ALL DIFFERENT FLAVORS OF SYNCHROTRON SINGLE CRYSTAL X-RAY DIFFRACTION EXPERIMENTS

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Abstract This lecture reviews the main concepts, applications and capabilities of different non-conventional approaches to single-crystal x-ray diffraction (SXD) experiment utilizing synchrotron radiation for applications in high-pressure research. You will learn how such experiment can be designed and performed to best answer the scientific goals of your study and, at the same time overcome the main technical limitations imposed by the high-pressure device and type of measurement. The emphasis will be placed on experiments that cannot be performed using laboratory instruments, *e.g.* involving ultrahigh (>50 GPa) pressures, poor quality samples, laser heating in diamond anvil cell (DAC), *etc.* The main goal of the presentation is to convince you that even if you are not an expert crystallographer, with good understanding of the general basic principles of synchrotron SXD experiments in a DAC you can successfully use these techniques as valuable and easy tools in your own high-pressure research.

Keywords: Synchrotron experiments, structure determination, single-crystal diffraction, phase transitions

1. Introduction

Conventional methodology (utilizing monochromatic beam and four circle diffractometer with point detector) for single-crystal XRD experiments has been developed and optimized shortly after the first automated diffractometers became available in late 1960s and has served the crystallographic

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community very well since then (see *e.g. Arndt and Willis*, 1966; *Busing and Levy*, 1967). The introduction of area detectors in the 1990s has brought some revolutionary improvements into the data collection time, ease of diffractometer operation and sensitivity (*e.g. Burns*, 1998), but at the same time turned the diffractometer more into a black box that operates in a push-button mode. This mode usually works very well in application to crystals in air, but often is not quite adequate for experiments involving samples enclosed in diamond anvil cells (DACs). DAC introduces several important obstacles into the experiment, which significantly affect the quality of the intensity data and the coverage of reciprocal space (amount of independent observations that can be acquired). Since the very beginning of the automated diffractometry high-pressure crystallographers have strived to define optimal data collection and data reduction strategies geared towards retrieving highest-possible quality data from the SXD experiment in a DAC and developed such custom solutions as the $\phi = 0°$ positioning mode (*Finger and King*, 1978), 8-position peak centering (*Hamilton*, 1974; *King and Finger*, 1979; *Dera and Katrusiak*, 1999), multiple-ψ intensity measurement (*Loveday et al.*, 1990). *Miletich et al.* (2001) presented a thorough review of the high-pressure crystallographic solutions and techniques for SXD experiments with lab diffractometer.

The availability of synchrotron x-ray sources, and development of beam-lines specializing in high-pressure diffraction experiments has brought yet another significant revolution into high-pressure crystallography, enabling researchers to work with much smaller samples, reach much higher pressure and study more complex solids (*e.g.* proteins). However, despite all the great advantages of SXD techniques, synchrotron single crystal experiments remain much less frequently utilized than synchrotron powder diffraction experiments. The main reasons for this situation are lack of understanding of basic principles and (mostly unjustified) fear of sophistication. I will try to convince you that a well designed and executed synchrotron SXD experiment can, in fact, be much easier than a powder experiment, and will, in most cases, provide you with data characterized by a far superior information content and quality.

While the conventional experimental strategy for SXD experiments is ideal for crystals of reasonable (above 0.020 mm) size in air, and large incident beams (above 0.100 mm), characteristic of laboratory diffractometers, it is often suboptimal or even inadequate for experiments in diamond anvil cell involving synchrotron radiation. The main reasons for that are:

- Access limitations introduced by the design of the DAC
- Presence of additional diffraction signal (backing plates, diamonds, pressure medium)

- Time constraints (*e.g.* necessity to collect data containing maximum information at multiple pressure steps within the constraint of synchrotron beamtime)
- Instrument imprecision (for beam sizes below 0.005 mm and very small crystals (0.001–0.005 mm) keeping the illuminated volume of the crystal constant during rotation is almost impossible)
- DAC rotation limitations (*e.g.* for experiments at high pressure during laser heating)

Because of these reasons, a lot of developmental efforts have recently been devoted to designing and testing alternative ways of performing SXD experiments at synchrotron high-pressure beamlines. These new experimental approaches, which retrieve the same information content and provide the same (or superior) data quality as the conventional methods, allow to circumvent most of the problems intrinsic to DAC.

The main objective of this lecture is to provide a comprehensive introduction to SXD crystallography at high pressure as well as critical review of the most promising experimental approaches alternative to conventional monochromatic SXD experiment.

2. Why SXD Experiment is Usually Better than a Powder Experiment

A typical single crystal XRD experiment provides three classes of direct observations: (i) crystal orientations and diffracted beam orientations at which diffraction peaks occur (ii) intensities of the diffracted beams (iii) energies/wavelengths of the diffracted beams. From these measurements, the following secondary and directly interpretable information can be derived:

- Lengths of reciprocal vectors corresponding to each diffraction peak
- Orientation of reciprocal vectors corresponding to each diffraction peak
- Orientation matrix
- Miller indices
- Structure factor amplitudes
- Systematic absences/space group
- Structure factor phases
- Structure model (atomic positions, occupancies, thermal displacement parameters)
- Electron density distribution

The main difference between single crystal and powder experiment is that in the latter it is not possible to measure/determine orientations of reciprocal vectors, but only their lengths. While this may seem like a small loss, it has very significant consequences for data analysis/information retrieval:

- In powder diffraction determination of the unit cell, space group and assignment of Miller indices are usually ambiguous.
- Because of one dimensional character of the powder XRD data peak profiles often overlap and peak intensities cannot be measured independently.
- Peaks at high resolution (small d-spacings, below ~1.5 Å) contribute very little to indexing and unit cell refinement as their Miller index assignment is very ambiguous).

In addition to the above general shortcomings of powder diffraction, there are also important high-pressure specific limitations such as insufficient particle statistics, especially after laser heating treatment (due to recrystallization), uniaxial strain induced peak broadening and coexistence of multiple phases within one sample. It cannot be denied that powder XRD at high pressure is a well established and very successful technique, but it has to be realized that majority of its successes apply to very simple systems (elements, oxides, binary compounds).

3. Basic Principles of SXD

Diffraction (scattering of intense and directional diffracted beam(s) originating from the crystal) occurs when the Bragg condition for the given reciprocal vector is satisfied at a given *crystal orientation* and for the *available incident wavelength*. At a given crystal orientation each reciprocal vector requires a different specific wavelength for the diffraction to occur. At a given fixed wavelength there is a set of crystal positions (defined by rotation of the reciprocal vector on a surface of cone with axis along the incident beam) at which diffraction for a given reciprocal vector occurs. In order to observe sufficient number of peaks one of the variables has to be varied. Diffraction occurs regardless of the detector used, and the detector position, but the detector is needed to provide the observation.

Capturing the diffraction event on a detector constrains the intensity, direction and energy (only if the incident beam is monochromatic, or with a polychromatic incident beam, if the detector has energy resolution) of the diffracted beam. The angle between the diffracted and transmitted beams (Bragg angle), together with diffracted beam energy define the length of the corresponding reciprocal vector.

In a polychromatic experiment with stationary sample the crystal orientation is constant, therefore measuring the directions, intensities and energies of the diffracted beams provides complete SXD information. In a monochromatic experiment with area detector, on the other hand, diffraction images are collected while the sample is rotated, and the complete

measurement involves determination of the directions and intensities of diffracted beams as well as crystal orientations at which these intensities reach maximum.

4. Differences and Similarities Between Monochromatic SXD Experiments with Point Detector and with Area Detector

The conventional monochromatic SXD technique using 4-circle diffractometer and point detector, and utilizing the high-pressure specific data collection strategy can be successfully applied at synchrotrons to pressures as high as 50 GPa (*Friedrich et al.*, 2007) however, the long data collection time, and user-attention-intense data collection process are often prohibitive for synchrotron environments.

One of the major advantages of using point detector is the ability to collimate the diffracted beam and discriminate the signal originating from the sample crystal from other signals (powder diffraction from the backing plates, diamond reflections, parasitic scattering, *etc.*). Additionally, point detector experiments provide a much more detailed information about the evolution of crystal mosaicity (related to *e.g.* to uniaxial strain) by allowing to measure high resolution rocking curves (*e.g. Angel et al.*, 2007). High quality of the intensity data that can be achieved through diffracted beam collimation often allows more advanced data analysis such as retrieval of deformation electron density using maximum entropy method (*e.g. Yamanaka*, 2005).

SXD experiments require as large as possible angular access to the sample and are usually performed with DACs equipped in x-ray semi-transparent backing plates. The plates most commonly used in lab experiments are made of Be metal. With the use of point detector the powder diffraction signal which originates from the transmitted beam passing through the downstream Be backing plate can be rejected by collimation of the diffracted beam. Use of Be backing plates in synchrotron SXD experiments with area detectors is not very convenient, as the very textured Be powder pattern significantly contaminates the signal originating from the studied sample.

One of the most important differences between monochromatic SXD (mSXD) experiment with point and area detector is peak positioning. In point detector experiment the sample is positioned individually for measurement of every peak. As a result, the data collection time depends significantly on the number of reflections measured (and as a consequence on the size of the unit cell and crystal symmetry). This strategy requires that the orientation matrix of the crystal is determined very precisely prior to the actual data collection.

In area detector experiments peak intensities are captured in the diffraction image "on the fly", while the sample rotates. Since the surface area has a large angular coverage, multiple diffraction events are recorded in the same image without the necessity to "aim" for each peak specifically. In principle, it is possible to record a good quality dataset without any prior knowledge of the crystal orientation. This significantly speeds up the experiment, and makes it lees attention-demanding. Availability of diffraction images with multiple diffraction peaks is also very convenient in experiments involving phase transitions, as it provides an immediate qualitative evidence that a discontinuous change has happened.

There is a general belief that SXD experiments with area detectors produce unit cell information with quality inferior to that coming out from point detector instruments, however this is mostly due to hardware configurations (mostly very short sample-to-detector distance) used in CCD lab diffractometers which do not emphasize high quality unit cell parameter measurements and result in relatively large uncertainties of peak d-spacing determination. In fact, in a properly designed synchrotron SXD experiment the unit cell parameter determination can be more precise than in a powder experiment, because peaks at very large Bragg angle can be unambiguously indexed (using their three-dimensional coordinates, instead of just the lengths) and used in the unit cell refinement.

Monochromatic SXD experiments utilizing area detectors (CCD and image plate) have been successfully carried out at GSECARS, Sector 13 APS and several other high pressure beamlines throughout the world to pressures as high as 200 GPa.

5. Monochromatic Experiments with Area Detectors

5.1. STANDARD STEP-SCAN APPROACH

Standard monochromatic SXD experiments are performed using small angular step technique, in which the step size is adjusted to capture every diffraction peak in several consecutive images and allow determination of the angle at which the maximum peak intensity occurs by peak fitting (of peak intensity integrated within one image as a function of the rotation angle). Unfortunately, step scan mSXD experiments performed at synchrotrons bring several inconveniences:

1. They produce very large volumes of data. With a standard 0.3 degree step scan a single dataset at one pressure point usually consists of more than 1,000 images. Processing of such large numbers of images is quite time consuming and their storage is expensive.

2. Data collected only is step-scan mode does not provide an easy way of looking at "global picture". If data processing is not performed in real time an interesting phenomenon can be overlooked at the time of performing the data collection.
3. Collecting every image involves time spent for a detector readout, which for certain types of detectors can be very significant (for MAR345 image plate detector readout of one image in full resolution mode takes over 2 min). With large number of images collected the total time lost for readout quickly becomes prohibitive.
4. With high quality and very small crystals and with tightly focused beam peak profiles are often much narrower than the typical 0.3 degree angular step.
5. With very short exposure times (often in the sub-second range) the synchronization of the rotation motor speed with the shutter becomes challenging.

The simplest solution to most of the above problems, which is applicable to crystals of small to medium unit cell is to follow up the step scan with a data collection involving accumulation of the whole (or large part) of the accessible angular range or simply algebraically merging the step images. Such wide-rotation image provides the "global" picture of the diffraction, assures constant rotation speed and significantly shortens the data processing time. There are, however, also few disadvantages of the wide-rotation approach, such as:

- It is not possible to avoid strong diamond peaks which are captured in the same single image as all of the sample peaks.
- With large unit cell crystals the spacial overlap of the peaks might become a problem.

5.2. DUAL-SLEW APPROACH

From the point of view of best possible utilization of the valuable synchrotron beam time it would be optimal if a complete SXD information could be retrieved from a single wide rotation (WR) image. This would mean that a full data collation at a single pressure could be accomplished in a matter of seconds. Such data would most likely be of mediocre coverage and redundancy, but could provide possible insight into slower dynamical processes. Unfortunately, single wide-rotation image does not carry the information about the rotation angle at which each peak maximum occurred. This information is not needed, as long as a sufficiently accurate orientation matrix is available (*e.g.* determined at lower pressure), but in case of a displacive phase transitions peak indexing for the new phase without step scan data becomes very challenging.

In order to solve this problem a new data collection approach, referred to as Dual Slew Approach (DSA) inspired by a method recently patented by Bruker AXS (*Hooft*, 2008, private communication) has been introduced and tested at high pressure beamlines of GSECARS and HPCAT, Advanced Photon Source, ANL.

In a DSA data collection no step scan images are needed. The experiment consists of collecting only two WR images. During the first image accumulation the sample is rotated (usually about the vertical, omega/phi axis) and the detector remains still. When the second image is recorded, the sample rotation is the same as in the first image, but it is accompanied by a second continuous motion, which changes the position of the diffraction peaks on the detector e.g. (detector rotation or translation along, or across the incident beam, chi-rotation, etc.). The magnitude of shift of the detector position for each peak depends on when, during the accumulation the peak passed through its diffraction maximum. Therefore, the maximum intensity rotation angle for each peak can be retrieved by measuring the shifts of the detector pixel coordinates. The DSA method brings several important advantages:

- Complete SXD information can be obtained in a much shorter time just (two accumulations). The gain is especially significant for image plate detectors that have readout times as long as 2–3 min per image.
- The second DSA image records information about peak rocking curves and thus provides some more insight into the strain/mosaicity conditions.
- The precision of the peak rotation angle determination can be controlled by adjusting the magnitude of the second motion, and precision much higher than usually achievable in step scans can easily be accomplished.

6. Beyond Monochromatic Experiments – Polychromatic and Variable Energy SXD Techniques

In addition to monochromatic experiments, single crystal diffraction at high pressure can also be successfully performed with polychromatic incident beam. The two varieties of this method utilize solid-state energy-dispersive point detector (the EDX approach) and non-energy dispersive area detector (Laue method). The EDX method was very popular and quite successfully used in the 1980, but currently fell out of fashion mostly because of the relatively long data collection time (comparable to point detector mSXD experiments) and much more complicated than in mSXD peak intensity corrections. The classical Laue approach has never been widely utilized at high pressure because it does not provide direct information about reciprocal vector lengths and therefore does not allow determination of equation of state.

6.1. VARIABLE MONOCHROMATIC EXPERIMENT (VMSXD)

Ice et al. (2005) described the concept and first experimental tests of high-pressure variable monochromatic (energy scan) experiments with area detector. In vmSXD experiment the sample remains still and incident energy is varied to bring multiple diffraction peaks to a diffracting condition. The diffraction images are collected in a step scan mode, with each image collected at a different energy. Peak energies are determined by fitting of the energy-rocking curves in a manner analogous to angular rocking curve fitting in the mSXD experiment. The vmSXD can be conveniently combined with a wide energy range (WER) image accumulation (analogous to RW images in mSXD), which then provides a global picture of diffraction in one image and can be used conveniently for structure amplitude retrieval. The WER image, is essentially a limited-range (pink beam) Laue image, and alone does not contain the information about the reciprocal vector lengths. The vmSXD approach can also utilize the concept of DSA. If two WER images are recorded, and during the second image acquisition, the continuous energy change is accompanied by a continuous sample rotation (or detector motion), the peak energies can be retrieved my measuring the magnitudes of the peak shifts.

7. Structure Solution and Refinement at Ultrahigh Pressures

In general the information retrieved from an SXD experiment can be used for the purpose of determining the crystal structure if the following conditions are satisfied:

- The unit cell and space group are determined correctly, or at least a proper but unconventional unit cell/space group is assigned.
- The peak intensities are measured with sufficient precision and accuracy. The measure of precision is internal consistency factor of measured intensities R_{int}, which reflects agreement between the measured values of peak intensity for symmetry dependent peaks.
- Sufficient signal to noise level for the peak intensities is obtained.
- Necessary corrections (Lorenz, polarization, absorption, extinction) are applied.
- Sufficient number of peaks intensities are measured and sufficient coverage of the asymmetric part of the reciprocal space is available. From the experimental point of view the above requirements should be satisfied if:
- The sample crystal is of sufficient quality.

- The stress field is sufficiently isotropic.
- The illuminated sample volume remains sufficiently constant.

8. Between Single Crystal and Powder

While the information content of a single-crystal experiment is usually far better than that that of a powder experiment, it is not always possible to preserve the integrity of a single crystal throughout the whole pressure range of interest. Reconstructive phase transitions, anisotropic stresses, as well as high temperature gradients can irreversibly turn the single crystal sample to a powder (*e.g. Sowa and Ahsbahs*, 2006). There are multiple examples that even in such cases pursuing single-crystal style analysis of the coarse powder/bad single crystal samples can lead to retrieval of important and not obtainable by other means information (*e.g. McMahon*, 2005).

It is possible today to deal relatively routinely with crystal twinning and occurrence of multiple grains of one or several different phases present in the incident beam at the same time. In fact, recent reports demonstrate feasibility of single crystal analysis with samples composed of hundreds of such grains (see *e.g. Vaughan et al.*, 2004). The ease of peak indexing and ability to determine structures of unknown phases are not the only benefits of SXD approach. With application of methods known as 3D x-ray microscopy (see *Poulsen*, 2004 for a recent review) details of texture, strain and stress state, and epitaxial relations can be deduced from multigranular samples. Even in case if the sample is composed of small grains and of relatively poor diffraction quality, but exhibits high preferred orientation, collection of three-dimensional data in an SXD manner (pole figure measurement) may yield very valuable information (e.g. decomposition of overlapping peaks) that can be critical in deciphering the nature of the crystal structure (*Wessels et al.*, 1999; *Baerlocher*, 2004).

9. Conclusions

Synchrotron single crystal x-ray diffraction experiments can undoubtedly serve as a very valuable tool in studying structure and behavior of solids under high pressure. The unequivocal determination of the unit cell and space group, the structure factor amplitude information free from ambiguities caused by peak overlap and broadening characteristic of powder diffraction, and the ability to efficiently work with crystals in 1–10 μm size range, as well as reach pressures in excess of 200 GPa make it a truly unique experimental method.

With the recent significant efforts located at the synchrotron beamlines specializing in high-pressure research and focused on creating custom setups, optimized new methodology and specialized data acquisition and analysis software for SXD experiments at ultrahigh pressures the technique becomes not only more and more easily available to the broad community of high-pressure scientists, but also significantly less sophisticated and more user friendly.

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