

Implementation



Toward Nanoscale?





Precision and Detail

• **Reciprocal space** methods classically measure average properties to a high precision

Generally utilise periodic samples

• Extension to non-crystalline or semicrystalline samples and the measurement of inhomogeneity

- Pair Distribution Function analysis
- Total Scattering
- Direct space methods can measure local inhomogeneities
- Extension to shorter length scales is a serious but achievable technical challenge
 - Very rigorous implementation to achieve high accuracy results
- · Ultimately we aim for simultaneous hierarchical characterization

• Collect high-energy, quantitative data on all length scales, of the distributions of properties

Single Crystal Studies

Small and bad crystals

- 10s of microns
- Bad mosaic / twinning
- Air sensistivity

Fine details

- Spin–Flip systems
- Orbital Ordering
- CDW
- (Incommensurate) Superlattices
- (Anomolous Diffraction)





Self-assembly into complex structures

- · Ligand Self-assembles into complex grids, helices, zippers ...
- Information storage

Lehn Group, Barboiu Group 1998–2008



Self-Assembled Organometallic

Weak intermolecular forces Frustration

- •Packing
- •H-bonding
- Ionic interaction
- → Small, Poor Unstable Crystals



10s microns, twinned, air sensitive, poor mosaic single crystal Solved, refined with 5000 parameters

Saalfrank et al., *Chem. Eur. J.*, 8(2) 493 (2002).



Solving/Refining Crystal Structures: Bridge the Gulf...





Powder/CCD 35 parameters Data Collection 1 s

Single Crystal/CCD 5000 parameters Data Collection 1h



1000 micron beam + turning









































50 micron beam

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30 micron beam

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Experimental Realization

ID11 @ FSRF Moderate to high energy (25 - 100 keV) Absorption Extinction Resolution Data: set of 2d rotation images CCD camera Small beam size Down to 2 x 5 μm² (50 x 150 nm² – 2007) Tunable Fast acquisition 100 s / complete data set • (powder – 10 ms) Detector (budget) limited



Flowchart for 3dxrd







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Determination of Unit cell

Mean - Median pixel by pixel image

- Pseudo-powder pattern
- Averages out errors





Determination of Unit cell

Mean - Median pixel by pixel image

- Pseudo-powder pattern
- Averages out errors



Determination of Unit Cell





Determine Orientation Matrices



Generally need three unambiguous peaks



Solution and Initial Refinement





Intra-grain Merging/Filtering

Filter

- Data quality
 - I/ σ
 - Spot shape
 - Distance from another (known) reflection
- Equivalent reflection statistics
 - deviation from average
- Expected value
- Skewed outlier distribution
 - Outliers due (mostly) to unindexed peaks
- Reweighting
 - Usually filter throughout, reweight at the end





Cupric Acetate Monohydrate

Simple small molecule Each individual crystal data set incomplete

Decomposing?

Structure solution / Refinement Compare to single crystal and powder refinements



Indexing/Unit cell

pseudo-powder indexed with Ito

a = 13.175 b = 8.569 c = 13.868 $\beta = 117.02$ C2/c



18k/130k spots assigned to crystallite



Merging/Filtering/Scaling

Low internal redundancy

- No intragranular equivalent filtering
- Individual data sets incomplete
- Corrupt, complete data set
 - Heavily filtered
- sufficient for structure solution (direct methods)
 Initial constrained refinement

Cycling







Generation of Final Scales

Histograms of $k|F_c|^2/|F_{obs}|^2$ Peak position gives scale factor Fit peak

- Gaussian
- Error bar





Final Refinement

After several iterations, get a good refinement

• GOF R-factors fine

$$\cdot R_1 = 5.7$$

Data quality R-factors still high

- $R_{sym} = 13.6$
- Redundany ~ 3.5
- Data/Parameter ratio ~ 8
 - •795/98



Single Crystal Refinement

Large crystal

- 30 x 30 x 30 µm³
- Collected data with the same detector
- Complete, redundant (4) data set
- $\cdot R_1 = 1.8$



Powder Refinement

High Resolution Power Diffraction Data From ID31




Comparison of Refinements

Single crystal refinement is "correct answer"

- Unconstrained refinement
- All bonds very accurate and precise
- Thermal ellipsoids look correct
- Found, refined water H-atoms (isotropically)
 - Not uniquely fixed by molecular symmetry



Comparison of Bond lengths

Bond	Single Crystal	Multicrystal	Powder	$\mid d_{mc} - d_{sc} \mid \times 10^{3}$	$ \mathbf{d}_{pow} - \mathbf{d}_{sc} \times 10^3$
Cu-O1	1.9880(8)	1.985(5)	1.981(4)	3	7
Cu-O2	1.9962(8)	1.991(7)	1.985(4)	5	11
Cu-O3	1.9431(9)	1.945(7)	1.924(4)	2	18
Cu-O4	1.9575(9)	1.963(7)	1.949(4)	6	8
Cu-O5	2.1588(14)	2.149(8)	2.149(9)	11	11
< \Delta (Cu - O) >				5.4 (31)	11.0 (24)
01-C1	1.2601(12)	1.259(11)	1.246(7)	1	14
O2-C1	1.2613(14)	1.257(11)	1.296(8)	4	35
O3-C3	1.2612(15)	1.273(11)	1.309(8)	12	48
O4-C3	1.2588(14)	1.242(10)	1.271(8)	16	12
< \Delta(0 - C) >				8.2 (92)	27.3 (39)
C1-C2	1.5022(15)	1.497(13)	1.563(8)	5	61
C3-C4	1.5055(18)	1.519(13)	1.496(9)	14	9
< \Delta (C - C) >				9.5 (92)	35 (6)
O5-H7	0.829(19)	0.85(13)		20	
O5-H8	0.73(2)	0.99(13)		260	
H7-O5-H8	117.3(13)	101(11)			
< \Delta (C - H) >				140 (180)	

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Thermal Factors

Single crystal > Multicrystal \gg Powder

Could not get meaningful anisotropic thermal factors for C atoms in powder refinement

Could not refine H atom thermal factors unconstrained in multicrystal refinement

	Cu	0	С	Н
Single Crystal	А	A	A	I
Multicrystal	А	Α	Α	R
Powder	A	Α	I	_



Thermal Factors

	$[(u_{eq} \text{ or } u_{iso})/u_{eq,sc} - 1] \times 100$		$[(u_3/u_1)/(u_3/u_1)_{sc} - 1] \times 100$	
	Multicrystal	Powder	Multicrystal	Powder
Cu1	4	-29	9	178
01	-1	27	0	191
02	2	32	5	163
03	-7	21	-22	104
04	2	13	-6	-3
05	6	30	10	5
C1	1	76	22	
C2	2	27	-4	
C3	6	37	33	
C4	2	49	9	
H7				
H8				
Absolute deviation	3.3	34.1	12.0	107.3
Mean deviation	1.7	28.3	5.6	106.3



Conclusion

Multi-crystal method gives single-crystal quality

- Bond lengths
- Anisotropic Thermal Factors
- H atoms
- At least for simple problems...

Improvements to algorithm

- Find robust parameters for blind data reduction
- Empirical "absorption" correction
- Improve cycling to include intensity extraction
 - 3d Rietveld



3d Microscope \rightarrow 3d Nanoscope

Access to all relevant length scales

- 10pm: charge distributions
- Ă: molecular structure
- nm: crystal structure
- 10 nm: initial nucleation
- 100 nm: dislocations/intragranular structure
- µm: intergranular interactions
- mm: bulk structures

Total Simultaneous Characterisation

- Crystallography: structure of each grain
- Microstructure: stacking faults, microstrain...
- Grain Statistics: size, strain, stoichiometry...
- Distributions of properties rather than means.
- Relationship between grains

Grain Mapping

- Quantitative Tool: Not just images
 - 6-dimensional characterisation
 - Doesn't relay on Z-contrast
- *Now: resolution limited by detector technology*
- Future: Structured scintillaters



A three-dimensional detector for hierarchical characterisation

Three Dimensional Detector





Grain map from grain centre fits



Grain positions, orientations, lattice parameters all simultaneously refined from multi-crystal data

"grain boundaries" from Voronoi calculation: if the grain centre falls in the middle of the reconstructed grain, perhaps nothing is missing.

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Better representation?



Here the colours fall away from the centre of mass and end at the boundaries – so that missing or vacant areas become more apparent...



Could add some orientational information



The axes are placed at the crystal centre (this is for one layer).



Rotations after each step

Depicted are the Rodrigues vectors of subsequent rotations after straining a sample





Projection in plane



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Also correlate with grain size distribution





Layer by layer maps



These are constructed using only grains with a match above and/or below



Resistor: Compare different layers

The grains found in different layers are compared based on their orientations and refined positions in order to try to locate the same grain in different layers.

The results in this case are quite complete and unique: most grains match only one other grain in the next layer with precision $<0.3^{\circ}$ and $50 \ \mu$ m.



This can also give a sort of grain size distribution in z.



High Resolution Grain map

A combination of detectors allows the high resolution map to be constructed while we characterize simultaneously:

> •Grain Shape •Grain Position •Crystal Structure •Strain State

For each crystal independently









Allow Total Characterisation





Collaborators at ESRF

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Outlook

• Spatial resolution is now 1 step away from ultimate target

Spatial ~ 10s nm

• These goals will be technically feasible in the next decade

• Technical proposals aim to ensure our compatibility to exploit new development











Diffractometer mount



Both the global y and z translations will be on "reversible" airpads

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Final Conclusion

Beamline evolution follows the path proposed by the last review, with continued evolution as scientific fields develop or regress....

Extension of the line Refactoring the optics Refactoring the diffractometer

Advanced feedback schemes based on image recognition



Ultra-high resolution detector



Resolution for direct mapping experiments is essentially determined by detector resolution

We propose to participate in the development of a new kind of detector, which aims to deliver ~100nm resolution



FIB Microscope

- Surface characterization prior to X-ray experiment
- Surface modification or marking for metrology
- Destructive measurement after the experiment
- Used overnight to machine optics (CRLs, zone plates...)
- Sell time on the machine





Ultra high precision measurements

Ultra-high precision crystallography has most of the same needs as our other experiments,

- High Energy
- Beam Stability
- Beam Homogeneity
- Synchronization
- Detector Calibration
- Data Weighting
- Data Extraction

The beamline is currently being optimised with these concerns in mind, which are also important for PDF, Topo-Tomo, ECT, Holography...

What is medium-term solution? On main station, side station, new beamline...



Pixel Detector

- Photon counting, allowing proper statistics without gain corrections.
- Energy discrimination to minimize effects of fluorescence, Compton, etc.
- Good dynamic range.
- Constant response
- Continuous readout, allowing shutter-less operation
 - Eliminates shutter jitter issue
 - No rewind/acceleration/deceleration issues
 - Infinitely fine slicing
- Almost no electronic background, minimizing peak tail discrimination issues.

Unfortunately, does not yet exist...



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A three-dimensional detector for hierarchical characterisation



New opportunities with submicron beams

Example: Crystallization mechanisms in oxide or metallic glasses Different Possibilities (nucleation in bulk, nucleation at defects, spinoidal decomposition), large theoretical activity

Today, Nucleation mechanisms are deduced from

- Final microstructure
- Powder diffraction

Data are often ambiguous and incomplete We aim to directly measure the nucleation mechanism

- In the bulk
- With ~second time resolution
- For scales down to ~nanometers

By simultaneously measuring the evolution *and* interactions of 100s of nuclei.



New opportunities with submicron beams

Example: The drive toward minaturisation has produced objects which require real nano-scale beams to be mapped

Variations in strain over the tiny features in modern electronic chips, in which a wire may only be a few crystals wide, have large effects on the chip's performance and lifetime

Direct mapping with diffraction gives not just spatial information, but also

- grain sizes,
- grainorientaions
- strain state
- The relations between grains.





Why a new hutch

- Improve focusing ratio
- Purpose built for temperature and vibration control
- Refactor optics and diffractometer after generations of evolutionary development
- Independent foundation
- More room $(2\pi r)$



Current Status of ID11

Building complete Commissioning began in Dec 2006 User experiments since Feb 2007 1st experimental station operational Moderate focus optics upgraded 10 Hz Feedback implemented Diffractometer upgrade in progress

ID11



Schedule

- Scientific Program
 - Statistics
 - Scientific Background
- Experimental Realization
- Current Challenges
- Ongoing Evolution
- A. Bytchkov J. Wright C. Gundlach
- Proposed Evolution
- Conclusion



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A. Bytchkov J. Wright C. Gundlach

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Why Nanofocus?

• Our techniques for high spatial resololution depend on having a limited (<1000) number of crystals in the beam)

- The smallest features which may be measured depend on the sample mosaic, size and the size of the focal spot
- We aim to characterise the sample on multiple length scales (Å mm)
- With a smooth transition from direct (mapping/reconstruction) to derived (crystallography) characterisation


Why Nanoscale?

Direct structural studies of phenomena on the submicron to nanoscale, in the bulk, have never before been possible.

This scale is crucial in determining long-range materials properties such as strength, elasticity, etc.

Classical descriptions of these properties, based on average or derived descriptions of their submicron bulk strucutre, are waiting to be tested

Essentially every experiment we've done so far contradicts the classical models, which ignore

- Heterogeneity
- Inter-grain interactions



- Optics
- Thermal drifts
- Ambient vibrations
- · Vibrations during rotations
- Source size broadening
- Flux density reduction
- Sample Positioning
- Sample metrology

Mon

· 25 - 125 Kev



- Foint or time focus
- Wide an export of monorchromators

Si Nanolens

 The nost advanced area technically





Optics

Thermal drifts

- Ambient vibrations
- · Vibrations during rotations
- · Source size broadening
- Flux density reduction
- Sample Positioning
- Sample metrology

Everything moves!
Default sample + optics mounts not optimised at all for thermal stability
Diffractive/Refractive optics multiply effect:
Best case: ~µrads/°C for diffractive/refractive optics
i.e., microns at 1 m, 10s nm at 10 mm
Multiply with effects of everything else



in the stack





~µm amplitudes on **floor**, up to high frequencies

Position – configuration		Horizontal AC OFF	Horizontal AC ON	Vertical AC OFF	Vertical AC ON
ID11 Floor	0.5 m	0.56 (0.09)	0.53 (0.08)	0.85 (0.14)	0.70 (0.12)
	3m	0.50 (0.08)	0.48 (0.08)	0.94 (0.15)	0.76 (0.13)

- Optics
- Thermal drifts
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- · Vibrations during rotations
- · Source size broadening
- Flux density reduction
- Sample Positioning
- Sample metrology

ID11 - Laue Monochromator - 2nd crystal - Vertical (Z) PSD - Effect of roughing pump



Everything moves!



CRL – nanofocusing lenses





Charge Ordering: Beyond Valence Sums



Using anomalous Diffraction to achieve an independent measure of oxidation state







Charge Density Studies



Determine charge distributions beyond the spherical atom limit



Single Crystal Studies

Good structures from bad crystals Fine details from decent crystals





Software

Up to 1 Tb/day at the moment – has to be at least preprocessed psedo-online Much development has been carried out in the last several years

Fable project, for data acquisition, reduction and analysis...demonstrations during BL visit



Diffractometer and environment

Mechanical specifications necessary to perform sub-micron experiments are now realisable. Real spatial resolution determined not by beam size, but by diffractometer and metrology.

Two current experimental stations:

EH1 for large, heavy experiments with moderate (>10 μ m) focusing. New diffractometer installed last year.

EH3 for micro and sub-microfocusing (~100nm static, ~750 nm 360° rotation): new diffractometer is being acquired.

A variety of detectors and sample environments are available



- Optics
- Thermal drifts
- Ambient vibrations
- Vibrations during rotations
- · Source size broadening
- Flux density reduction
- Sample Positioning
- Sample metrology

Feedback scheme

- BPM near the sample, activating Piezo on optics (i.e., Laue monochromator) angle (=position)
 - Could predict offset via temperature/angle measurements if no BPM available
- Hardware feedback currently functioning at ~10 Hz
- 200 nm rms stability of ~µm beam on s time scale







Optics

Challenges 60 Al collimating Be Collimating ocussing (150 microns) Problem: twice as far fro Solution: Collimator/Condensor based on CRLs Thermal drifts In white beam Without Collimator: Ambient vibrations 40 ●Variable number of AlfBe refises 1.0 mm²) Vibrations during rotations V(0) * 100 •Collimate (Moves source to infinity) Source size broadening Improves energy/spatial resolution 30 Flux density reduction •Focus to 1mm @23 m to 150 µm @ 100 m Similar to acceptance of nano-optics Sample Positioning •25-125 keV Sample metrology 20 •Huge flux increase In fabrication (early 2008) 10 20 40 60 80 100 120 Energy (keV)



- Optics
- Thermal drifts
- Ambient vibrations
- · Vibrations during rotations
- Source size broadening
- Flux density reduction
- Sample Positioning
- Sample metrology

Below 2 μ m there is a transition Need a big effort in this area

- Interferometry?
- Image recognition?











Primary Monochromator



New horizontal Laue-Laue monochromator gives excellent flux, beam stability and homogeneity.



Focussing Optics								
Optical Element(s)	∆E/E	Focus Achieved (horizontal × vertical, μm)	Energy Range (keV)	Maximum Flux in spot (photons/s)				
Saggital Bragg/Bragg	10-4	200 ×	23 - 64	10 ¹⁴				
CRL + Bragg/Bragg	10-4	3×1.0	23 - 99	10 ¹²				
CRL + Laue/Laue	10 ⁻² ~10 ⁻³	3 imes 1.0	30 -140	10 ¹⁴				
nCRL + Bragg/Bragg	10-4	0.50 imes 0.25	23 - 80	10 ⁹				
nCRL + Laue/Laue	10-2~10-3	0.50 imes 0.25	30 - 80	1011				
Bent Laue	10 ⁻² ~10 ⁻³	× 1.2	35 -100	10 ¹⁴				
KB + Bragg/Bragg	10-4	4 imes 2.5	25 -100	1014				
KB + Laue/Laue	10 ⁻² ~10 ⁻³	4 imes 2.5	25 -100	5×10 ¹⁴				
Bent Laue + ML (h)	10-2	4 imes 1.2	50 - 80	5×10 ¹⁴				



Focussing Optics





Focussing Optics



Laue vertical monochromators - High flux and stability for line beams



Focussing Optics



Single or crossed multilayers - high flux but stability more critical



CRL - Transfocator



Adjustable number of lenses for focus between 25 - 50 keV (current model) In vacuum model for focus (100 - 150 µm) or collimation between 25 - 125 keV



CRL – nanofocusing lenses











Can be crossed for 2d focusing



Conclusions

- Many Challenges remain, but goals are achievable
- Proposed extensions will
 - Close the scale gap
 - Allow the characterisation of "intermediate" ordered structures