Lectures - Thursday, June 19

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SYNCHROTRON RADIATION FOR MATERIALS SCIENCE AND POWDER DIFFRACTION

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There are many different applications of synchrotron radiation in materials science. Actually, they use nearly all well-known remarkable properties of the synchrotron radiation: high intensity, high brilliance, wavelength tunability, low divergence etc. Different kinds of samples can be studied; powders, thin films, bulk samples, small particles, small areas of bulk samples. In particular, non-ambient conditions and time resolved experiments are of great interest.

Main applications

High-resolution powder diffraction

One of the most frequently used experiments of powder diffraction with synchrotron radiation is high-resolution powder diffraction with a resolution of about an order better than in conventional (laboratory) diffraction and and still working at very reasonable intensity and necessary measurement time. High-resolution powder diffraction beamlines can be found at nearly all synchrotrons worldwide. The use of high-resolution experiments is of particular interest in the several problems. For example for complex mixtures unique determination of quantitative or sometimes even qualitative determination of *phase composition* is difficult. The information content of measured diffration pattern in terms of interplanar spacings (peak positions) and intensities is closely related to the resolution. If this is too low, the phase analysis may be impossible in principle. Another example of need of high resolution is the *structure refinement* or *structure determination* for low-symmetry phases or structures with large unit cell which is for example the case of biological materials or zeolites. The high-resolution setup reduces significantly overlapping of peaks the effect which complicates any minimalization procedures used for structure refinement. Since peaks are narrower, the peak positions can be estimated more accurately, the peak overlap diminishes and a more accurate 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 measured 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 beneficial. This can be easily generated for selected elements by choice of the wavelength from the broad white synchrotron 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 can often be even neglected. Moreover, high intensity reduces the noice and makes investigation of fine microstructural details (distribution of crystallite size, arrangement and correlation of structural defects) possible.

Pair distribution function

The 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 also very efficient 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.

Microdiffration

Diffraction on extremely small diffracting volumes, small set of crystals or even single microcrystals are of interest in several different scientific branches. In pharmaceutical research, in organic chemistry, in research on the field of forensic science and art, in the investigation of microporous materials etc. Moreover, the spatial resolved X-ray diffraction experiments can give unique information inhomogeneous materials, functionally graded samples, or in materials which are somehow in-homogeneously mechanically, chemically or thermally treated. The X-ray microdiffraction (X-ray rocking curve imaging) with spatial resolution on μm scale or even below can be used for analysis and quantification of spatial distributions of crystal lattice misorientations, for determination of defects densities and for detection of local lattice quality in crystalline specimens. 3D XRD grain mapping, called also 3D X-ray microscopy, can be nowadays performed at ESRF (ID11) or at two beamlines in Argonne National Laboratory. The shapes, morphology, orientation dependences and

even growth of individual grains with temperature can be studied.

Analysis of orientation dependence of microstructure (stresses, textures)

The studies of orientation dependences of microstructures are of great importance in materials science, for example for mechanically treated (deformed materials), thin films etc. The 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.

Analysis of thin films

The 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 it 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. Moreover, 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.

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MATERIALS SCIENCE BEAMLINE AT SYNCHROTRON ELETTRA IN TRIESTE

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Introduction

Materials Science Beamline (MSB) at ELETTRA, Sincrotrone Trieste is probably the most complex device used in synchrotrons, which was proposed, designed and manufactured mainly by Czech companies and institutes and financed from European and Czech funds. In the present time it is operated in close cooperation of three partners - Institute of Physics of the ASCR, Charles University and Sincrotrone Trieste by the international team with Czech participation. This 10 years long experience with construction, operation, maintenance and never-ending improvement of MSB would be useful for currently proposed ambitious project of Central European Synchrotron Laboratory (CESLAB) in Brno.

ELETTRA

Synchrotron ELETTRA was proposed as a soft X-ray complement of ESRF Grenoble in 80's. A decision to build the two 3rd generation synchrotron facilities was taken in 1986 and construction of ELETTRA began in 1991, reaching commissioning in 1993. In contrast to older facilities, 3rd generation sources are dedicated for synchrotron radiation not only from bending magnets, but also from many of insertion devices (undulators, wigglers). They have low emittance and then small beam size. ELETTRA storage ring with a circumference 259 m has double bend achromate structure with 24 bending magnets and 11 long straight sections dedicated for insertion devices [1]. Energy of circulating electrons was originally proposed to 1.5 GeV with full energy injection from linac, but early it was increased to 2.0 GeV with injection at 1.0 GeV. Later, the new mode with 2.4 GeV energy was introduced (25% of user time). The latest development represents a new full energy injection device consisting of 100 MeV linac with a 2.4 GeV booster. Abandoned old linac will be rebuilt and become the core of the FERMI@elettra 4th generation light source (free electron laser).

Materials Science Beamline

History

The idea to build relatively simple and cheap beamline using bending magnet radiation with photon energy in the range 20-1000 eV for the wide range of application in materials science jointed together people from many institutions leaded by Institute of Physics in Prague. Materials Science Beamline was proposed for the first time as Italian-Czech project for financing from Central European Initiative in 1996. The second attempt in 1997 was successful and MSB was supported by EU grant for transfer of high technologies to the east European countries. Main components of the beamline (UHV chambers for all optical elements with fine mechanics) were designed and manufactured by Delong Instruments, Brno in period 1998-99. Final assembly began in 1999 and commissioning followed in 2000. First experimental station attached to the Materials Science Beamline was UHV chamber with Scienta 200 analyzer from Karl Frenzens University, Graz (2000-2002). From 2002 it was replaced by the chamber from ELETTRA fitted with Phoibos 150 electron analyzer and other equipment from Charles University, Prague. This experimental chamber is continuously upgraded and works on MSB up to now. In 2008 a new grating chamber manufactured in Bestec Berlin was installed. It conserves optical concept, but introduces state-of-the-art components of the fine mechanics including actuators and high precision angular encoders.

Beamline description

Materials Science Beamline is attached to the bending magnet exit 6.1 on ELETTRA storage ring. To cover photon energy range 20-1000 eV a grazing angle reflective optics with gold coating in the UHV chambers was used. The first optical element is a toroidal mirror focusing light sagitally onto the entrance slit and tangentially onto the exit slit. Due to the incidence angle 4° from the optical surface, hard X-ray is absorbed and only visible, ultraviolet and soft X-ray light reflects downstream. A plane grating monochromator based on the SX-700 concept has plane mirror determining the angle of incidence on the plane grating, while the spherical mirror focuses the diffracted light onto the exit slit. After exit slit the light beam is refocused to the sample by the toroidal mirror that deflects the beam in vertical plane [2]. Schematic optical layout is on figure 1.

End station

The key component of the beamline is end station allowing not only experiments with synchrotron light, but also in-situ sample treatment and its characterisation by supplemental methods. In the experimental chamber it is possible to use Ar^+ sputtering, LEED, HeI lamp for UPS (Ultraviolet photoelectron spectroscopy), Mg+Al X-ray tube for XPS (X-ray photoelectron spectroscopy), various evaporators and off-course sample heating and cooling during all experiments. High pressure expositions and sample clean-

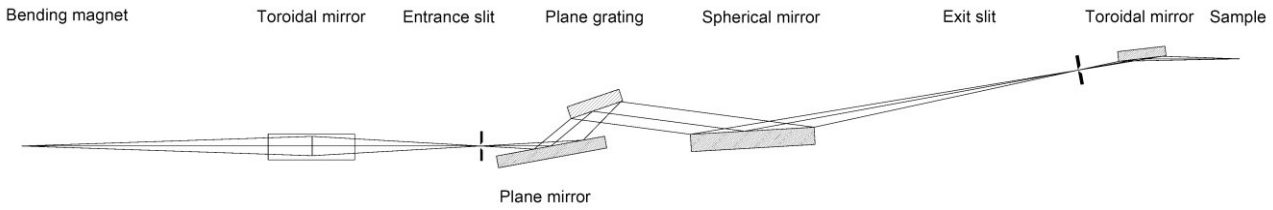

Figure 1. Optical layout of MSB, side view (not in scale).

ing can be done in neighbouring preparation chamber. Fast entry allows sample entering from ambient with atmospheric pressure to the UHV chambers in 20 minutes.

Synchrotron radiation photoemission spectroscopy

The main experimental method used at MSB is photoemission spectroscopy. In contrast to UPS, when excitation energy is 21.218 eV (HeI lamp) or XPS with excitation energy 1253.6 eV (Mg K-) and 1486.6 eV (Al K-), the synchrotron radiation on MSB represents a tuneable light source covering the whole gap between classical UPS and XPS. There are more advantages – small and selectable energy bandwidth (10 500 meV) and focus to the small spot on the sample (100 100 μm). The practical result is, that synchrotron radiation in combination with SPECS Phoibos 150 electron energy analyzer can distinguish not only between different elements, but also between different sites of atoms by analyzing of chemical or surface core level shifts only ~0.1 eV large. Tuning of excitation energy changes information depth (due to variation of electron inelastic mean free path) as well as focusing on specific element (due to photoionization cross section dependence). Near Edge X-ray Absorption Fine Structure (NEXAFS) can be measured only with tuneable photon source. Photon flux on the sample as a function of photon energy is displayed on figure 2.

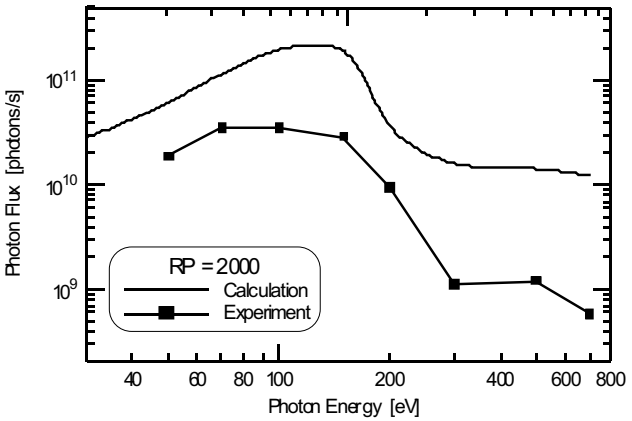

Figure 2. Photon flux as a function of photon energy for resolving power E/dE = 2000.

Scientific output

During its seven years history MSB produced nearly 50 scientific papers and other 10 are submitted or in press. As an example can be mentioned work about valence-charge fluctuations in the Pb/Si(111) system [3] or photoemission study of CO adsorption on ordered Pb/Ni (111) surface phases [4].

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