



MATERIALS SCIENCE – POWDER DIFFRACTION BEAMLINE

Milan Dopita^{1,2}, Radomír Kužel¹

¹Department of Condensed Matter Physics, Faculty of Mathematics and Physics,
Charles University, Ke Karlovu 5, 121 16 Praha 2, Czech Republic

²Institute of Materials Science, Technical University Bergakademie Freiberg, Gustav Zeuner Str. 5, D-09599
Freiberg, Germany

Abstract

The X-ray diffraction is, without question, one of the most important techniques for the non-destructive materials structure investigation. Although the convenient laboratory X-ray equipment improved significantly within last decades, there still exist topics and effects which are, using laboratory equipment, unattainable. Limits and restrictions of conventional X-ray diffraction are relevantly shifted or wiped away using synchrotron radiation source. In our contribution, we discuss topics which are planned to study on Materials Science – High Resolution Powder Diffraction beamline, the most suitable experimental settings for majority of requested tasks as well as institutions or scientific groups and fields of their interests which manifested their pronounced interest on participation on proposed beamline.

Introduction

High resolution powder diffraction beamline should serve for different tasks of structural studies of materials in the form of powders, polycrystalline bulk materials, thin films and epitaxial layers. It is proposed for diffraction experiments which require high resolution in energy and scattering angle as well, and it is primarily optimized for experiments on polycrystalline materials, however the microdiffraction experimental settings allows its application to the high resolution scattering studies of the single-crystals too. Therefore, it could also be called the Material Science beamline. Most of the famous properties of synchrotron radiation can be of use – high intensity and high brilliance, wide energy range, low divergence. For all the applications, free selection of wavelength from the white beam is important. This beamline should operate in the energy range 8 – 50 keV (1.5 - 0.25 Å) which cover most of the needs of material science community and satisfy the conditions of scientific research topics planned on this beamline. Requested accessible energy range inevitably determines the use of the superconducting wiggler with short period length as the insertion device for the Material Science beamline.

Main applications of powder diffraction and advantages of synchrotron radiation

High-resolution powder diffraction

Nowadays, by using of high-resolution powder diffraction a resolution about an order better than in conventional diffraction can be achieved still at very reasonable intensity. The use of high-resolution experiments is of particular interest in the following problems. *Phase analysis* of complex mixtures when unique determination of neither quantitative nor qualitative determination of phase compo-

sition is difficult. The information content of the diffraction pattern in terms of interplanar spacings (peak positions) and intensities is closely related to the resolution. If this is low, the phase analysis may be impossible in the principle, in particular cases. *Structure refinement* or structure determination especially for low-symmetry phases or structures with large unit cell which is for example the case of biological material or zeolites. High-resolution setup reduces significantly overlapping of peaks the effect which complicates any minimalization procedures used for structure determination. Since peaks are narrower, peak positions can be estimated more accurately, peak overlapping diminishes and a more complete intensity data set can be extracted. Combination of several diffraction patterns collected at different conditions can be of great use. In textured samples, different patterns at different sample orientations can be collected and the pole function for a few well separated reflections calculated. With this information the orientation distribution function for each reflection can be found, so that a set of linear equations can be established, in which the integrated intensities of the texture-free sample are the unknowns. For both phase analysis and structure determination anomalous scattering can be very useful. This can be easily generated for selected elements by choice of the wavelength from the wide spectrum. *Line profile analysis* can offer information on mean crystallite size, crystallite size distribution, microstrain and/or dislocation densities or even types. Practical limits of conventional analysis for crystallite size and dislocation densities are up to 200-300 nm and down to about 10^{14} m^{-2} , respectively. High-resolution setup can shift significantly the limits by reducing the instrumental broadening that must be deconvoluted and moreover high intensity reduces the noise. This means that in some cases the instrumental broadening can be neglected at all and in other cases this allows to study finer microstructural details (distribution of crystallite size, arrangement and correlation of structural defects).

Microdiffraction

Diffraction on extremely small diffracting volumes, small set of crystals or even single microcrystals are of interest in several different scientific branches. Nominally, in pharmaceutical research, in organic chemistry, in research on the field of forensic science and art, in investigation of the microporous materials etc. The spatial resolved x-ray diffraction experiments are moreover important in investigation of the materials with function gradients and generally for the diffraction investigation of inhomogeneous samples. The X-ray microdiffraction (X-ray rocking curve imaging) with spatial resolution on μm scale can be used for analysis and quantification of spatial distributions of crys-

tal lattice misorientations, for determination of defects densities and for detection of local lattice quality in crystalline specimens. The experimental setup planned for the micro-diffraction experiments can be further used for the single-crystal diffraction.

Pair distribution function

Study of pair distribution function (PDF) has been revitalized in last few years. Originally, this was usually of interest for amorphous materials but it has been shown that it is the only method for structural characterization of nanomaterials, study of local order in materials showing average disorder, and even very helpful for structure refinement. In order to determine the function it is necessary to use high energy radiation to be able to perform measurement to large Q vectors, and position sensitive detectors (like 2D detectors) for data with good statistics at high Q values.

Analysis of orientation dependence of microstructure (stresses, textures)

Studies of orientation dependence of microstructures are of great importance in materials science, for example for mechanically treated (deformed materials), thin films etc. Measurement requires complete mapping of diffraction peak positions (determination of the residual stresses), intensities (description of the preferred orientation of crystallites - texture) or even line width (microstrain determination and estimation and study of the microstructural defects types and distribution). This can be performed much more efficiently with synchrotron radiation and area position sensitive detector. Another approach to the problem is to replace global analysis by the local one which means 3D grain-by-grain (spatially resolved) mapping of the material. Such a procedure can yield unique information namely in an inhomogeneous materials, functionally graded samples, or in materials which are somehow in-homogeneously mechanically, chemically or thermally treated. Spatially resolved X-ray diffraction can be more efficient using the hard X-rays.

Analysis of thin films

Investigation of thin layers or low dimensional structures incorporates whole variety of problems which are often not possible to overcome using classical X-ray equipment. In addition to the classical problems as is for example the low diffracted intensity, the investigation of the thin films requires other specific features. First of all, this is necessity on reduction or setting of the analyzed depth. This is usually done by setting of the appropriate low angle of incidence of the primary beam in the glancing angle X-ray diffraction (GAXRD). High intensity of synchrotron radiation in combination with excellent energy resolution makes that technique convenient for investigation of the nanocrystalline coatings and observation of the partial coherence effects in thin layers and nanocrystalline materials. Another experimental techniques suitable and often used for the coatings, epitaxial layers, multilayers and semiconductor thin films investigation, are for example X-ray reflectometry (XRR) giving the information on electron density and surface roughness and also information on the

number of layers, periods, interface roughness in the case of multilayers, or the grazing incidence diffraction (GID) which can provide information on sample structure in the lateral direction. Using of highly coherent synchrotron radiation in combination with its high intensity and possibility of the wavelength tunability greatly exceeds the potential of conventional laboratory X-ray diffraction equipment and makes the use of the synchrotron radiation necessary for the detailed investigation of thin layers/multilayers.

Measurements under non-ambient conditions

Probably one of the highest importances of synchrotron radiation, thanks to its high intensity and tunable wavelength, is the efficient possibility to perform all experiments under non-ambient conditions – low and high temperatures, high pressures and applying of external (electromagnetic) fields. In particular, the pressure is a powerful thermodynamic variable that allows the direct control of the interatomic distances and in combination with thermal treatment it can be used for novel supra-hard material synthesis or the structural characteristics obtained from temperature / pressure measurements can be used for the equation of state determination. Low temperature measurements can yield unique information on magnetic properties and generally on the electron structure of solids. Fast phase transitions, chemical reactions in solid, liquid or solid-gas state can be fully structurally characterized only when using synchrotron radiation. Moreover, the scattering of synchrotron radiation can be easily combined with in-situ spectroscopic studies like Raman or infrared. In-situ sample preparation like thin film deposition or hard material synthesis would also be of interest.

Requirements

The latest setup proposed in MSPD beamline in Alba synchrotron (February - July 2007) seems to be very suitable, at least as a starting point in beamline design, also for needs of our crystallographic community and material research groups (see the list below) which plan to participate and to perform their experiments on projected beamline. Specifically the experimental requirements on proposed beamline cover: high resolution and in-situ powder diffraction, single crystal, high pressure diffraction on powders and single crystals, spatially resolved microdiffraction. In addition, texture - stress analysis and thin film analysis is of interest as well as the experiments in non-ambient conditions and external fields, as it was formerly described in more details. The beam line should be able to operate in energy range from 8 keV to 50 keV. This will cover most of the needs for the materials science community. In particular the high energy region (30 – 50 keV) provides an optimum energy range for high pressure experiments; it is also desirable for high resolution powder diffraction experiments and PDF studies. The energy range has determined the type of source (a superconducting wiggler with short period length), and the implemented techniques the number of experimental stations (2-3). Moreover, the main accent on the optical and experimental station design should be focused to the compactness and the possibility to easily change the



beamline setting without major, long time consuming, realignments.

Energy range: Maximum: 8-50keV (1.5 - 0.25 C) Typical: 20-40keV (0.6 - 0.3 C)

Energy resolution: 2×10^{-4} E/E

Typical beam sizes (H x V): $5 \times 2 \text{ mm}^2$ down to $30 \times 20 \text{ m}^2$

Incident beam optics:

The next paragraph briefly describes the planned beamline design and main parts of the optical and experimental hutches. The beamline should basically operate in two modes depending on the required energy and experimental settings; in a mirrored mode for the energy range from 8 to 40 keV and for energies higher than approximately 40 keV in un-mirrored mode.

Filters

The optical elements are preceded by a variable white beam filter to strip off the low energy part of the wiggler spectrum and reduce the heat load on the downstream optics.

Mirror

The collimating bent silicon mirror will be installed to reduce the heat load on the monochromator, to suppress higher harmonics and to collimate the beam in the vertical direction, thus increasing the energy resolution. This is necessary in order to achieve high resolution powder diffraction data. The energy range in the mirrored mode is defined by the mirror coating and grazing angle. To cover a wide energy range without the need of major realignments the mirrors will be operated at a fixed glancing angle, and it will be covered by several stripes made from different materials (Si, Rh, Pt, Ir) to achieve different energy ranges between 8 – 40 keV.

Monochromator

The monochromator will produce a monochromatic beam with energy resolution E/E of about 2×10^{-4} in the 8 – 50 keV range. The monochromator can principally be designed either as a double-crystal monochromator or as a channel-cut monochromator. Considering pros and cons of both mentioned monochromator types, the use of double-crystal monochromator will be preferred. To reduce the influence of the thermally induced distortion, caused by high heat load, both collimating mirror and monochromator must be externally cooled during its operation.

Focusing KB system with Multilayers

The pair of Kirkpatrick-Baez (KB) focusing mirrors can be used in both mirrored and un-mirrored settings. In both modes the KB-multilayer mirror can be applied as additional focusing option in the energy range between 20 and 50 keV. The KB mirrors will serve for focusing of the incident beam for the spatial resolved diffraction, single-crystal diffraction and their use is essential for the microdiffraction experiments, where the beam should be focused to the area of about $30 \times 20 \text{ m}^2$. For high-angular resolution powder diffractometry these mirrors has to be removed from the beam path to produce a parallel incident

beam on the powder sample. They can be, for instance, made with either lateral or in-depth grading (super-mirrors) and double layer spacing of 2 nm.

Sample stage

Principally at least two sample stage systems are proposed for this beamline; the two-circle goniometer for transmission and reflection high resolution powder diffraction geometry and four-circle or kappa goniometer for microdiffraction and single-crystal diffraction settings.

For the purposes of the high resolution measurements the powder diffraction stage has to be equipped with diffractometer having the angular accuracy better than $1 \times 10^{-3}^\circ$ and step $1 \times 10^{-4}^\circ$, moreover for the precise measurements the accurate alignment of the sample with respect to the incident beam is necessary. Therefore the sample stage allowing movements in order of microns or tens of microns in z and xy position respectively is requested. Planned detection system (detectors) consists of the multi analyser detector setup for precise high resolution diffraction experiments and a fast curved position sensitive or silicon strip detector for time resolved X-ray diffraction. The geometry of the powder diffractometer has to allow mounting of various sample supports primarily an additional Eulerian cradle, holder for rotating capillaries with optional movement along the capillary axis, flat-plate sample holder with spinner, or placing different sample environments on a lifting table that can easily be moved to the diffractometer. Examples of such sample environments are: liquid-nitrogen cryostream with broad temperature range and high temperature stability, continuous liquid-helium flow cryostat with spinning capillary and flat-plate adaptors for temperature range from 2.2 K to 350 K, high temperature chamber, reaction cell for in situ studies, diode laser furnace for capillaries, stress rig to apply mechanical load while measuring the residual strain, humidity chambers, etc.

For microdiffraction experimental settings a full four-axis instrument or the kappa goniometer for flexible sample orientation and complete data collection to high theta values at small crystal to detector distances will be selected. The sphere of intersection of axes should be as small as possible (less than 5 microns) to avoid the problems with sample misalignment during measurement with smallest planned focus size ($20 \times 20 \text{ mm}$). The spatially resolved diffraction techniques require additional precise sample translation stage for micro positioning. It's necessary to find a diffractometer that accommodates both techniques without major changes in the hardware. Further it is also important to have enough free space around the diffractometer to be able to install additional equipment like the low temperature system, lasers, positioning video microscope and other sample environments.

Detecting systems

For different diffraction techniques, which we plan to perform on proposed beamline, we require different types of detectors. The main detector for the high resolution powder diffraction station will be a multi analyzer stage with 5-7 detectors with analyzer crystals. Time resolved experi-

ments can be performed on very different time scales nevertheless fast detection system is needed for such types of experiments. We plan to equipped powder diffraction stage with a curved 1-dim PSD or better with curved silicon strip detector which is feasible for less than one second measurement. The microdiffraction / single-crystal station will be in basics equipped with a point detector as well, however for fully efficient measurements fast readout CCD area detector is required. For some application the large apertures, high dynamic range and low intrinsic noise at long exposures of Image Plate can be beneficial as well.

Possible extensions

Combination of powder diffraction with EXAFS and other spectroscopic methods can be considered.

Potential users of Materials science beamline

In the table below there is a list of laboratories which showed high interest in measurements at the proposed beamline and other potential users (without specifications) from the Czech and Slovak Republics. However, users coming from other close countries are expected, namely Austria, Poland and Hungary but also for example Slovenija, Croatia, Ukraine where there are many laboratories dealing with powder diffraction.

Interesting links:

Some links to the related beamlines (powder diffraction, material science, etc.) working or under construction in Europe.

ALBA (Spain); beamline High Resolution Powder Diffraction,

<http://www.cells.es/>

ANKA (Germany); beamlines PDIFF, NANO,

<http://ankaweb.fzk.de/>

Diamond (UK); beamline I11,

<http://www.diamond.ac.uk/>

ESRF (France); beamlines BM01, ID3, BM05, ID10B, ID11, ID13, ID15A/B, BM20, ID22, BM25, ID31, ID32,

<http://www.esrf.eu/>

HASYLAB (Germany); beamlines B2, BW1, C, D3, D4, F1, F2.1, G3, W1, W2,

<http://hasylab.desy.de/>

MAX-lab (Sweden); beamlines I711, I811,

<http://www.maxlab.lu.se/>

SLS (Switzerland); beamline X04SA,

<http://sls.web.psi.ch/>

Appendix

List of some Czech and Slovak scientific groups showing prominent interest in performing experiments on Materials Science – Powder Diffraction Beamline

Institution: **Faculty of Mathematics and Physics, Charles University, Prague**

Contact: R. Kužel, S. Daniš

Interests: high-resolution powder diffraction, thin films

analysis, 3D grain mapping

Materials: nanocrystalline materials, deformed materials

Institution: **Faculty of Science, Charles University, Prague**

Contact: V. Goliáš, J. Plášil

Interests: high-resolution powder diffraction, microdiffraction

Materials: new minerals

Institution: **Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University**

Contact: N. Ganev

Interests: stress and texture analysis

Materials: steels

Institution: **Institute of Physics, Academy of Sciences of the Czech Republic, Prague**

Contact: M. Čerňanský

Interests: high-resolution powder diffraction, thin film analysis, analysis of orientation dependence of microstructure, measurement under non-ambient conditions, pair distribution function

Materials: nanocrystalline materials, deformed materials, shape memory materials

Institution: **Institute of Physics, Academy of Sciences of the Czech Republic, Prague**

Contact: K. Knížek

Interests: high-resolution powder diffraction

Materials: transition metal oxides

Institution: **Institute of Chemical Technology, Prague**

Contact: J. Maixner, B. Kratochvíl, M. Hušák, R. Pažout

Interests: high-resolution powder diffraction, structure solution from powder or microcrystal data, thin film analysis, microdiffraction, EXAFS

Materials: Pharmaceutical substances, Al-Ti-Si alloys, minerals, nanocrystalline materials, rare-earth elements in silicate and borate glasses

Institution: **Geological Institute, Academy of Sciences of the Czech Republic**

Contact: R. Skála

Interests: diffraction under non-ambient conditions (hP/hT), texture analysis of natural highly-deformed materials

Materials: minerals and synthetic compounds relevant to planetary crusts and cores, highly deformed rocks, materials from UHP terrains

Institution: **Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic**

Contact: P. Bezdička

Interests: high-resolution powder diffraction and microdiffraction with potential interest in analysing samples from the field of art, archaeology

Materials: micro-samples of artworks, clay minerals, nanomaterials



Institution: Institute of Nuclear Physics, Academy of Sciences of the Czech Republic, Rez near Prague

Contact: P. Lukáš, P. Strunz, P. Mikula

Interests: high-resolution powder diffraction, in-situ studies

Materials: shape-memory alloys, steels

Institution: Faculty of Science, Palacky University, Olomouc

Contact: Z. Trávníček, J. Filip, J. Walla, O. Schneeweis

Interests: high-resolution powder diffraction

Materials: structure solution, nanocrystalline materials

Institution: Faculty of Science, Masaryk University, Brno

Contact: J. Marek, J. Pinkas, M. Nečas, V. Vávra

Interests: high-resolution powder diffraction

Materials: structure solution, minerals

Institution: Institute of Materials Physics, Academy of Sciences of the Czech Republic

Contact: B. David, P. Roupcová

Interests: in situ measurements of high-temperature phase transformations and their kinetics

Materials: nanocrystalline powders

Institution: University of Pardubice

Contact: L. Beneš, M. Steinhart

Interests: time-resolved diffraction, high pressure

Materials: layered compounds, intercalates, nanocomposites

Institution: Laboratory of Physical Chemistry, Research Institute of Building Materials, Brno

Contact: D. Všíanský, T. Staněk

Interests: qualitative and quantitative phase analysis, phase transitions, high temperature powder diffraction

Materials: cementitious materials, ceramics, secondary industrial materials (ashes, slags etc.).

Institution: Zentiva, a.s., Praha

Contact: H. Brusová

Interests: high-resolution powder diffraction, non-ambient conditions, PDF

Materials: structure solution, pharmaceuticals, nanomaterials

Institution: Institute of polymer engineering, Faculty of Technology, T. Bata University, Zlín

Contact: M. Hřibová, F. Rybníkář

Interests: high-resolution powder diffraction, thin film analysis, texture, PDF, SAXS, non-ambient diffraction

Materials: synthetic polymeric materials, polymer blends, biopolymers, geopolymers

Institution: Czech Geological Survey

Contact: F. Laufek

Interests: high-resolution powder diffraction, structure solution and refinement

Materials: minerals, intermetallics containing Te, semiconductors

Institution: National Museum Prague

Contact: J. Sejkora

Interests: high-resolution powder diffraction, microdiffraction

Materials: minerals, mineral-like phases

Institution: Institute of Criminalistics Prague

Contact: M. Kotrlý

Interests: high-resolution powder diffraction, microdiffraction, phase analysis

Materials: nanomaterials, forensic samples

Institution: Institute of Physics, Slovak Academy of Sciences, Bratislava

Contact: M. Jergel

Interests: high-resolution powder diffraction, thin films analysis, anomalous powder diffraction, microdiffraction, measurements under non-ambient conditions

Materials: metallic thin films and multilayers, granular thin films, metallic nanoparticles, hybrid structures (top-down & bottom-up)

Institution: Institute of Physics, Slovak Academy of Sciences, Bratislava

Contact: P. Švec

Interests: high-resolution powder diffraction, high-intensity small spot size analyses, high-temperature measurements, measurements in liquids and molten alloys

Materials: metals, alloys, textured structures, oriented and functionally graded materials, short-range and medium range ordered systems, local order in melts.

This list is still incomplete.

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