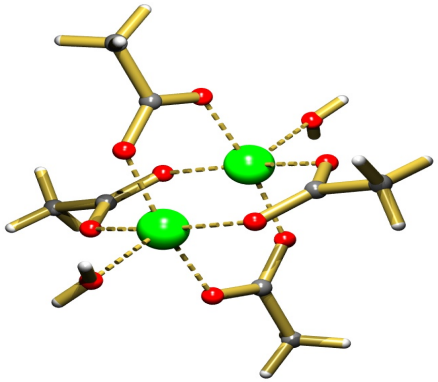
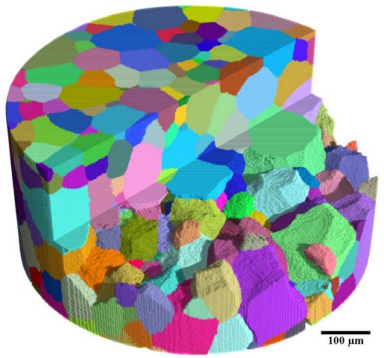
Multicrystal diffraction





DTU, Denmark: C. Gundlach, P.C. Hansen, D. Juul Jensen, E.M. Lauridsen, L. Margulies, J. Oddershede, U.L. Olsen, W. Pantleon, H.F. Poulsen, S. Schmidt, H. Simons Uni Copenhagen: H.O. Sørensen

ID11, ESRF, France: A. Götz, A. King, W. Ludwig MPIbpc, Göttingen: J. Davaasambuu, S. Techert
G.B.M. Vaughan, J. Wright Uni Oxford: K. Paintankar, E.F. Garman

---

Sector 1, APS, Chicago: J. Almer, U. Lienert Carnegie-Mellon: C. Hefferan, S.F. Li, A. Rollett, R.M. Suter.

Lawrence Livermore: J. Bernier Cornell: M. Miller ……

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DANISH NATIONAL RESEARCH FOUNDATION

DanScatt

ESRF

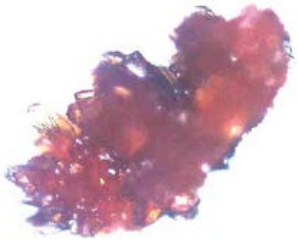
Argonne NATIONAL LABORATORY

DTU

Diffraction

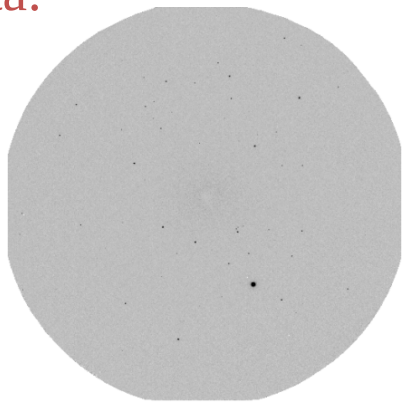
Single Crystal

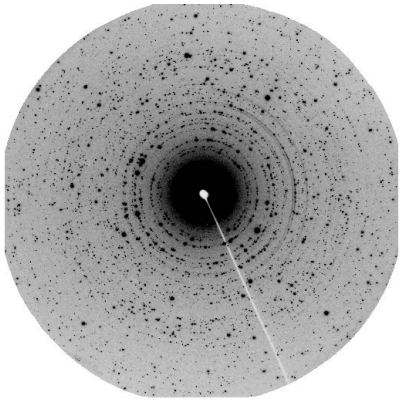
Multicrystal

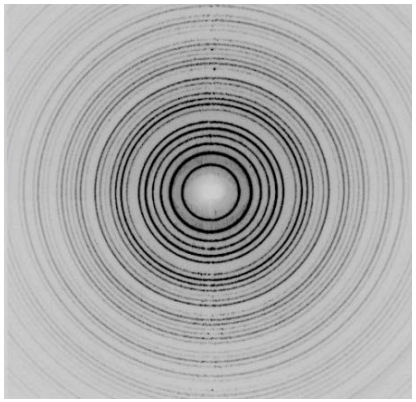


Powder

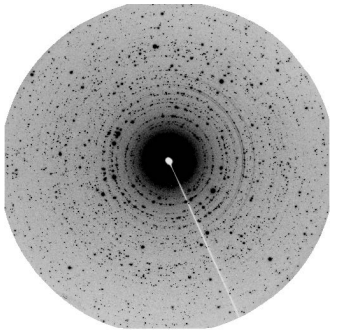
X-ray data:







Case for multicrystal diffraction



Microstructure

- Grain statistics and maps: phase, orientation, stress, 3D shape
- Grain dynamics and grain interactions

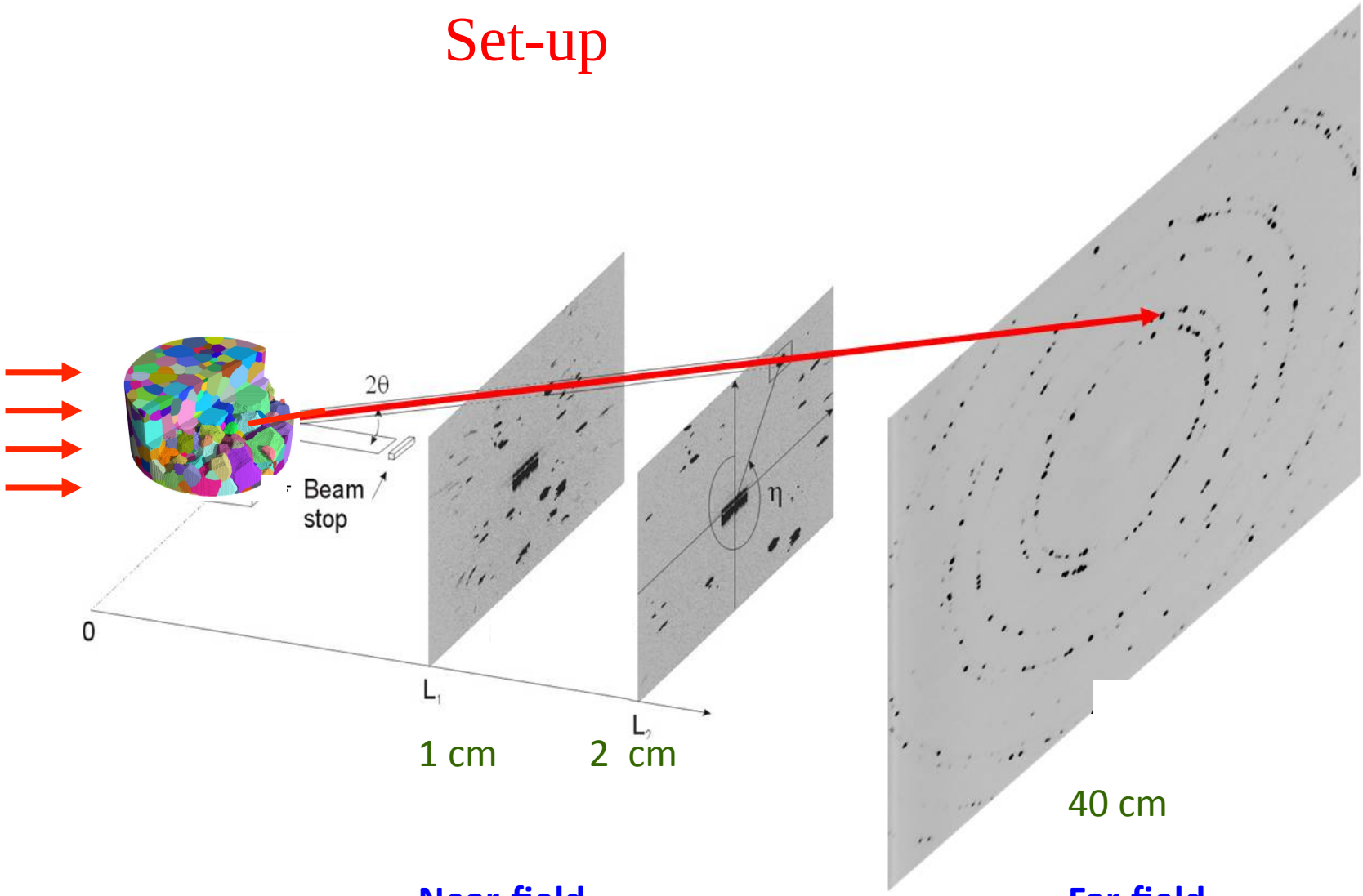
Samples

- Does not comply with powder diffraction
- Minority phases (10^{-9} volume fraction)
- Screening of samples

Accuracy

- Crystallography: more redundancy than single crystal work
- Strain: measure not only radial strain

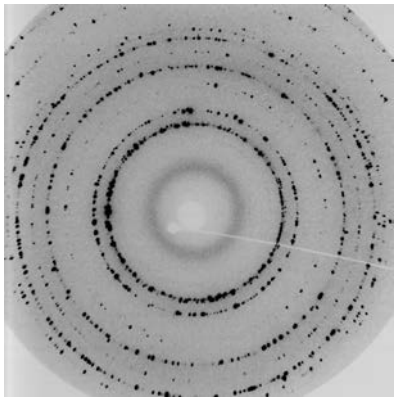
Set-up



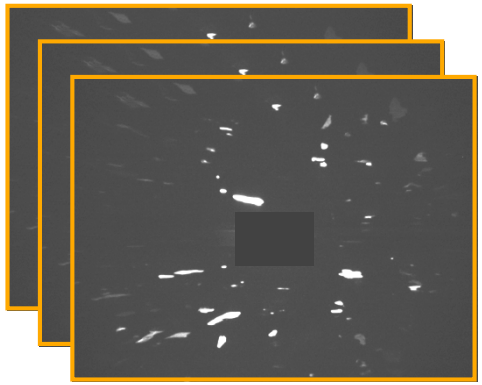
H.F. Poulsen. *Three-dimensional X-ray Diffraction Microscopy* (Springer, 2004)

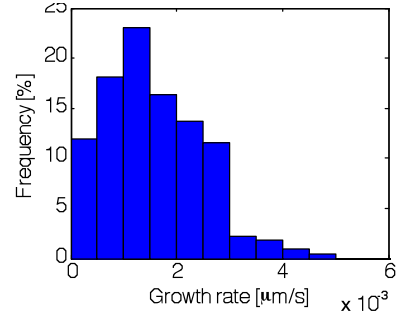
Data analysis

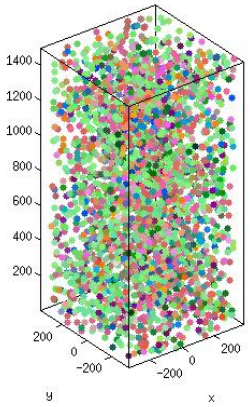
1. Grain identification:

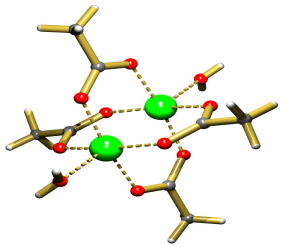


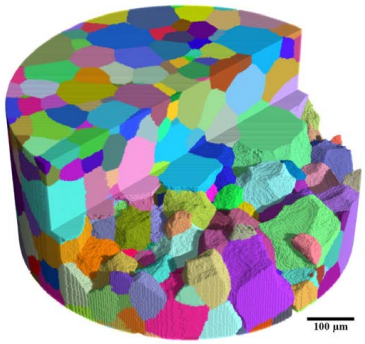
2. Grain shape:







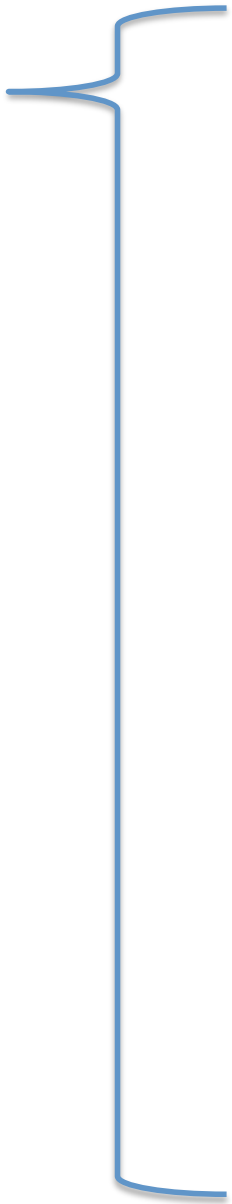




Distributions CMS maps Structure solution & refinement 3D Orientation maps

Data analysis

- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation

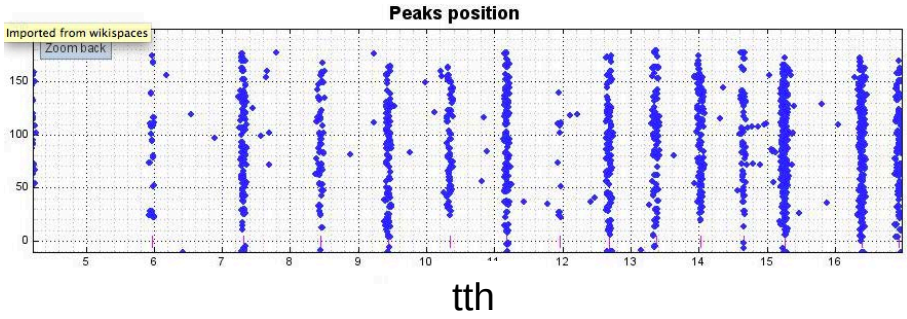


- Use NIST powder diffr. standards

Data analysis

- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation

-Use powder diffraction methods



ImageD11 program by J. Wright*

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*sourceforge.net/apps/trac/fable/wiki/imaged11

Data analysis

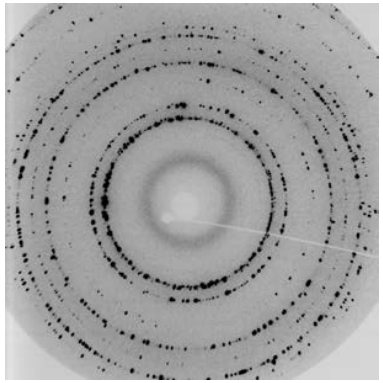
- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation

Peak profiles

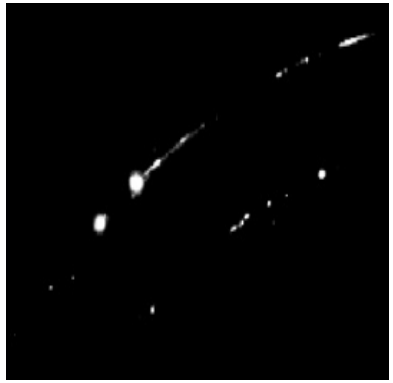
Typical: CMS within 10% of pixelsize

Limitations:

Peak Overlap

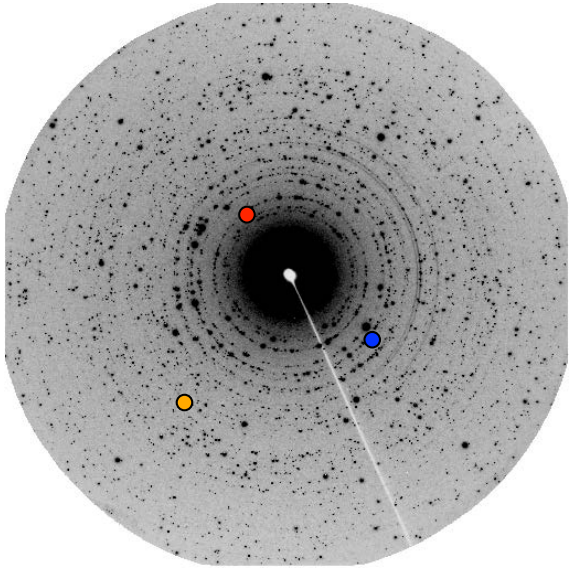


Plastic deformation

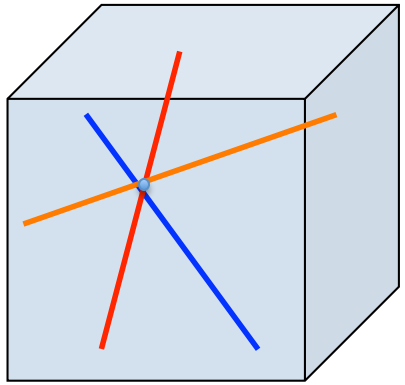


Data analysis

- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation



Orientation space:



Data analysis

- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation

Simulation of monodisperse Al with conservative errors: $(\sigma_{2\theta} = 0.025^{o}, \sigma_{\omega} = 0.125^{o}, \sigma_{\eta} = 0.05^{o})$

Nr grains	Grains correct	Reflections correct	Analysis time
1000	1000	99.2%	3 min
3000	3000	97.4%	50 min

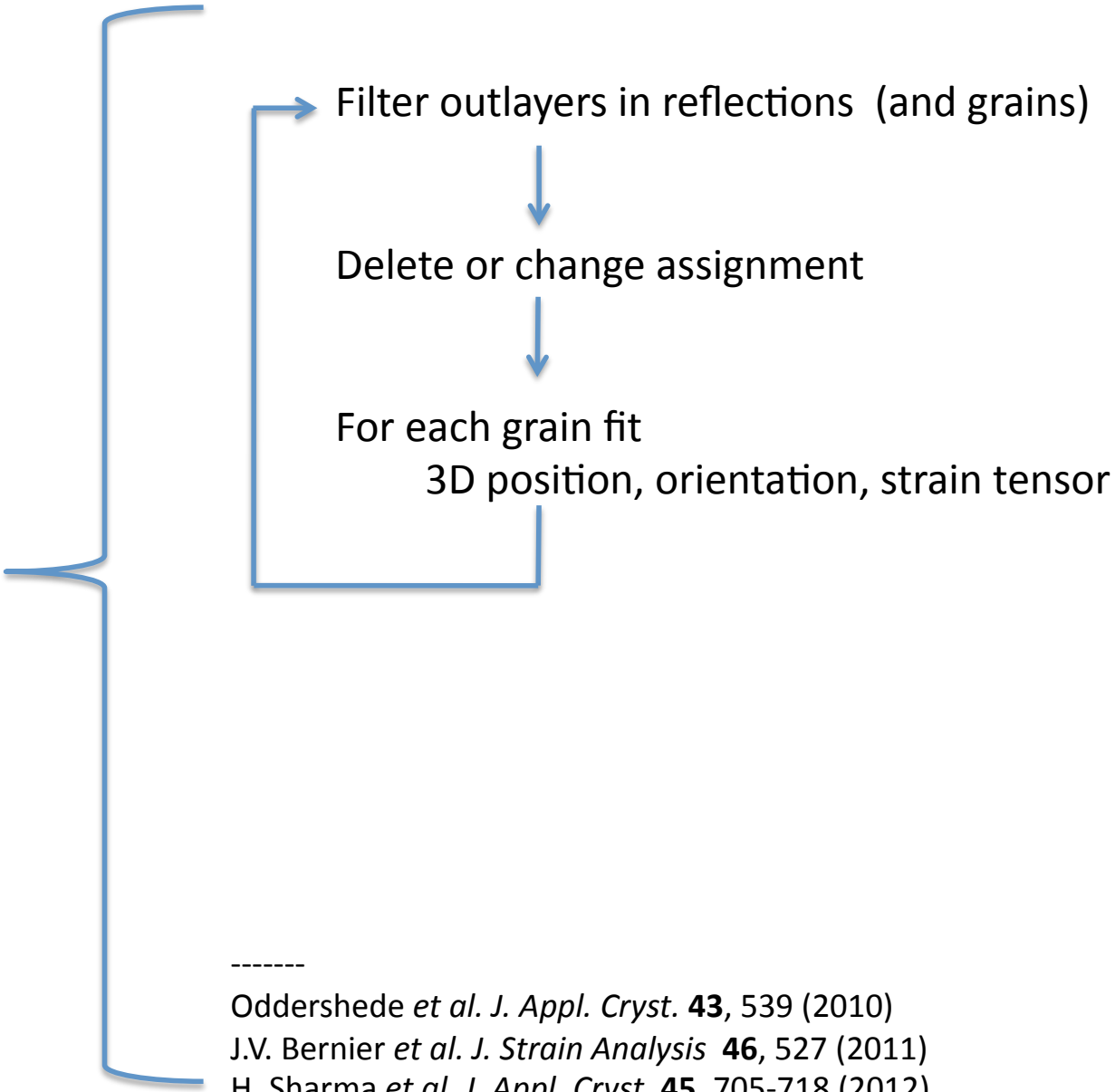
*S. Schmidt. Grainspotter. *J. Appl. Cryst.*, in review

Other Indexing programs:

E.M. Lauridsen *et al. J. Appl. Cryst.*, **34**, 744 (2001)
W. Ludwig *et al. Rev, Sci. Instrum.* **80**, 33905 (2009)
J. Wright. ImageD11 software (2009)
J. Bernier *et al. J. Strain Analysis Eng. Design.* **46**, 527-547 (2011)
H. Sharma *et al. J. Appl. Cryst.* **45**, 705-718 (2012)

Data analysis

- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation



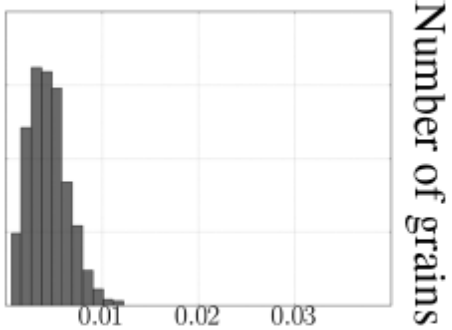
Oddershede *et al. J. Appl. Cryst.* **43**, 539 (2010)
J.V. Bernier *et al. J. Strain Analysis* **46**, 527 (2011)
H. Sharma *et al. J. Appl. Cryst.* **45**, 705-718 (2012)

Data analysis

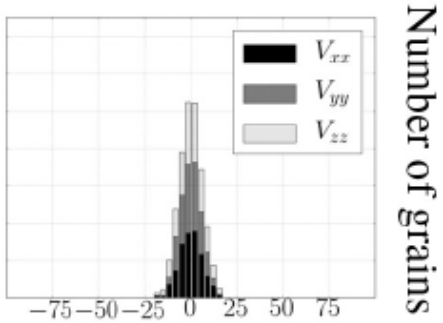
- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation

Simulation of 819 grains of Ti-7%Al (P6/mmc), 80 reflections per grain. Experimentally determined errors: $(\sigma_{2\theta} = 0.002^o, \sigma_\omega = 0.02^o, \sigma_\eta = 0.01^o)$

Orientation



Strain components



Error, σ: 0.003°

$6 \cdot 10^{-5}$ in strain

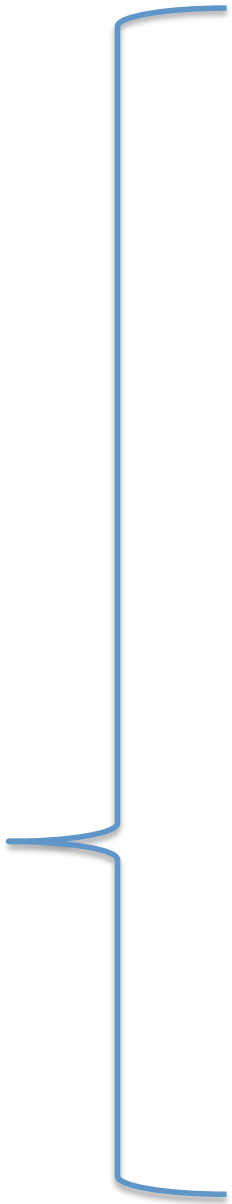
J.V. Bernier *et al. J. Strain Analysis* **46**, 527 (2011)

Oddershede *et al. J. Appl. Cryst.* **43**, 539 (2010)

H. Sharma *et al. J. Appl. Cryst.* **45**, 705-718 (2012)

Data analysis

- Calibrate instrument
- Find space group
- 3D peak search
- Indexing
- Filtering & fitting
- Crystallography
- Validation



Interface to SHELX, JANA2000, MOSFLM:

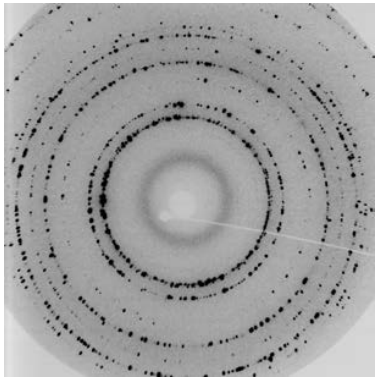
Refine grains independently

or

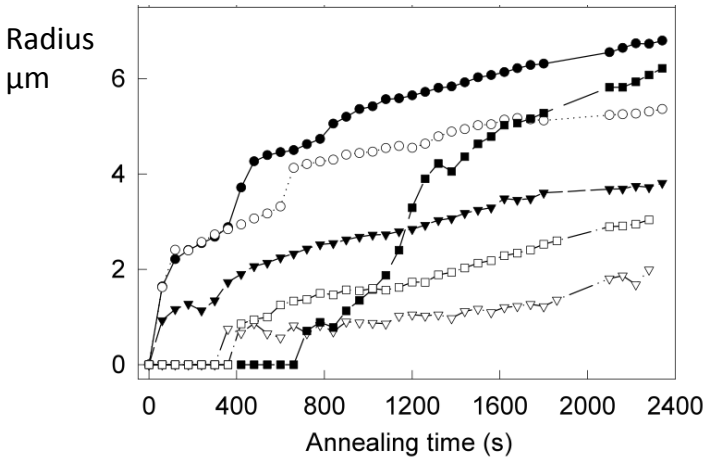
Merge and global refinement

Grain growth

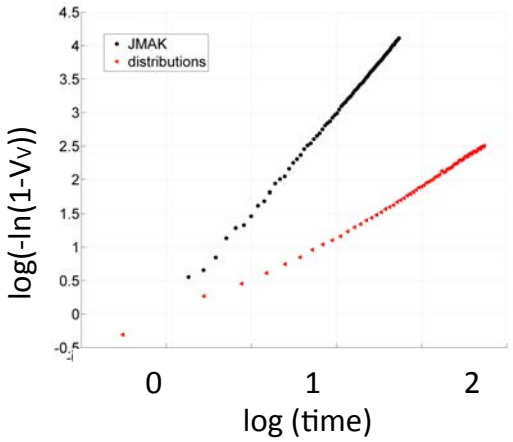
Watch spot intensities



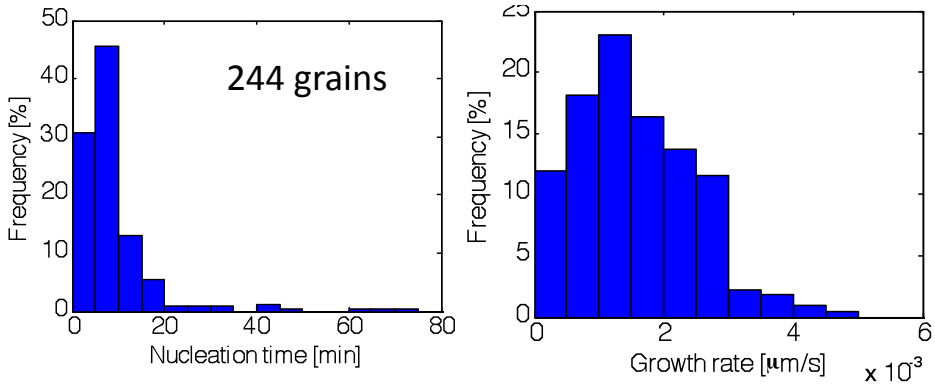
Growth curves:



New Avrami-type model



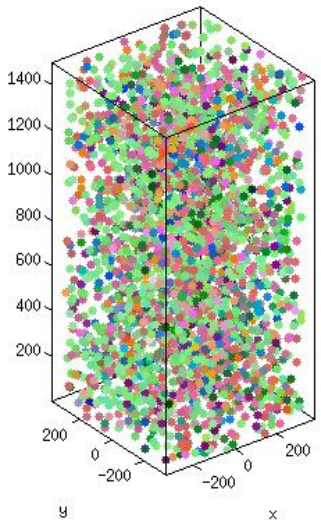
Statistics

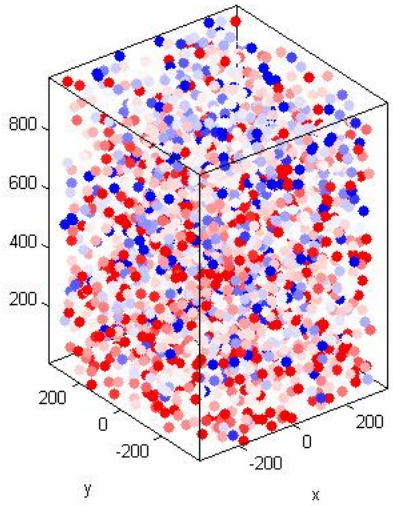


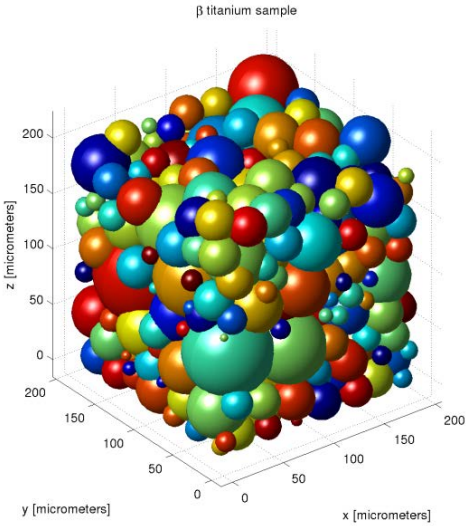
E.M. Lauridsen, H.F. Poulsen, S.F. Nielsen, D. Juul Jensen. *Acta Mat.* **51**, 4423 (2003).

Grain properties mapping

CMS position of 2842 grains in an IF steel sample:



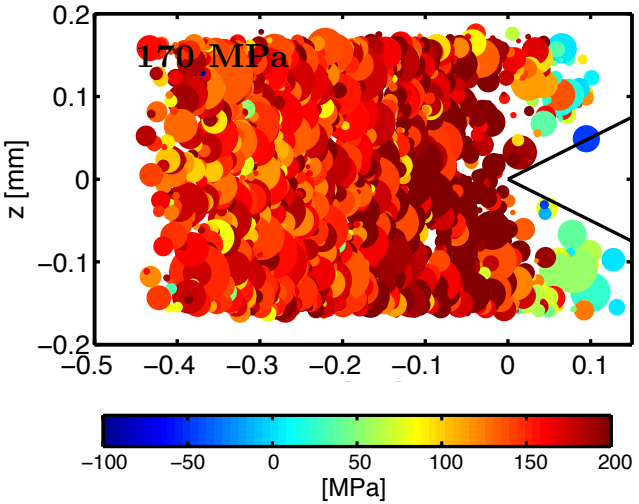


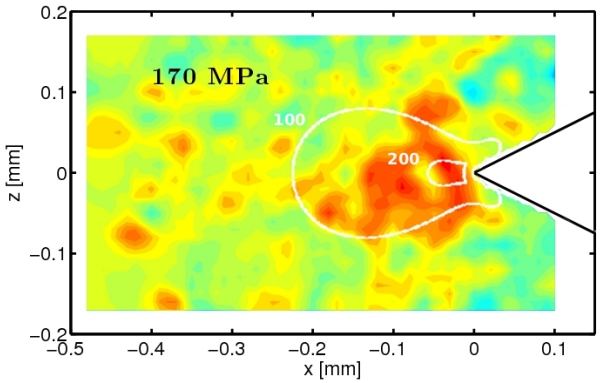


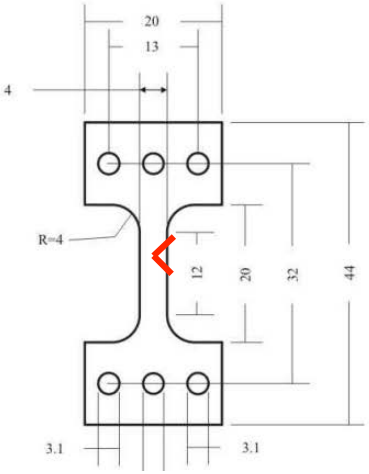
Position + orientation	elastic strain tensor	volume
2 μm 0.05 deg	$\Delta E/E = 10^{-4}$	10% relative

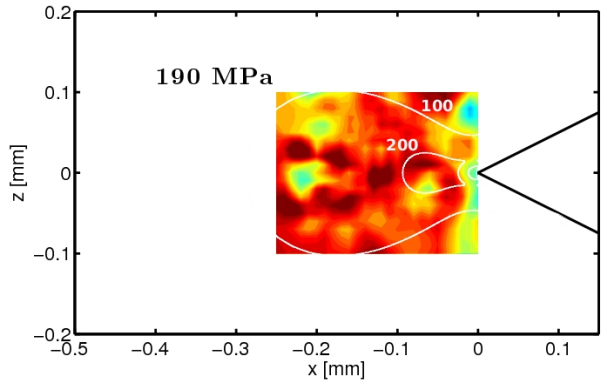
J. Oddershede, G. Winther, H.F. Poulsen, L. Margulies, M. Kobyashi,, S. Schmidt, J. Wright, W. Reimers.

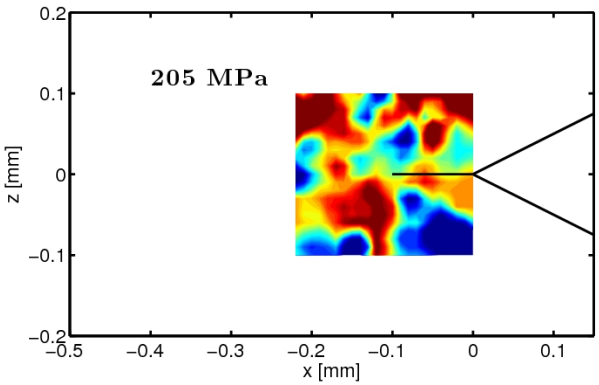
Stress mapping around a crack in Mg









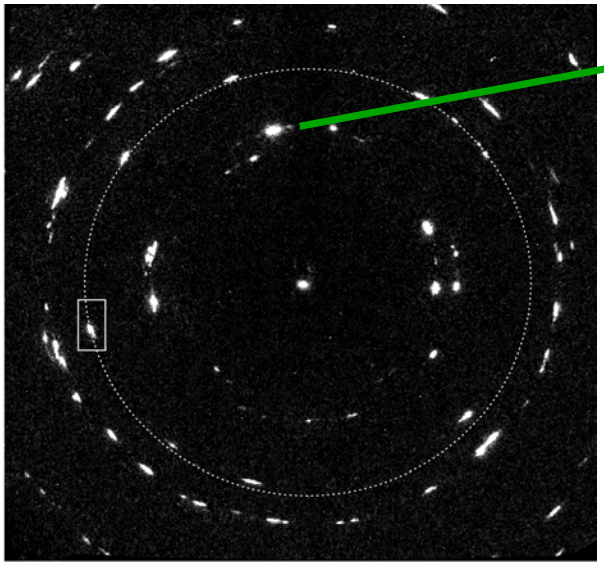


J. Oddershede, B. Camin, S. Schmidt, L.P. Mikkelsen, H.O. Sørensen, U. Lienert, H.F. Poulsen, W. Reimers.
Acta Mater. **60,** 3570-3580 (2012).

Peak broadening: resolving sub-grains

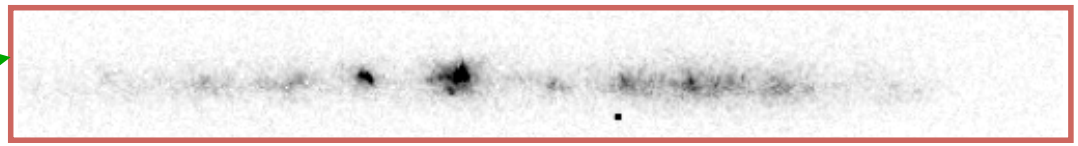
Ex: Cu deformed to 5%

Grain-scale

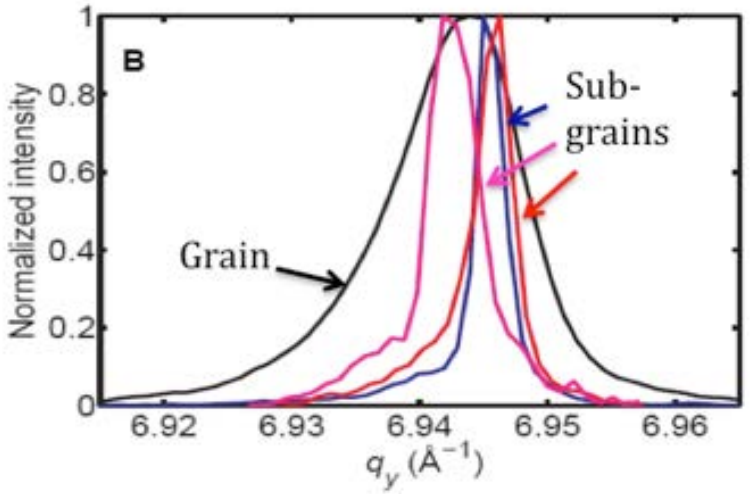


Zoom

Subgrain-scale



0.001 deg



B. Jakobsen, H.F. Poulsen, U. Lienert, J. Almer, S.D. Shastri, H.O. Sørensen, C. Gundlach, W. Pantleon Science **312** (2006) 889-892

Crystallography on small molecule

Validation:

$Cu(C_2O_2H_3)_2 \cdot H_2O$.

70 grains of size < 1 micron

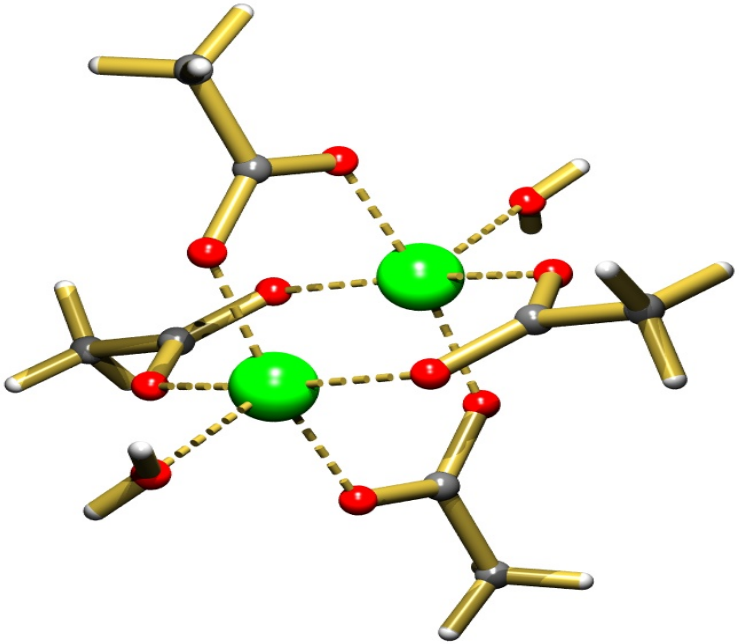
Cell ~1400 Å^3 (C2/c)

R_1 = 5.7

Compare to

Powder diffraction

Single crystal diffraction



G.B.M. Vaughan, S. Schmidt, H.F. Poulsen. *Z. Krist*. (2004) **219**, 813-825

Comparison of Bond lengths

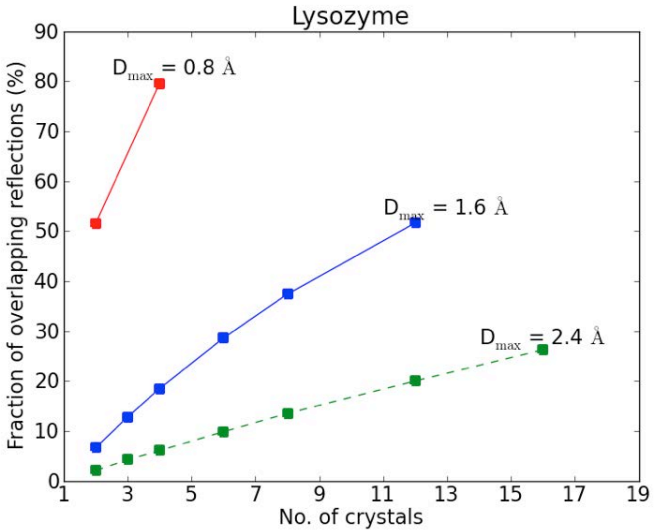
Bond	Single Crystal	Multicrystal	Powder	$\lvert d_{mc} - d_{sc} \rvert \times 10^3$	$\lvert d_{pow} - d_{sc} \rvert \times 10^3$
Cu-O1	1.9880(8)	1.985(5)	1.981(4)	3	7
Cu-O2	1.9962(8)	1.991(7)	1.985(4)	5	11
Cu-O3	1.9431(9)	1.945(7)	1.924(4)	2	18
Cu-O4	1.9575(9)	1.963(7)	1.949(4)	6	8
Cu-O5	2.1588(14)	2.149(8)	2.149(9)	11	11
$< \Delta (Cu - O) >$				5.4 (31)	11.0 (24)
O1-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
$< \Delta(O - C) >$				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)	

Comparison of Thermal Factors

	ΔU_{eq} in %		$\Delta (u_3/u_1)$ in %	
	Multicrystal	Powder	Multicrystal	Powder
Cu1	4	-29	9	178
O1	-1	27	0	191
O2	2	32	5	163
O3	-7	21	-22	104
O4	2	13	-6	-3
O5	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

Proteins

Spot overlap:



5 cubic insuline crystals:

Crystal identifier	I4-0	I4-2	I4-5
Resolution range (Å)	55.1-1.9 (2-1.9)	31.9-1.9 (2-1.9)	26.6-1.9 (2.0-1.9)
Number of refl Total Unique	 67286 6391	 67962 6395	 67089 6341
Completn	100(100)	100(100)	99.9(100)
Multiplicity	10.5(10.9)	10.6(10.9)	10.6(10.9)
R_{meas}	0.12(0.3)	0.08(0.3)	0.07(0.2)
I/s(I)	21.5(7.4)	24.9(9.6)	28.6(12.2)
Wilson B ($Å^2$)	16.6	18.4	17.7

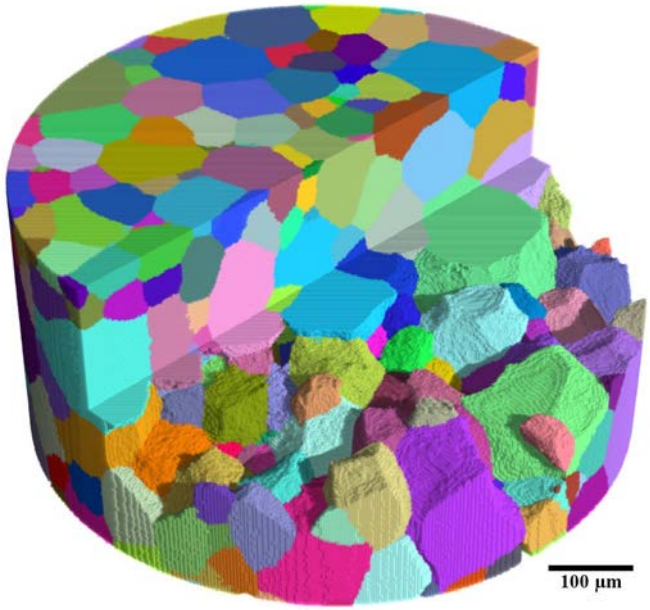
Merged: $R_{p.i.m}$ = 0.015

Paithankar, KS , Sørensen, HO , Wright, JP, Schmidt, S, Poulsen, HF & Garman, EF, *Acta Cryst D* **67**, 608-618 (2011).
Overview: H.O. Sørensen *et al. Z. Kristallogr*. **227** 63-78 (2012)

3D grain mapping

DCT:

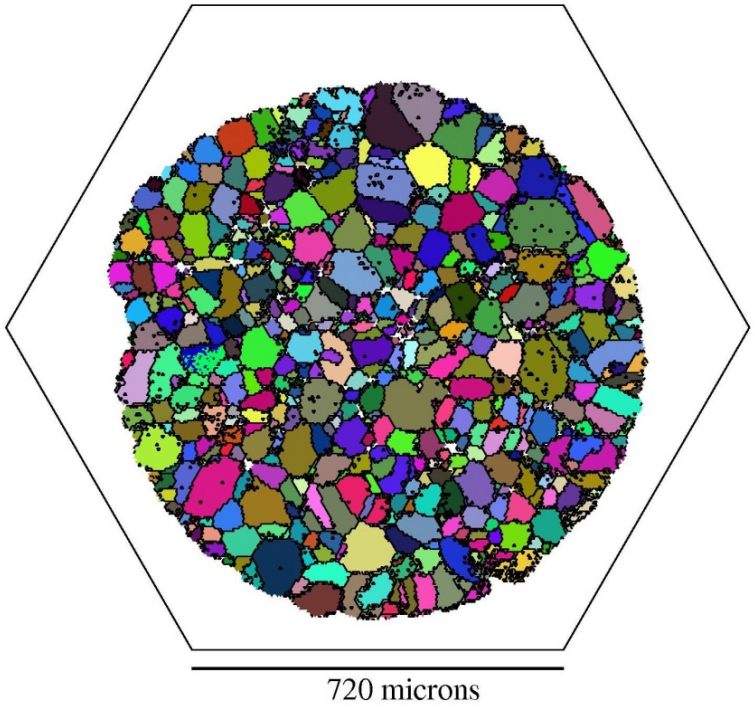
Mapping β-Ti at ID19, ESRF:



G. Johnson, A. King, M. G. Honnicke, J. Marrow and W. Ludwig. *J. Appl. Cryst.* (2008) **41**, 310-318,

Layer-by-layer:

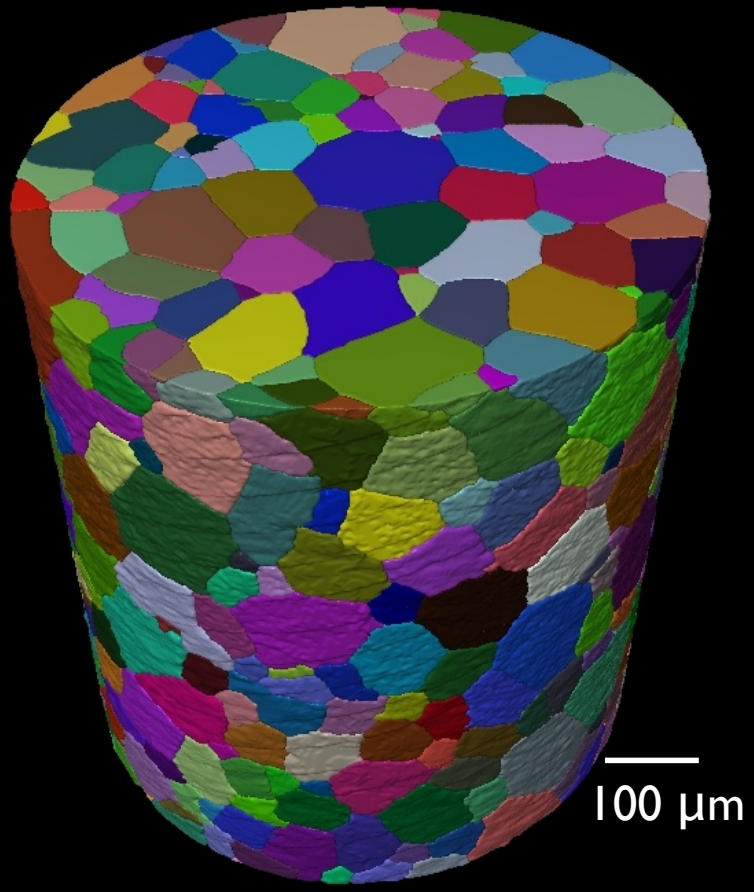
Mapping pure Ni at sector-1 at APS:



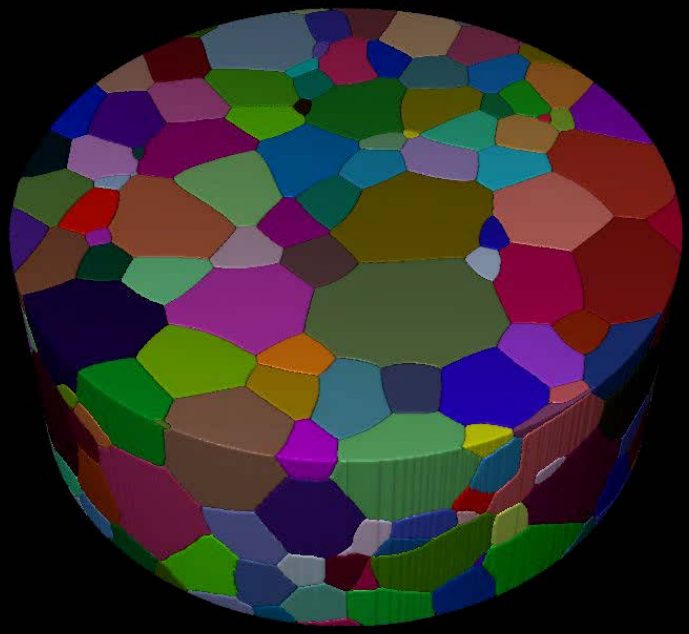
C. M. Hefferan, S. F. Li, J. Lind, U. Lienert, A. D. Rollett, P. Wynblatt, R. M. Suter, *Computers, Materials and Continua* (2009) **14**, 209-219

Grain Growth in Titanium

Experimental results



Phase field simulations



Risø: E.M. Lauridsen, S. Poulsen, A. Lyckegaard.

Northwestern: P. Voorhees, I. McKenna

Navy Resarch Lab: R. Fonda

ESRF: W. Ludwig, A. King, S. Rolland

Instruments

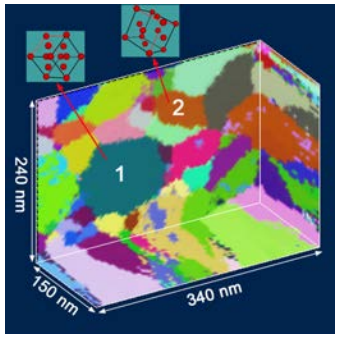
Beamlines

ID11 @ ESRF
1-ID @APS
HEMS @ PETRA-III
(CHESS, Spring-8, …)

Neutrons:

ESS-DTU collaboration

Electrons*:



1 nm

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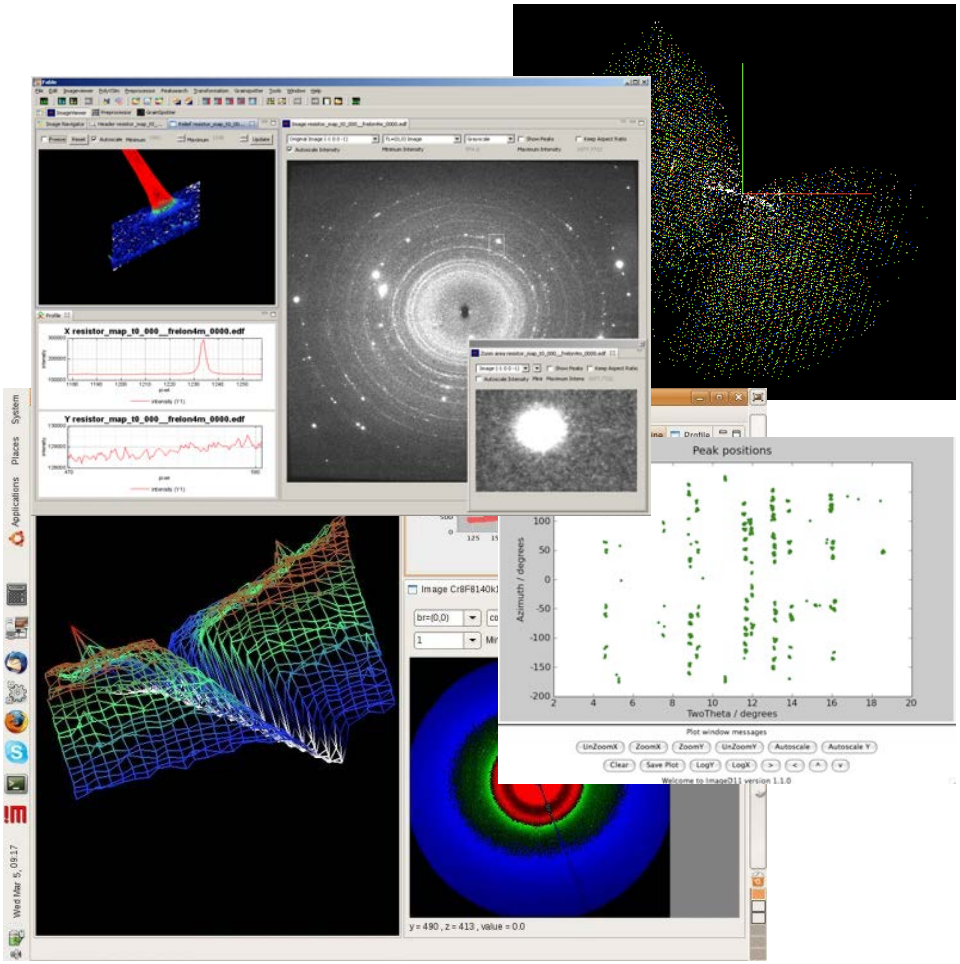
*H.H. Liu et al., *Science* **332**, 833 (2011)

Software

FABLE:



Available on Sourceforge

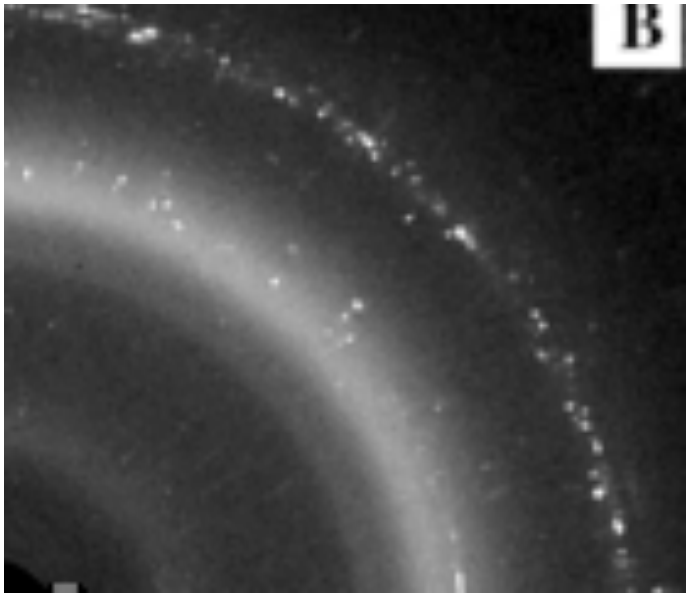
Perspective 1:

More complex samples

Limitation:

Size distribution

Bad grains



Solution 1: Model as

N multigrains

+ very strongly textured powder pattern*

Solution 2:

Avoid segmentation

Full forward modeling

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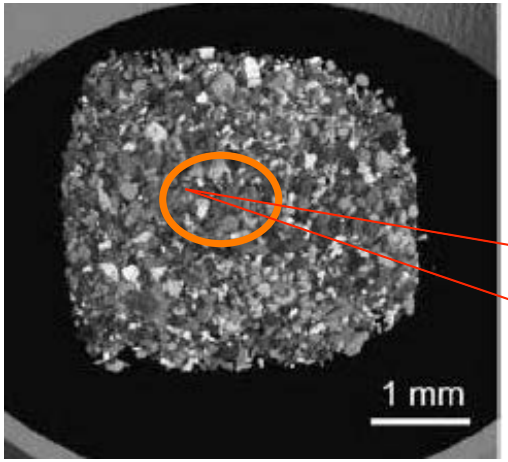
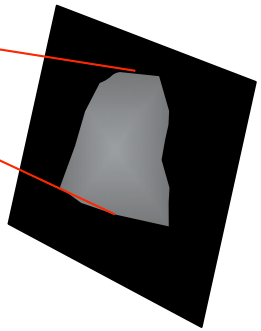
*I. G. Kazantsev *et al. Inverse Problems* **25**, 105009 (2009)

Perspective 2:

Local diffraction & imaging



Lens



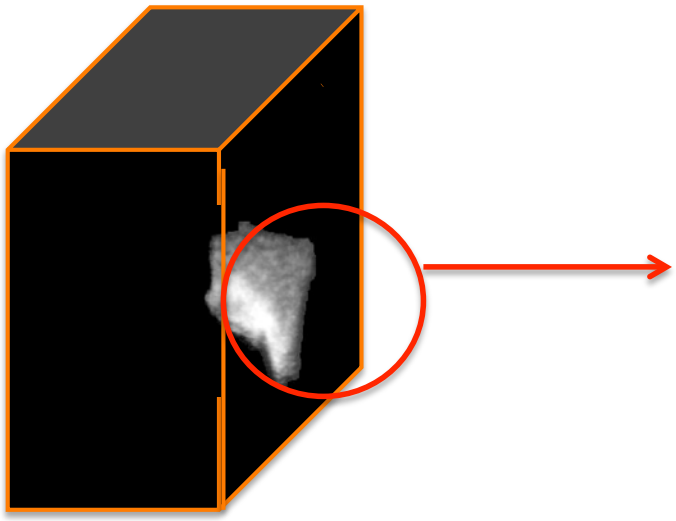
- Overcomes spot overlap problem
- Enlarge grains

Detector

Alternative: diffraction tomography and PDF tomography

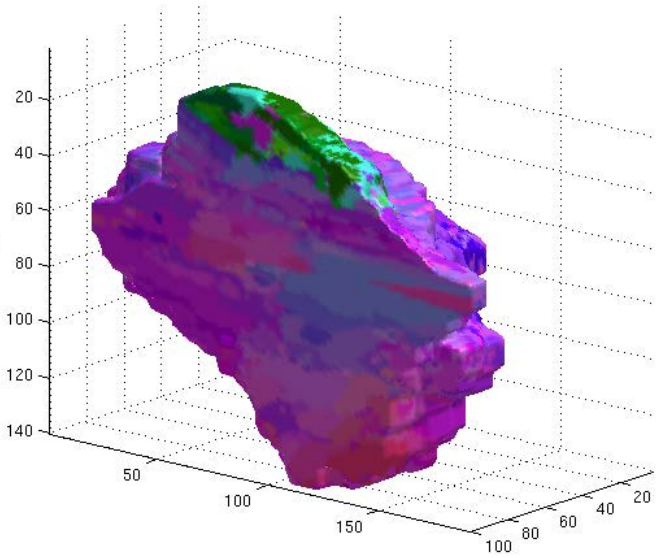
Demonstration: subgrains in Al

Grain mapping



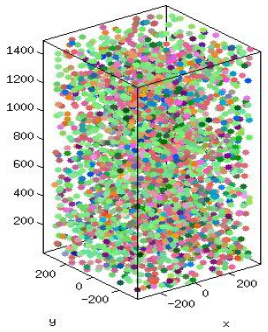
0.7 mm

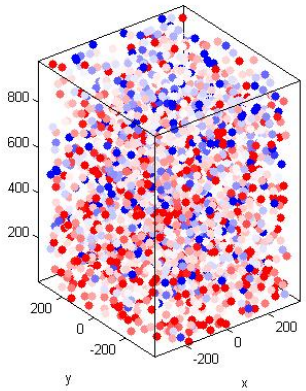
X-ray microscopy

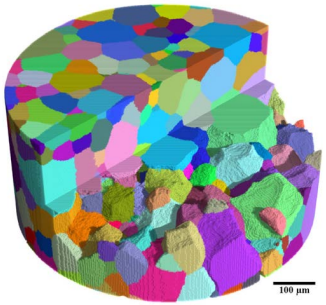


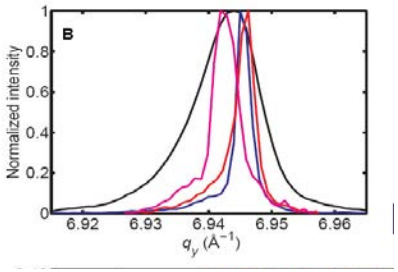
Resolution 200 nm

Accuracy in multigrain crystallography









Orientation
0.05 deg

elastic strain tensor
$\Delta E/E = 10^{-4}$

3D maps
1-2 µm

Peak-profiles
$\Delta Q = 0.001$ Å^{-1}

Small molecules

Na (H2PO4) 2H2O
31 crystals
Rsym 2.6%

Proteins

Cubic Insuline, 5 crystals
R_{meas} 0.08- 0.14 each, $R_{p.i.m}$ ~ 0.03 each
Merged: $R_{p.i.m}$ 0.015

H.O. Sørensen *et al.* Multigrain crystallography. *Z. Kristallogr.* **227** (2012) 63–78