Electron Crystallography and Precession

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Electron crystallography

Electron crystallography is the study of crystalline (in a wide sense) compounds by electrons. Compared to X-ray crystallography, electron crystallography has several important advantages;

a) electrons (unlike X-rays) can be focused into an image, allowing microscopy

b) due to the much stronger interaction of electrons with matter, samples millions of times smaller than those needed for X-ray crystallography can be used, allowing real nano-samples to be studied.

The back-side of using electrons is that this strong interaction can lead to multiple scattering even in very thin samples, which can make the information hard to interpret.

Electron crystallography

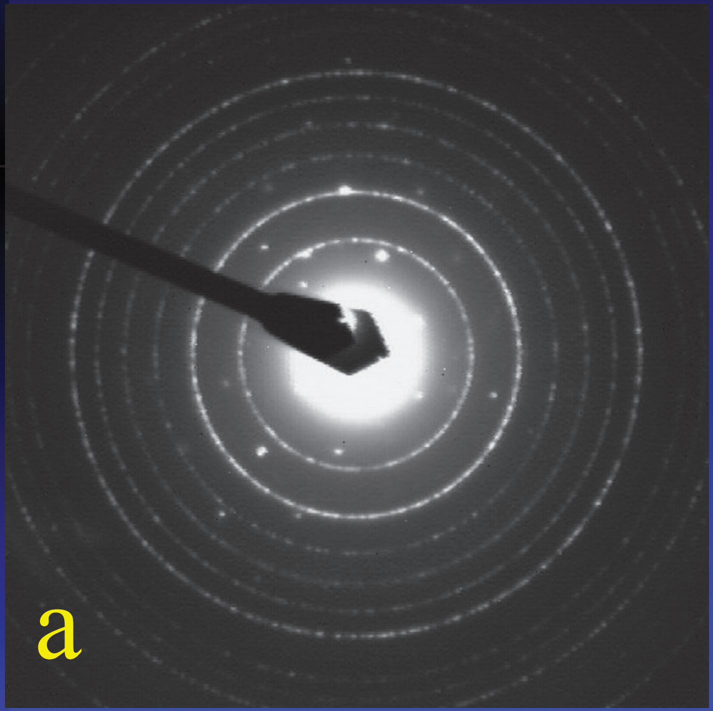
Roughly speaking, we may divide electron crystallography into two main categories;

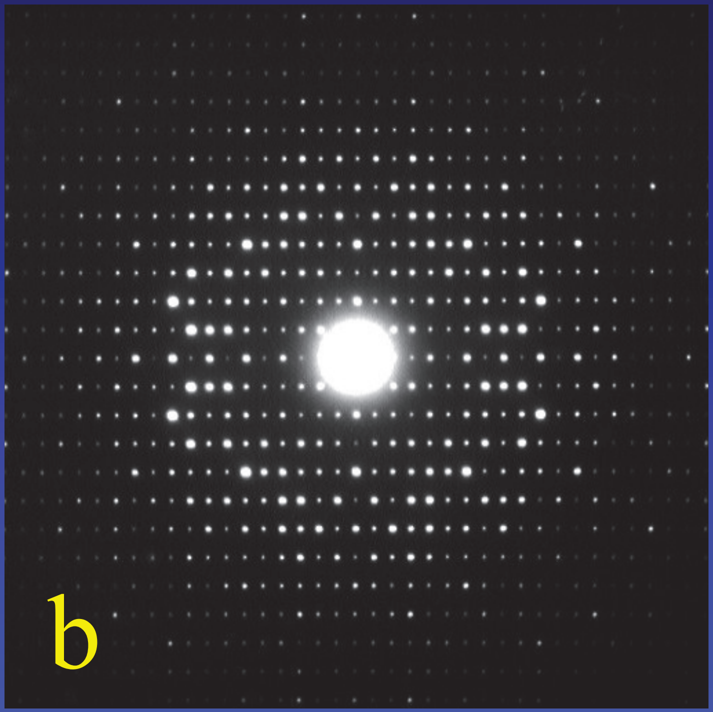
1. Identify known phases
2. Determine 3D structure of new unknown phases

While the first is of more interest to industry, the second is more exciting in academia.

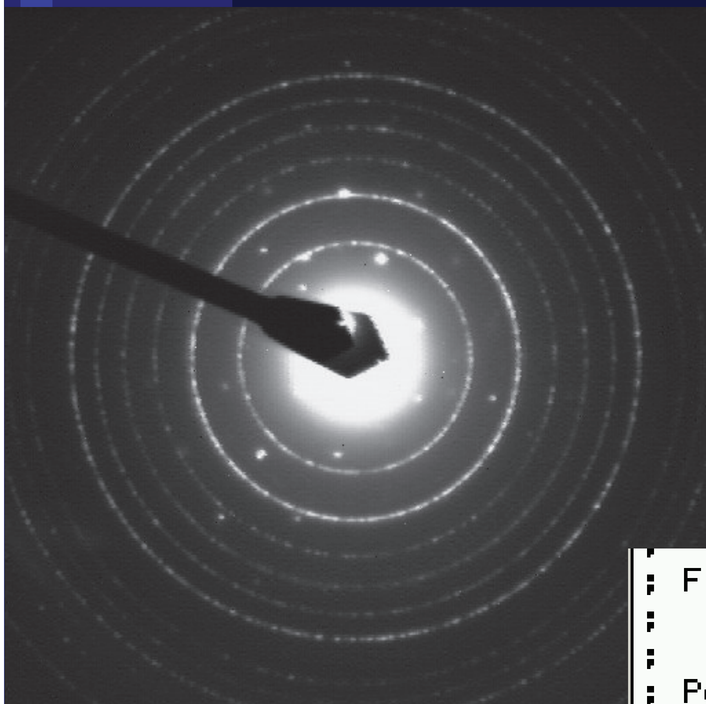
1. Identify known phases

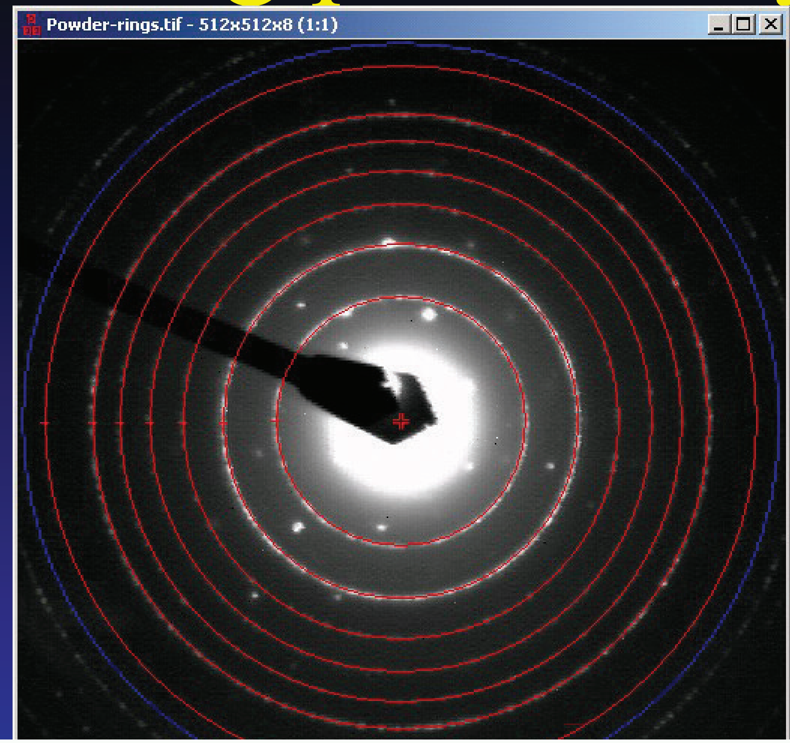
a. Multiple crystals ”powder” diffraction
b. Single, individual crystals





Quantify powder ring patterns by ELD



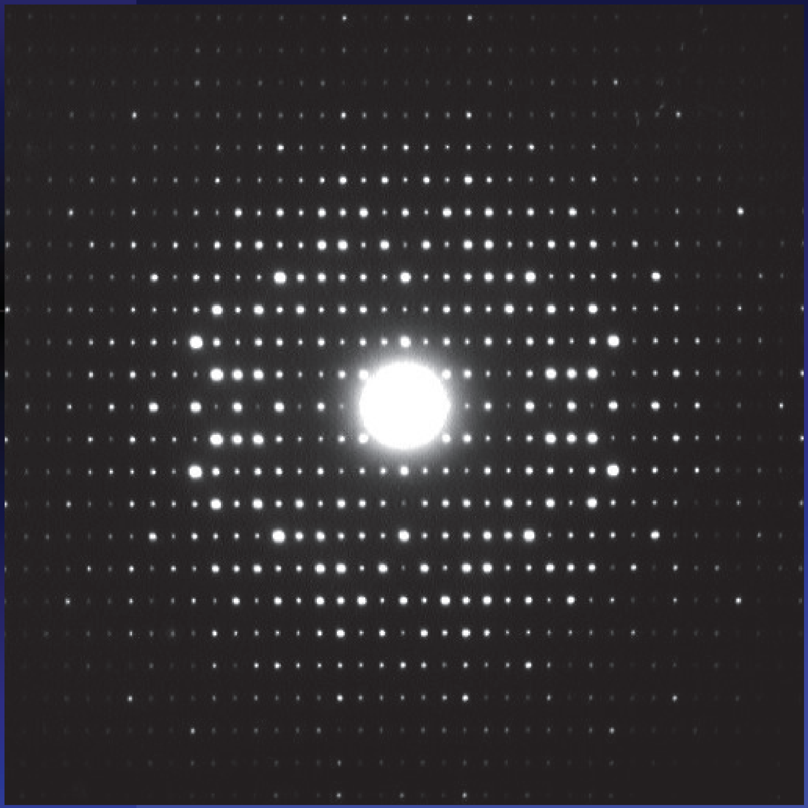


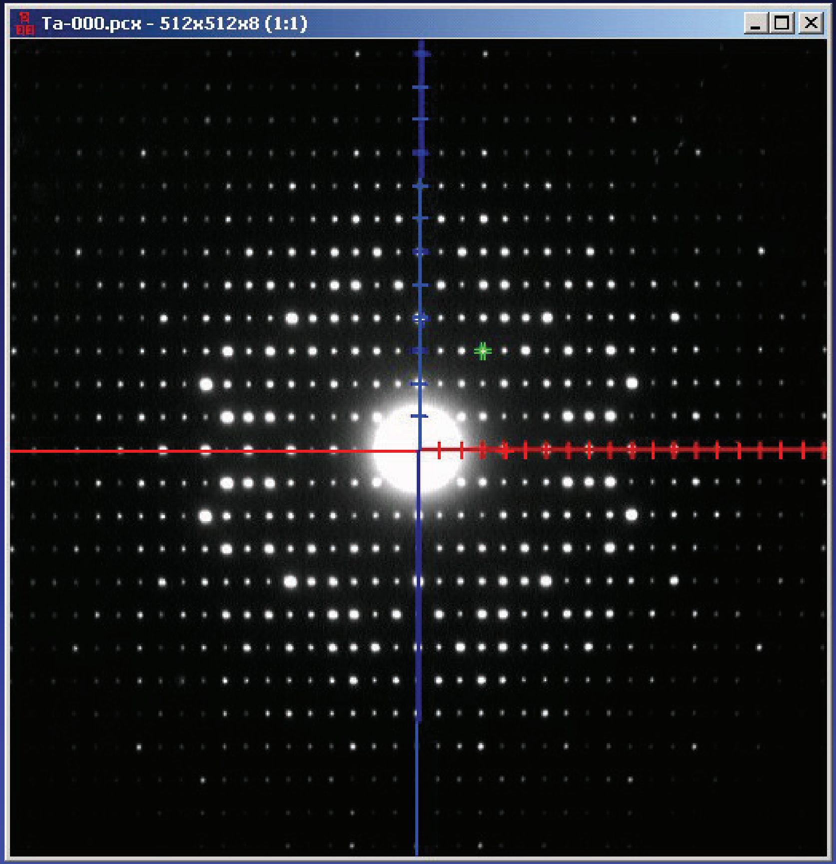
; File : C:\Program Files\Calidris\CRISP\Sample Images\Powder
;
;

; Peak ;number	Radius pixels	d-value (Å)	Width pixels	Width (Å)	Int.	Scaled intens
1*	83	4.1181	2.04	0.10	164	5414
2*	118	2.8997	2.04	0.05	304	10000
3*	144	2.3666	2.04	0.03	38	1251
4*	167	2.0500	2.04	0.02	46	1524
5*	187	1.8314	2.04	0.02	42	1397
6*	205	1.6704	2.04	0.02	119	3921
7*	237	1.4442	2.04	0.01	17	560

Single, individual crystals

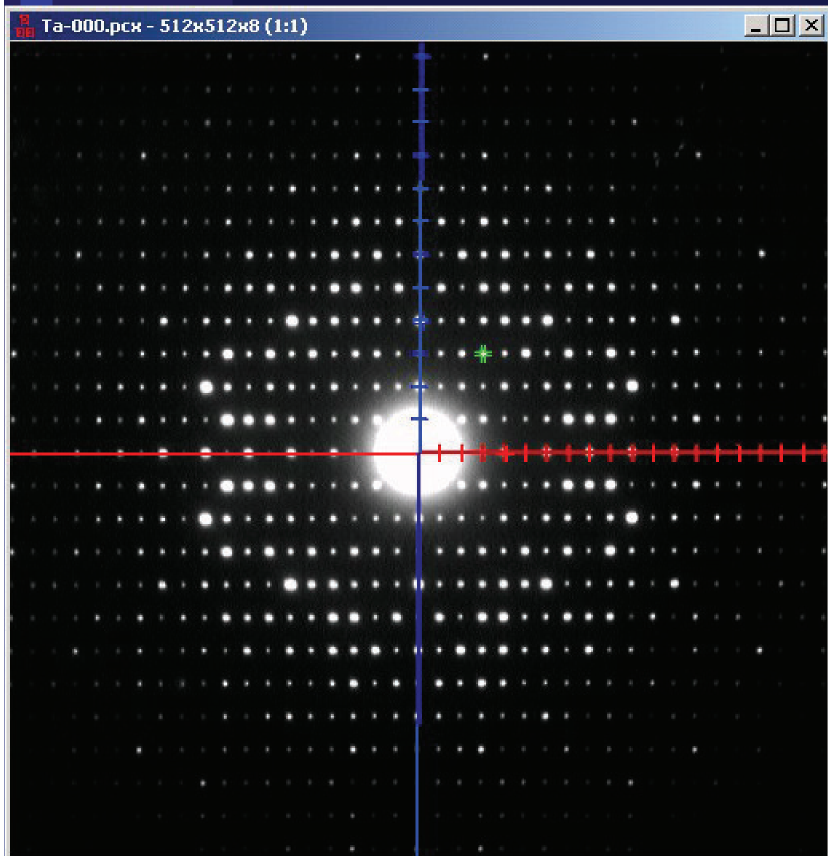
First: find the crystal axes directions and unit cell dimensions

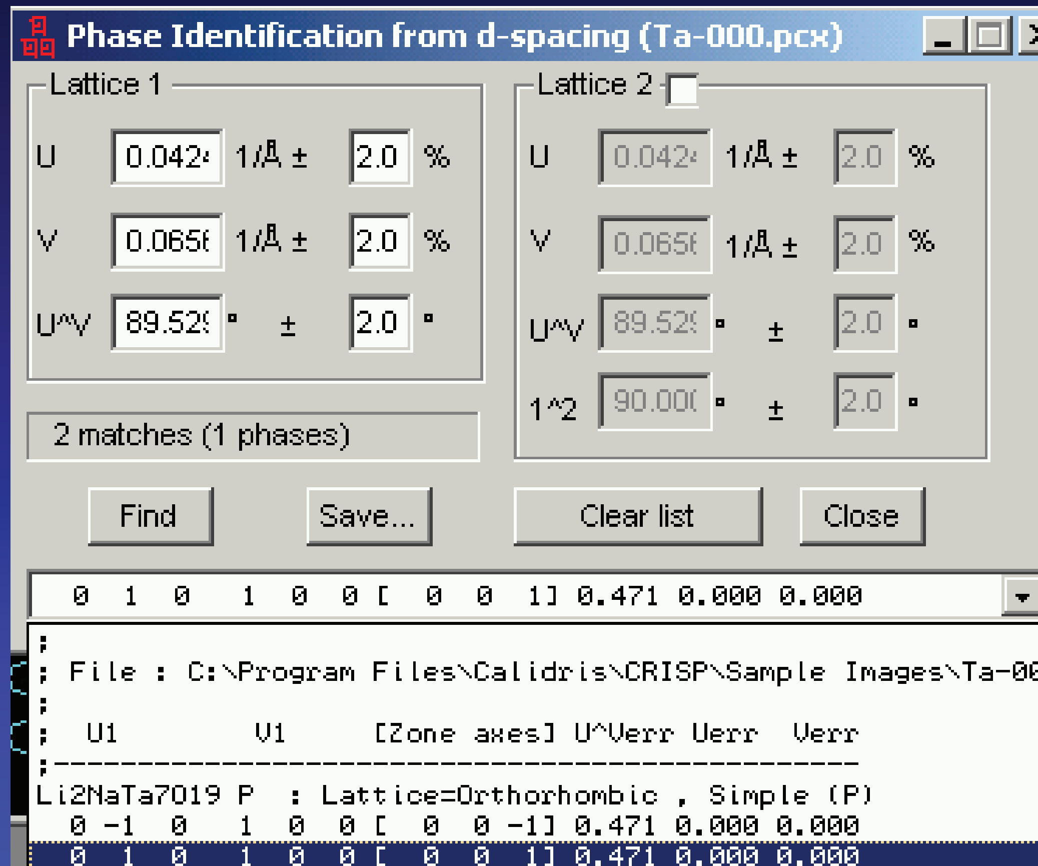




Single, individual crystals

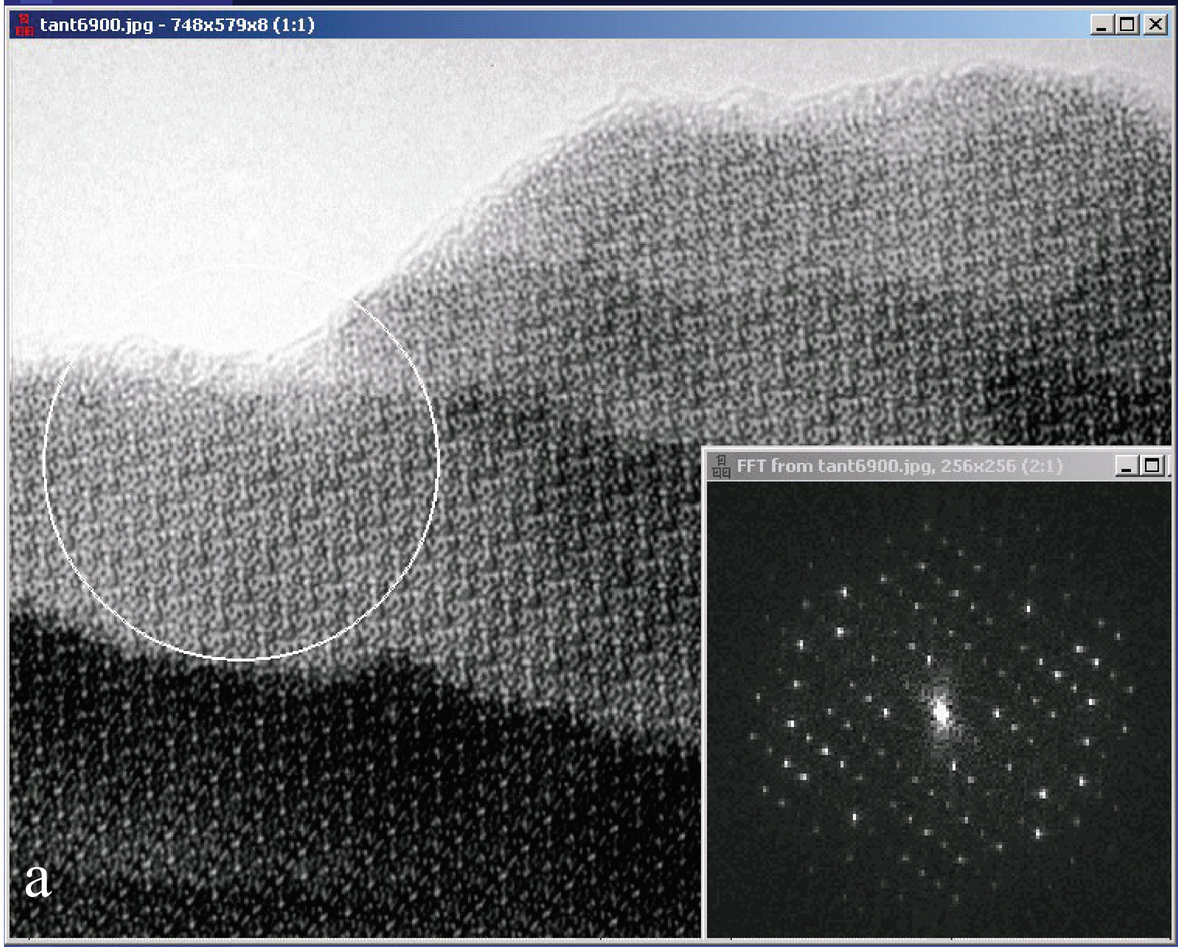
Second: identify the phase and orientation, using PhIDO

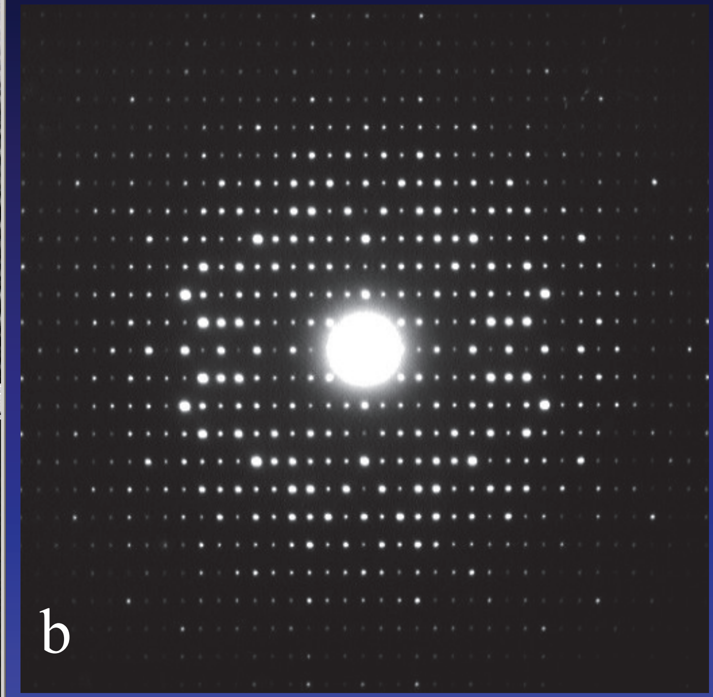




New, unknown phases:

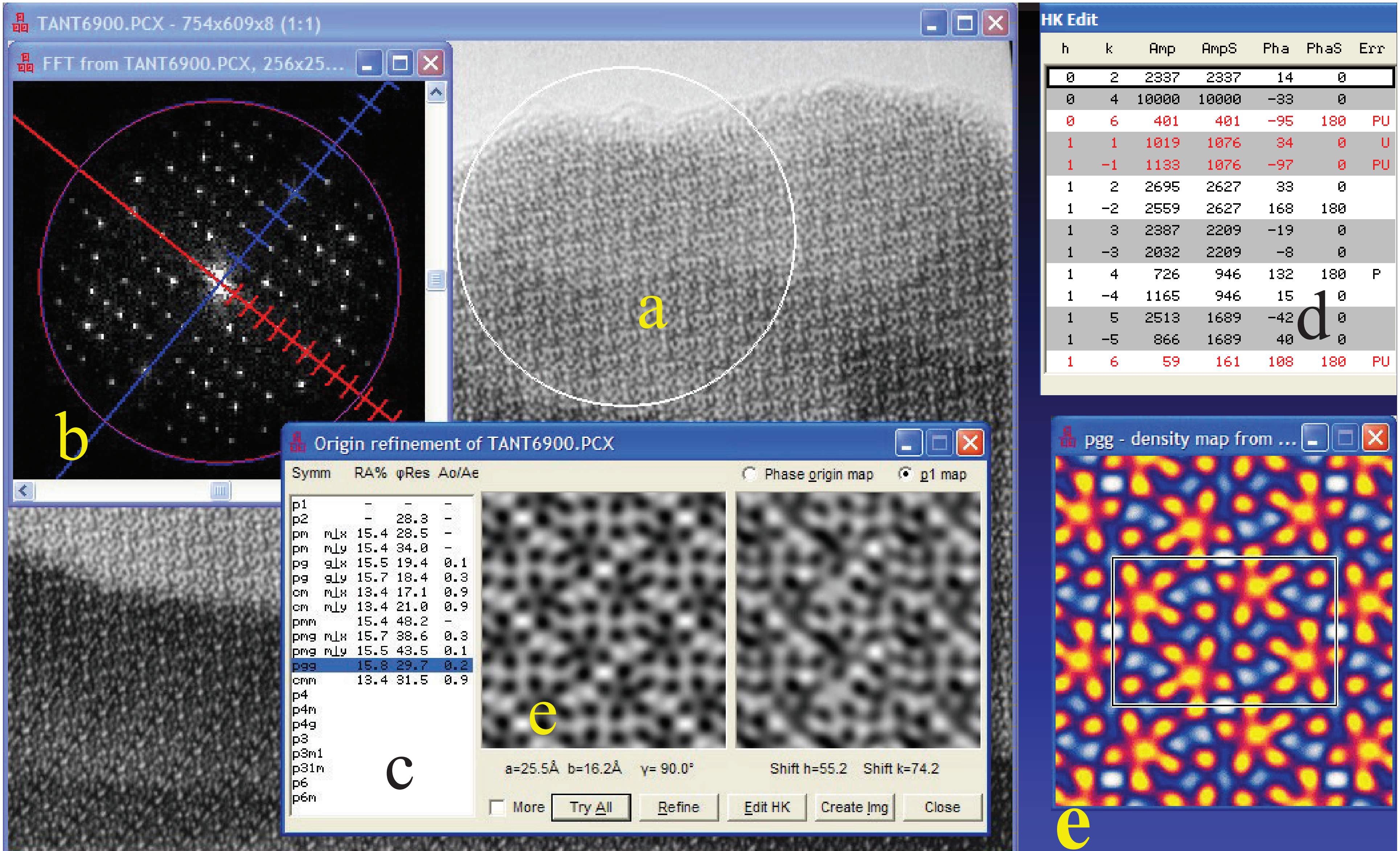
Structure determination from single crystals using EM images and/or electron diffraction patterns





a) EM images contain the crystallographic structure factor phases needed for solving a crystal structure

b) X-ray and electron diffraction (ED) patterns lack the phase information, but go to higher resolution than EM-images (~1Å rather than ~ 2Å).



a) EM image of a tantalum oxide with b) its Fourier transform (FT). The crystal lattice axes are marked red & blue. c) The crystal symmetry *pgg* is determined from the numerical phase values d) read out from the FT and imposed on the data, resulting in e) a solved structure. All Ta atoms are seen. The program CRISP from Calidris is used.

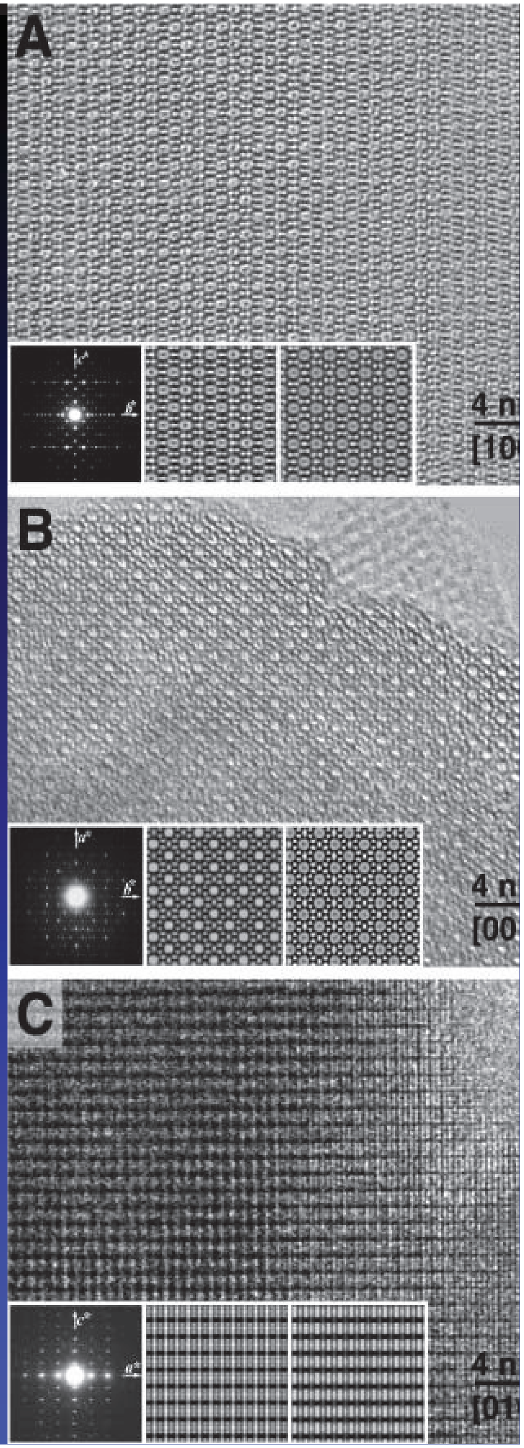
New, unknown phases:

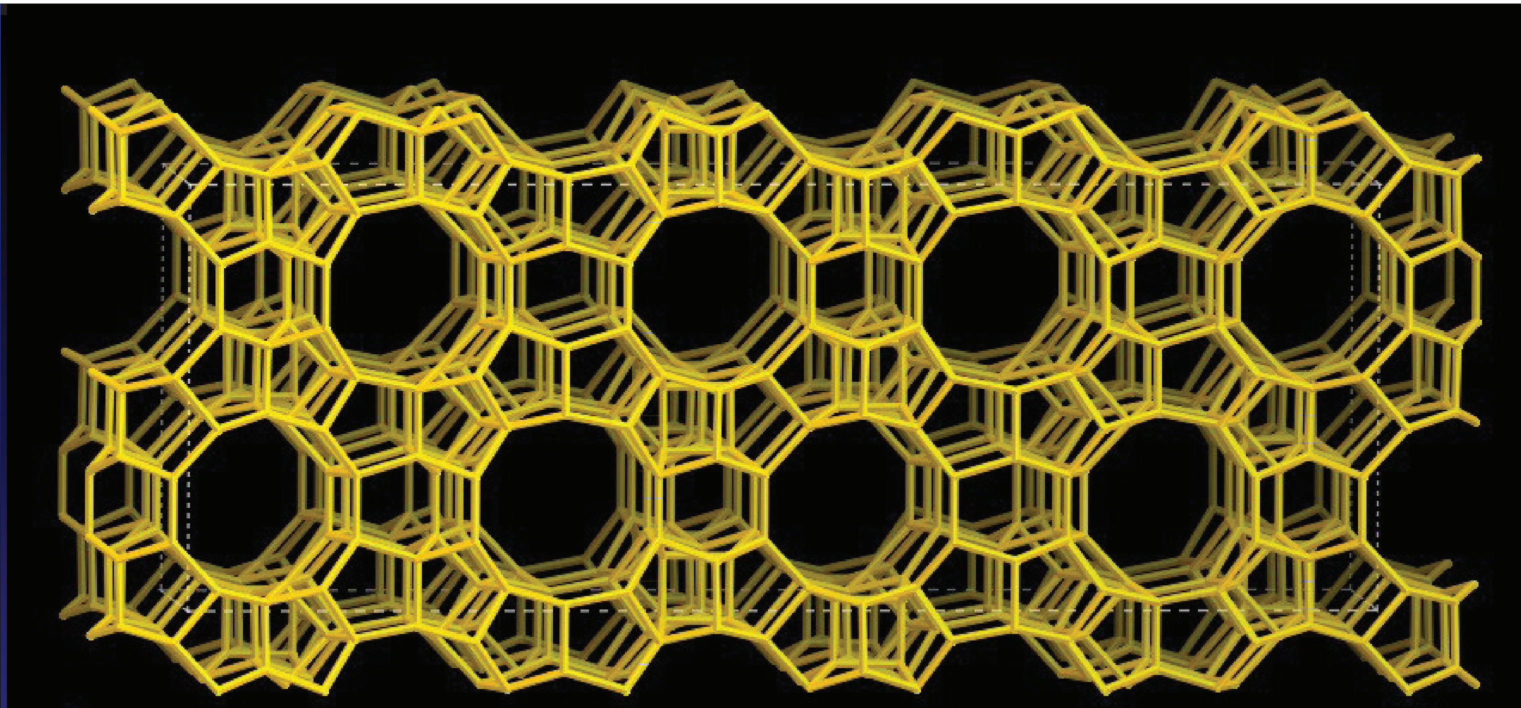
3D data (with phases) is needed for complex structures

Here a zeolite; a porous silicate, is solved from the 3 axial projections

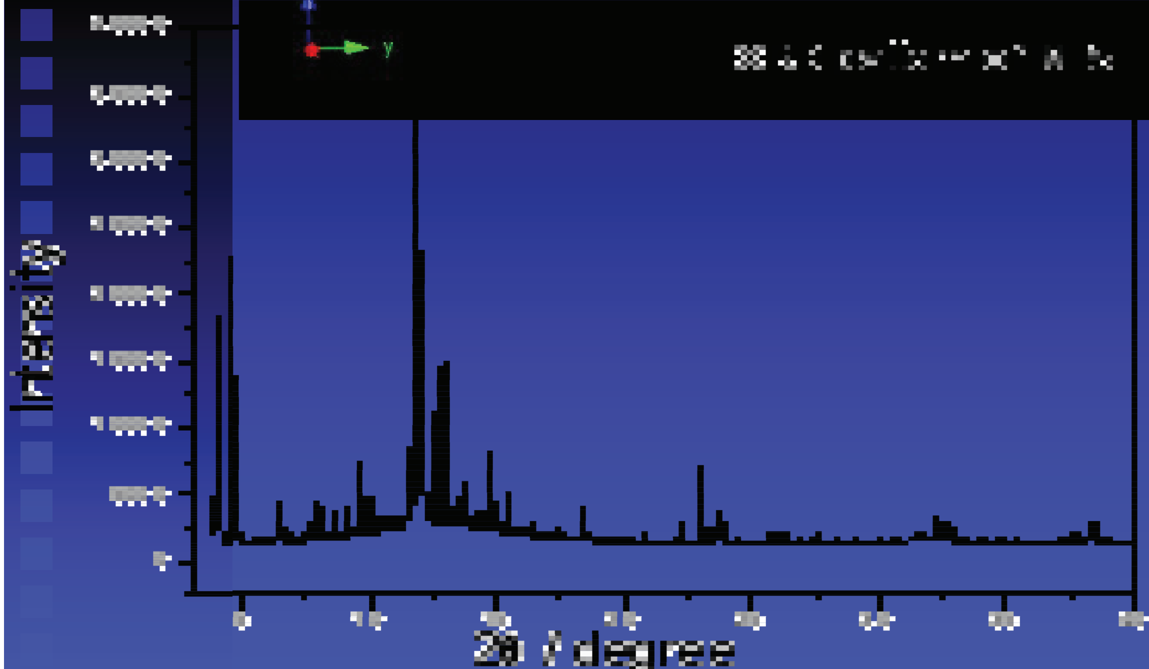
Baerlocher,C., Gramm,F., Massüger,L., McCusker,L.B., He, Z.B., Hovmöller,S. and Zou,X.D. Structure of the Polycrystalline Zeolite Catalyst IM-5 Solved by Enhanced Charge Flipping.

Science 315 (2007), 1113-1116





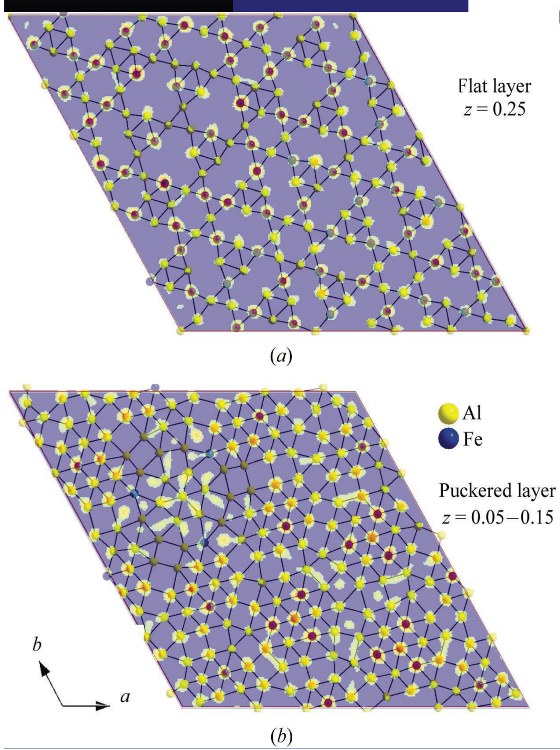
Above: One unit cell of the zeolite IM-5.

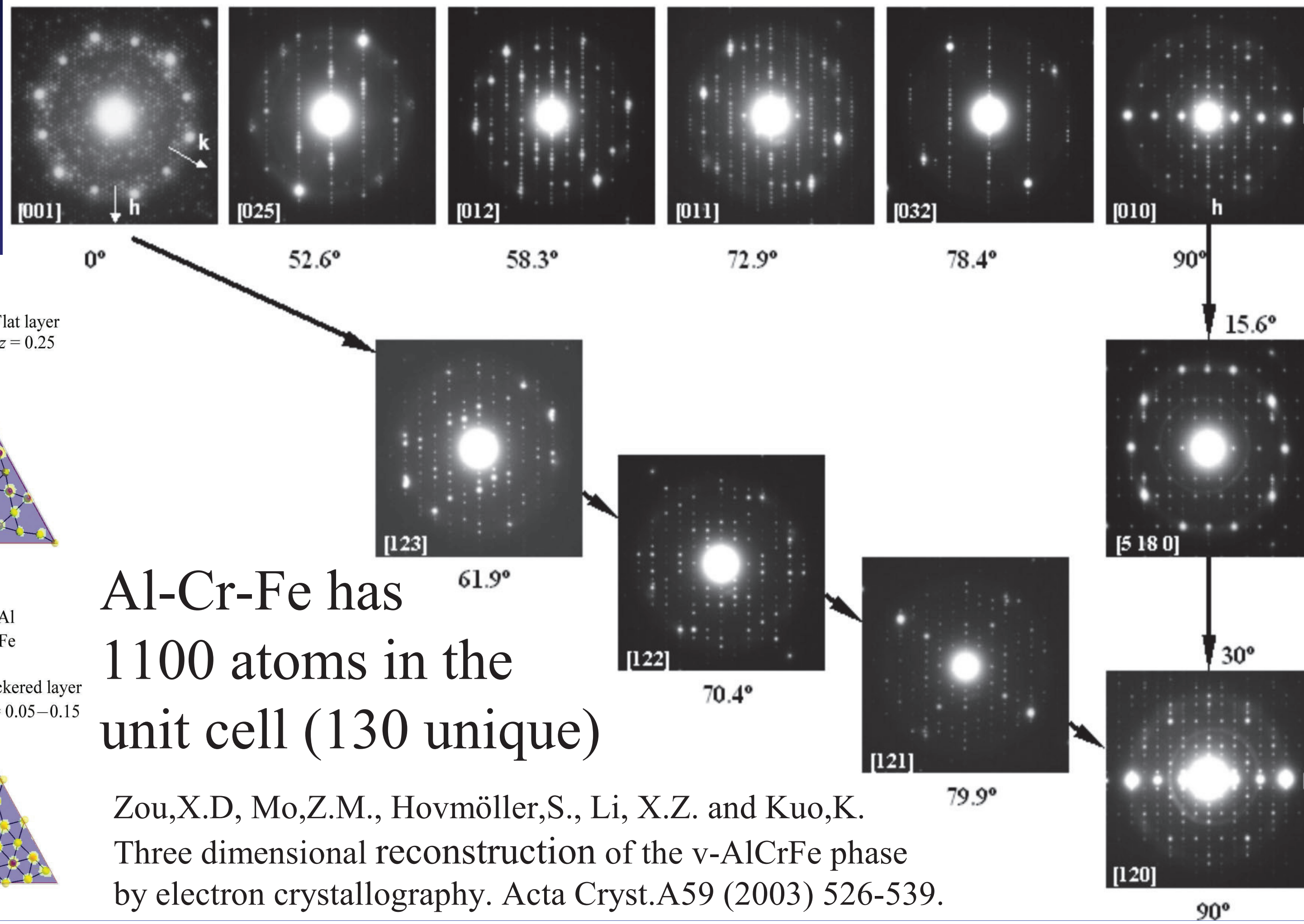


This structure could not be solved from the X-ray powder diffraction pattern (left) due to its complexity, but it was solved from EM images.

New, unknown phases:

Also EM and ED from diagonals are needed for solving very complex structures

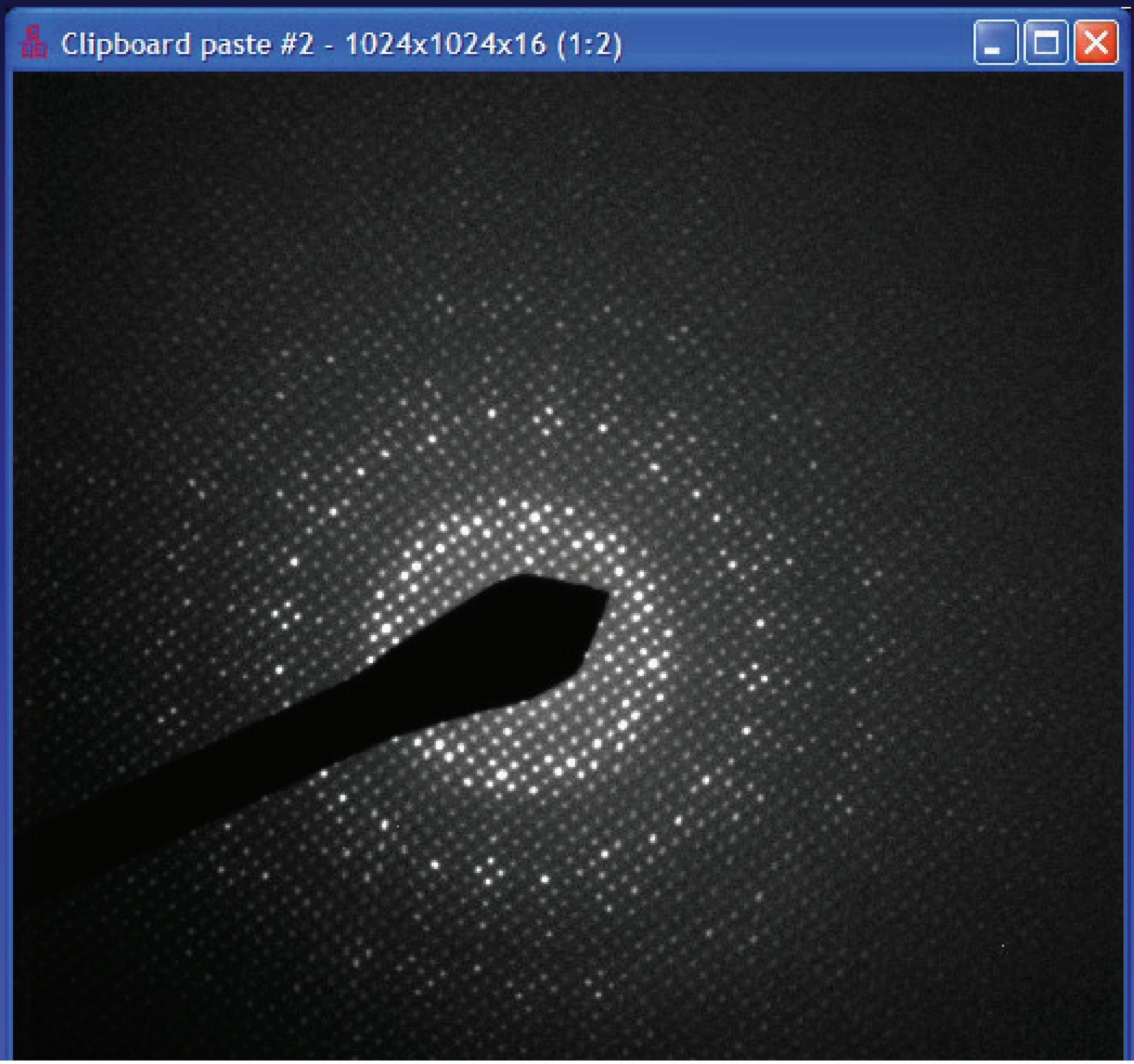




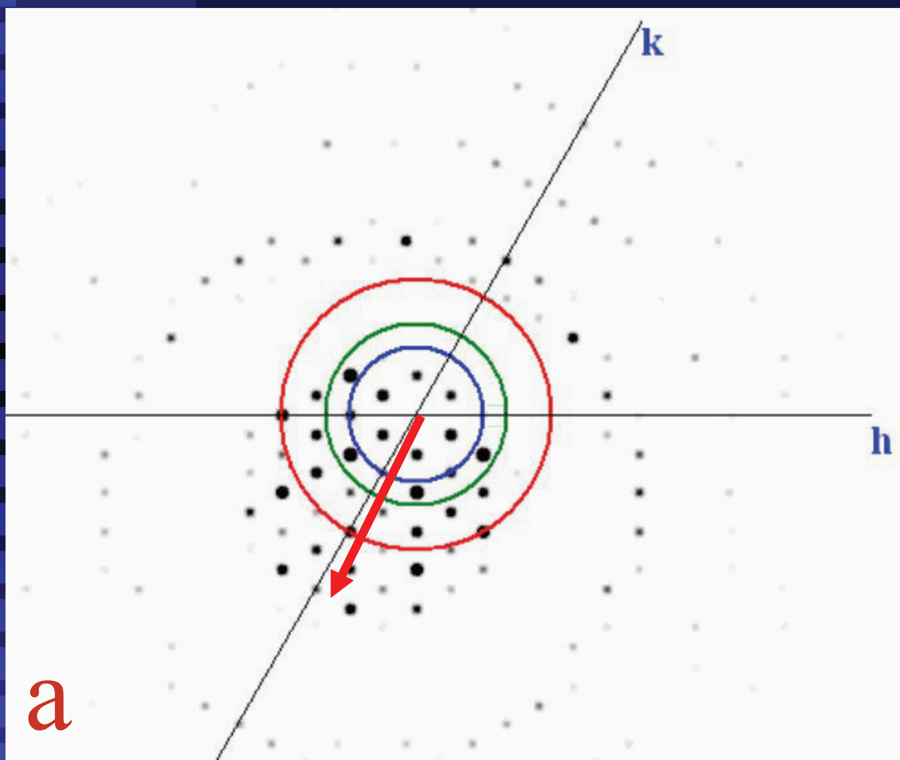
Al-Cr-Fe has 1100 atoms in the unit cell (130 unique)

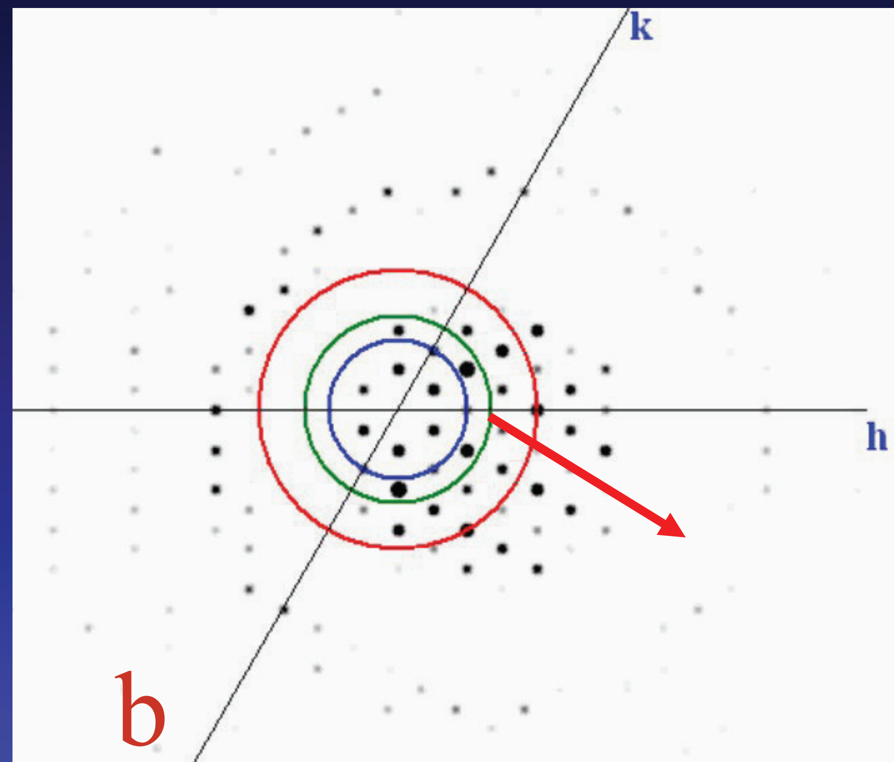
Zou,X.D, Mo,Z.M., Hovmöller,S., Li, X.Z. and Kuo,K.
Three dimensional reconstruction of the v-AlCrFe phase by electron crystallography. Acta Cryst.A59 (2003) 526-539.

A major problem in electron crystallography is how to avoid multiple scattering. Precession can help.

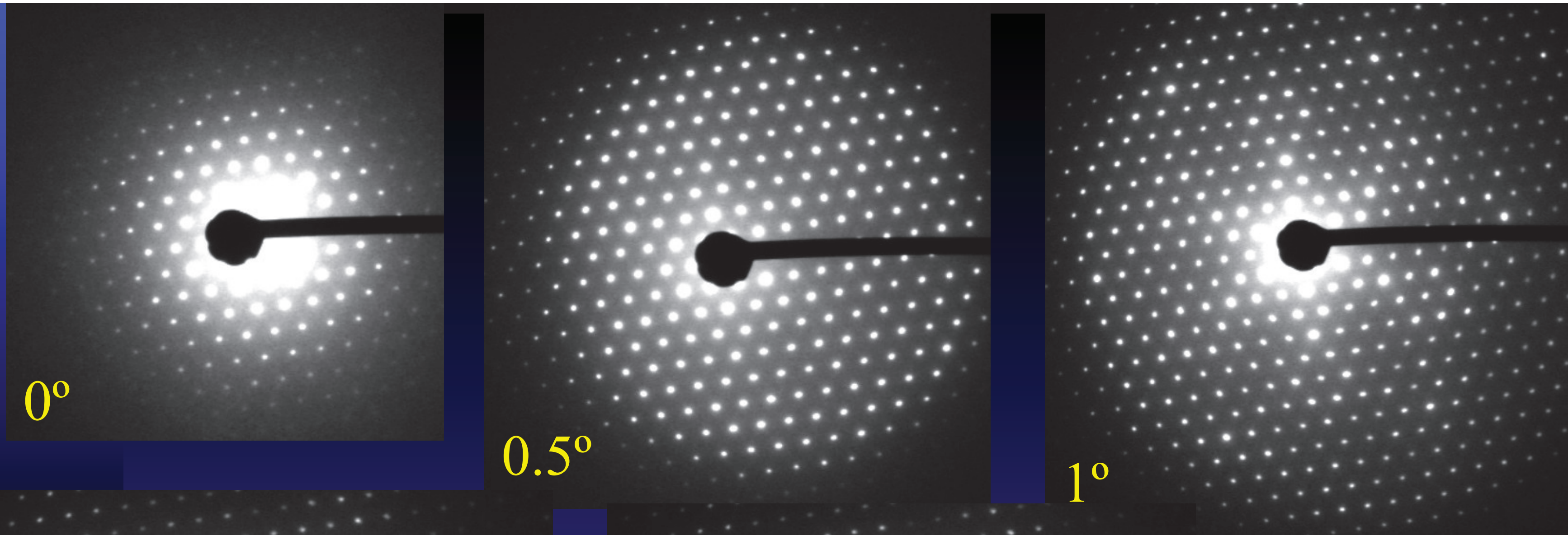


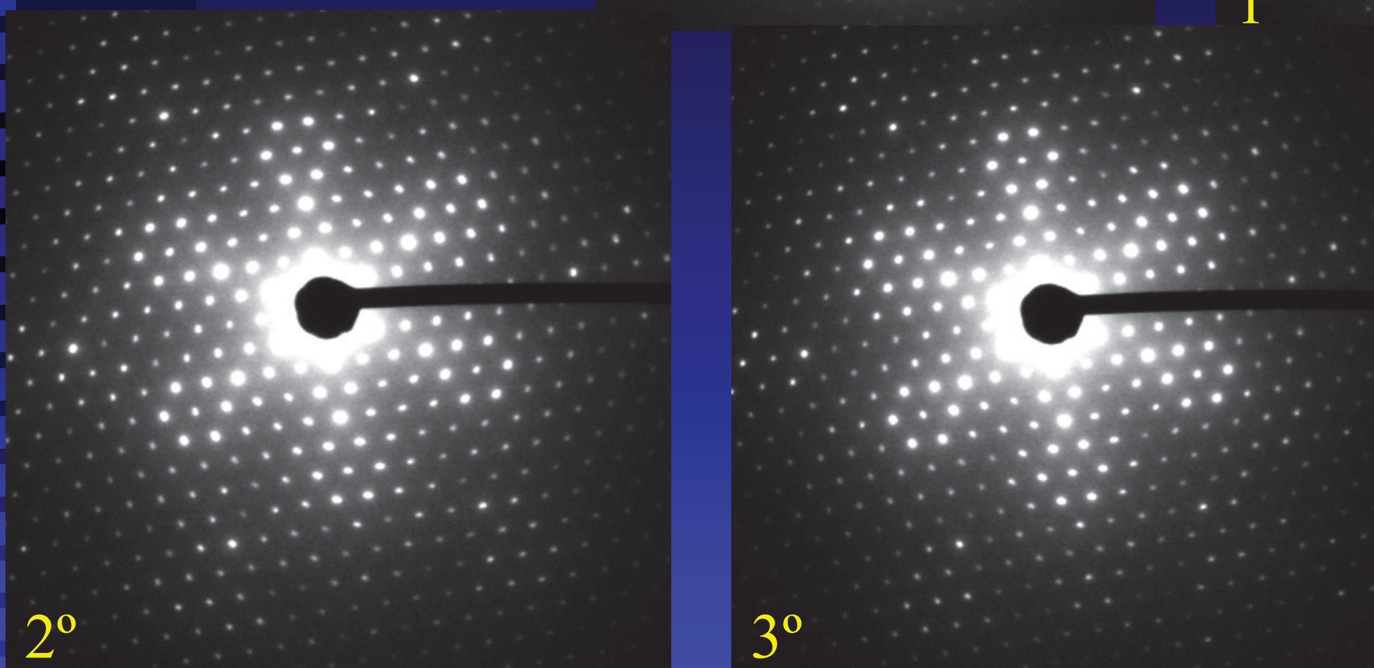
In precession, the electron beam is rotated in a conical way, such that a crystal aligned along a certain direction becomes misaligned (by up to about 3º). The rotation can be done at any speed, form 1 Hz to 100 Hz.





Here, the crystal is misaligned by about 1º along the direction indicated by the red arrows. The beam is rotated, so the final image becomes the sum of many different misoriented diffraction patterns.





As the precession angle increases from 0º to 3º, the diffraction pattern goes to higher resolution (i.e. more diffraction spots are seen).

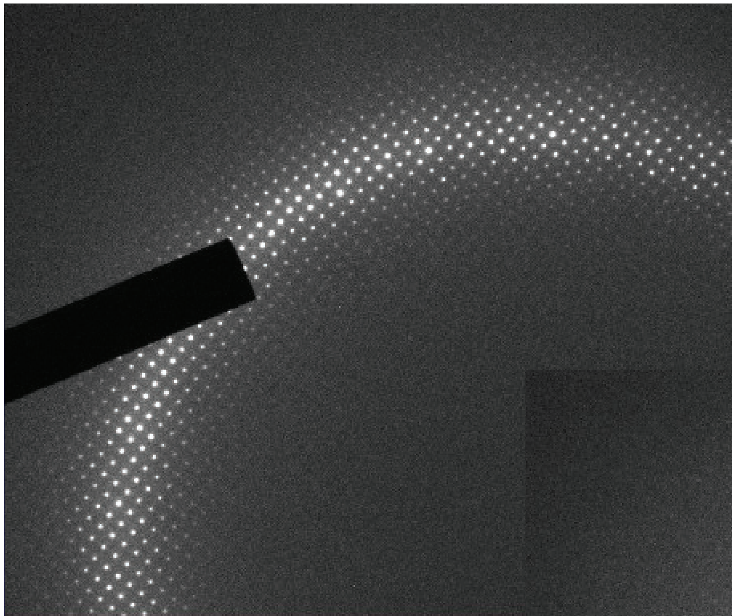
But most importantly: the relative intensities become evident. Notice how all intensities are equal in 0.5º; this is the situation of traditional electron diffraction (called SAED) – no structural information is present there.

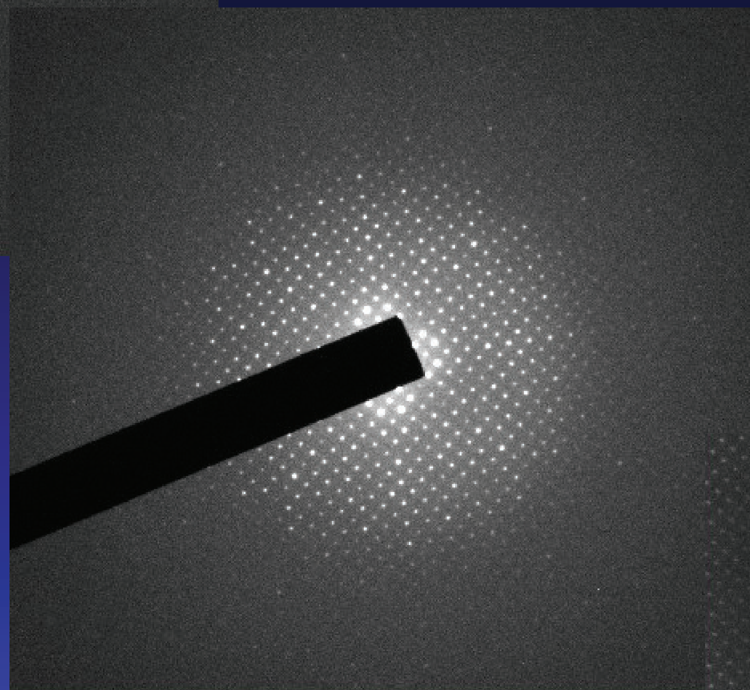
Precession or rotation patterns for 3D data sets?

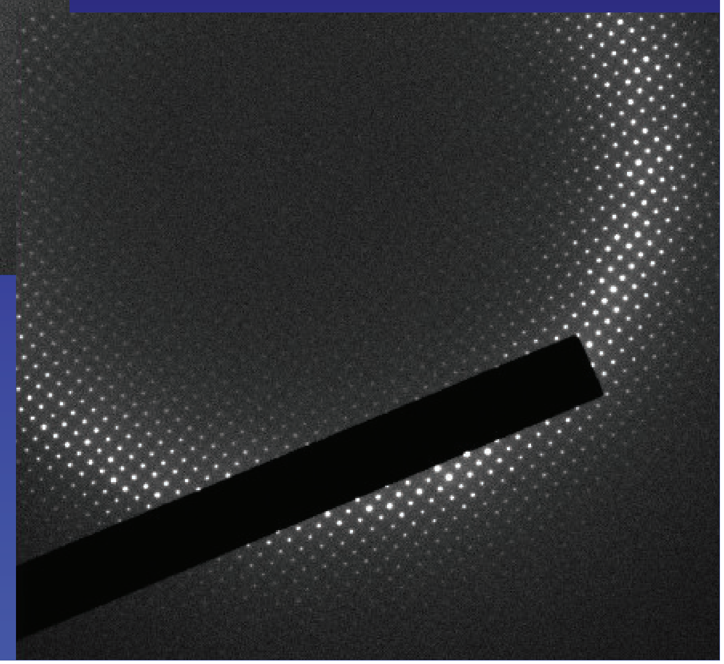
Precession is superb for obtaining high quality electron diffraction patterns from zone axes.

But for collecting complete 3D electron diffraction data, another method is needed; the rotation method. Here, either the crystal or the electron beam is rotated continuously over a large range, from for example 0º to 90º. For practical reasons, each frame may contain only a fraction of a degree. Several crystals (differently oriented on the grid) may be needed for collecting a complete 3D data set. The exact range of tilt angles needed for a complete 3D data set depends on the symmetry. Triclinic crystals need larger tilt ranges while cubic crystals need smaller tilt ranges.

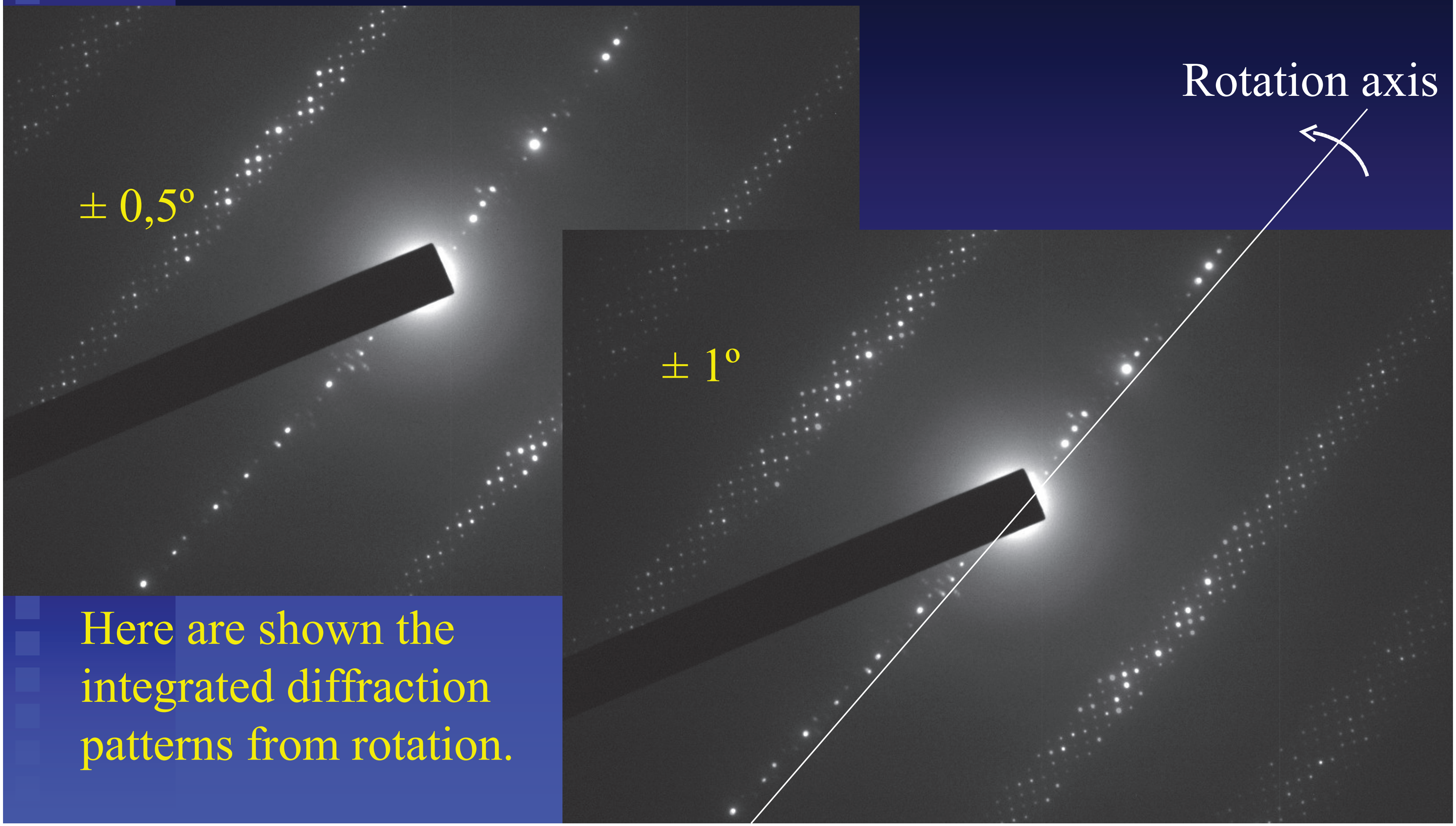
Individual frames of a rotation series







Collecting complete 3D electron diffraction data using rotation or tomography



Here are shown the integrated diffraction patterns from rotation.

Conclusions:

There are many new methods being developed within electron crystallography. These allow fast and accurate data collection, both for analysis of known phases and crystal structure determination of new, unknown compounds.

The new methods precession and rotation allow us to collect electron diffraction with less contributions from the unwanted multiply scattered electrons.

Acknowledgements

- Peter Olynikov: programming rotation
- Xiaodong Zou: crystallographic image processing and zeolites
- Daliang Zhang: rotation data movies
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