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Shifts:	**Local contact(s)**: J. Wright, G. Vaughan, C. Gundlach	*Received at ESRF:*

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Report:

This report summarizes key results over the last year within the scope of LTP ME1162. Significant progress has been made toward the development of improved high resolution detectors, including structured scintillators to improve efficiency as well as the design of a 3D detector to further the grain mapping technique towards highly deformed materials. Algorithm and software development has also progressed within the last year, and examples of work involving mapping of stress states in polycrystals and mapping of deformed microstructures is presented. Finally, highlighted experimental results are shown in the areas of grain rotation during plastic deformation, nucleation during recrystallization, and boundary migration.

Detector development

Structured scintillators

Currently high resolution imaging at synchrotrons is based on the use of detectors, where a homogeneous flourescence screen is coupled by microscope optics to a CCD. In the 30-200 keV range such detectors are fundamentally limited in terms of resolution and efficiency. As described in the last annual report, Risø and KTH Sweden are pursuing R&D in structured scintillators, in part funded by ID15. The scintillators comprise regular arrays of very deep and narrow pores in Si filled with CsI:Tl. The resulting structure acts as a waveguide to the light emitted, promising efficiency gains of one order of magnitude.

In 2008 a new procedure for making the pores (dry etching) was developed: this is better suited for upscaling the process. Batches with distances between pores of 1.4 μm and 4 μm and pore depths of 40-100 μm were succesfully tested at ID11 and ID15. The screens will be implemented in new detectors at both beamlines in first part of 2009. Other synchrotrons (APS, SPRING-8, PETRA, Maxlab, Diamond) have expressed an interest in this technology.

3D detector
During 2008 a high resolution 3D detector has been designed; the installation and commissioning of this detector on ID11 is planned for March 2009. The design will utilize 2 high resolution structured scintillators in series coupled to optics and CCD cameras at right angles to each other. Both screens will be semi-transparent to diffracted x-rays, which will allow a third larger area detector (Frelon) to be placed downstream. In this way, 2D images can be simultaneously recorded at three different distances from the sample. The detector is a joint ID11-Risø project, to which **Risø has contributed ~100 k€ - this investment is in addition to what was promised in the LTP.**

Combining the information gathered at all three detector distances during analysis will greatly enhance the capability of the 3DXRD microscope. In particular we expect the detector to facilitate fast and reliable 3D mapping of deformed microstructures. To our knowledge this is the first true 3D x-ray detector in the world. As such we see this as a prototype for other types of hybrid detectors.

Software development and demonstration

The ID11-Risø lead collaborative plan for 3DXRD related software development is detailed in the proposal for the EU grant: TotalCryst. In 2008 Risø contributed ~3 manyears. The plan and progress reports can be found at www.totalcryst.dk. The final result – the FABLE package - will be an integrated set of tools for analysing 3DXRD data on line and at home (preprocessing, indexing, structure solution & refinement, grain mapping, visualisation). The shareware runs on both LINUX and Windows, supports the use of clusters, and can be run both by command lines and using GUIs. FABLE programs and documents can be downloaded from http://fable.wiki.sourceforge.net/. A school aiming at introducing users to FABLE will be held at ESRF 1-4 April 2009.

Mapping the stress states of grains within polycrystals
A vast majority of all engineering metallic materials are polycrystalline, and due to elastic and plastic anisotropies between the grains residual stresses which influence the material properties develop during deformation. The residual stresses of type II - that is between the individual grains - are related to the elastic strain tensors of the grains via the stiffness tensor. The elastic strain tensors of grains embedded in the bulk of a polycrystalline material can be determined by means of 3DXRD microscopy with an accuracy of $\Delta\varepsilon = 10^{-4}$. However with existing software so far at most 10 grains have been analysed (Martins et al., Mat. Sci. Eng. 2004; A387-389:84.), where 100-1000 are required for typical applications.

To overcome this obstacle, in 2008 we developed a new algorithm FitAllB in collaboration with W. Reimars at TU Berlin (work funded by the BMBF, Germany)[1]. FitAllB fits the centre-of-mass grain positions, orientations and strain tensors for all illuminated grains (3+3+6 parameters per grain) based on 3DXRD farfield and (optional) neafield data. In addition the relative volumes of the grains are calculated based on the peak intensities, so using tessellation a 3D orientation and stress/strain map of the polycrystal can be obtained. A major challenge for the method is peak overlap, especially for textured and/or deformed materials. Experimentally this can to some extent be handled by scanning the sample with a line beam to reduce the illuminated sample volume. Initial tests on both simulated and experimental data have shown that even for moderately deformed materials 200 simultaneously illuminated grains can be handled. Running FitAllB takes less than a minute per grain.

In the first experiment FitAllB was used to determine the grain resolved elastic strain tensors for an IF steel sample at 0 and 3 % ex situ tensile elongation. Both near- and farfield 3DXRD data were collected for 1 mm of the sample using a beam height of 10 µm and mapping the layers consecutively. Fig. 1a shows the centre of mass of the identified grains in each layer in the undeformed state. As the grains are elongated along the vertical tensile axis a grain shows up as a necklace of similarly coloured points, where the colour is related to the grain orientation. In total about 2000 grains were mapped in the undeformed state. The centre of mass of these in 3D are shown in Fig. 1b. The map of the deformed state is more uncertain, but it was possible to identify with certainty 1200 matching grains between the undeformed and 3 % elongated state. Fig. 2a shows

[1] An alternative program for deducing the strains of individual grains has been made by J. Wright from ID11.

where these grains are positioned within the sample and how large the absolute values of the strain components along the tensile axis are for the undeformed state. Fig. 2b shows the same for the 3 % elongation. Note that the strain levels at 3 % elongation on average are substantially higher than for the undeformed state. Further analysis is in progress.

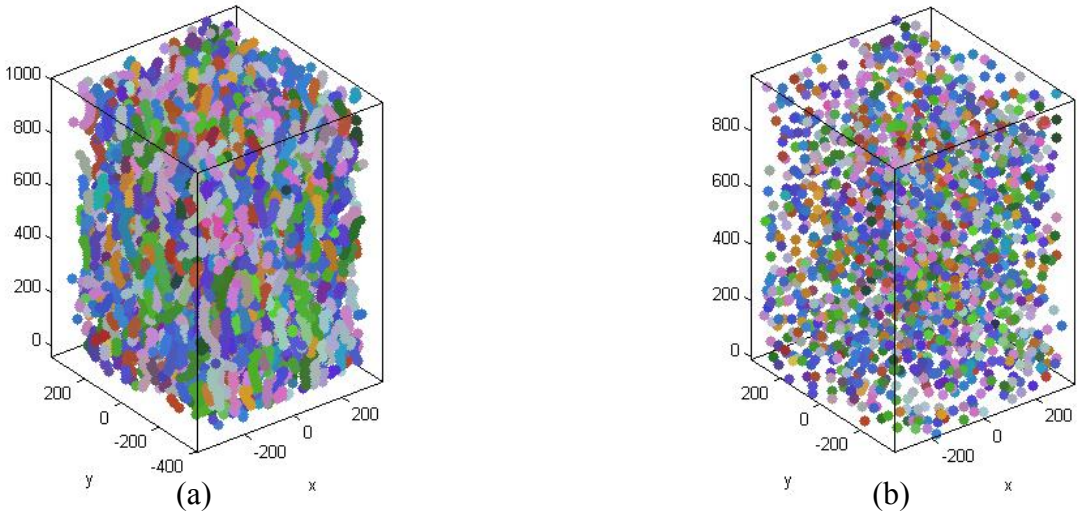


Fig. 1. Maps of grain orientations. a) Undeformed state. Centre of mass of each grain identified in consecutive layers with a height of 10 µm. Grains with different crystallographic orientation are coloured differently. b) Undeformed state. Centre of mass of the ~2000 grains in 3D. The units are in µm.

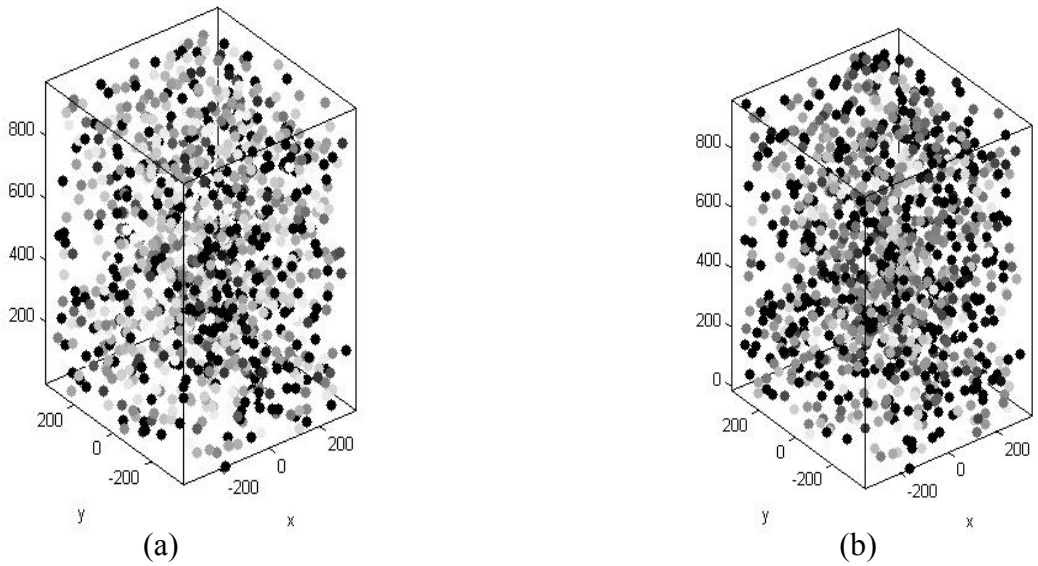


Fig. 2**.** Maps of grain strains. Centre of mass of about 1200 grains that can be matched at 3% elongation. Colour coding according to the absolute value of the strain component along the tensile axis. White corresponds to no strain and black corresponds to an absolute strain larger than 0.001. a) Undeformed state b) 3% strain.

3D orientation map of deformed specimens

Several programs have been developed for mapping the morphology of grains in 3D in undeformed specimen based on 3DXRD nearfield data. The GrainSweeper algorithm is the workhorse (see e.g. [2]). During 2008 it was shown that with small modifications of the program the local orientations in moderately deformed samples can be reconstructed as well. The method is quite robust as it can handle missing - as well as - saturated data (which is often the case). Furthermore, it was shown that grain maps could also be constructed

based on data from farfield detectors, although at a reduced spatial resolution. The modified GrainSweeper program can now handle data from either near or farfield detectors as well as near and farfield combined.

Several data sets have been tested at ID11 ranging from deformed single crystals, with small internal orientation spread to heavily deformed as shown below. An example of such a map is shown in Fig 3 (from the study of nucleation in 30% deformed Aluminium, see below). The map is not perfect and work is ongoing to perform more thorough tests, but these results are promising. The performance is expected to improve substantially when the new 3D detector is installed.

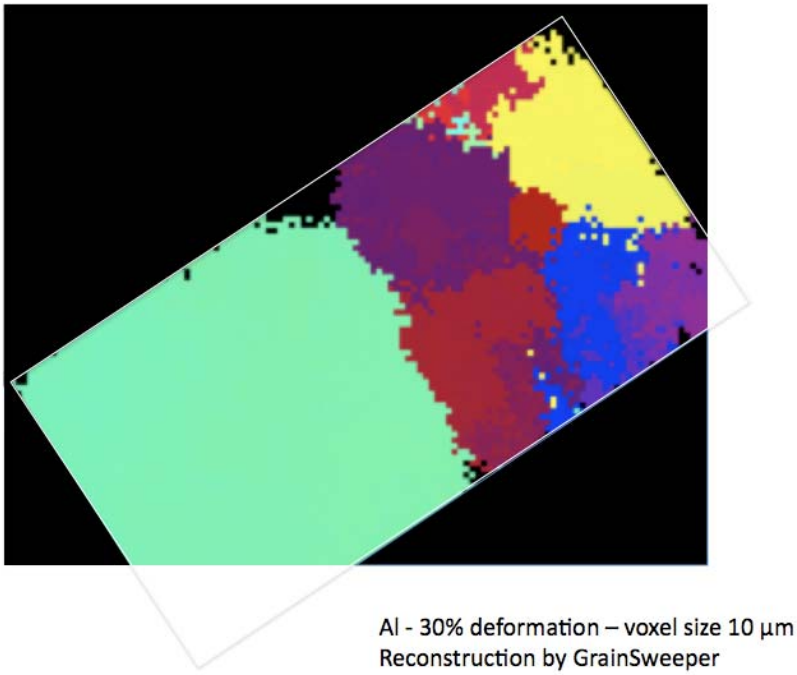


Fig. 3: Orientation map of one layer in a 30% deformed Al sample using far-field 3DXRD data. The outline of the sample is marked in white while colours indicate orientations. The sample is mapped layer by layer using a beam focused in one direction.

Selected Research Highlights

Nucleation of Recrystalization

The study of nucleation of recrystallization is similar to looking for a needle in a haystack as nucleation is a very rare event. Also, traditional surface methods suffer from one of two problems; either the same area can be examined before and after nucleation, which means that the nucleation process will be affected by the free surface and thus may not be representative. Alternatively, the sample can be polished after nucleation, but then the evidence of what was present before nucleation has been lost. Using 3DXRD, we may examine nucleation in the bulk, mapping the same volumes before and after to learn more of the mechanisms behind nucleation.

An experiment was performed to study bulk nucleation in high-purity aluminium non-destructively. A sample was prepared from 30% deformed 99.996% aluminium with a cross section of 600×1000µm. The sample was mounted in a furnace in the beam, which was focussed vertically to 7µm. The beam width of 1500µm covered the entire cross section of the sample. A setup with two detectors at distances 1.2 and 17cm from the sample was used in order to obtain both spatial and orientation information. 97 layers were characterized before and after annealing to 320°C, allowing direct comparison of the microstructure before and after nucleation.

Using the Grainspotter software, 6 nuclei in the interior of the sample were identified, and their positions, volumes and orientations determined. Fig. 4 shows the positions of these nuclei.

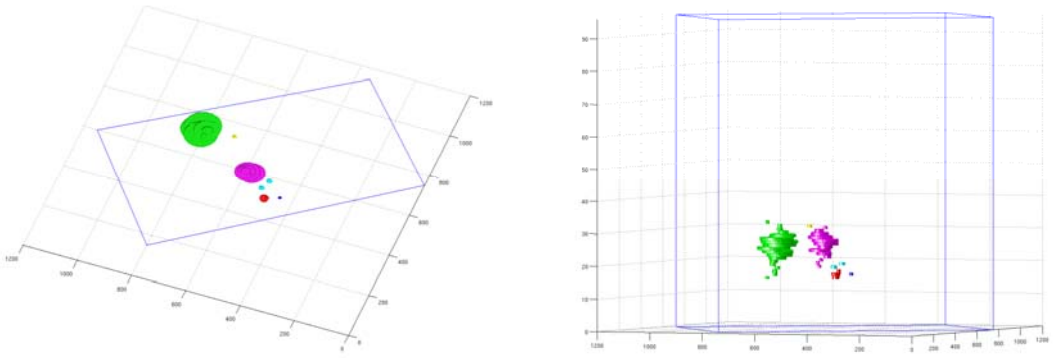


Fig. 4: The positions of the 6 nuclei. The volume of the nuclei in each layer has been calculated using the diffraction spot intensities and a reference scan, and these volumes have been plotted as disks.

Currently we are in the process of reconstructing the 3D orienation map of the deformed structure – an example of one such layer is shown in Fig 3 above. By combining the spatial information of the found nuclei in Fig 4 with orientations maps as in Fig 3, the influence of the local environment on the mechanism of nucleation can be observed in truly bulk conditions for the first time. Such data will provide novel information on the exact nucleation sites and allow orientation correlations between the deformed state and the formed nucleus to be extracted. To do this as a bulk study is particularly interesting because of recent reports from surface studies of nuclei with a wide range of orientation relations to the deformed state.

Graín Rotations in IF Steel

Previous 3DXRD experiments on the lattice rotations during tension of a number of individual aluminium grains (fcc crystal structure) revealed a strong grain orientation dependence of the rotations but the grains were not fully illimunated and the analysis did not include any spatial information about the grain environment. Following up on this an experiment on IF steel (bcc crystal structure) was conducted but this time the aim was to monitor the behaviour of all the grains in the sample and to obtain a map of their spatial distribution. The sample was investigated at 0, 3, 6 and 9% elongation. The tensile elongation was conducted ex-situ. Initially the sample had a cross section of 700x700 μm^2 but at 9% deformation the sample dimension was reduced to about 400x400 μm^2 by etching to limit the amount of spot overlap. The mapping was done with a beam height of 10 μm and at 0, 3 and 6% elongation consecutive layers were mapped while the spacing between layers at 9% was 20 μm. At all strains a sample length of 1 mm was mapped.

It was not possible to find all grains in the deformed specimens. However, ~1200 grains were identified both at 0 and 3% elongation (as shown above in Fig 1 from the work on mapping stress states) which is sufficient for a statistical analysis. Fig 5 shows the corresponding rotation of the crystallographic tensile axis. Preliminary analysis indicates that the rotations are grain orientation dependent and that the rotation is in the opposite direction of those observed previously in aluminium with a fcc crystal structure. This is in agreement with the theoretical expectation.

Further analysis is in progress. This will include

1) correlations between average grain rotation and {grain volume, distance of grain to free surface, grain stress state}
2) correlations between average grain rotation and grain neighborhood. We are in the process of reconstructing a full 3D map for the undeformed case, enabling us to identify all neighbors to each grain.
3) information based on the intra-grain rotations and stresses, as evidenced in the variation as a function of layer, cf. Fig 1a.

If succesful, it is evident that this analysis will be far more comprehensive than any previous studies.

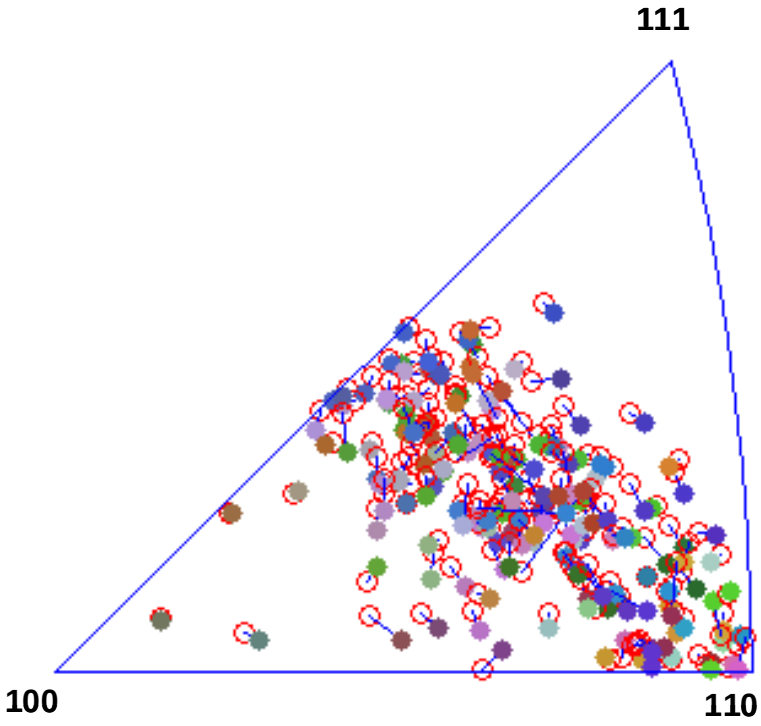


Fig. 5. The rotation of crystallographic tensile axis from 0 to 3% elongation (open and solid symbols, respectively) for grains in a subset of the mapped layers. The triangle represents an inverse pole-figure, a way of representing orientation space.

Observation of boundary migration during recrystallization

Previous in-situ 3DXRD and topotomo investigations by our group have revealed that the migration of boundaries during recrystallization is far more complex than so far considered. Even in the most homogeneous deformed matrices, the migration is not smooth, but typically occurs in jumps and quite extended protrusions may form locally on the migrating boundary. This was the most common pattern observed, but also at least 1 facet has been seen which moved with a constant speed for more than 20h (during a 72h anneal experiment).

As a follow-up to these early findings, new experiments have been conducted in collaboration with Wolfgang Ludwig from INSA-Lyon using the topotomo technique. With this technique the diffraction vector of one diffraction spot of a recrystallization nucleus is brought parallel to the rotation axis of the stage, so that this nucleus is always in diffraction condition. Tomographic reconstruction using the different projections of the diffraction spot gives a reasonably accurate measurement of the shape of the growing grain (spatial resolution of order 3 μm).

Two single crystal orientations, Cube and Goss, of Al-1050 were cold rolled to 30% thickness reduction and received a hardness indent of 2 kg to initiate the nucleation at the top of the sample. The deformation substructure of both orientations is known to be different (long narrow microbands for Goss, and more or less equiaxed cells for Cube). Both samples were heated at low temperature to start the nucleation. Once a growing nucleus was detected this nucleus was put into a permanent diffraction condition and 18-72 projections of its shape were measured in between short heating intervals during recrystallization. In this way the growth of a nucleus into the deformed matrix is monitored.

Fig. 6 shows the 0° projections of diffractions spots of nuclei growing into a matrix of Cube orientation at different timesteps. The growth of the monitored nucleus into the Cube matrix indicates a growth in different directions at a constant speed, while the growth of the nucleus into the Goss matrix clearly shows protrusions and a quirky motion of the moving boundary.

A full 3D reconstruction of the growing nuclei, a further analysis of the boundary misorientation and substructure morphology, as well as correlating the boundary movements with a map of large second phase particles are work in progress.

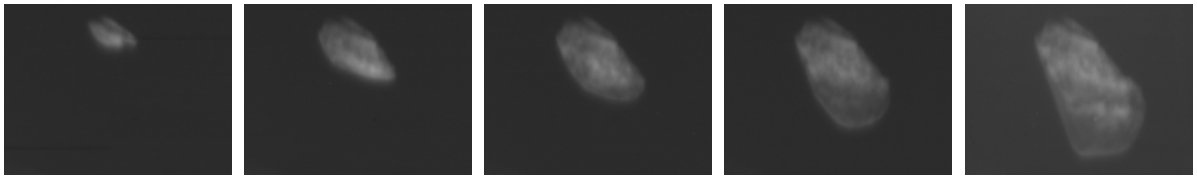


Fig. 6. Projection of a diffraction spot in a near field detector of a growing recrystallization nucleus into a 30% cold rolled Cube matrix growing at 300°C, snapshots at time = 0 s, 585 s, 990 s, 1530 s and 2200 s. The width of each image is 500 μm.

Totalcrystallography

Risø and ESRF are partners in the EU 6th framework program TotalCryst. A main aim of this program is to transfer the 3DXRD approach to use within pharmacy, time resolved studies in chemistry and structural biology. Part of the beamtime within this LTP has been reserved for tests and demonstrations on such specimens. Other studies have been done at ID11, ID14 and ID09B based on independent beamtime applications. TotalCryst highlights from 2008 are

Pharmacy

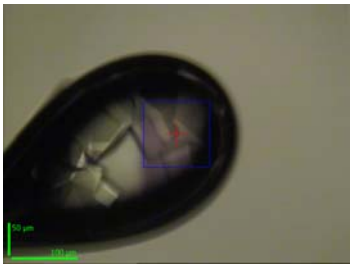
- The polycrystal indexing program GrainSpotter has been generalised such that specimens with *unknown* space group can be indexed. Each of the simultaneously illuminated grains can then be individually analysed by conventional single crystal structure solution and refinement programs, opening up a new route in crystallographic research. In a first experiment at ID11 a small molecule sample (a variant of the small molecule compound BCCP) with about 20 grains was successfully refined.
- A major limitation is the possible overlap between diffraction spots, in particular when grains are mosaic. An algorithm was demonstrated at ID11 that extends the application range of the TotalCryst approach considerably by first determining an orientation distribution function (ODF) for each grain and then using projections of the ODF for the actual peakfitting.

Time-resolved studies of photochemistry

Several successful experiments were made, headed by the group of S. Techert at the MaxPlanck Institute for Biophysical Chemistry at Göttingen. We refer to the experimental report for beamtime MI900.

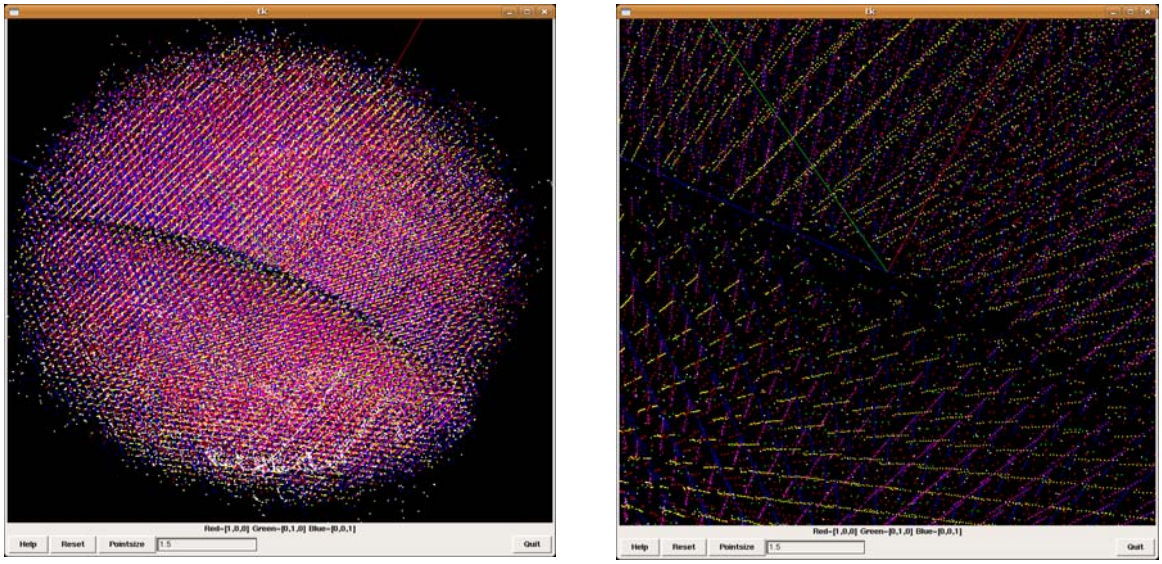
Structural Biology

The quality of the molecular structure of protein crystals determined from data collected at 3rd generation synchrotron sources often suffers from radiation damage. Even though attempts are made to minimize the radiation damage in various ways it is impossible to fully remove.
Using the TotalCryst methodology we can collect data on several crystals simultaneously (e.g. mounted in a loop, see figure to the right) and combine these data sets into one. The radiation damage can then be significantly reduced by reducing the crystal rotation range, e.g. from 100 degrees to 20 degrees.



One major problem with this approach is foreseen to be spot overlap. In close collaboration with E. Garman and K. Paithankar from the University of Oxford, we have investigated the degree of spot overlap both in simulated protein diffraction patterns and experimental data on polycrystals. We find that the overlap for e.g. 4 crystals of cubic insulin is less than 0.2 up to 2 Å resolution.

Measurements have been performed on cubic insulin and tetragonal lyzosyme at ID14-4 having from 2 to 6 crystals in the beam. We managed to index the diffraction patterns with FABLE programs ImageD11 (J. Wright) and GrainSpotter. In Fig 7 the reciprocal lattice vectors are plotted for a sample consisting of 5 cubic insulin crystals.



(a) (b)

Fig. 7. 3D plot of reciprocal space, showing the diffraction spots observered from a 5 grain multicrystal of insulin. Vectors from the same grain have the same color, illustrating the successful indexing. a) shows the full data set., b) shows the central part of the vectors from a).

The orientation matrices for the 5 grains were fed one at a time into the single crystal crystallography program MOSFLM (Leslie, A.G.W., (1992), Joint CCP4 + ESF-EAMCB Newsletter on Protein Crystallography, No. 26.) to integrate the data individually for each grain.

Publications in 2008 from work done in connection with ME-1162

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2) Schmidt, S., Olsen, U.L., Poulsen, H.F., Sørensen, H.O., Lauridsen, E.M., Margulies, L., Maurice, C., Juul Jensen, D., "Direct observation of 3-D grain growth in Al-0.1%Mn," *Scripta Mater.*(2008) **59**, 491-494.
3) Thorton, K., Poulsen, H.F., "Three-dimensional materials science: An intersection of three-dimensional reconstructions and simulations," *MRS Bulletin* (2008) **33**, 587-595.
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5) Olsen, U.L., Schmidt, S., Poulsen, H.F., "A high-spatial-resolution three-dimensional detector array for 30-200 keV X-rays based on structured scintillators," *Journal of Synchrotron Radiation* (2008) **15**, 363-370.
6) Winther, G., "Slip systems extracted from lattice rotations and dislocation structures," *Acta. Mater.*(2008) **56**, 1919-1932.
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8) West, S.S., Schmidt, S. Juul Jensen, D. "Experimental quantification of nucleation," In: Energy materials. Advances in characterization, modelling and application. Proceedings **29** Risø international symposium on materials science, Risø (DK), 1-5 Sep 2008, 383-389.
9) Poulsen, H.F., Nielsen, S.F., Olsen, U.L, Schmidt, S., Wright, J. "Novel synchrotron based techniques for characterization of energy materials" In: Energy materials. Advances in characterization, modelling and application. Proceedings **29** Risø international symposium on materials science, Risø (DK), 1-5 Sep 2008, 101-122.

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