# PANALYTICAL USER'S MEETING

## EXPERIENCE FROM ALMELO LABORATORY

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The aim of the project was to test selected X-ray optics modules and to measure in nonconventional experimental arrangements as well as to study structure of the samples.

### Samples

Various types of X-ray optics in different diffraction geometries were tested on tree types of samples: a high quality epitaxial layer of GaMnAs, polycrystalline Cu samples prepared by severe plastic deformation and magnetron sputtered $TiO_2$ nanocrystalline thin films.

### Position sensitive detectors X'Celerator and PIXcel

Both position sensitive detectors (PSDs) X'Celerator and a prototype of new detector PIXcel were available on an horizontal MRD system. The MRD system with the selected incident beam optics (a hybrid monochromator or a stand-alone mirror) was used mainly for high resolution experiments and parallel beam geometry. Hence, we utilized these detectors for reciprocal map measurements (Fig. 1 and 2) and for a measurement in the parallel beam geometry with a low take-off angle (Fig. 5).

### Comparison of Hybrid and 1 monochromators

The 2X hybrid mirror/monochromator was used for the high resolution measurements of the GaMnAs layer sample. The intensity gain was excellent with good angular resolution (Fig. 3). Only for higher diffraction angles (006 diffraction) the broad spectral band-pass of the monochromator induced a significant broadening of the GaAs substrate peak.

Both monochromators, the hybrid and the 1 one, were tested on polycrystalline Cu samples prepared by severe plastic deformation. The intensity of the focusing 1 monochromator was very good, it was possible to utilize all the advantages of the focusing symmetrical geometry (programmable slits, PSD detector). The shape of the peaks profiles was well defined (Fig. 4, potentially of enough quality to make possible evaluation of the dislocation density and arrangement). The intensity from the Cu sample measured by the 2X hybrid monochromator was lower. It is, however, necessary to consider that for this bulk polycrystalline sample the used parallel beam setup is not a good option. Just a very small part of the sample is irradiated in the symmetrical scan and it is not possible to use any PSD detector. On the other hand, in comparison with the Barthels monochromators available in our X-ray laboratory the intensity gain from the hybrid monochromator is much higher, hence also powder samples can be measured with excellent resolution.

Applications of both the alpha1 and the hybrid monochromators are well described in the X'Pert PRO User's Guide.

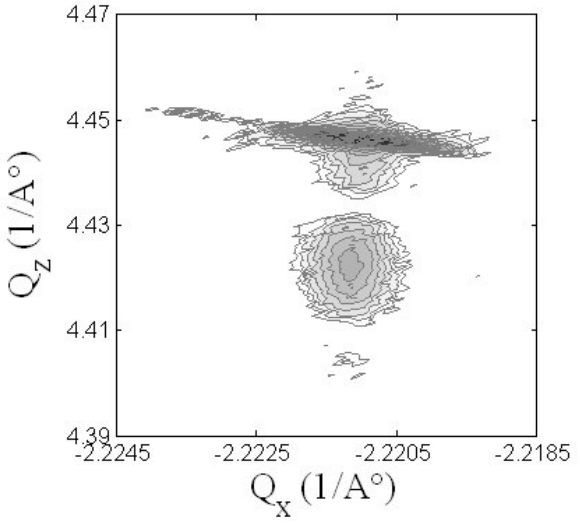


**Figure 1**. GaMnAs (204), hybrid monochromator, triple axis analyzer, 15 h, note that the (204) is a weak diffraction for zinc blende type semiconductor structures.

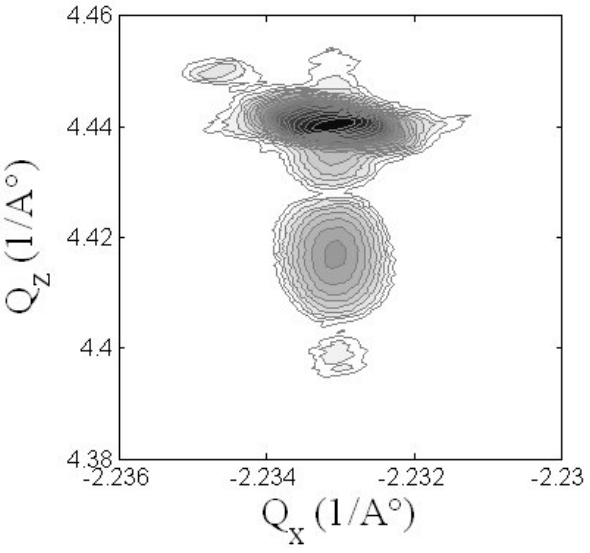


**Figure 2.** GaMnAs (204), hybrid monochromator, PIXcel, 2 h 20 min, 4x higher absolute intensity than with TA (Fig. 1).

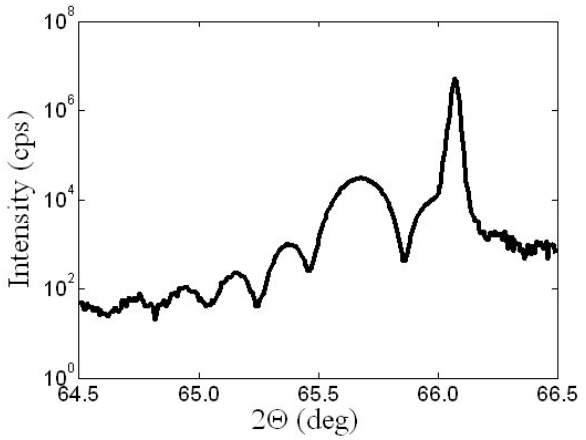


**Figure 3.** (004) diffraction of GaMnAs (50 nm), MPD, 2X Hybrid Monochromator, Mirror in the Diff. beam, 10 min.

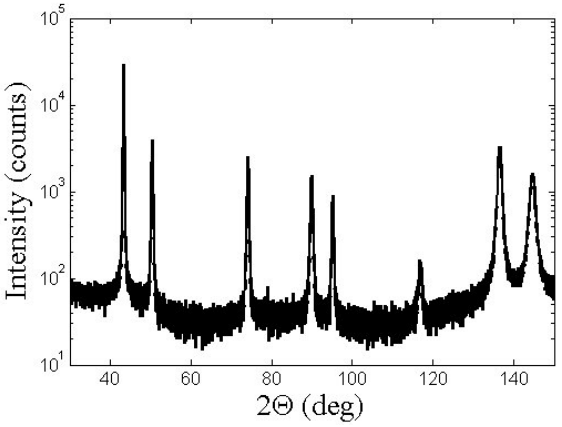


**Figure 4.** ECAP(1x) Cu sample, Alpha1 system, X'Celerator, 13 h.

## Measurement of thin films - grazing incidence vs. grazing excidence

The aim of this experiment was mainly to check usefulness of a PSD detector in the parallel beam geometry for study of polycrystalline thin films. To achieve a good resolution instead of the 2 scan with a low incidence angle the experiment was done in the grazing exit geometry. The scan, a little bit unconventional in the Data Collector software, with the same step in the both angles, incident angle as well as the diffracted angle 2 , was performed. The PSD detector was acquiring pattern for a certain range of diffraction angles 2 for each step of the scan. Hence a series of 2 scans for different take-off angles $_f = 2$ – were measured (Fig. 5). The exit angles were really low – close to zero. In principle, it should be possible to evaluate layer structure of the sample, however, it may be complicated by texture.

*The work is partially supported by the Academy of Sciences of the Czech Republic under the number KAN400720701.*

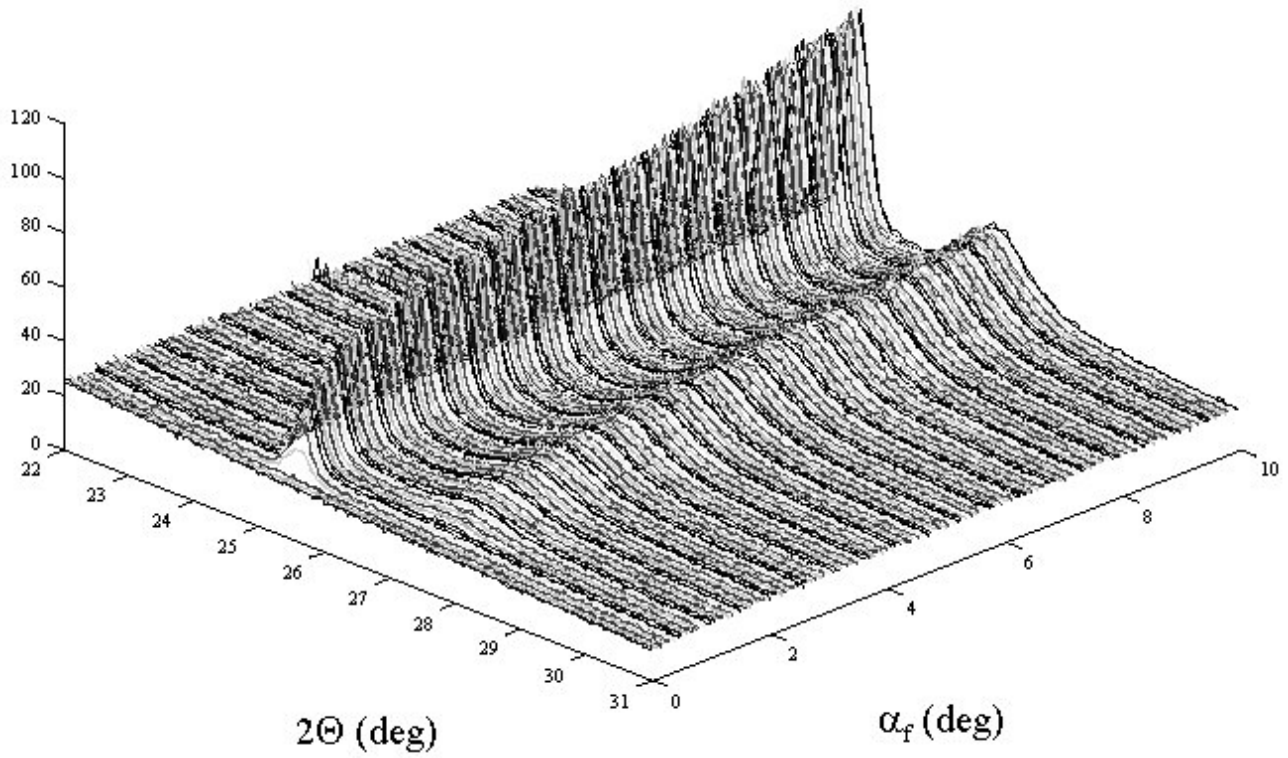


**Figure 5.** $TiO_2$ thin film on Si substrate: Part of the measured spectra with the PSD in the low exit angle geometry. Anatase (101) – the higher peak at the lower 2 angle, Rutile (110) – the lower peak at the higher 2 angle; range of the exit angle: 0 – 10 .

# MICRO-DIFFRACTION WITH A MONO-CAPILLARY: HOW TO SETUP OUR EXPERIMENT

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The experimental setup of a micro-diffraction experiment has already been described elsewhere [1]. One of the most important aspects of the micro-diffraction experiment is the alignment of a sample.

The spot on the sample that is to be analyzed can be determined by means of an alignment microscope. This microscope in attached to a PreFIX interface and it is equipped with a cross-hair in the ocular. This setup permits one to adjust samples with a precision of about 50 m. There is no way how to store the "*in situ*" information about the analyzed point or even about the precision of the system alignment.

Therefore we decided to modify this experimental setup using the alignment microscope. Together with IntracoMicro, Ltd. we constructed an optical interface for accommodation of a video camera in the position of the microscope eyepiece (fig. 1).


**Figure 1.** Mintron MTV-62W1P camera equipped with an optical interface.

This interface is equipped with a similar cross-hair that is also aligned with the optical system of our X'PertPRO diffractometer. Therefore it could be used in the same way as an optical eyepiece. Either an analog or a digital video camera with a "" sensor and C/CS lens can be used with this interface. The choice of a camera depends on what is the main purpose of the use of such attachment. If it is the preference of a good documentation of experiments, a digital camera may be in preference, as it permits the production of photographs with a better resolution and better reproduction of colors. If it is necessary to check the alignment of the system that needs to visualize the trace of the primary beam on the surface of a fluorescence disk, the analog camera, with its superior sensitivity, is absolutely necessary. The use of such a camera (with the sensitivity better than 0.01 Lux) can be very useful for a routine check of the system. An inferior resolution and color in accuracy are the drawbacks of that choice.

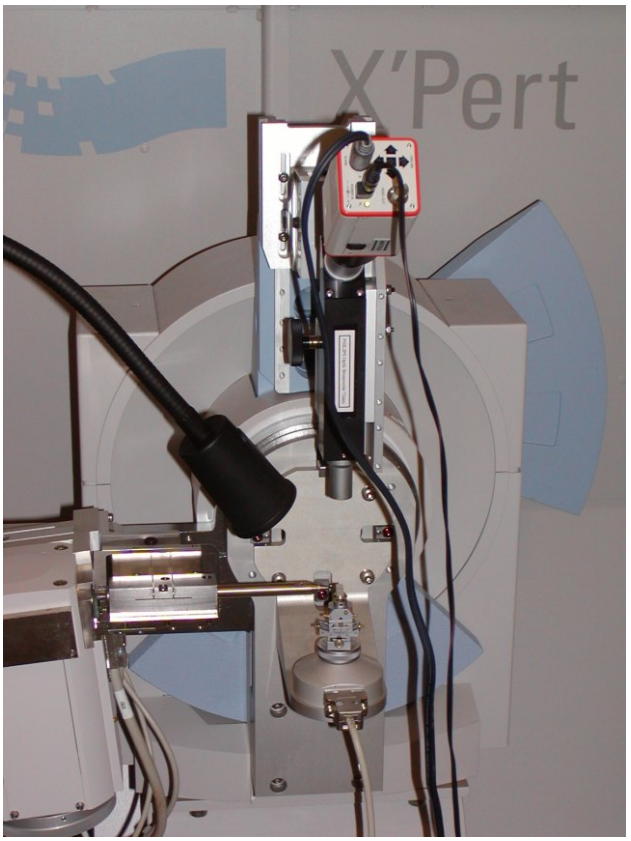


**Figure 2.** A video camera installed in the X'PertPRO diffractometer

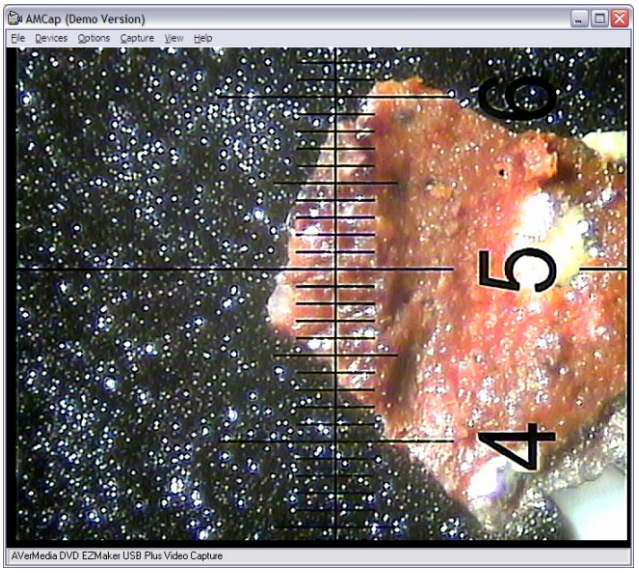


**Figure 3.** A typical photograph of the aligned sample that is to be analyzed.

After consideration of all benefits and drawbacks of the use of either an analog or a digital camera, we decided to install for our system the analog "Mintron MTV-62W1P" camera (fig. 1) with the minimum sensitivity of 0.007 Lux.

The overview of the experimental setup installed on our X'PertPRO diffractometer is shown in the figure 2.

Figure 3 shows a typical sample of a fragment that has been placed on a Si zero background sample holder and set up for X-ray powder micro-diffraction with the analyzed point (cross-hair)

The X-ray micro-diffraction with a conventional X-ray tube, focusing mono-capillary with a diameter of 0.1 mm, and a position-sensitive detector allows analysis of fragments as well as polished cross sections that permits us to deal with samples routinely prepared for optical or electron microscopy. The use of a video system for alignment of such samples significantly enhances the accuracy of positioning of samples and permits a routine check of adjustment of the whole system.

1. V. Šímová, P. Bezdička, J. Hradilová, D. Hradil, T. Grygar, *Powder Diffract.*, **20**, (2005), 224.

# TEXTURE AND STRESS MEASUREMENT WITH THE EULERIAN CRADLE ON MRD SYSTEM, DOUBLE-MIRROR SETUP

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## Measurement with the Eulerian cradle

For complete texture and stress analysis, it is necessary to measure reflections not only from the lattice planes parallel to the surface as in the Bragg-Brentano symmetrical -2 scans or at specific inclinations like e.g. for parallel beam 2 scans. Instead, information from large scale of inclinations is necessary. Either their diffraction peak intensities (for texture) or positions (for stress) are required. Traditionally Eulerian cradles are use for this purpose in combination with point focus of the tube and collimators. However, big disadvantage of this arrangement is significant defocusation and also loss of intensity. Therefore in modern diffractometers, polycapillaries (X-ray lens) are used behind the X-ray tube that transforms divergent beams into the beam parallel in all directions. There is still some divergence there but the suppression of defocusing effects and gain in intensity is significant. The arrangement can be in principle seen on Fig. 1 which differs only in one element, the Goebel mirror should be replaced by polycapillary module for texture and stress measurement (of course, also the tube should be rotated by 90 ° in order to use point focus).

Not only full texture measurement but also fast or scans can easily be done with the cradle.

Two software packages are available from Panalytical – X'Pert Texture and X'Pert Stress.

Texture software provide basic functions for display of pole figures in several views (Figure 2) and calculation of ODF – Orientation Distribution Function. There not many options for example for precise scaling of the plots and their export. Nevertheless, basic needs of texture characterization are met.

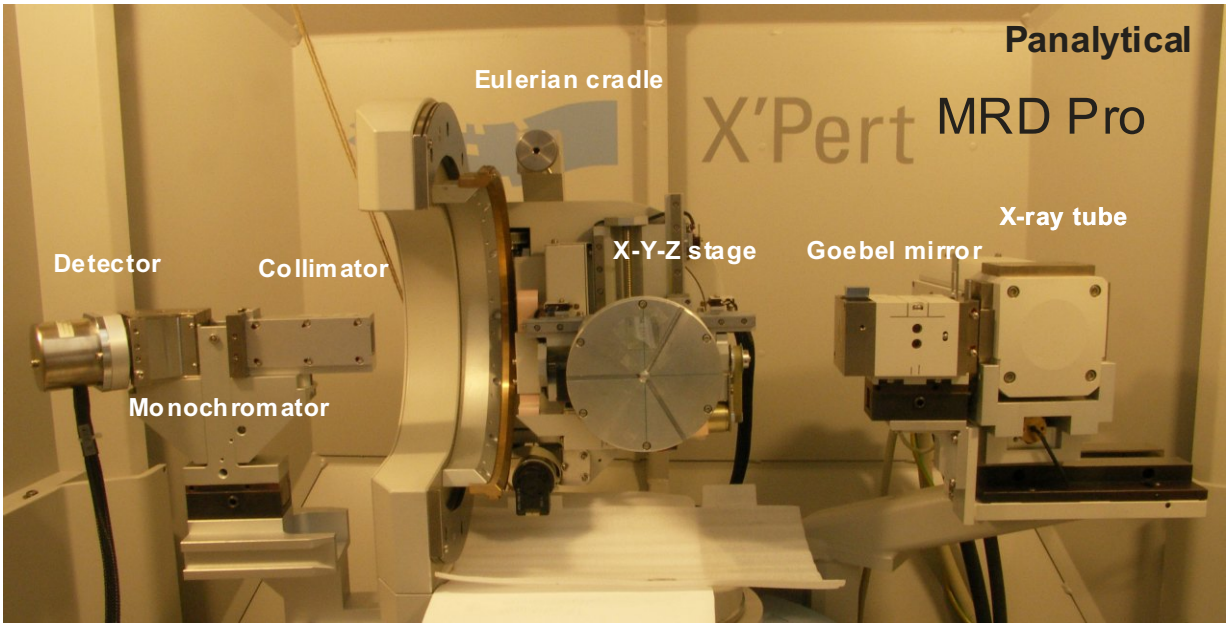


**Figure 1.** MRD Pro system with Eulerian cradle.

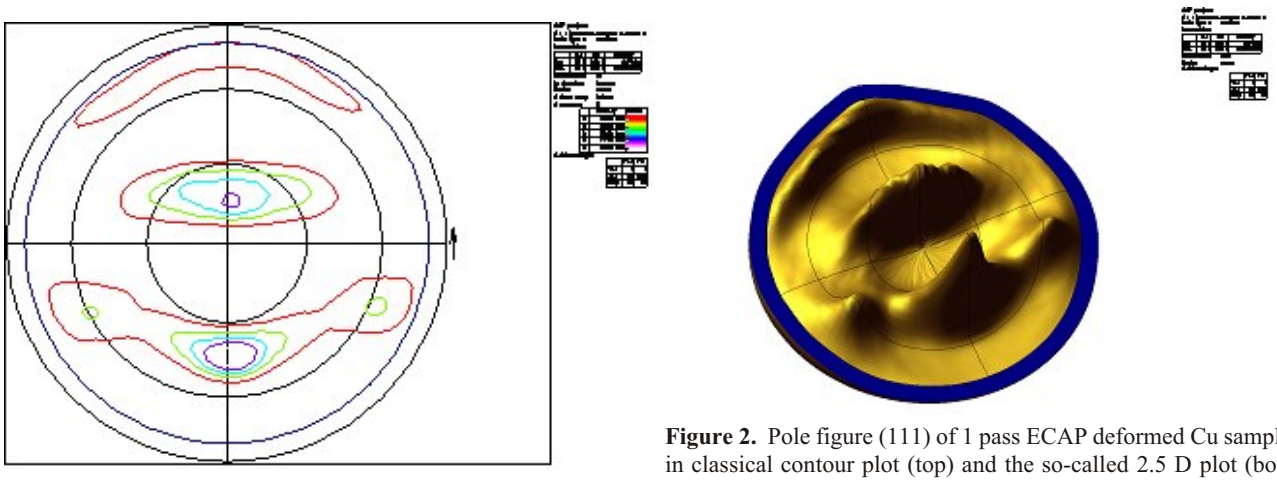

**Figure 2.** Pole figure (111) of 1 pass ECAP deformed Cu sample in classical contour plot (top) and the so-called 2.5 D plot (bottom).

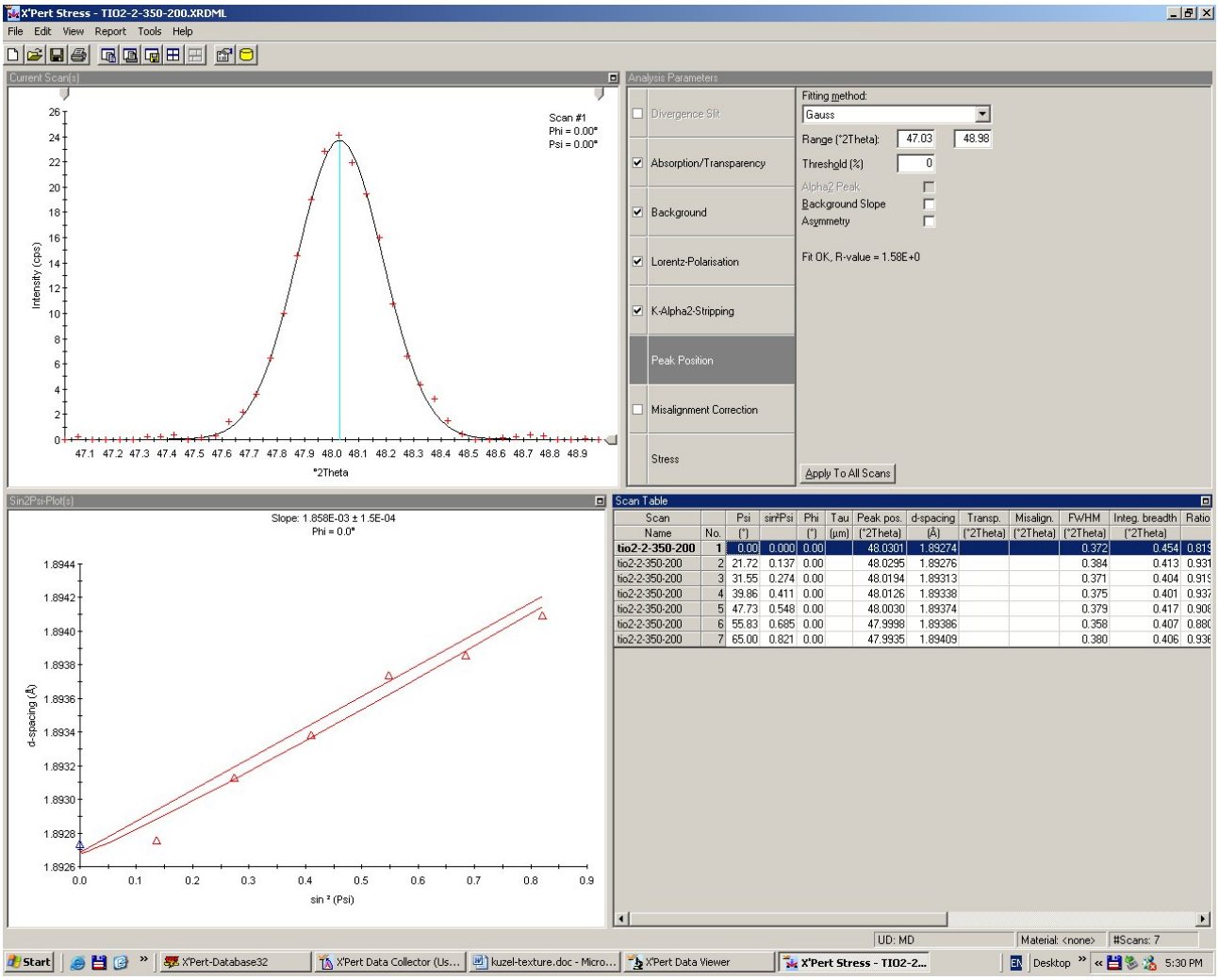


**Figure 3.** Basic screen of X'Pert Stress. Peak positions are determined automatically for all measured lines but the position of each individual peak of $\sin^2$ plot (left bottom) can be determined by different algorithm (center of gravity, parabola, Gauss, Lorentz, Pearson, pseudo-Voigt function, manually). The following corrections can be applied – absorption, transparency, Lorentz-polarization, misalignment, $K_2$ stripping.

The stress software (Figure 3) is very user-friendly. It allows both automatic and manual data processing and very fast and flexible stress evaluation not only in approximation of uniaxial stress (nonlinearity in $\sin^2$ plot, triaxial stress). Database of elastic constants for some materials can be used and modified by the user.

## Double-mirror setup

Nowadays, the measurement using parallel beam and Goebel mirror is more or less routine especially for thin films, when 2 scans with small angles of incidence are required. This arrangement gives quite high intensity but rather poor resolution that is 3-4 times worse than for the conventional Bragg-Brentano focusing geometry. In case of nanocrystalline films this is not that big problem because physical broadening is high. However, for the films with better crystallinity and not so high strains, the physical broadening is close to the instrumental one. In this case, the insertion of the second mirror in the diffracted beam can help. It converts the parallel beam to convergent one (focusing geometry) and resulting resolution is back close to the one of B-B setup. Picture of the setup on X´Pert Pro vertical system is on Fig. 4.

When to use this setup? In all cases, when high resolution and parallel beam on the sample are required simultaneously

*Thin film studies with low angles of incidence*. In this case, there is one significant disadvantage – the acceptance of the second mirror is very limited (to about 1.5 mm) so that the useful sample area is restricted by this dimension. It leads tothe intensity drop and may cause difficulties for samples with large grains.

*When precise specimen positioning in the goniometer axis is difficult – irregularly shaped surface, rough surface, usage of different chambers*. In such cases, even symmetrical - 2 scans may be of interest. They give not much lower intensities than focusing the BB setup with similar resolution. It is well known that focusing geometries are very sensitive to careful alignment. Double-mirror setup can overcome this drawback.

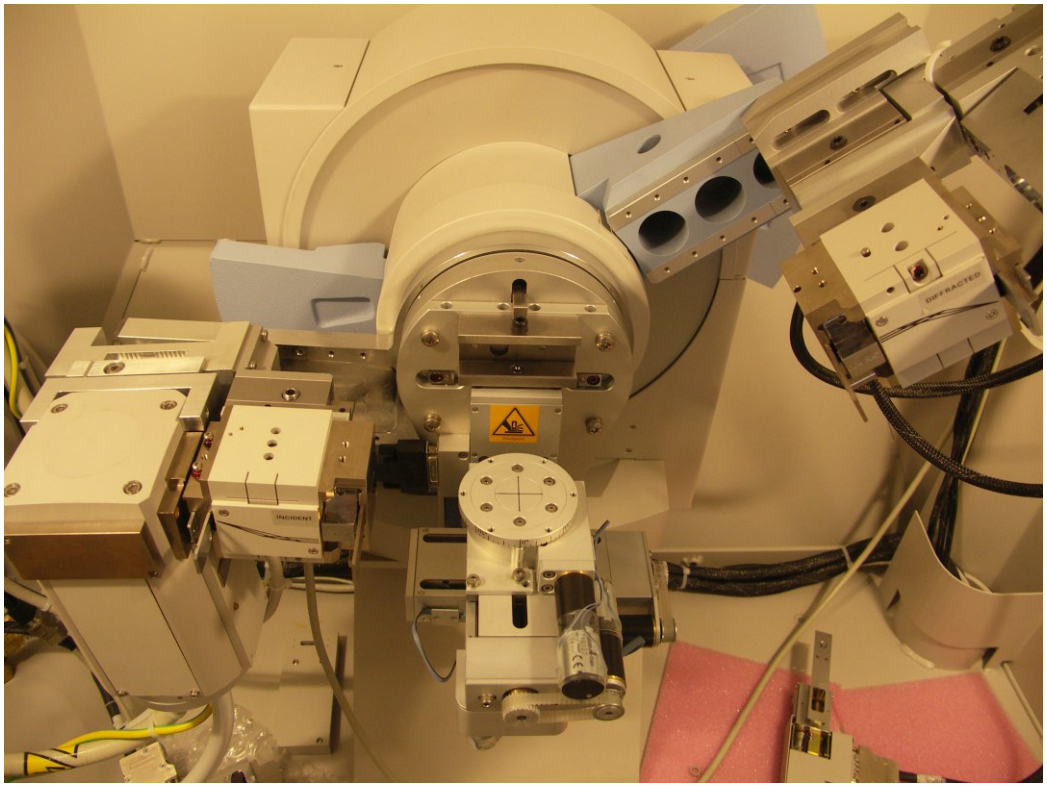

**Figure 4.** Double-mirror setup.

# KURS PROTEINOVÉ KRYSTALOGRAFIE

## CRYSTALLIZATION METHODS USED IN PROTEIN CRYSTALLOGENESIS

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Finding suitable crystallization conditions is the main problem to solve a protein structure by X-ray diffraction techniques.

In this lecture:

classical crystallization techniques based on evaporation used for screening and optimization of crystallization conditions utilizing the screening upon previously successful chemical cocktails,

advanced counter-diffusion technique that allows the screening for crystallization conditions in a wide range of supersaturation while suppressing concentration, of protein and precipitant,

cross-crystallization procedure based on using additives to modify crystal morphology and to improve diffraction quality,

will be discussed.

**Literature:**

Ivana Tomčová and Ivana Kutá Smatanová: Copper co-crystallization and divalent metal salts cross-influence effect – a new optimisation tool improving crystal morphology and diffraction quality. Journal of Crystal Growth, accepted for publication (2007).

Ivana Tomčová and Ivana Kutá Smatanová: Cross-crystallization as a new optimization tool of crystallization procedures. Materials Structure 14, 1, 3-5 (2007).

Ivana Kutá Smatanová, José A. Gavira, Pavlína Řezáčová, František Vácha, and Juan M. García-Ruiz: New techniques for membrane protein crystallization tested on photosystem II core complex of Pisum sativum. Photosynthesis Research 90 (3), 255-259 (2006).

Ivana Tomčová, Rui Miguel Mamede Branca, Gabriella Bodó, Csaba Bagyinka, and Ivana Kutá Smatanová: Cross-crystallization and preliminary diffraction analysis of a novel di-heme cytochrome $c_4$. Acta Cryst. F62, 820-824 (2006).

Julie Wolfova, Rita Grandori, Erika Kozma, Neal Chatterjee, Jannette Carey and Ivana Kuta Smatanova: Crystallization of the flavoprotein WrbA optimized by using additives and gels. Journal of Crystal Growth 284, 3-4, 502-505 (2005).

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## DEPOSITION OF MACROMOLECULAR STRUCTURES TO THE PROTEIN DATA BANK (PDB)

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Most grant agencies and virtually all journals require that the result of crystallographic or solution NMR analysis are deposited with a public database. In case of macromolecular structures, it is the Protein Data Bank ([1], PDB, http://www.pdb.org/) or the Nucleic acid Database ([2], NDB, http://ndbserver.rutgers.edu). Everyone involved in structure determination should keep in mind that structures that have been nurtured in laboratories for months and in some cases for years, will not be viewed in light of notebooks, log files from data processing and refinement, neither from endless coffee discussions in the laboratory but solely by their representation in the PDB. The deposition process therefore deserves attention and should be viewed as an important part of structure determination. The workshop will present the tools developed by the RCSB PDB that assist and simplify the deposition.

The main deposition tool is AdIt, deposition and validation tool, http://deposit.rcsb.org/. It is a web-based mmCIF editor. To deposit a structure, the user uploads the relevant coordinate and experimental data files and then adds any additional information. Each structure should be validated before deposition. Coordinates should be checked for format consistency and for quality of valence geometry using the Validation server (http://deposit.pdb.org/validate/). Web server http://pdb-extract.rcsb.org/auto-check/ allows non-trivial checking of coordinates versus x-ray diffraction data („structure factors“) using programs SFCheck, REFMAC, and CNS. Correctly formatted coordinates as well as collection and refinement statistics should be pro-

duced by the pdb_extract tool ([1], http://pdb-extract.rcsb.org/) that allows integration of refinement logs of most major refinement programs into PDB and/or mmCIF format and significantly thus simplifies the deposition. Identity of ligands present in the to-be-deposited structure should be verified using the ligand tool, currently at the web for „Ligand Depot“ (http://ligand-depot.rcsb.org/) that allows you to determine whether your ligands are correctly labeled, whether the right atom names were used, and whether these ligands are possibly new to the PDB.

All the mentioned web pages have available extensive tutorials, many steps have context-sensistive help and example pages and most of them are available as downloadable executable files as well as source codes.

The workshop will show deposition process using example files, possibly from participants.

***Acknowledgement***

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