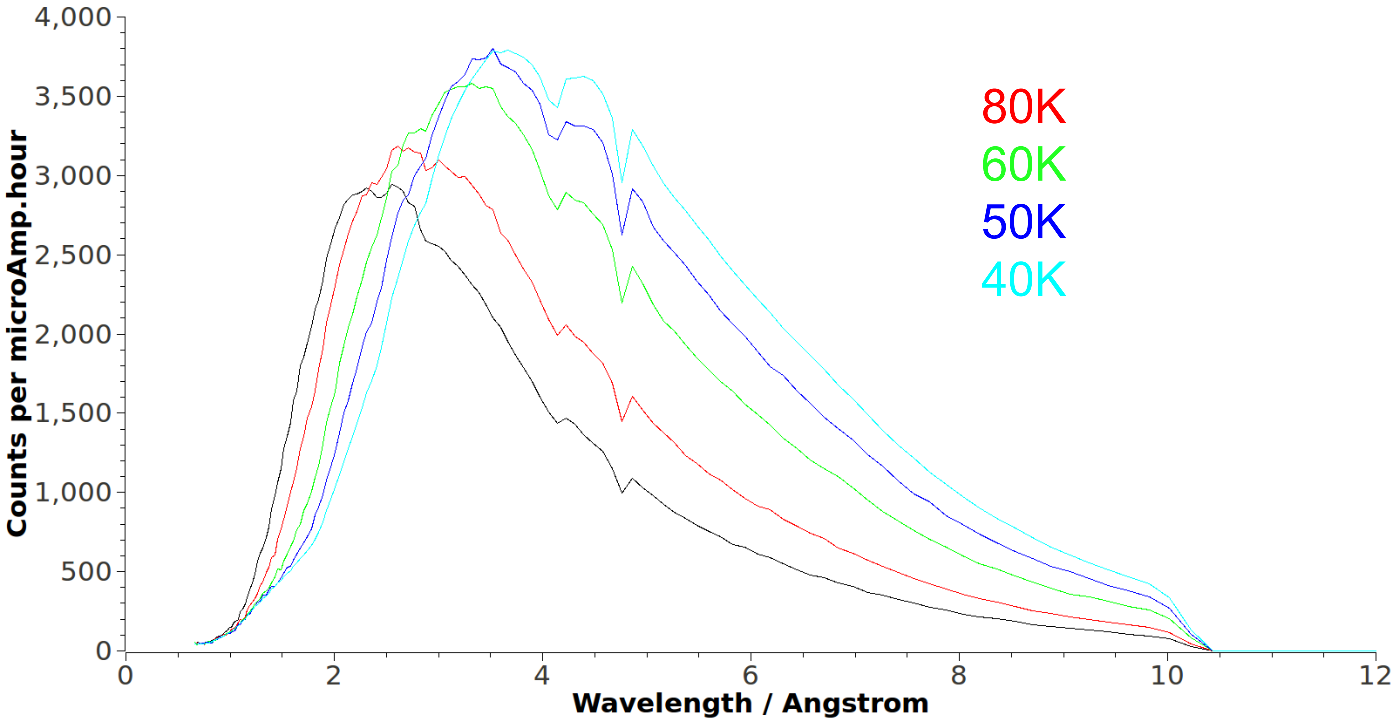
WISH moderator

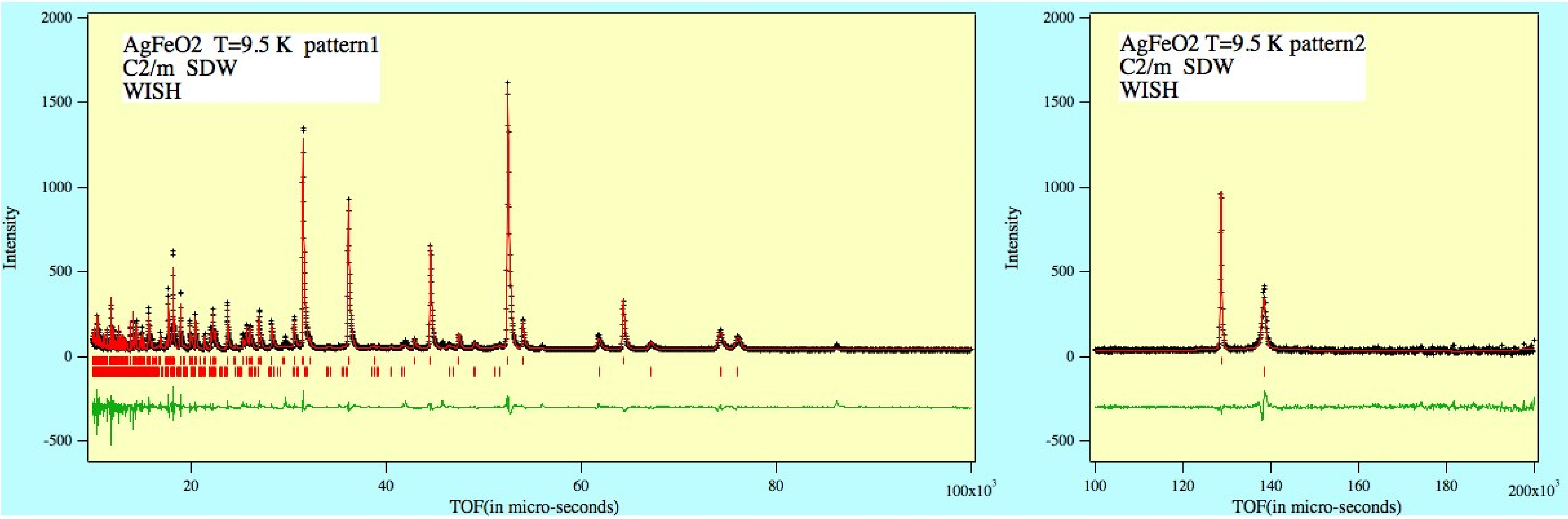
Solid methane : factor 5 gain at long λ (2 integrated)



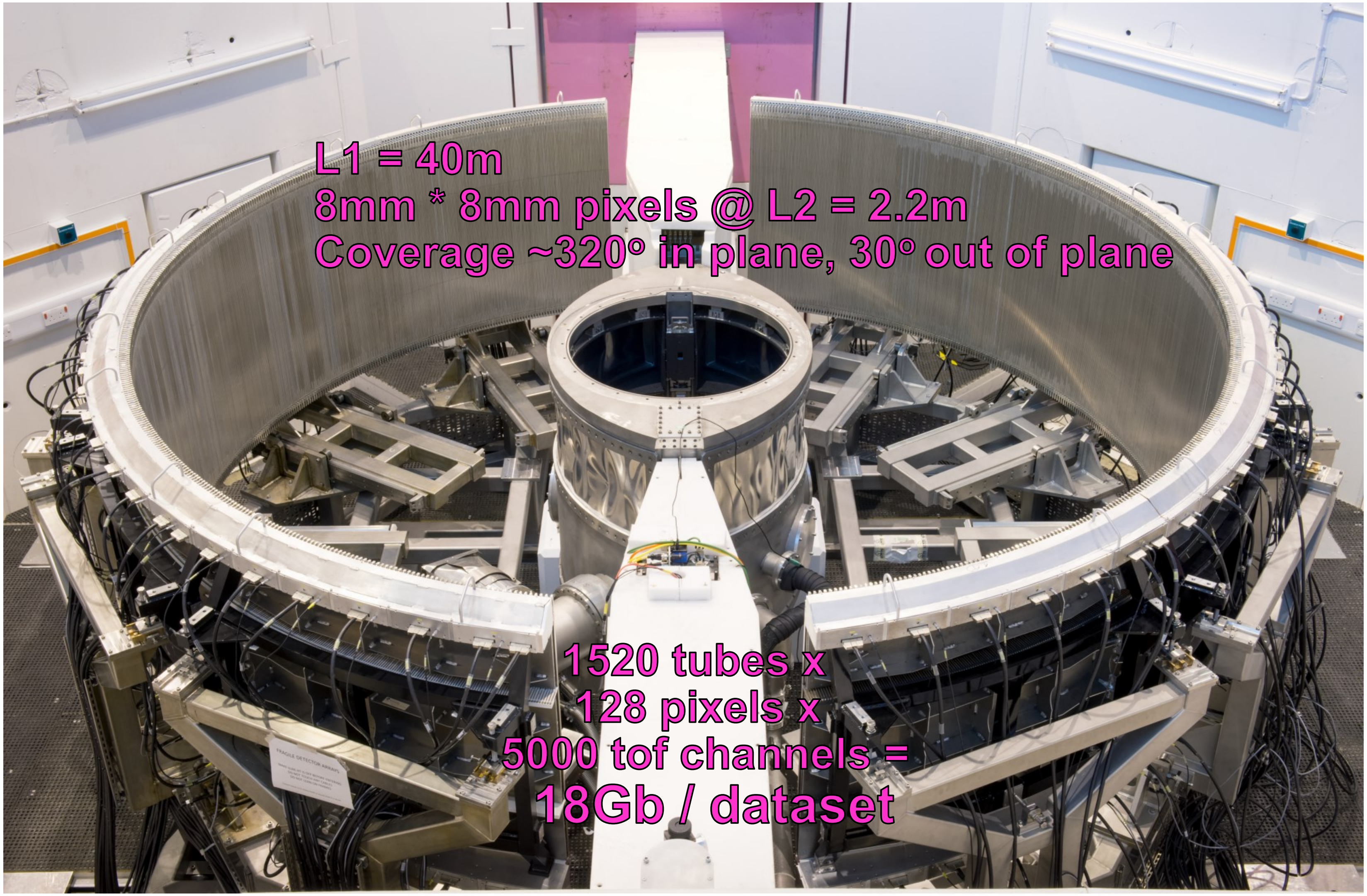
Refill every 18h

Double frame

0.5 to 10 Angstroms with backscattering resolution.
Lose factor 2 in flux, recouped by jaws to MR.
Can reach d=100 Angstroms at low angles.



For more details on this multiferroic delafossite AgFeO2, see Terada et al, Phys. Rev. Lett. 109 (2012) 097203



All 10 panels operational in 2014 (5 since 2009, ramping up second side since mid-2012)

Factor 2 for powders
Increased q-coverage for single crystal
(important for restricted geometry eg Pcell)

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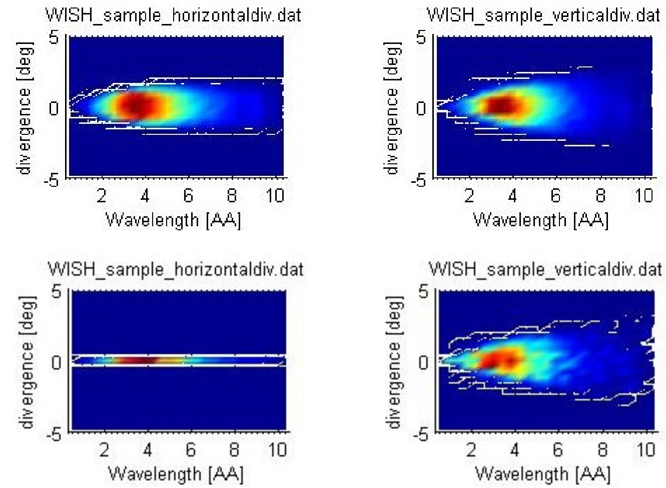
WISH design

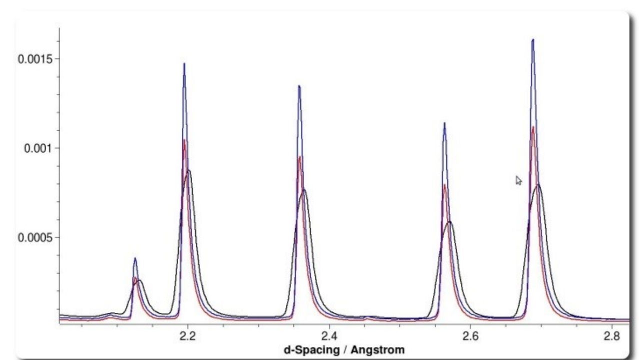
Transport : Elliptical guide

Background : Oscillating radial collimator

See Neutron News ***22****, 22 (2011) for details*



Divergence jaws :
Resolution / flux
Powder / single crystal



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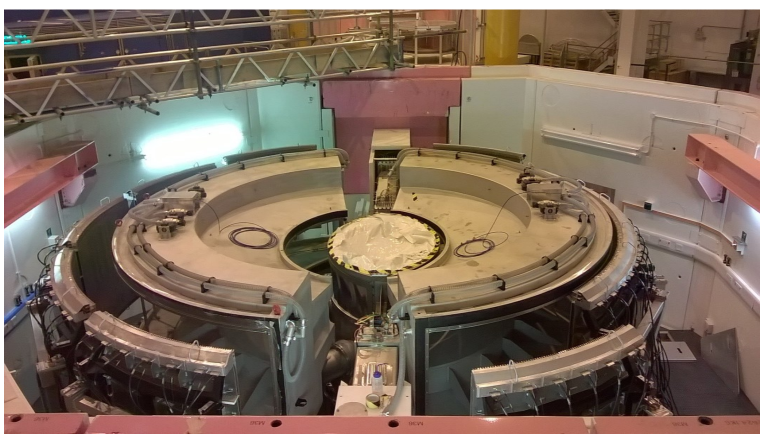
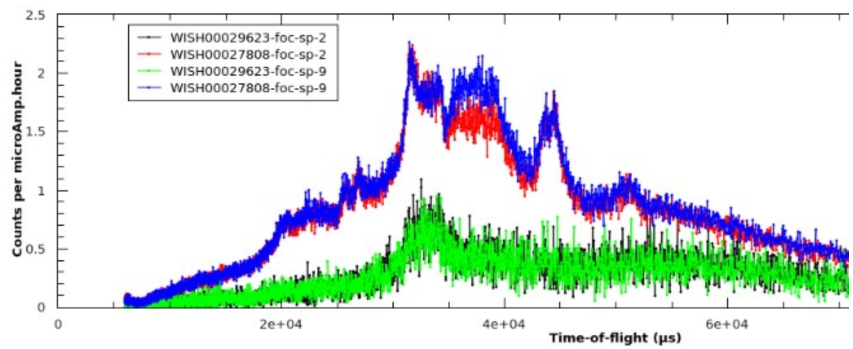
Recent upgrades

Reflector plug ~ 20% flux increase

Argon tanks

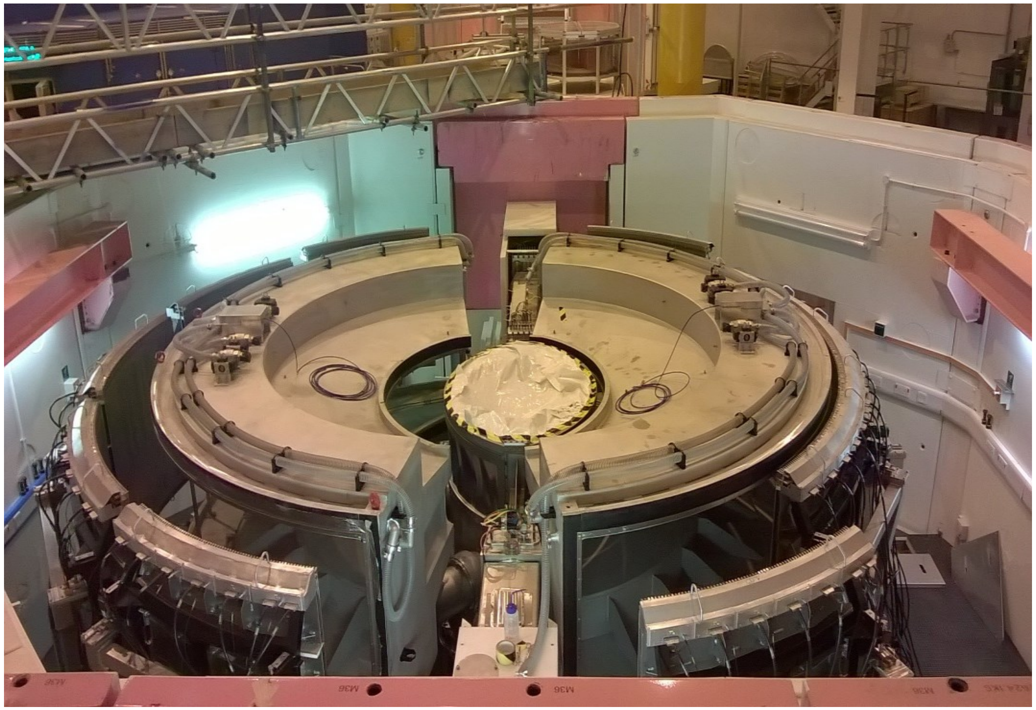


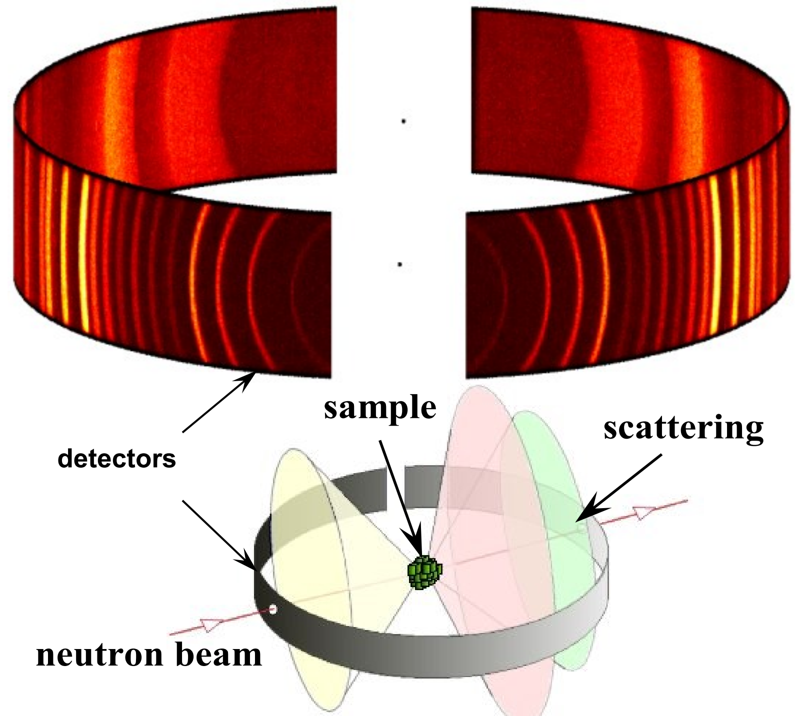
Less absorption in scattered beam



background reduction by factor 5 in low angle bank (bank2 shown)

Diffraction on a Pulsed Source (2)





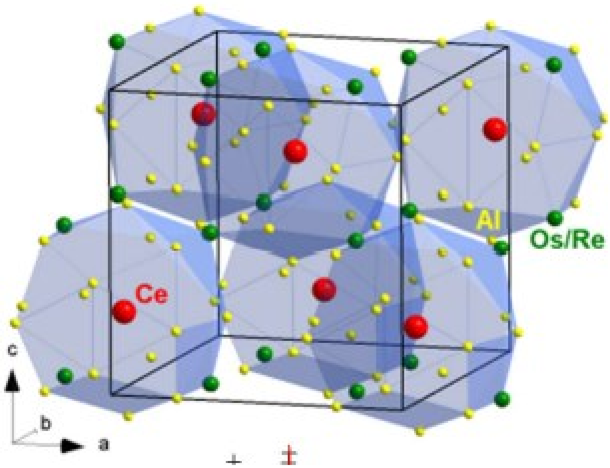
λ-range 0.35–20Å

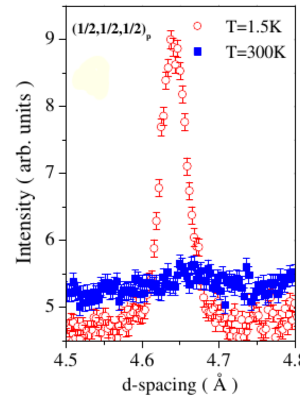
d-spacing range 0.4-100Å (0.4-10Å with $\Delta d/d \sim 0.003$)

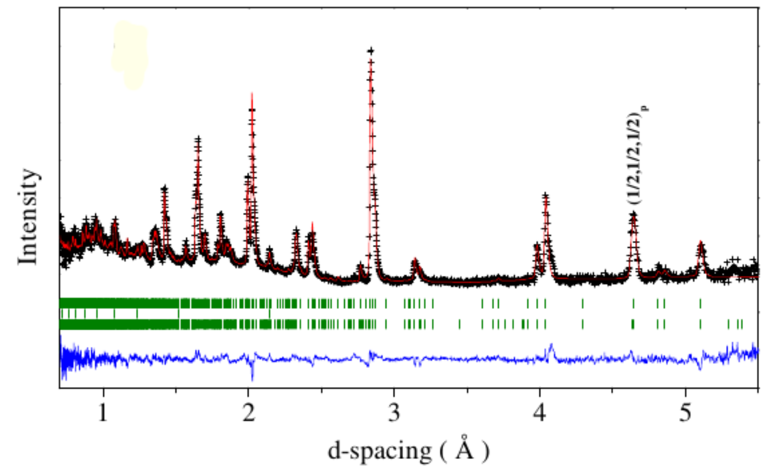
200 000 detectors focused into 5 histograms

Powder : very good at small samples/moments

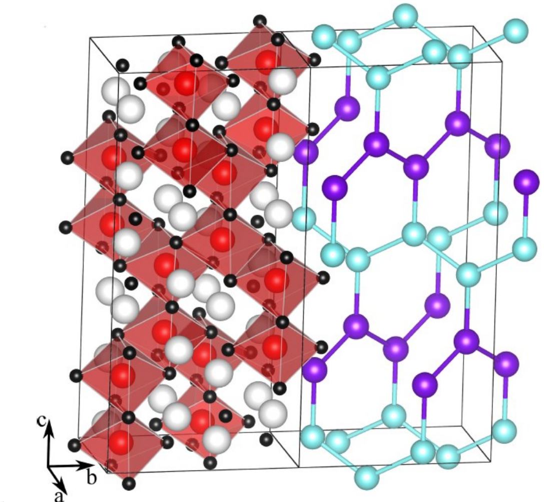
Magnetic structure of $BiSc_{0.5}Fe_{0.5}O_3$
20 mg



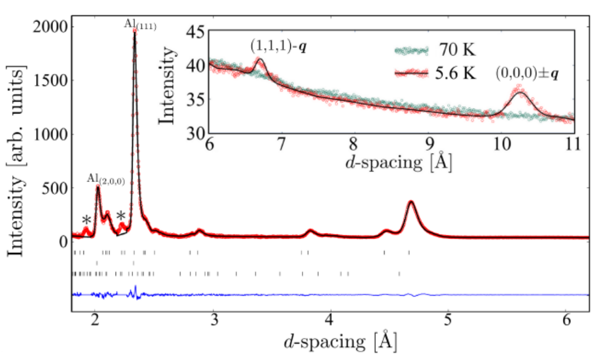




1-2-10 series, such as $CeRu_2Al_{10}$, 0.12 μ_B



Including on absorbing samples : βLi_2IrO_3 with 0.47 μ_B



Biffin et al,
PRB 90, 205116

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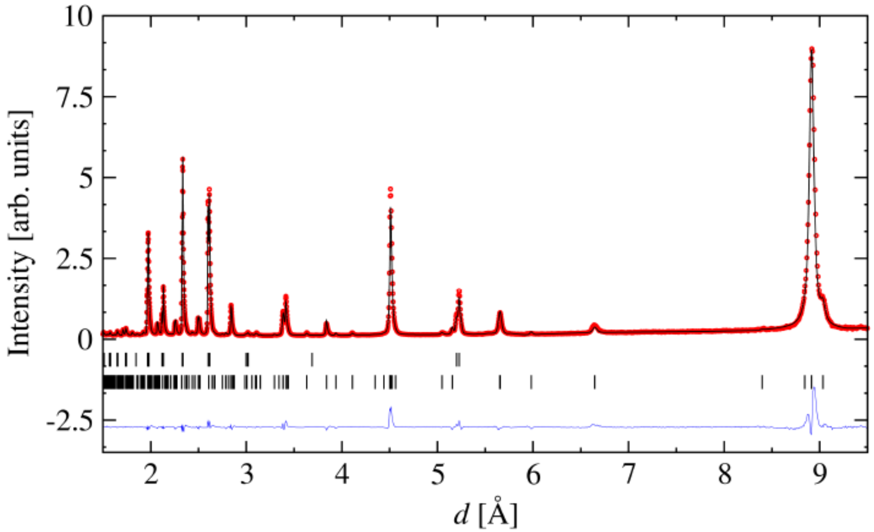
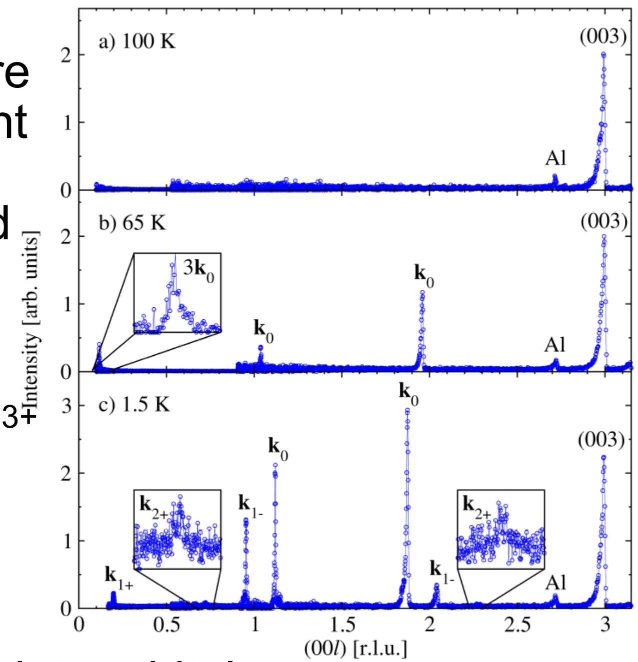
The most complex structure ? Low temperature phase of $CaMn_7O_{12}$

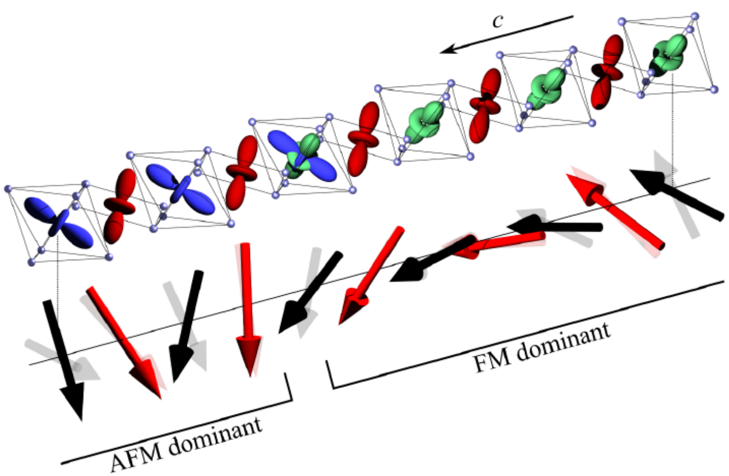
SX Sample : 200*200*200 μm



Multi-k structure is near constant moment Helix with modulated spin helicity which oscillate in phase with orbital occ. Mn^{3+}



Peak at d~65Å



Mag. PO locks into orbital wave at higher temp.

Temperature	Leading-order propagation vectors		
	Label	Components	Fundamental k_z
65 K	k_s	-	2.0788(2)
	k_0	$\frac{1}{2}k_s$	1.03942(9)
	$3k_0$	$3k_0$	0.1162(2)
2 K	k_s	-	2.0775(1)
	k_0	-	1.12354(8)
	k_{1+}	$k_s + k_0$	0.2031(4)
	k_{1-}	$k_s - k_0$	0.9554(4)
	k_{2+}	$2k_s + k_0$	0.7215
	k_{2-}	$2k_s - k_0$	0.0315

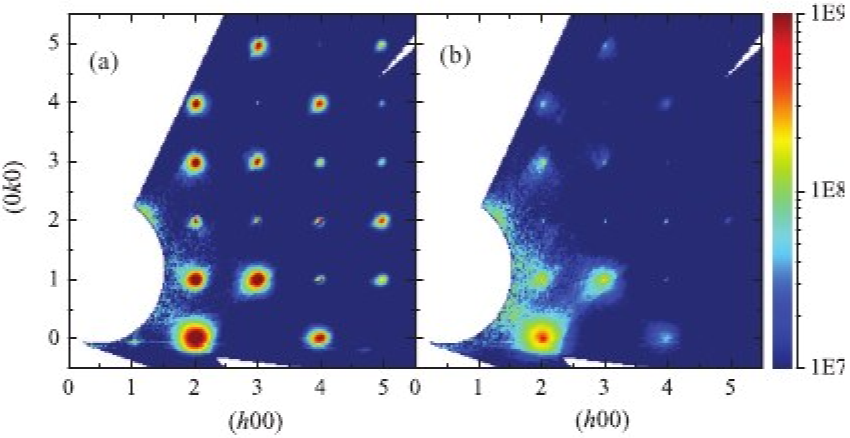
From 2012, SX starting with magnetic diffuse

PHYSICAL REVIEW B **88**, 024411 (2013)

Highly frustrated magnetism in $SrHo_2O_4$: Coexistence of two types of short-range order

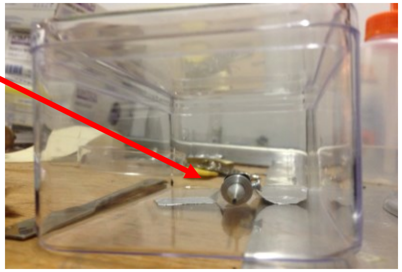
O. Young,[1] A. R. Wildes,[2] P. Manuel,[3] B. Ouladdiaf,[2] D. D. Khalyavin,[3] G. Balakrishnan,[1] and O. A. Petrenko[1]

0.9g sample. Ho^{3+} big moment (mK temperature)



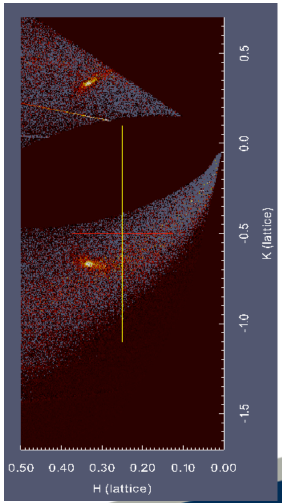
Diffuse scattering k=0 type.
D7 (and D10) data in different planes.
Rod like features in h0l along l=1/2 integers
→ 1d- correlation in real space.

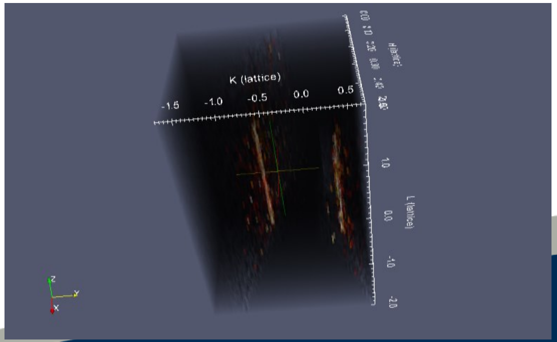
1x1x.1mm crystal
aligned
in basal plane
10, 35 38.5 & 150K
20 hours per run



$PdCrO_2$ orders at 37.5K
Diffuse scattering in H,K Plane accessing
1/3 1/3 l, & 1/3 -2/3 l

Scientific Reports 5 (2015) 12428





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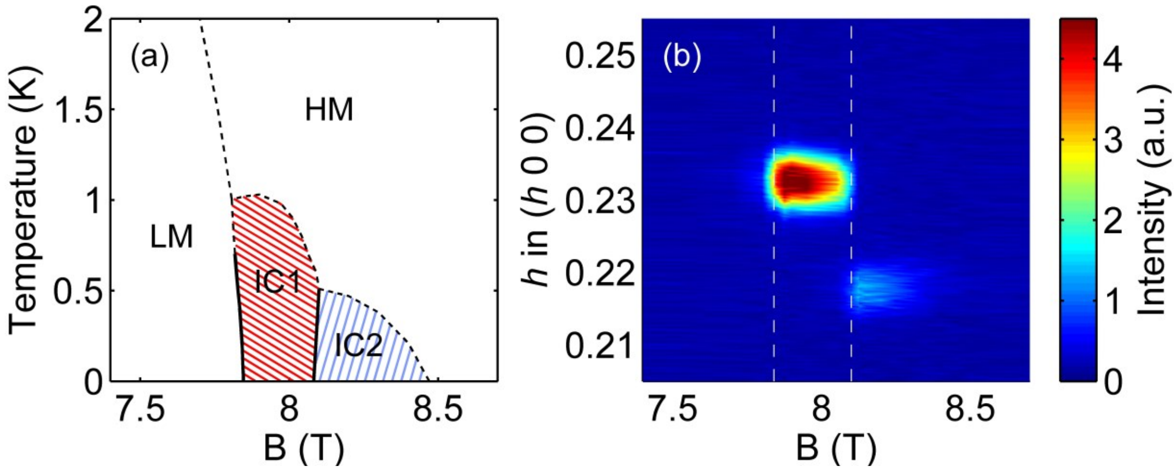
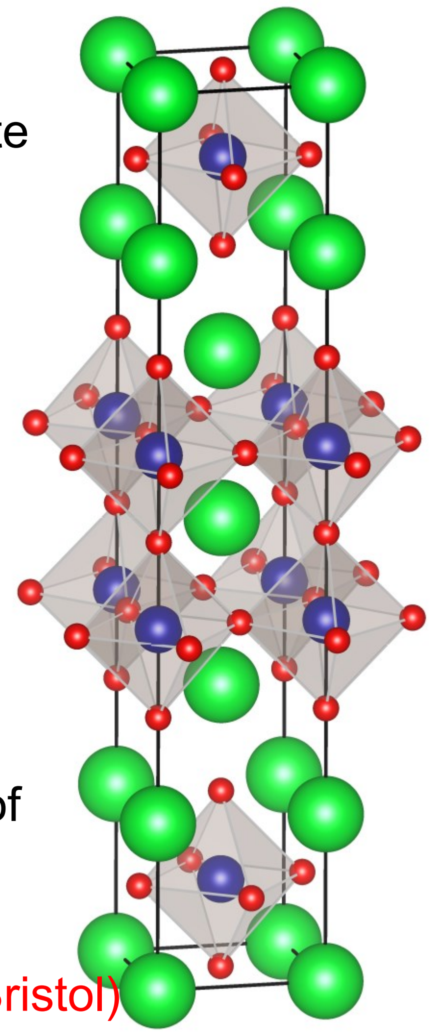
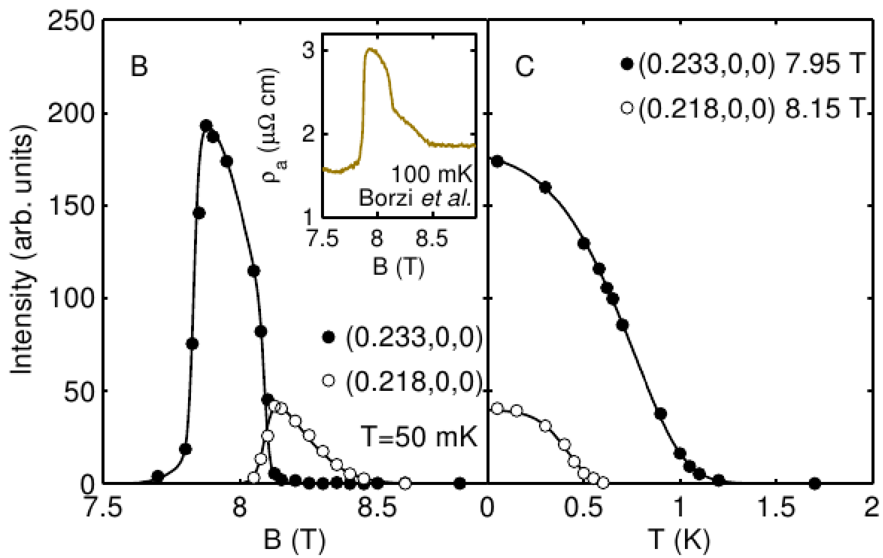
Magnetism studies with restricted geometry (1)

14T, dilution fridge



Perovskite





Metamagnetic at ~8T

Data reveals presence of <u>two</u> SDW

C. Lester / S. Hayden (Bristol)
Nature Materials

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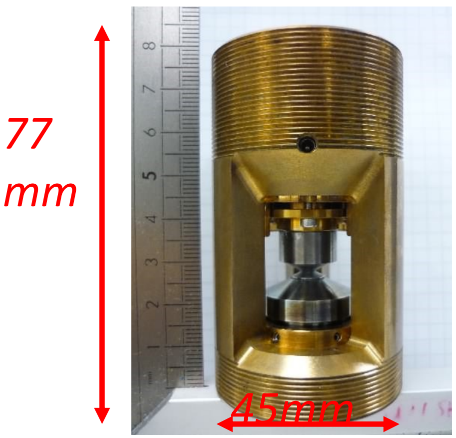
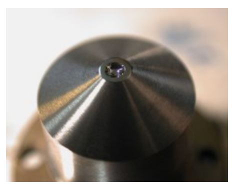
Magnetism studies with restricted geometry (2)

Hybrid anvil clamped cell (up to 10 GPa)

WC anvil

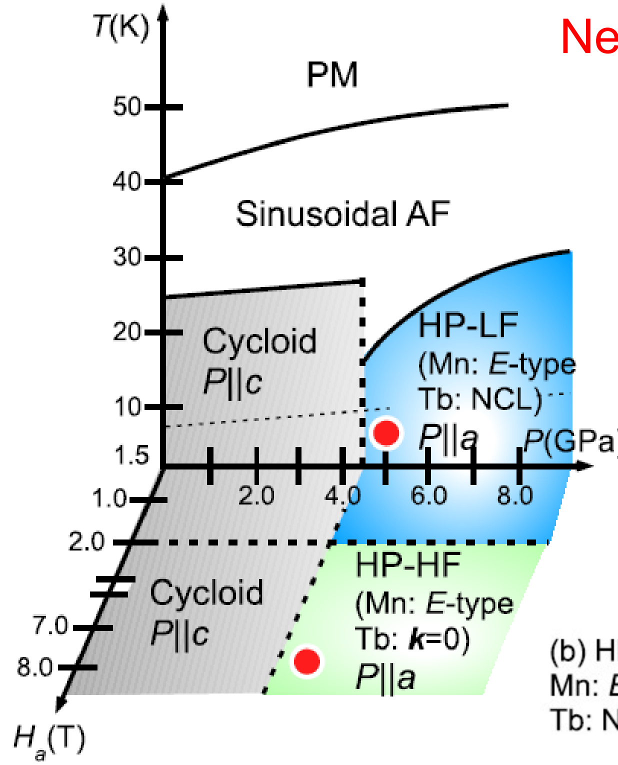




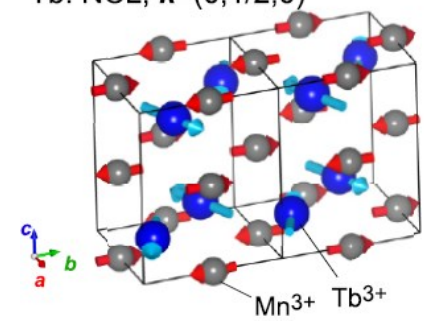
SiC anvil

Sample : **0.6 x 0.6 x 0.25 mm³**

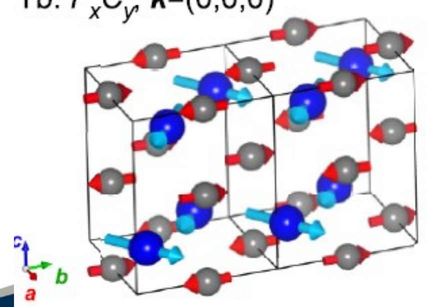
New phase diagram



(b) HP-LF (5.0 GPa, 0 T, 7.5 K)
Mn: *E*-type, ***k***=(0,1/2,0)
Tb: NCL, ***k***=(0,1/2,0)



(c) HP-HF (5.0 GPa, 8 T, 1.5 K)
Mn: *E*-type, ***k***=(0,1/2,0)
Tb: F_xC_y, ***k***=(0,0,0)



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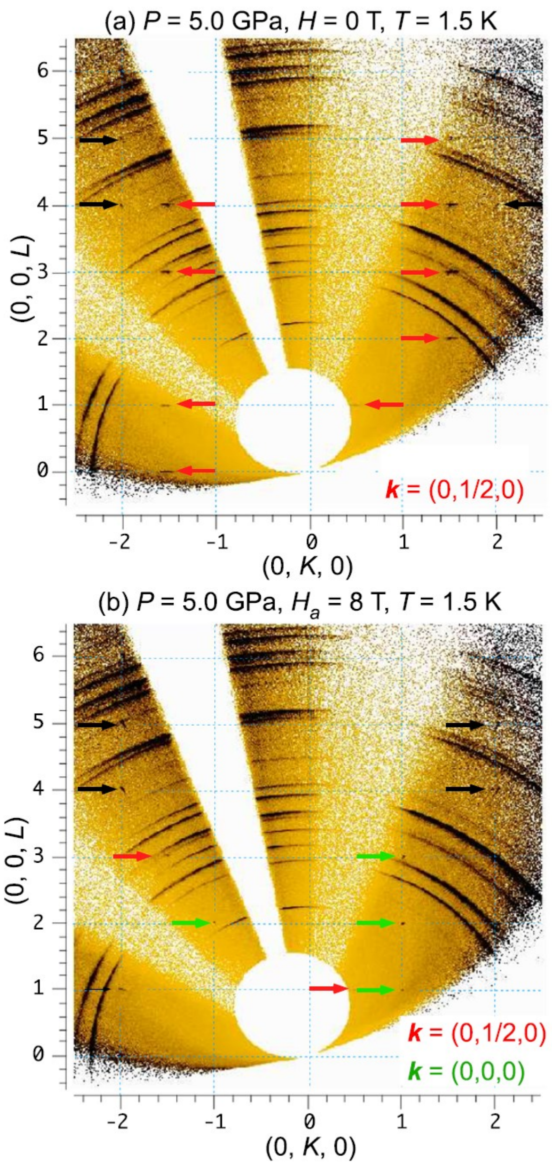
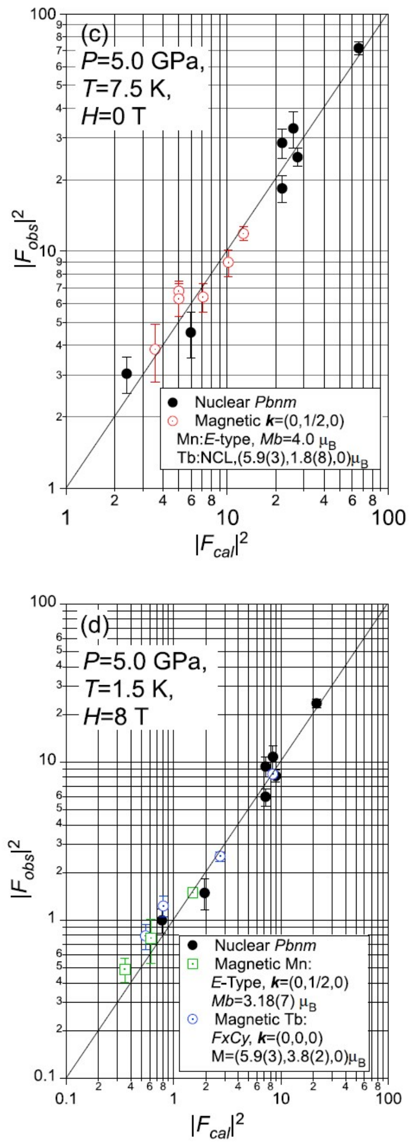
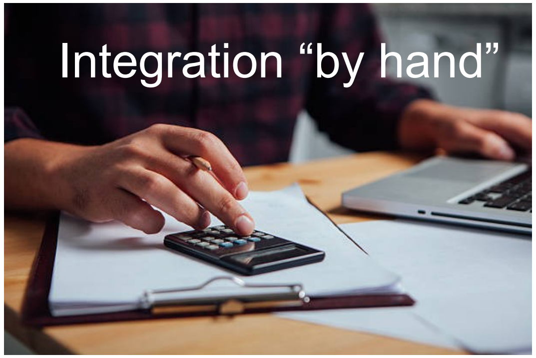
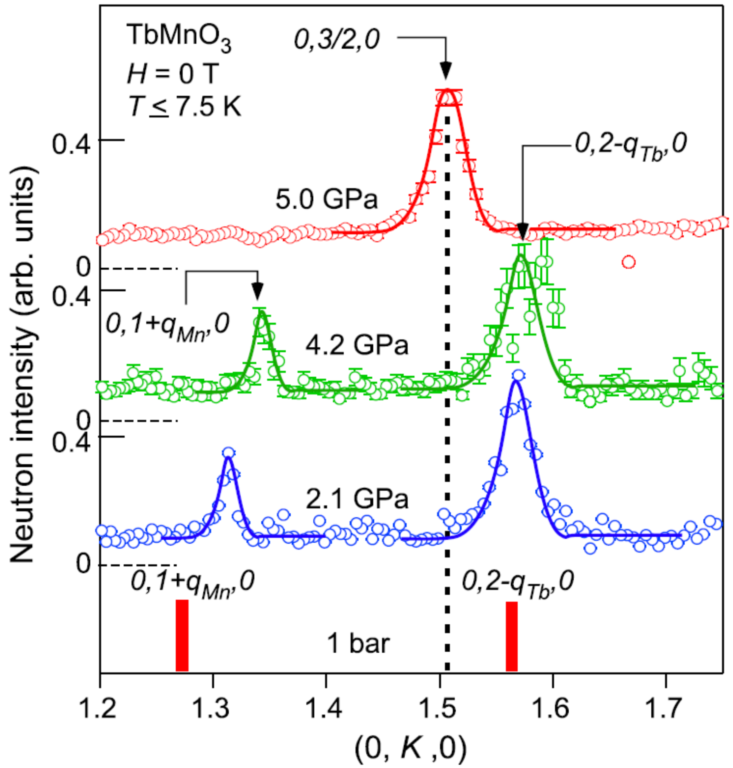
Magnetism studies with restricted geometry (2)









Thin films

Recent but successful programme

N Waterfield Price et al. Phys Rev Lett 117, no. 17 (2016): 177601.

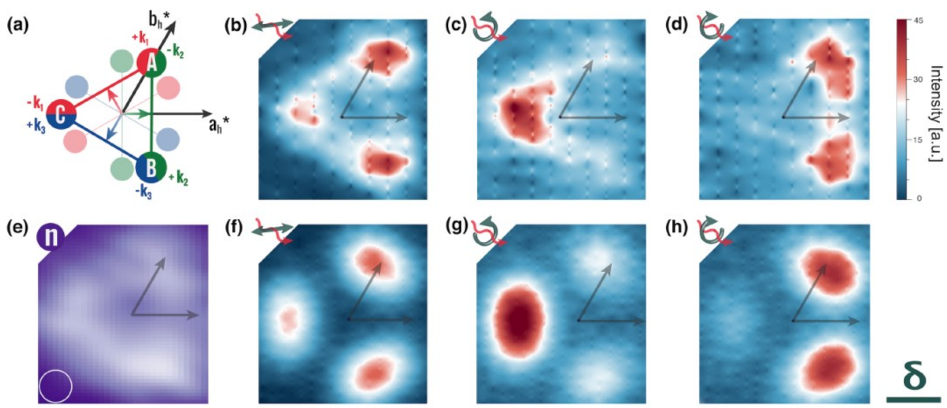
A Agbelele et al. Adv Mater 29, no. 9 (2016): 1602327.

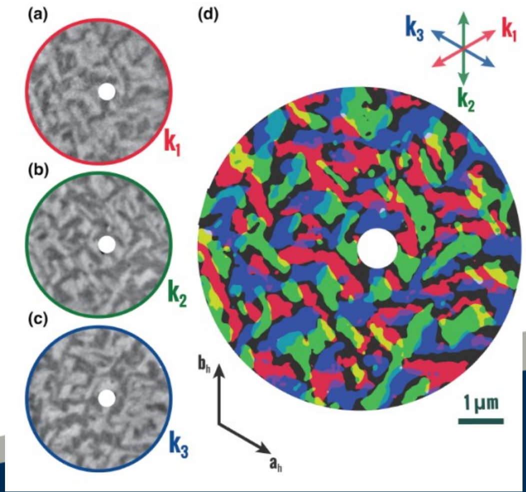
P Wadley et al. Nat Commun 4 (2013): 2322.

P Wadley et al. Sci Rep 5 (2015): 17079.

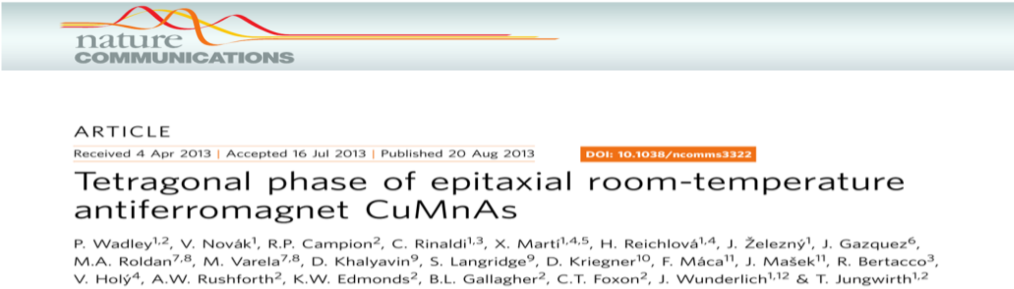
Often in conjunction with I16 and PEEM beamline at DLS

PRL 117 (2016) 177601 (ND confirms whole film is coherent twin pattern of monoclinic micro-domains.





Looking at (simple) thin films

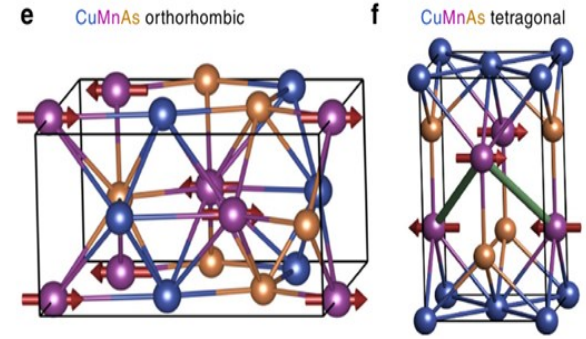

nature COMMUNICATIONS

ARTICLE

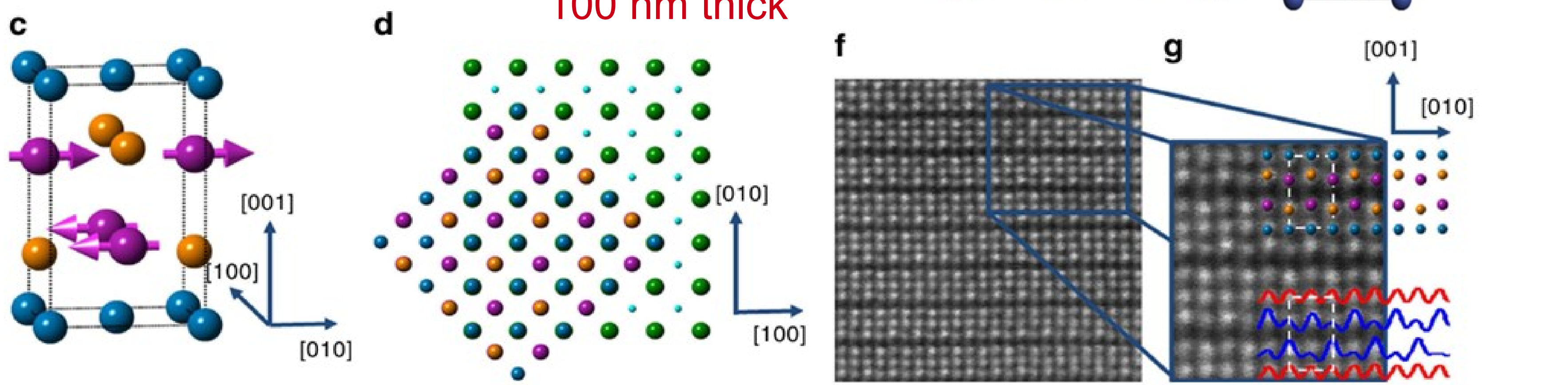
Received 4 Apr 2013 | Accepted 16 Jul 2013 | Published 20 Aug 2013 DOI: 10.1038/ncomms3322

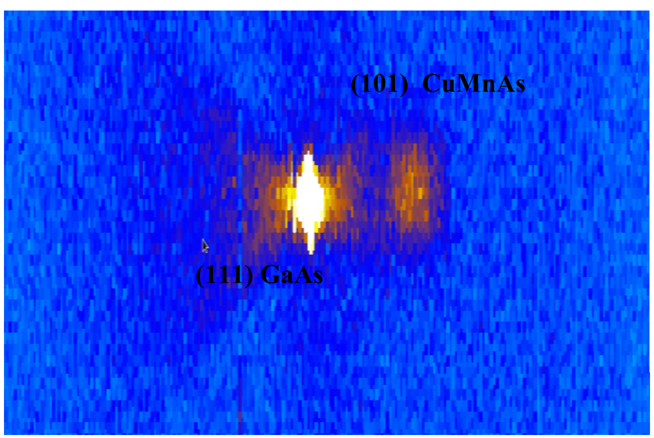
Tetragonal phase of epitaxial room-temperature antiferromagnet CuMnAs

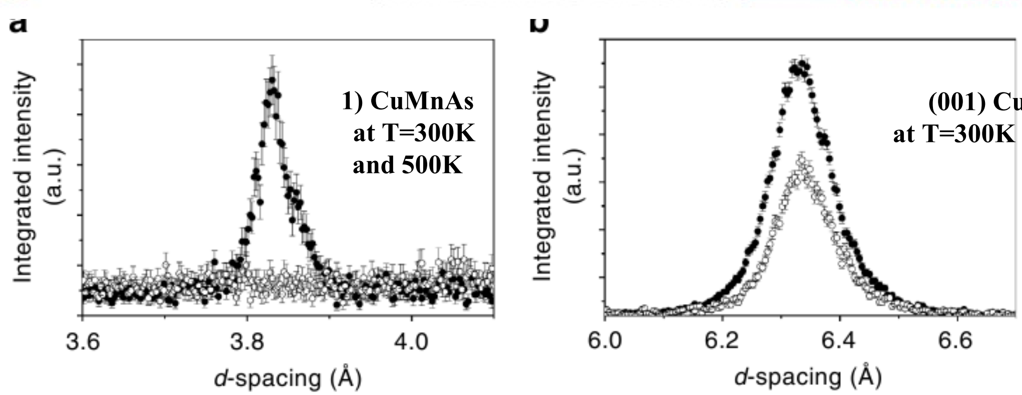
P. Wadley[1,2], V. Novák[1], R.P. Campion[2], C. Rinaldi[1,3], X. Martí[1,4,5], H. Reichlová[1,4], J. Železný[1], J. Gazquez[6], M.A. Roldan[7,8], M. Varela[7,8], D. Khalyavin[9], S. Langridge[9], D. Kriegner[10], F. Máca[11], J. Mašek[11], R. Bertacco[3], V. Holý[4], A.W. Rushforth[2], K.W. Edmonds[2], B.L. Gallagher[2], C.T. Foxon[2], J. Wunderlich[1,12] & T. Jungwirth[1,2]



100 nm thick







… But relevant for spintronics

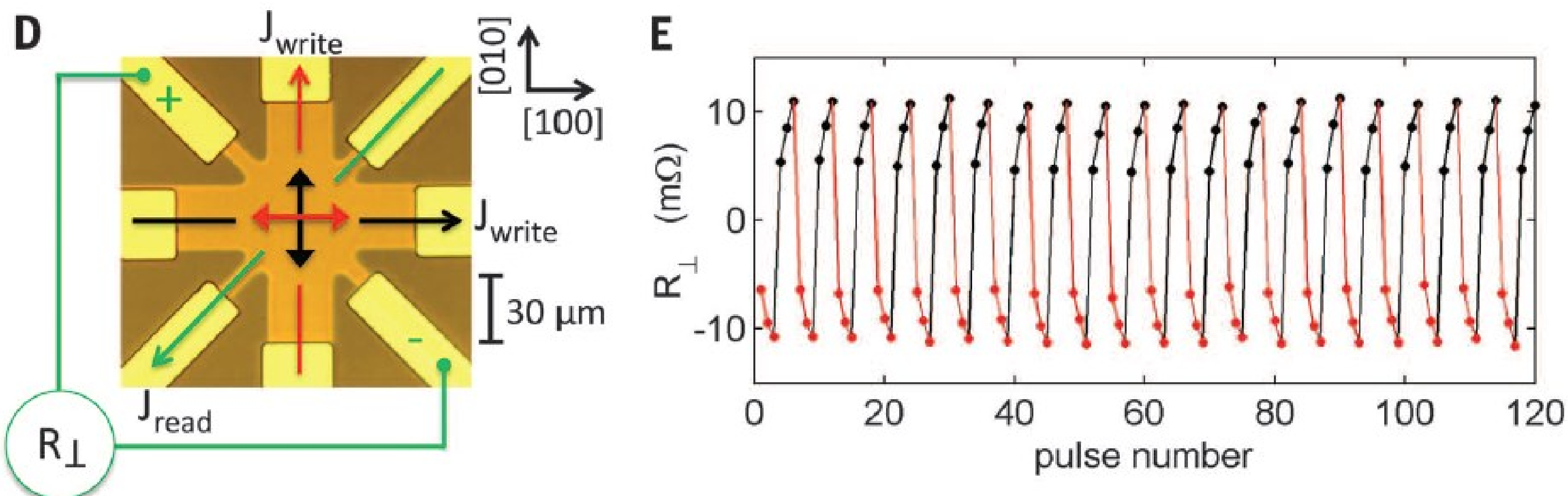
SPINTRONICS

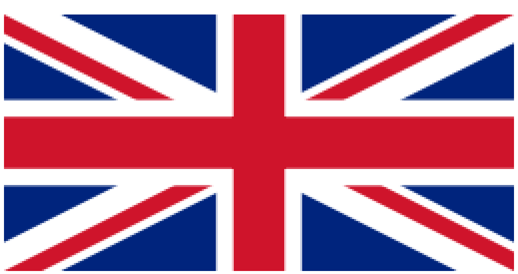
Electrical switching of an antiferromagnet

P. Wadley,[1*†] B. Howells,[1*] J. Železný,[2,3] C. Andrews,[1] V. Hills,[1] R. P. Campion,[1] V. Novák,[2] K. Olejník,[2] F. Maccherozzi,[4] S. S. Dhesi,[4] S. Y. Martin,[5] T. Wagner,[5,6] J. Wunderlich,[2,5] F. Freimuth,[7] Y. Mokrousov,[7] J. Kuneš,[8] J. S. Chauhan,[1] M. J. Grzybowski,[1,9] A. W. Rushforth,[1] K. W. Edmonds,[1] B. L. Gallagher,[1] T. Jungwirth[2,1]

Same sample, same team.
PEEM data at Diamond

Science 351 (2016) 587





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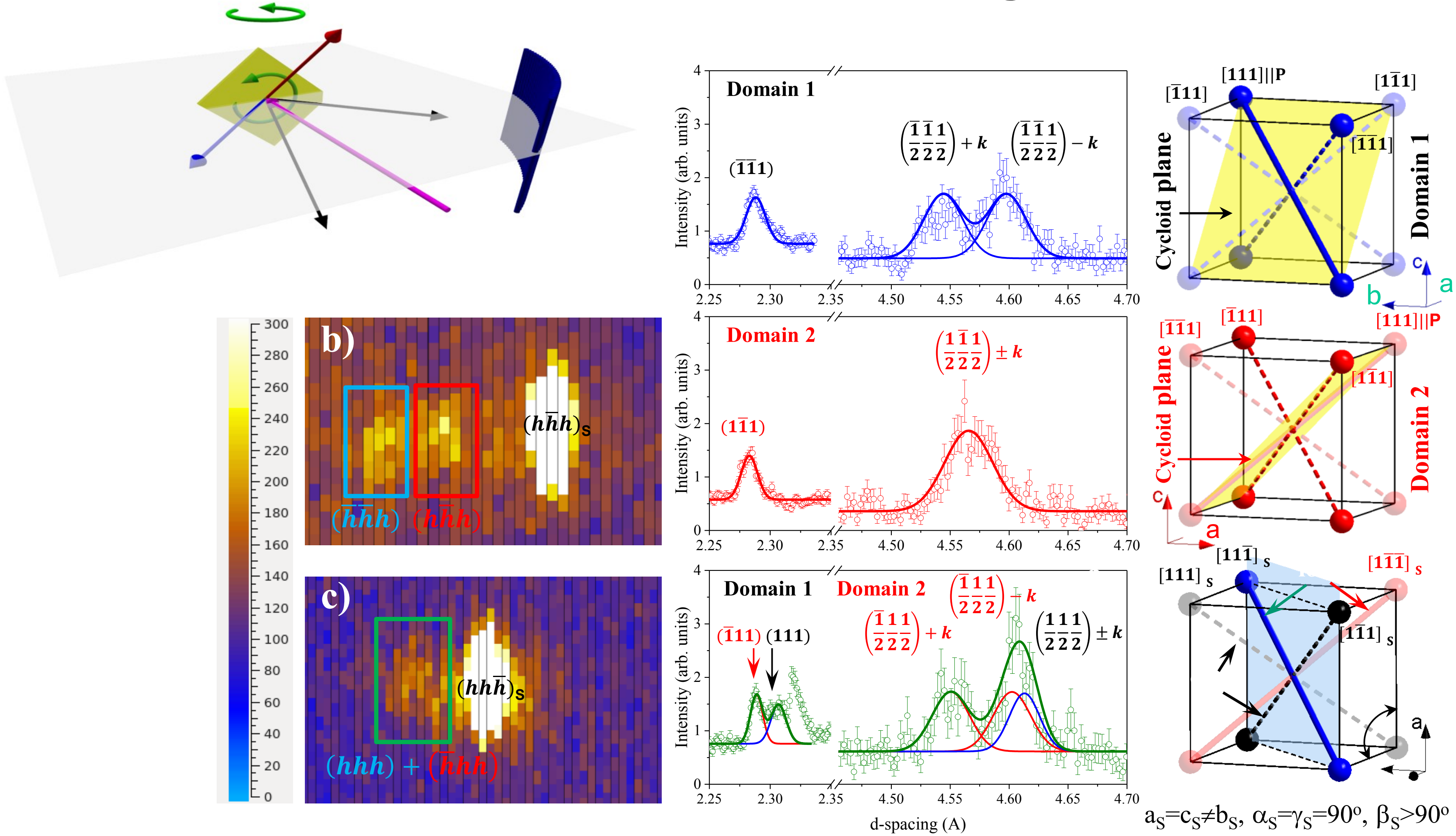
More complex case : $BiFeO_3$ thin films

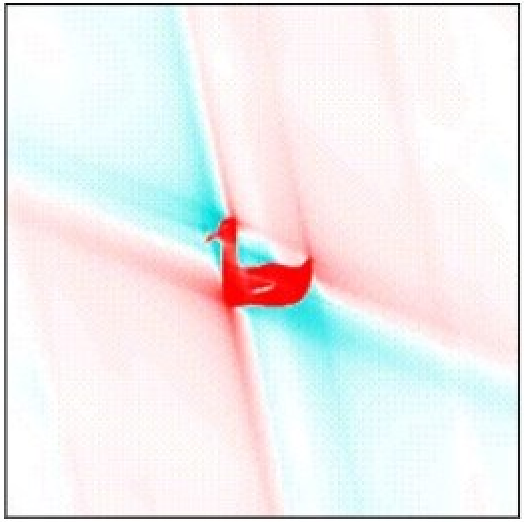


Samples Brahim Dkhil/Stephane Fusil (Centrale/Thales, Paris)

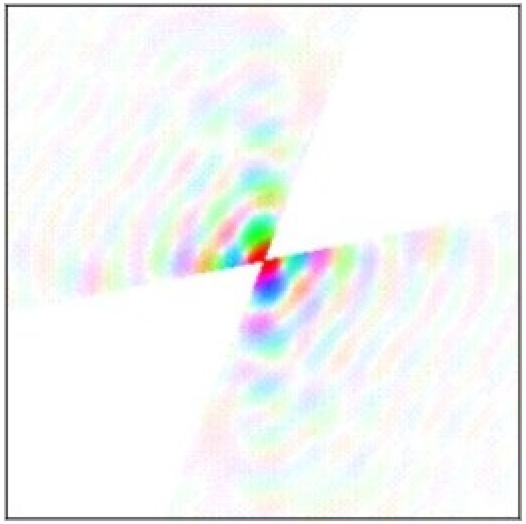
Sample : 5*5mm^2 * 30 nm

IKON15, 12/09/2018

Data coverage is absolutely crucial



If a segment of data is missing, features perpendicular to that segment will be blurred.



Crystallographic Interpretation:
Helices parallel to the missing data axis will become cylinders. Beta sheets parallel may merge into a flat blob. Beta sheets perpendicular to the missing data may be very weak. You could get into a lot of trouble with anisotropic temperature factors in this case.

Try not to omit *any* data. Collect it and use it.

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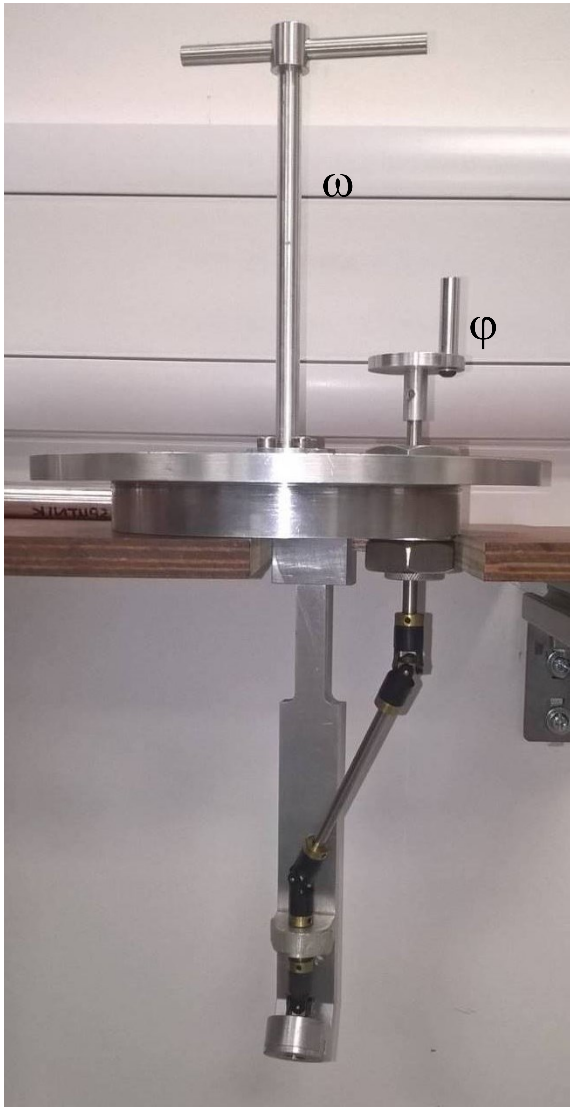
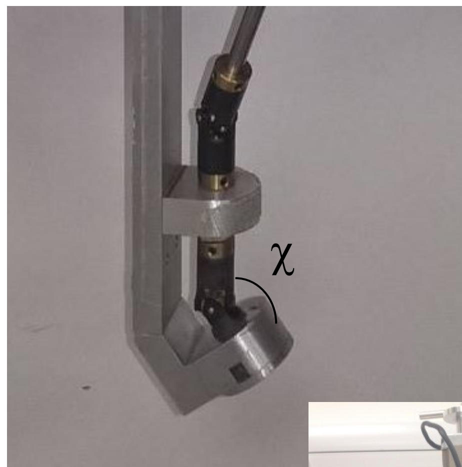
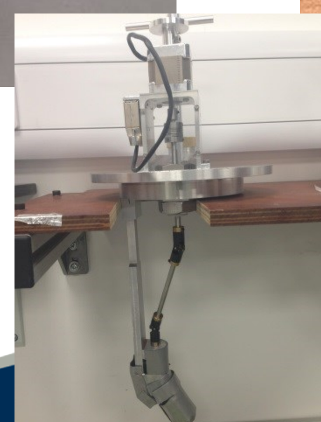
Towards qualitative refinements

Room Temperature “manual” goniometer



Allows two rotation axes one along the vertical direction ω
The second one φ at a fixed χ angle of 54 degrees.
A cryogenic version is on the way.



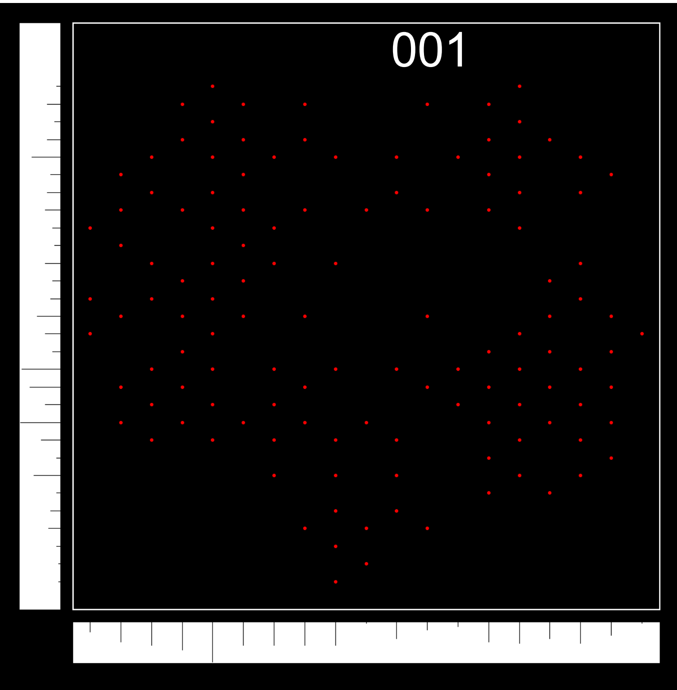


Ruby Al_2O_3 2mm sphere from D10

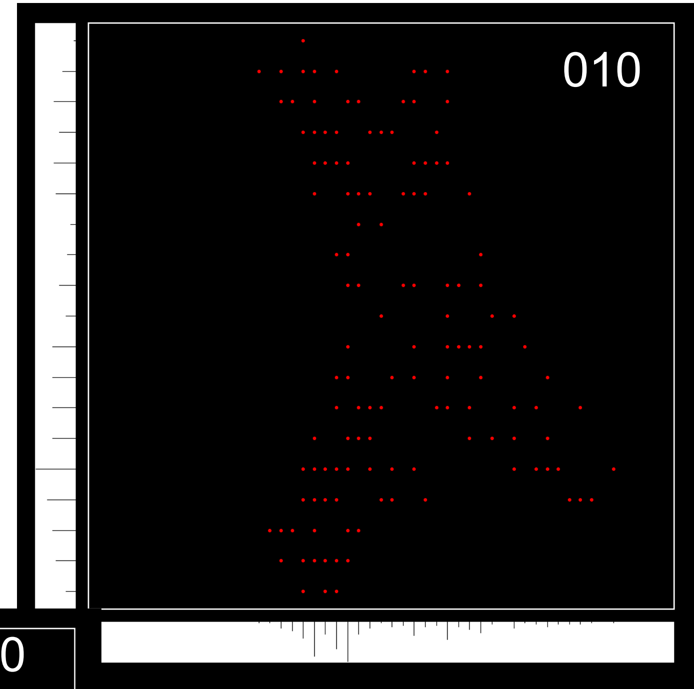
Motorised version (July 2018)
LT version (Oct’ 18)

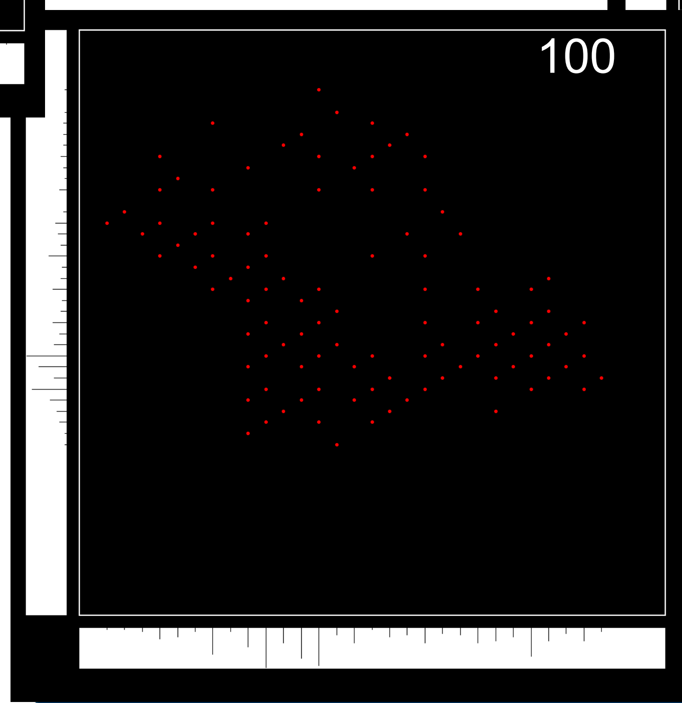
Data collection, integration and refinement

- 5 runs at ω= 0 φ= 0, ω= 90 φ= 0, ω= 180 φ= 0, ω= 180 φ= 15, ω= 180 φ= 90 of 15uA each ~20min
- Normalization by Vanadium and incident monitor
- Spherical integration in q space on predicted peaks not observed ones
- We collected 287 reflections with I/sigma>2, 203 I/sigma>3
- The coverage is not great but was a proof of principle for the gonio
- The refinement is performed with Jana2006 allowing anisotropic ADP's for Al and O



h(min)=-9, h(max)=9
k(min)=-9, k(max)=9
l(min) =-11, l(max)=21

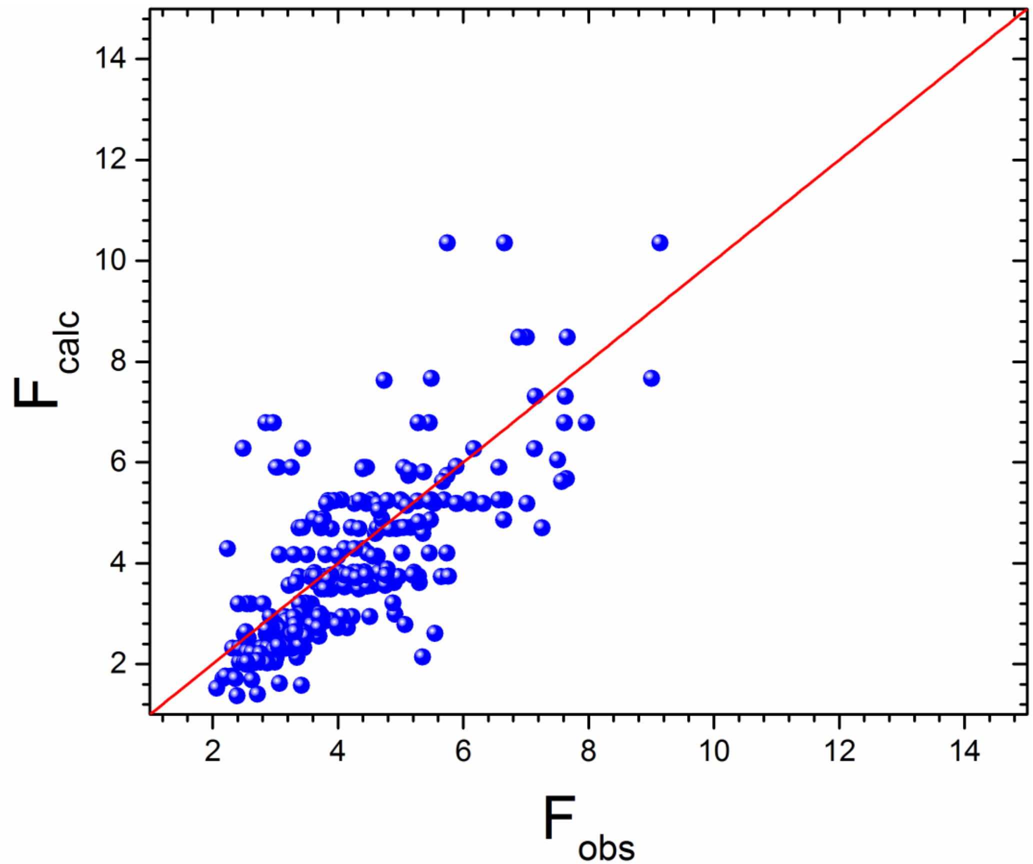




Space group R-3c

Cell parameters:
4.76(3) 4.76(3) 13.14(6)
90.0 90.0 120.0

Refinement



Without extinction correction
|R factors :
GOF(obs)= 2.09
R(obs)= 20.03 wR(obs)= 25.24

Also, Bugs/instrument specific tweaks along the way (error handling, 1% cutoff)

WISH Lambda range 0.8~10 Å previous test with NaCl and on users samples clearly indicate very large extinction correction probably related to the large wavelength range. Is something wrong?

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The scary plot

The scary plot

J. Appl. Cryst. (1975). **8**, 560

Neutron time-of-flight techniques for investigation of the extinction effect. By N. Niimura, *Laboratory of Nuclear Science, Tohoku University, Tomizawa, Sendai, Japan*, S. Tomiyoshi, *The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan* and J. Takahashi and J. Harada, *Department of Applied Physics, Nagoya University, Nagoya, Japan*

(*Received* 12 *March* 1975; *accepted* 31 *March* 1975)

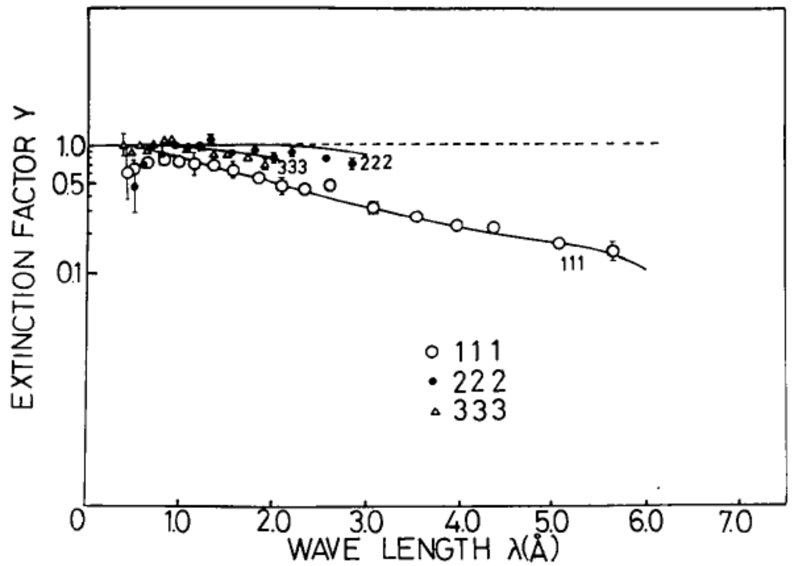
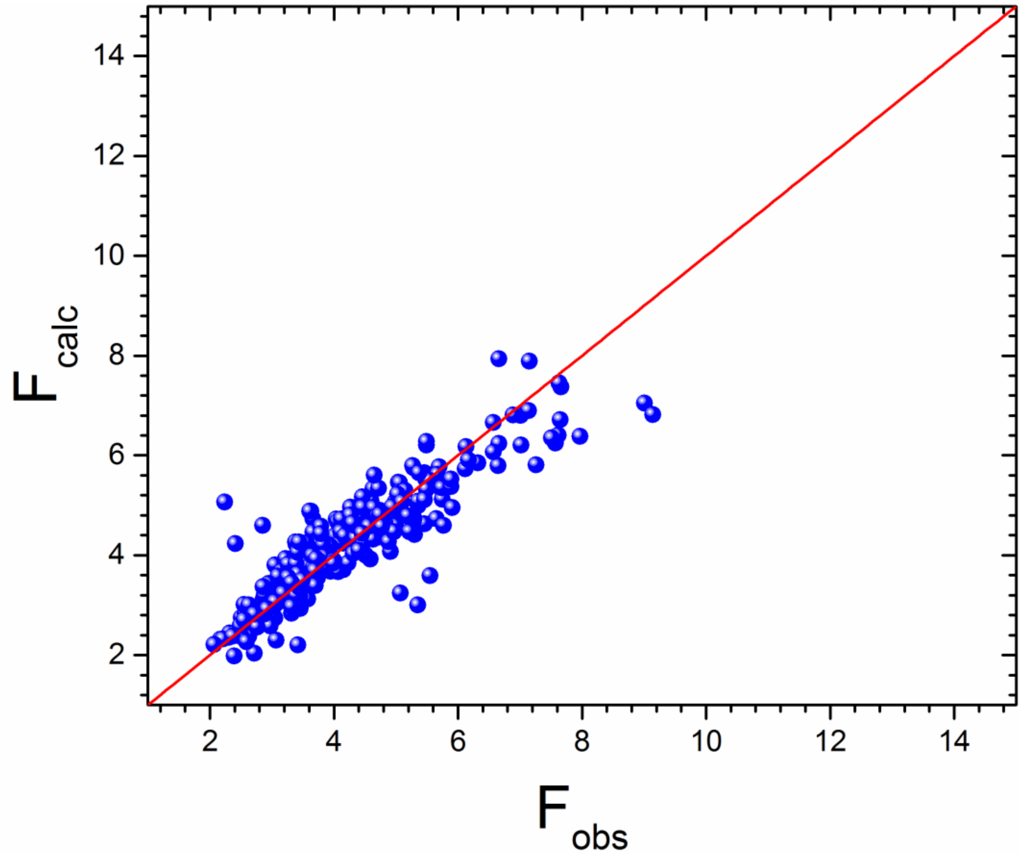


Fig. 2. The wavelength dependence of the extinction factor $Y(\lambda,F)$ for the 111, 222 and 333 Bragg reflexions. The solid curves show the calculations made on the basis of secondary-extinction theory (Becker & Coppens, 1974).

Refinement



With type I and type II secondary extinction assuming a Lorentzian distribution of the particle size (crystal domains).
We then had two refinable parameters particle size and distribution width.

R factors
GOF(obs)= 1.11
R(obs)= 9.35 wR(obs)= 13.19

We refined anisotropic ADP's for both O and Al and obtained physical values.
Gonio now motorised (soon at Low temperatures) and have developed methodology for collecting.

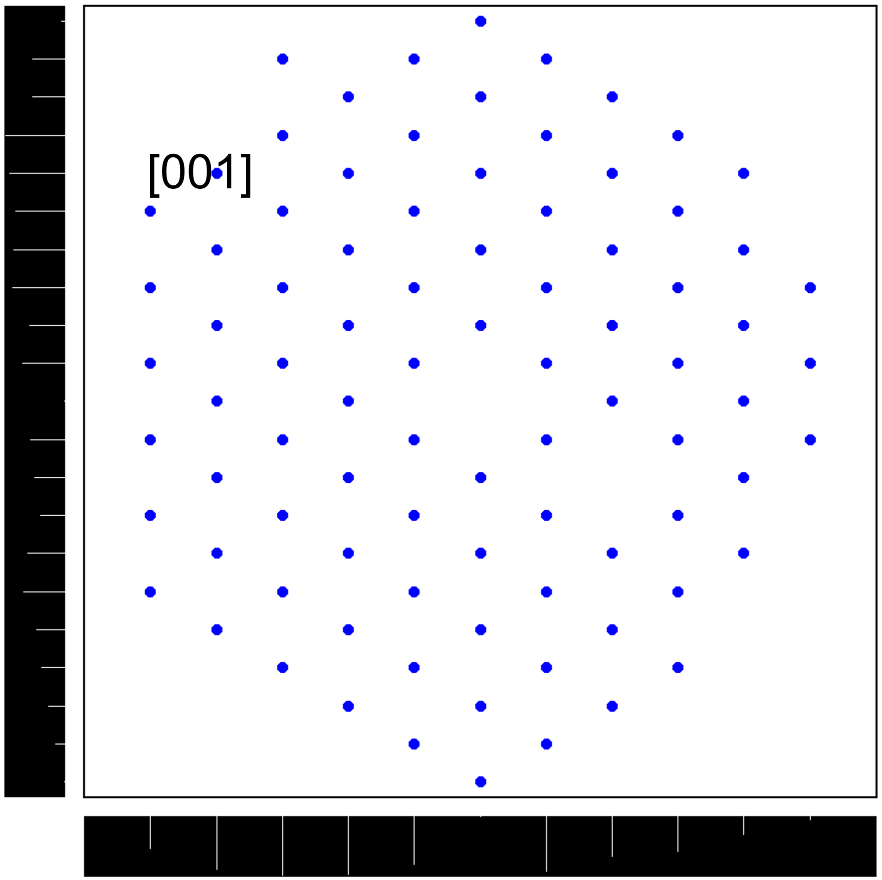
Ruby

LONG COLLECTION

Data collection, integration and refinement

- 23 runs at ω= 270, 210 and 150 and various φ. ~30 min per run
- Normalization by Vanadium and incident monitor
- Spherical integration in q space on predicted peaks not observed ones
- We collected 469 reflections with I/sigma>3
- The coverage is not excellent (need crystal planner to obtain a good collection strategy) but was a proof of principle for the goniometer
- The refinement is performed with Jana2006

Coverage



Structure solution from charge flipping using the superflip program.

Space group R-3c

Cell parameters:
4.81(3) 4.81(3) 13.58(7) 90.0 90.0 120.0

h(min) = -5, h(max) = 5
k(min) = -5, k(max) = 6
l(min) = -13, l(max) = 12

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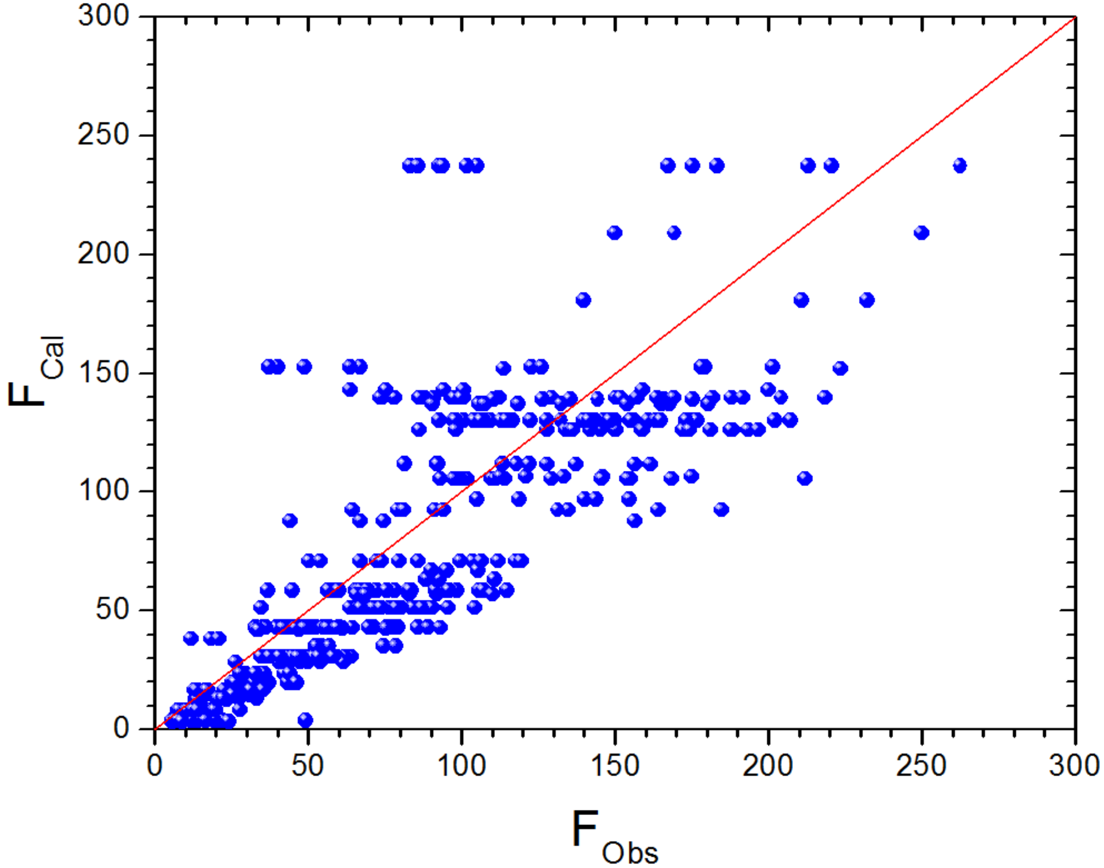
Refinement



GOF(obs)= 34.17
R(obs)= 30.73 wR(obs)= 35.38

No extinction correction, clear and strong lambda dependence of equivalent reflections

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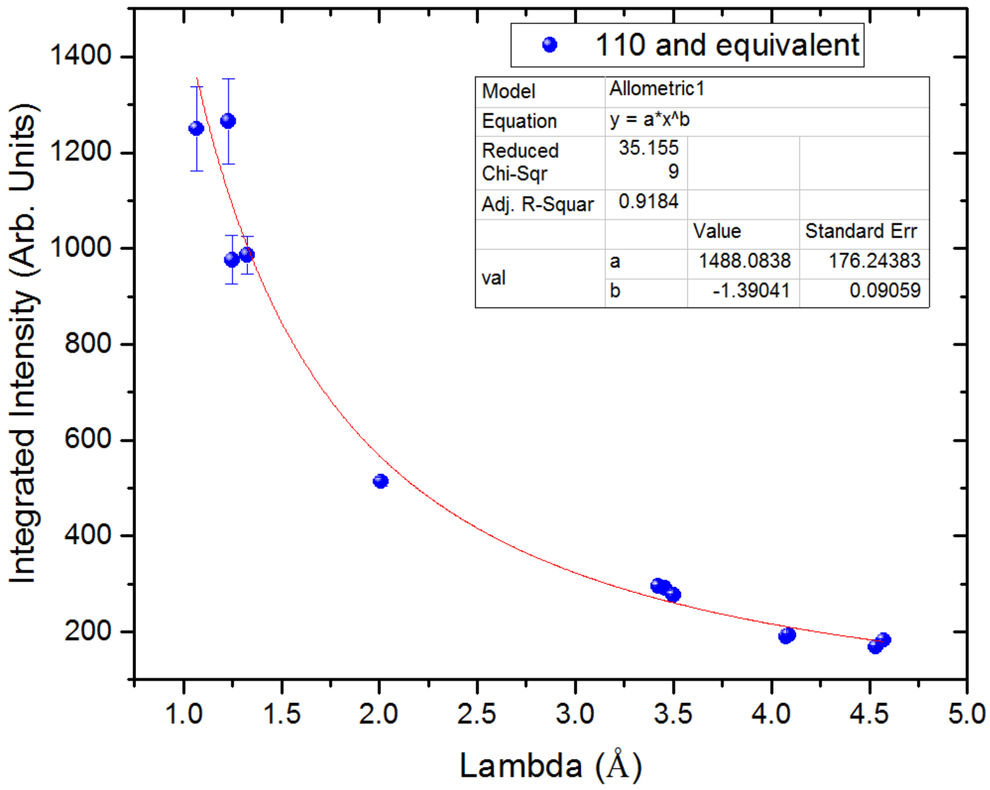
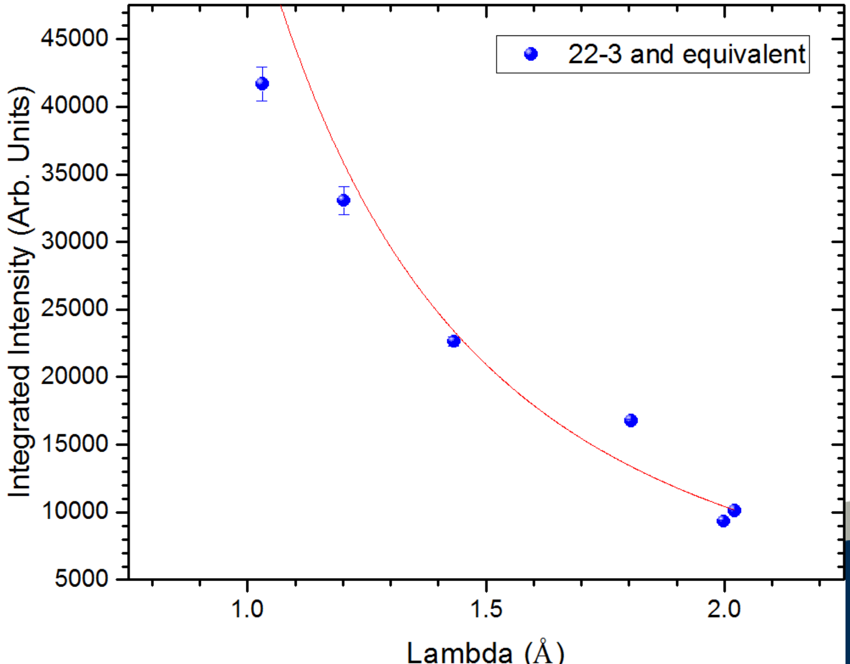
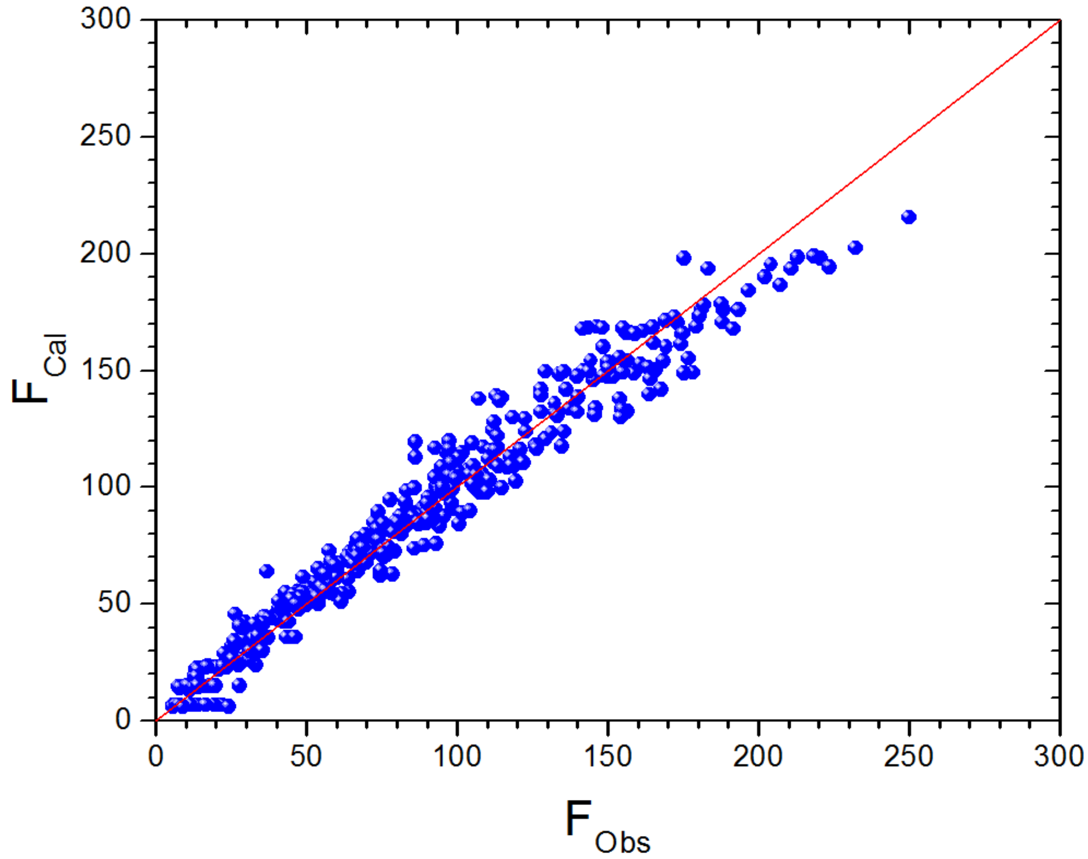
Refinement



Due to the wide lambda range on WISH ~1-10Å the effects of primary and secondary extinctions are quite severe.



Refinement



GOF(obs)= 9.77
R(obs)= 9.22 wR(obs)= 10.22

Refinement on 467 reflections
(16 rejected from the refinement)

Extinction model Type1+type2 with Gaussian distribution

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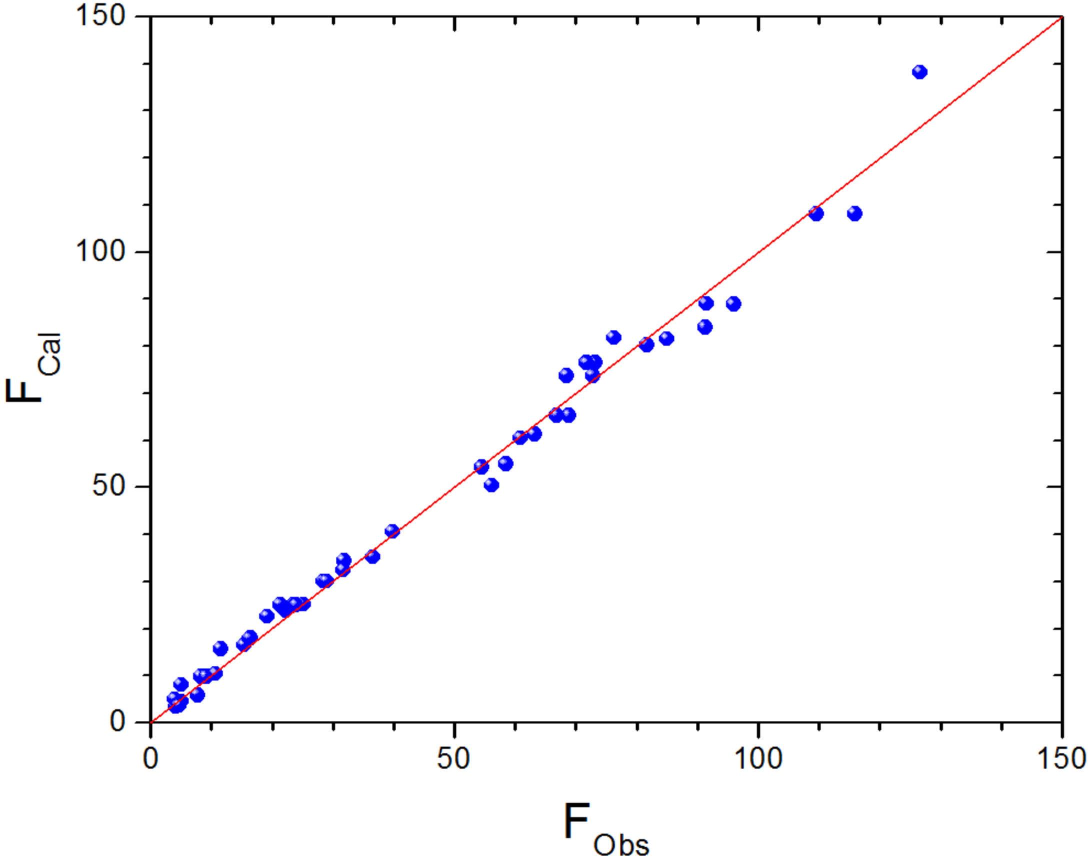
Refinement



"Corrected" refinement, apply the extinction correction to the observed intensity and after perform averaging.

GOF(obs)= 3.65
R(obs)= 5.84 wR(obs)= 6.24

Refinement on 49 reflections

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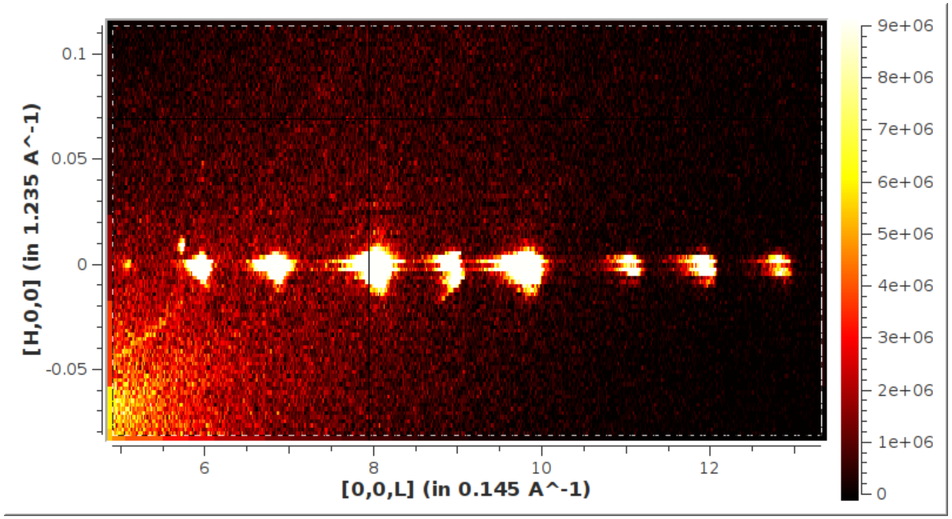
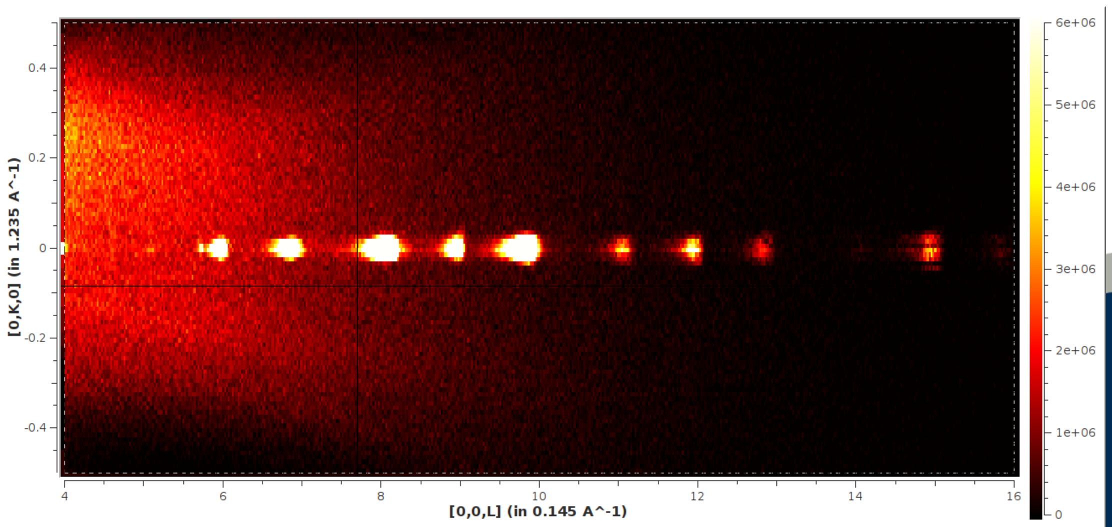
Peak overlap



The combination of large unit cell material plus low symmetry or an incommensurate modulation can give rise to a dense reciprocal space.

The strongly asymmetric peak shape of WISH plus a dense reciprocal space may lead to strong overlap if the spherical integration algorithm is used.



workplan

LT gonio coming now need to complete software!
UBs need to work for all angles (not just omega).
Cleverer way to get consistent UB matrices.
Treatment of errors to check with other modes of integration (eg ellipsoids)
Centroids should take into account peak asymmetry
Crystal planner essential!
Extinction and absorption modelling of complex shapes (sample environment and sample shape). Work starting on that (CAD drawing and 3D scanner).
Path of diffracted beam to feed into eg Jana.

3D profile fitting (a la SXD 2001)
Multiple UBs to deal properly with twinning or bad samples or P cell.

Incommensurate structures :
Generalize from 3D to 4D (need work on the peak workspace concept) -> Vicky's talk?

Nsxtools already has features such as crystal shapes determination as convex hull and Monte Carlo absorption correction, clever peak searches and weak peak integration (ellipsoid collision). Written in C++, python wrapper.
Big data student will test and see what mantid can use.

Topics of discussion

Common workflow ?

Observed vs predicted peaks

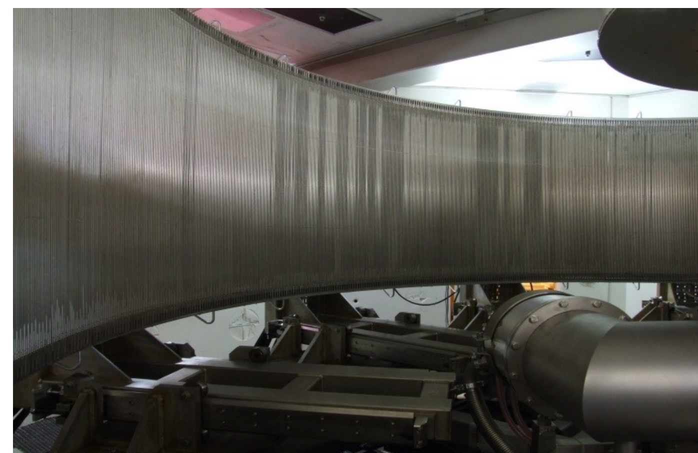
Anvred correction (fudge) ?

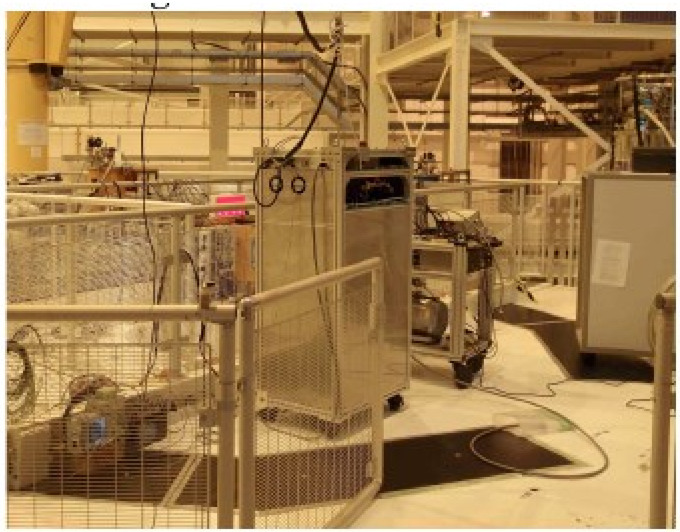
Good “calibration” samples

What does ManDi do ?

Xray community model for software effort ?

Thank you for your attention





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