APPLICATION OF AUTOMATED ELECTRON DIFFRACTION TO STRUCTURAL INVESTIGATION OF MOLECULAR CRYSTALS

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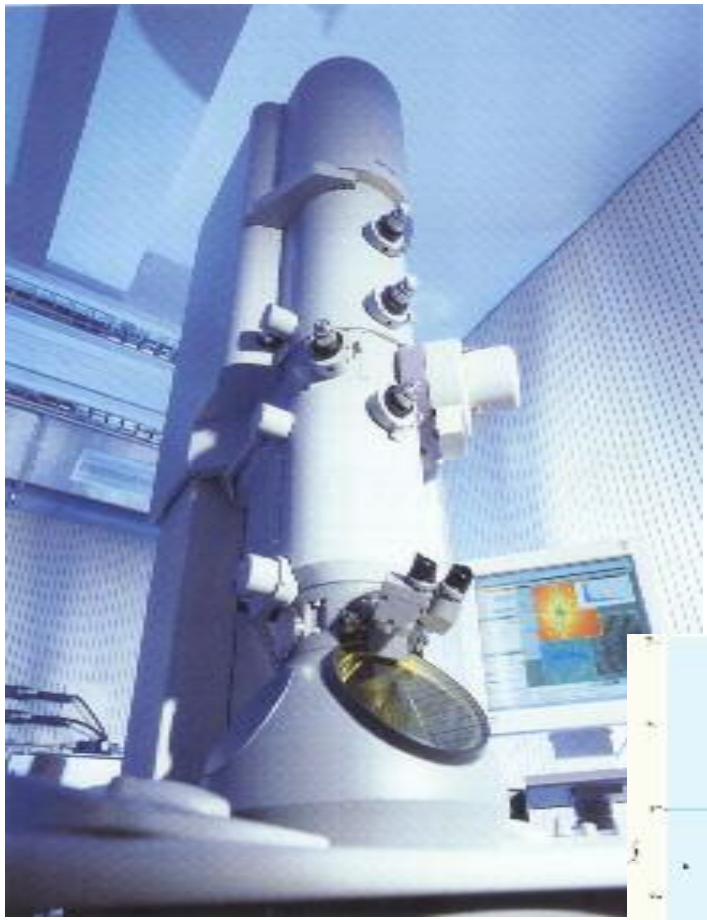
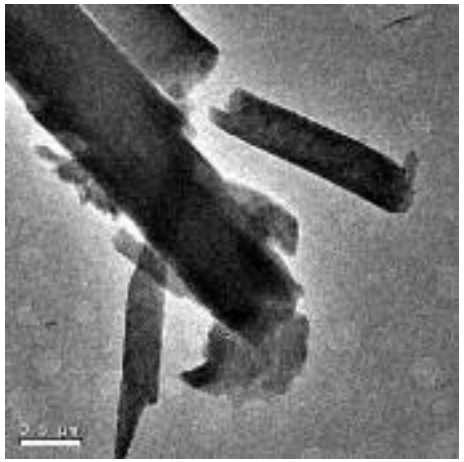
ICDD Website - www.icdd.com

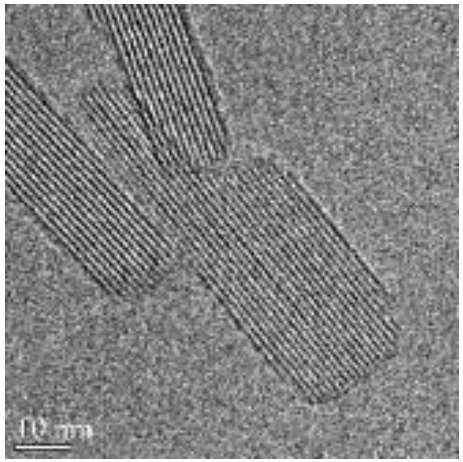
Transmission electron microscope (TEM)



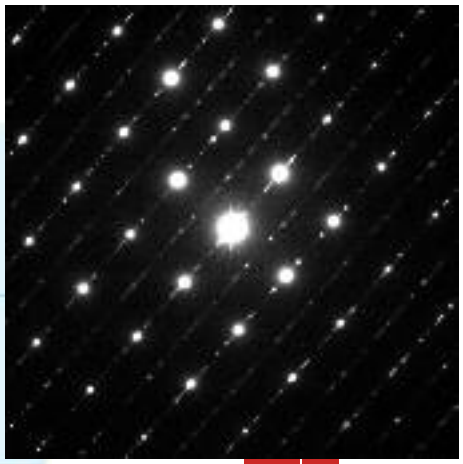
Imaging



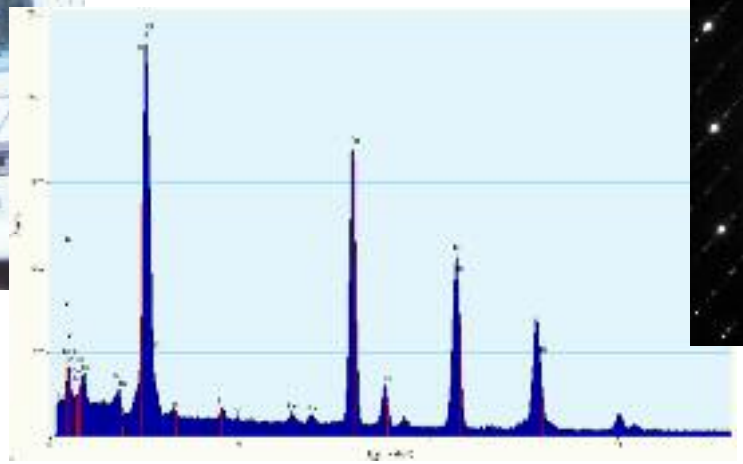
High-resolution imaging



Electron diffraction



Elemental analysis (EDX)



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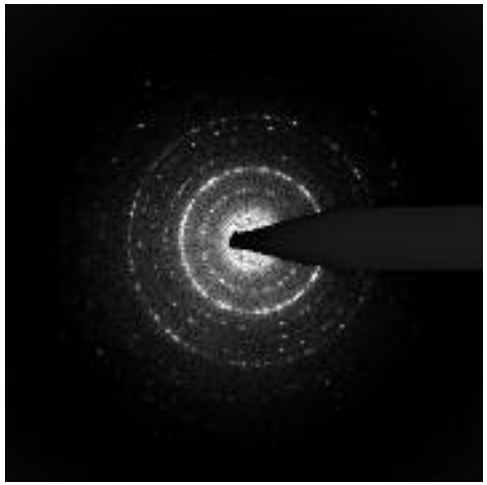
Powder electron diffraction

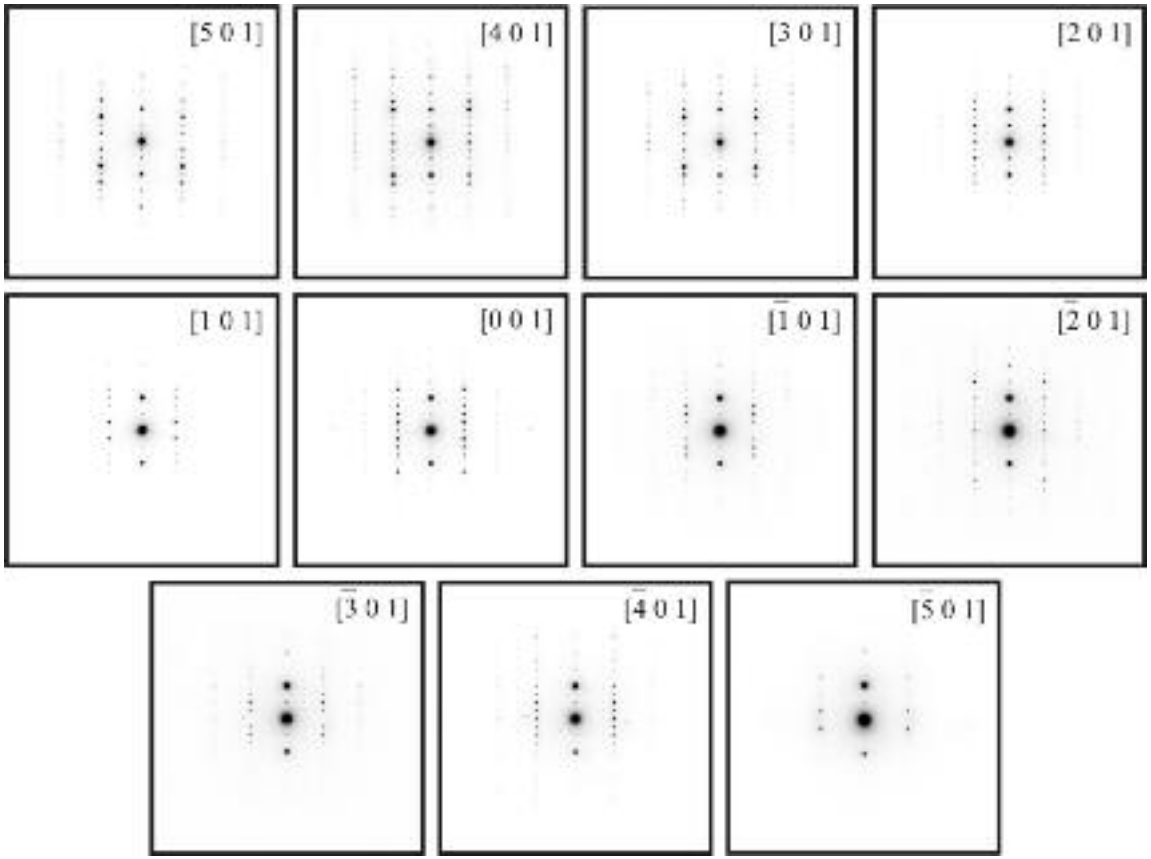


Pawley and Rietveld refinements using electron diffraction from $L1_2$-type intermetallic Au_3Fe_{1-x} nanocrystals duringtheir in-situ order–disorder transition

Zhiping Luo, Yolanda Vasquez, James F.Bondi, Raymond E.Schaak

Ultramicroscopy, 2011

Single crystal electron diffraction: tilt series



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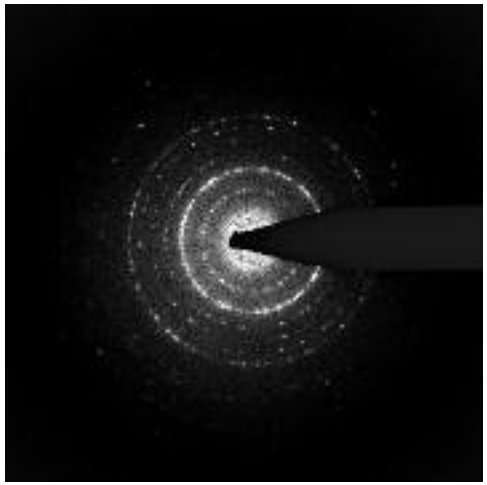
Powder electron diffraction



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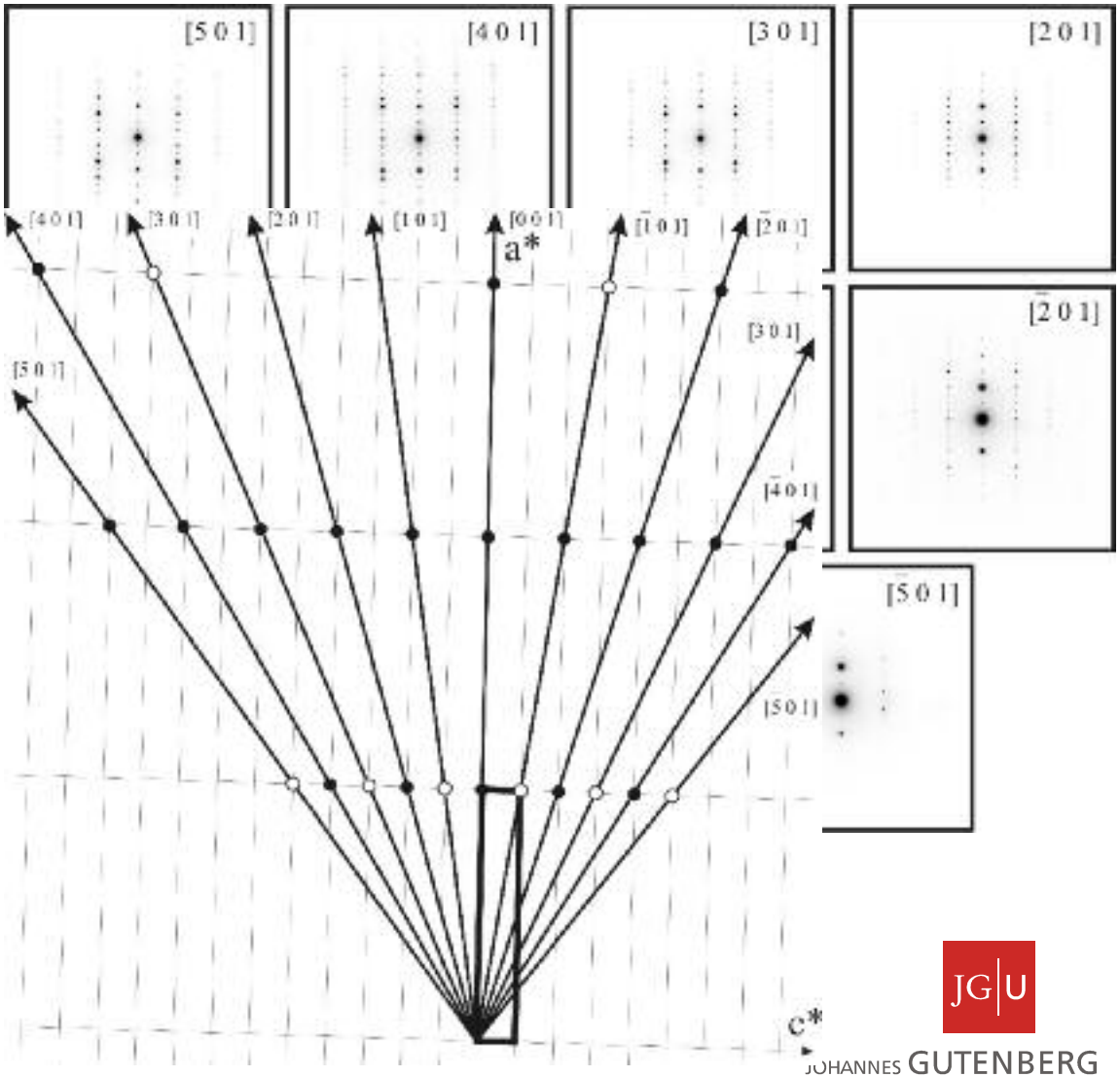

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Structure solution using zonal electron diffraction data: historical overview

Organic samples

Rigamonti, R., La struttura della catena paraffinica studiata mediante i raggi di elettroni, *Gazzetta Chimica Italiana* **66** 174-182 (1936)

D.L. Dorset, **Structural electron crystallography**, Plenum New York (1995)

Voigt-Martin et al., The use of simulation mehods to obtain the structure and conformation of 10-cyano-9,9'-bianthryl by electron diffraction and high-resolution imaging, *Ultramicrocopy* **57**, 29-43 (1995)

Biological samples
2D Protein crystals

Dorset, D.L., Direct structure analysis in protein electron crystallography: crystallographic phases for halorhodopsin to 6Å resolution, *Proc Natl Acad Sci USA* **92(22)**, 10074–10078 (1995)

→ Solution using structure factor phases derived from HRTEM

Kühlbrandt, W. et al. Atomic model of plant-light harvesting complex by electron crystallography, *Nature* **367**, 614, (1997) – 3.4 Å resolution

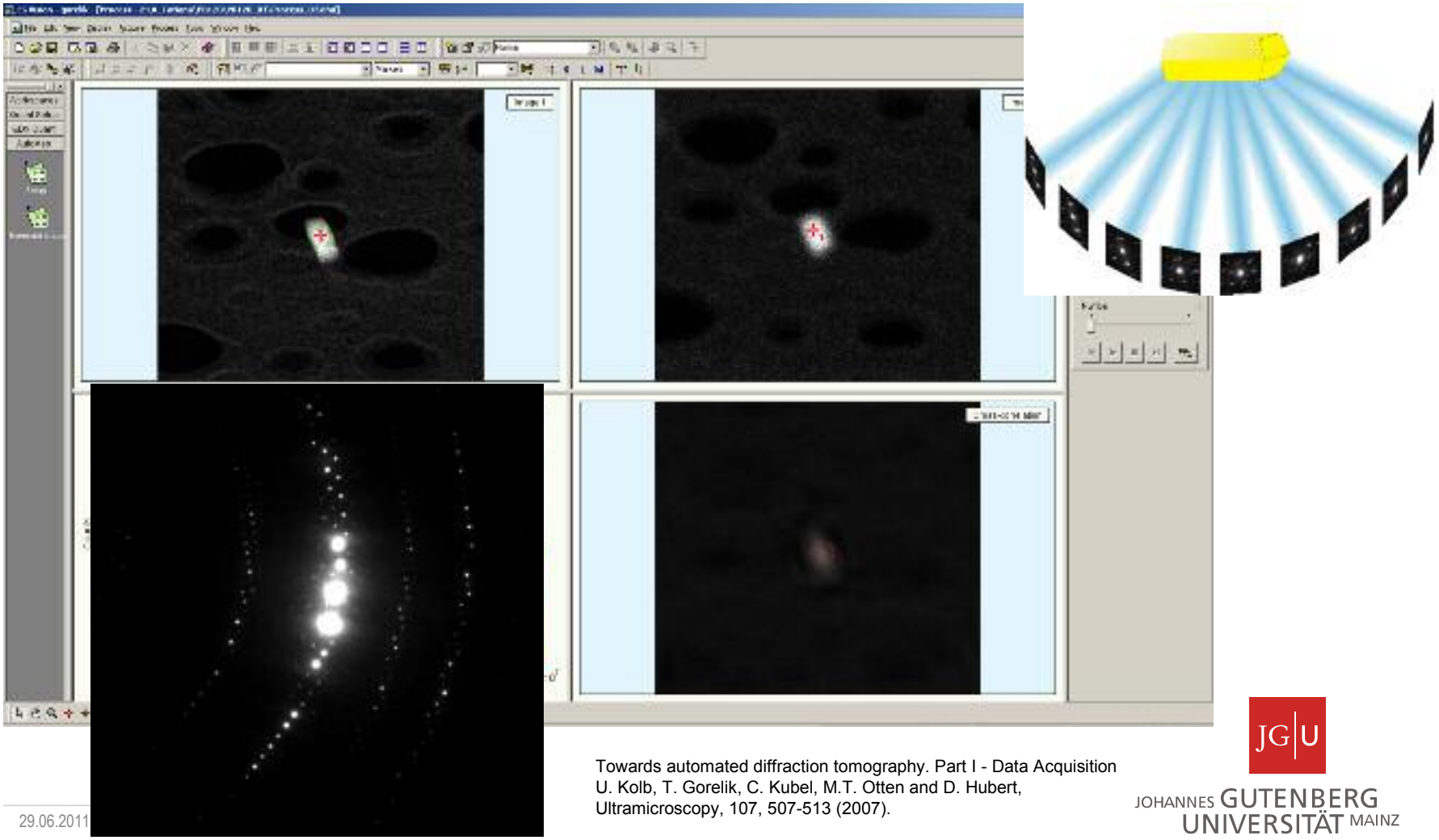
Inorganic samples (thin)

Weirich et al. A crystal structure determined with 0.02 Å accuracy with electron microscopy, *Nature* **382**, 144 (1996)

Hovmöller et al., Accurate atomic positions from electron microscopy, *Nature* **311**, 238-241 (1984)

AUTOMATED ELECTRON DIFFRACTION: THE EXPERIMENT

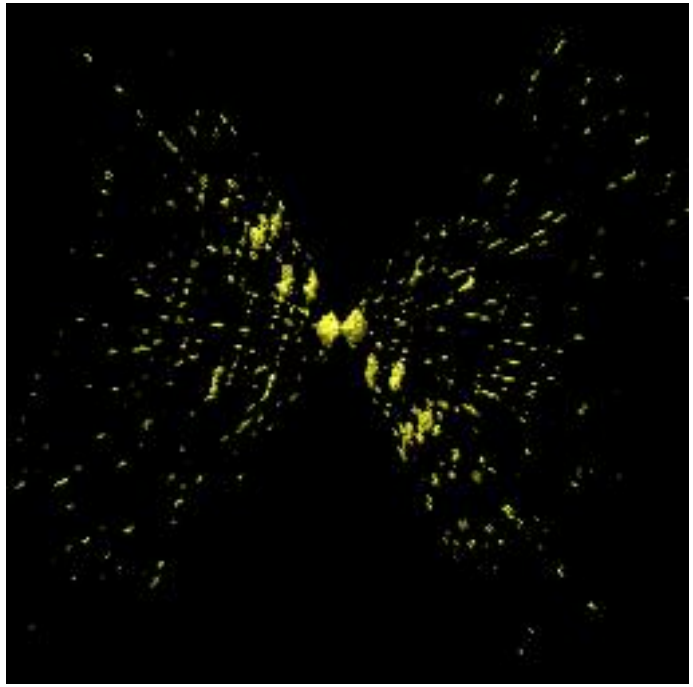
Automated electron Diffraction Tomography (ADT):
collection of the complete reciprocal data rather than zonal patterns

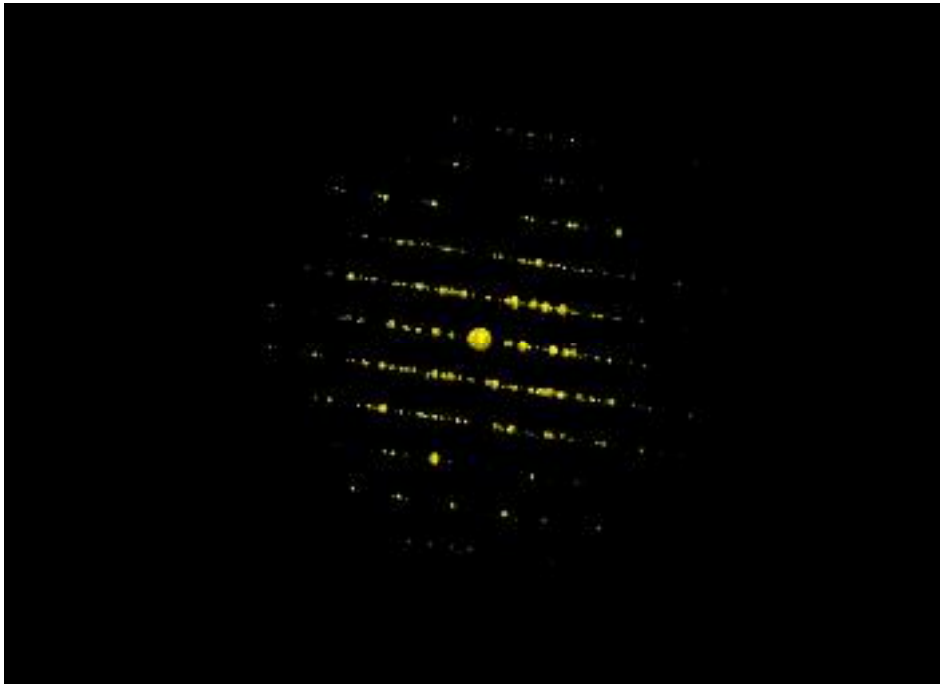


Towards automated diffraction tomography. Part I - Data Acquisition
U. Kolb, T. Gorelik, C. Kubel, M.T. Otten and D. Hubert,
Ultramicroscopy, 107, 507-513 (2007).

AUTOMATED ELECTRON DIFFRACTION: DATA PROCESSING

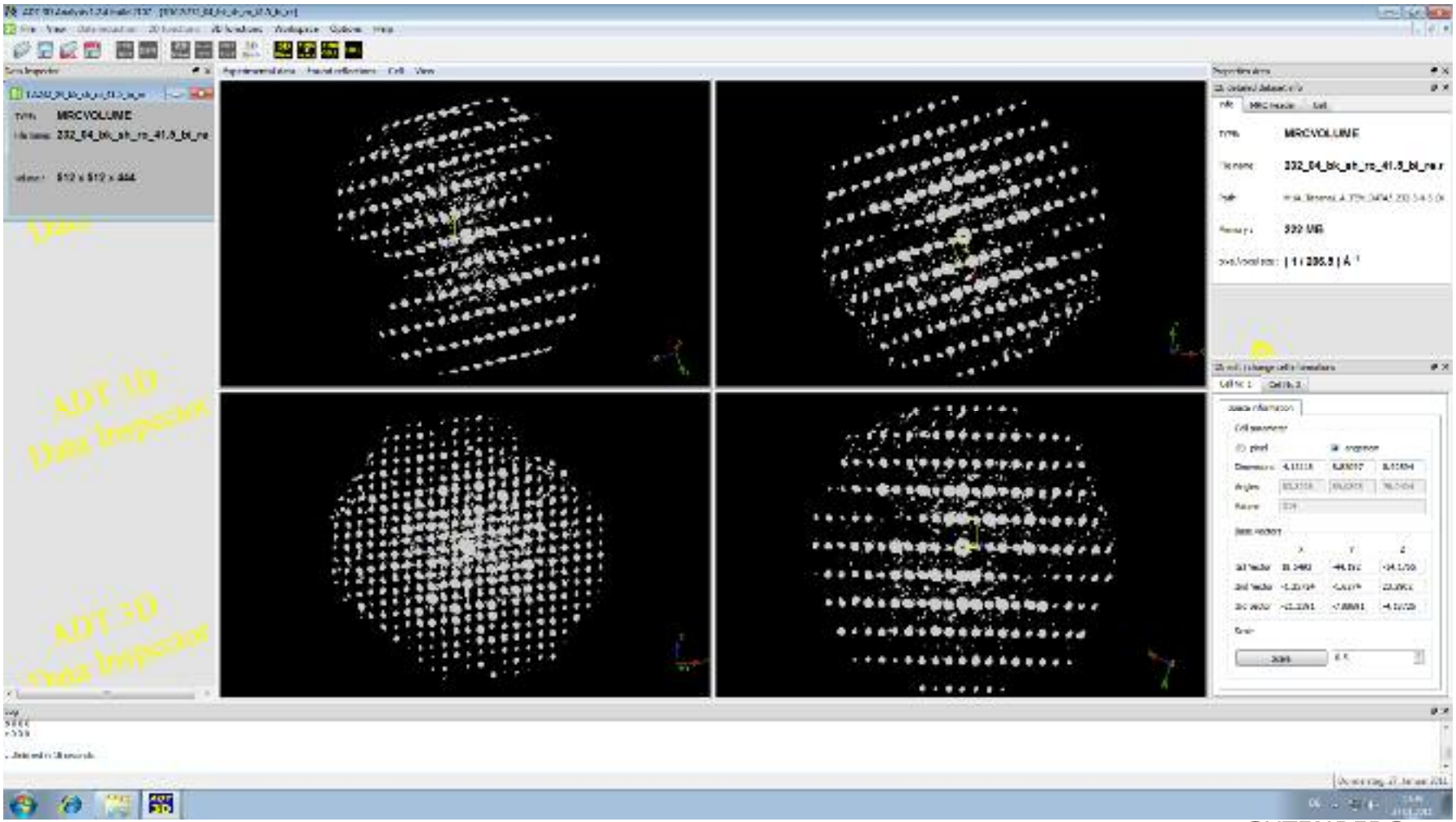
Automated electron Diffraction Tomography (ADT):
collection of the complete reciprocal data rather than zonal patterns



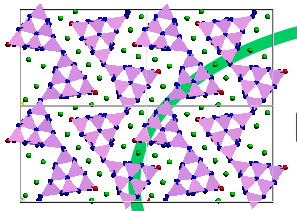


Towards automated diffraction tomography. Part II - cell parameter determination
U. Kolb, T. Gorelik, M.T. Otten, Ultramicroscopy, 108, 763-772 (2008).

Automated electron Diffraction Tomography (ADT):
collection of the complete reciprocal data rather than zonal patterns

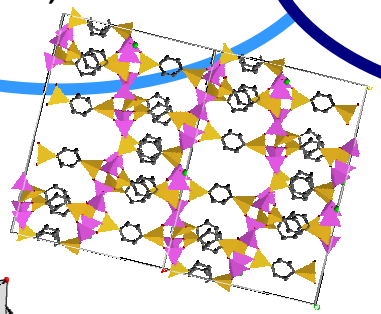


MORE THAN 30 STRUCTURES ARE SOLVED FROM ADT DATA BY NOW (16 OUT OF THEM - NEW)

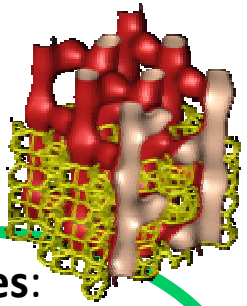


Phosphates:
SrP_3N_5O
$Ba_6Br_3P_{12}N_{17}O_9$

Organic-inorganic hybrids:
ECS3, ECS5

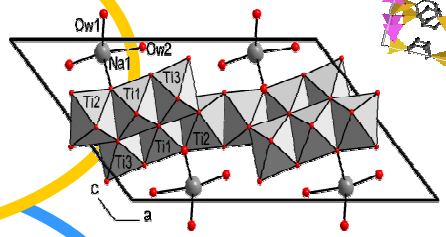


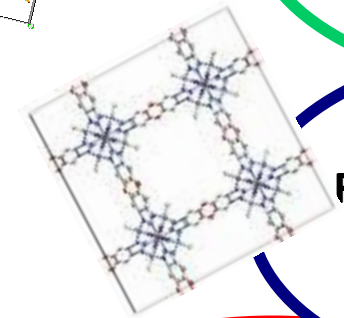
Organic:
NLO-active material
Organic pigments
Amides



Zeolites:
ZSM-5 ($Na_xAl_xSi_{96-x}O_{192}$)
Natrolite $Na_2Al_2Si_3O_{10}\cdot 2H_2O$
IM-5
RKL 040

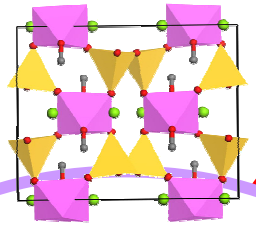
Oxides:
$Na_2W_4O_{13}$
$Li_2Ti_3NiO_8$
$NaHTi_3O_7\cdot H_2O$
$Na_2Ti_6O_{13}$





Metal Organic Frameworks (MOF):
MUF-4l
Basolite

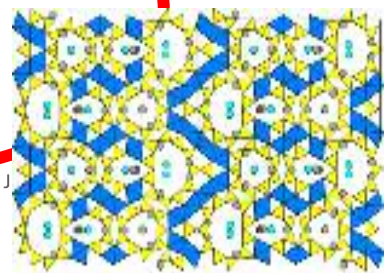
Intermetallic nanophases:
ZnSb, Zn_8Sb_7



Ca-compounds:
Calcite, Vaterite
Calcium silicate hydrate
$Ca_5Si_6O_{17}\cdot 5H_2O$

High pressure phases:
HP hydrous Al-pyroxene
$(Mg_2Al(OH)_2AlSiO_6)$

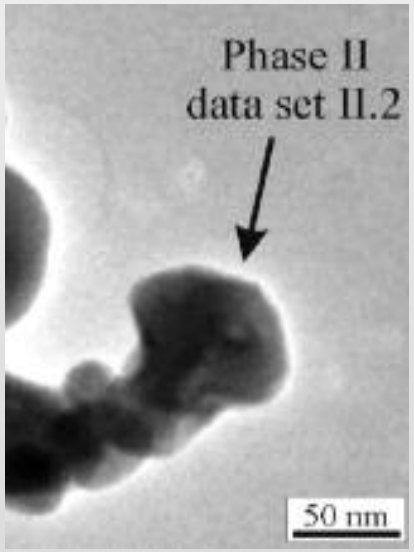
Minerals:
Mullite $Al_6Si_2O_{13}$
Sarrabusite
Charoite-96
Charoite-90



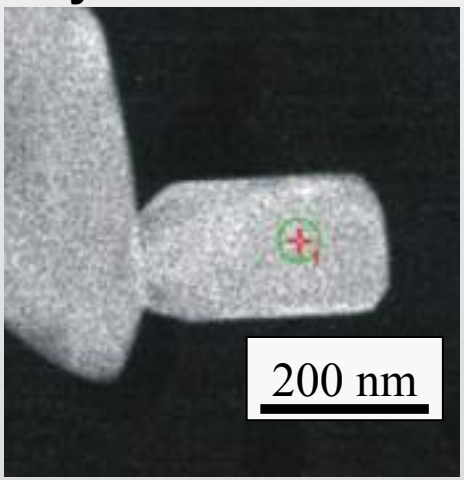
AUTOMATED ELECTRON DIFFRACTION TOMOGRAPHY

small crystals

Zn_8Sb_7 ~40 nm

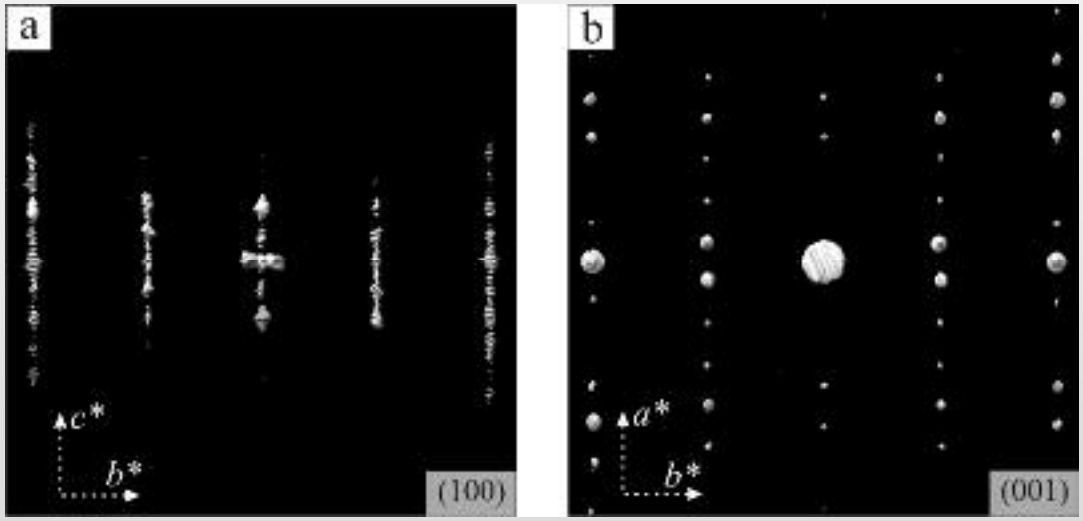


agglomerated crystals



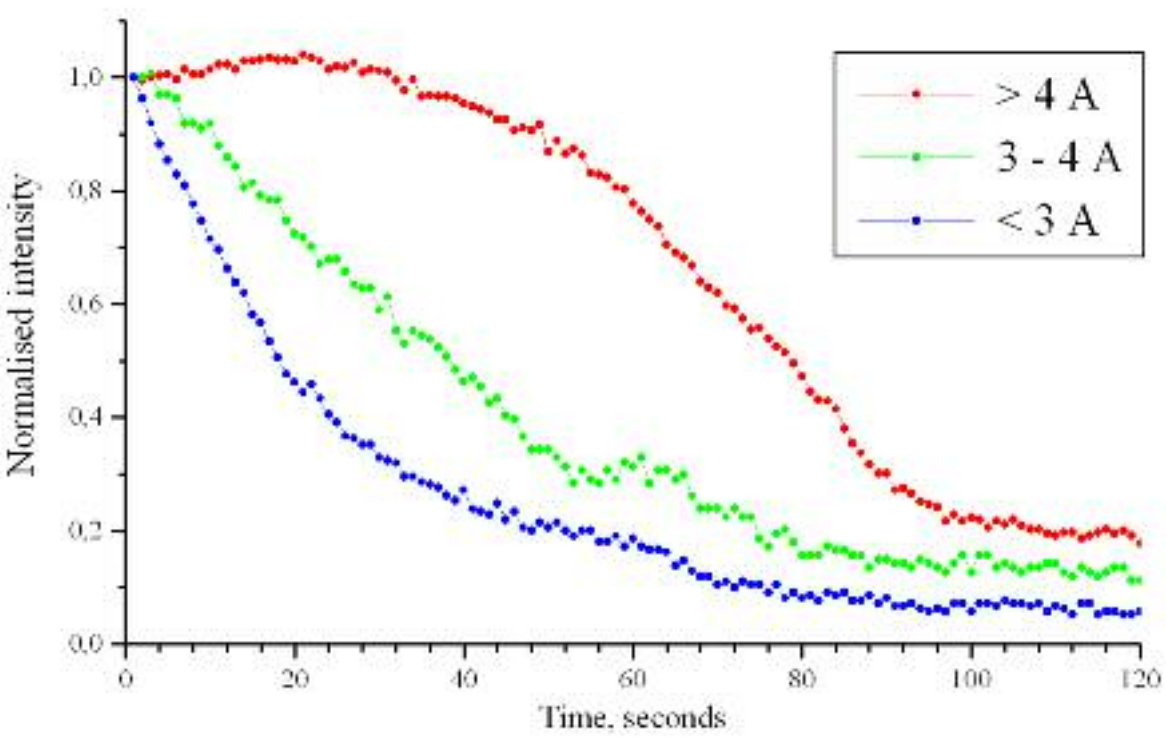
radiation damage

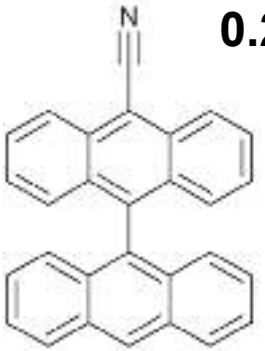
disorder

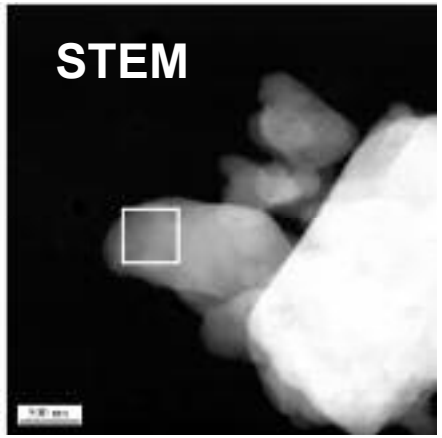


Radiation damage: CNBA

e-dose rate:
0.2-0.3 e/A^{2}s







STEM vs. TEM;
Distribute the dose (crystal bending!);
Cool the sample

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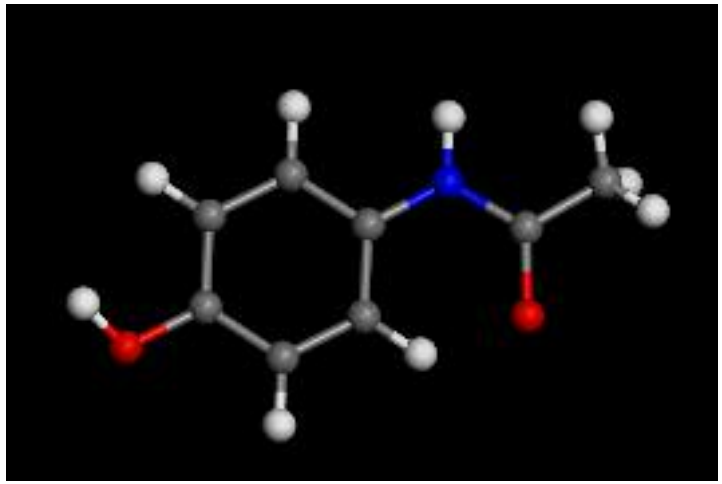
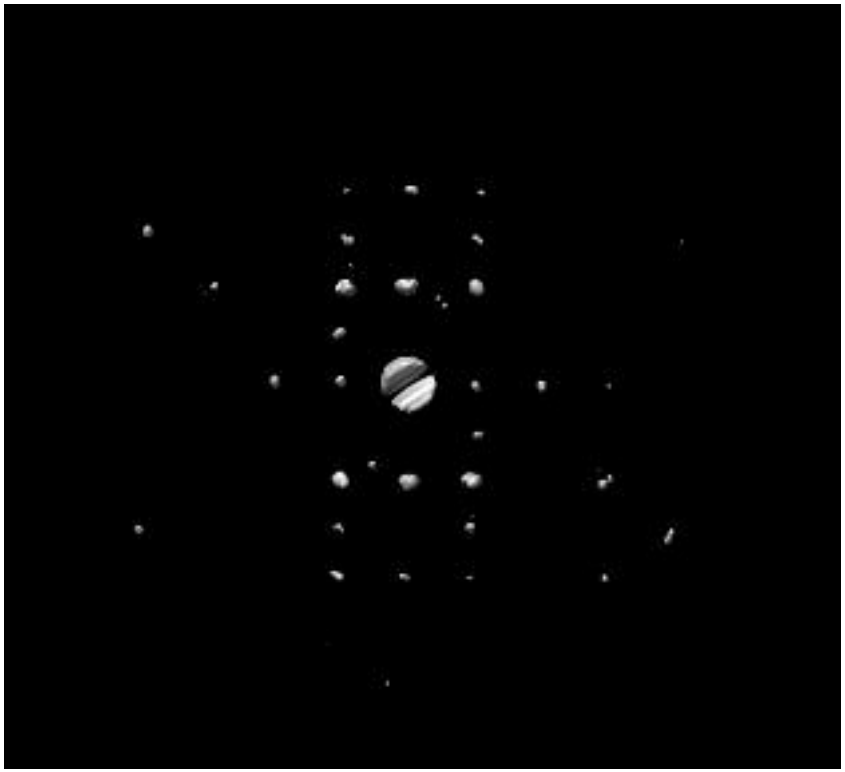
ADT: UNIL CELL PARAMETERS DETERMINATION

Orthorombic paracetamol (Pcab)



ADT	As given by Haisa et al., 1974
11.4 A	11.805 A
17.4 A	17.164 A
7.6 A	7.393 A
90.1°	90°
90.0°	90°
88.1° *	90°



Projection (010): extinctions along c* direction (b-glide plane)

Material provided by Elena Boldyreva, Novosibirsk State University

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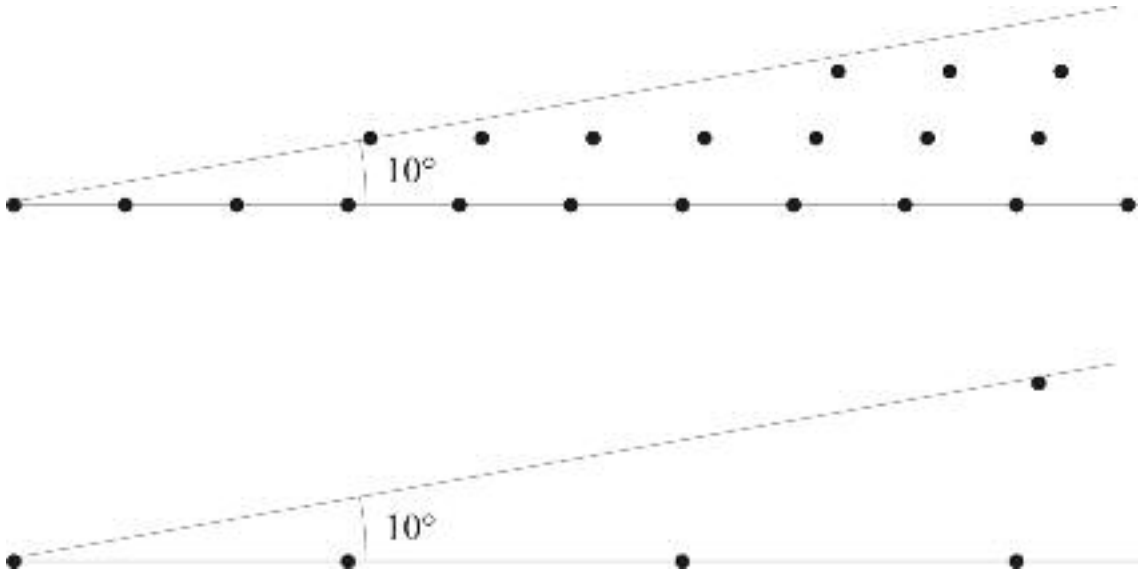
Orthorombic paracetamol (Pcab)



on

90.0°	90°
88.1° *	90°

Material provided by Elena Boldyreva, Novosibirsk State University

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Communications

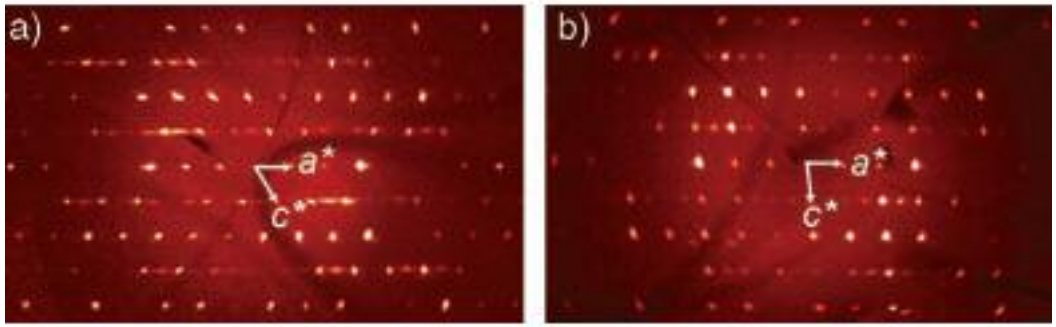
Polymorphism

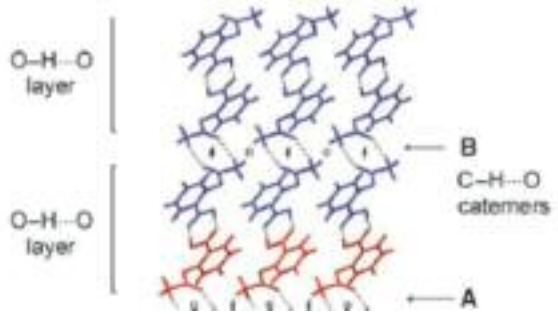
Angew. Chem. Int. Ed. 2007, 46, 618–622 DOI: 10.1002/anie.200603373

On the Polymorphism of Aspirin: Crystalline Aspirin as Intergrowths of Two "Polymorphic" Domains**

Andrew D. Bond, Roland Boese,* and Gautam R. Desiraju**

In the preceding paper, we highlighted the ambiguity that exists in the literature concerning the nature of crystalline aspirin.[1] In 2004, Ouvrard and Price demonstrated computationally that the long-established aspirin crystal structure[2–4] was amongst those predicted to be most stable, but they identified a slightly more stable structure as the thermodynamic minimum.[5] At the time, it was unclear whether the forms (Figure 1). In form I, the layers are arranged so that C–H···O interactions form centrosymmetric dimers (arrangement **A**, Figure 1). In the proposed form II, adjacent layers





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Conclusion

Caution during data acquisition

Lattice cell parameters determination is always possible …

Alternative structure solution approaches for medium-resolution data

Direct methods structure solution for high resolution data

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