High Resolution Powder Diffraction at the APS

Science

Definitive knowledge of the crystal structure of a material—inorganic, organic, or biological—is the gateway to understanding its physical properties, its chemical reactivity, and/or its biological functionality. It is the most fundamental aspect of any material. The increasingly complex chemistry and physics of modern materials demands that this structural information be obtained in a routine fashion and with state-of-the-art precision. Because most technologically critical materials only exist as polycrystalline solids, the definitive structural experiment requires high-resolution x-ray powder diffraction. Measurements must also be made with large dynamic range and great sensitivity, so that small signals may be discerned that indicate changes in structural detail or impurity phases – both highly important. Further, measurements must be rapid enough to meet the demand for the experiments and to be used for study of dynamic systems.

Powder diffraction is applied for study of materials of interest to fundamental physics, materials science, mineralogy, and biology. All of these impact DOE missions that are in the national interest including energy storage, remote sensing, environmental remediation, and metallurgical testing and validation. Examples of active problems in condensed matter physics and materials science follow.

The behavior of charge and orbital degrees of freedom is recognized as a powerful organizing principle for understanding the physics in transition metal oxides and chalcogenides. For example, the properties of colossal magnetoresistive (CMR) oxides depend critically on the relative occupation of z^2 and/or x^2-y^2 orbitals on Mn. Recent study of the spinel $CuIr_2S_4$ has revealed a novel charge-ordering motif in which Ir^{3+} octamers interleave with Ir^{4+} octamers. Examples of other systems that manifest charge and/or orbital order are Li-intercalated CoO_2 and spin-crossover compounds (e.g. cobalt oxides). Importantly it is the cooperative ordering of the charge and orbitals on either short- or long-range length-scales that determines the rich physics of manganites and other related systems. The examples given above demonstrate that the full breadth of charge order and orbital order remains to be discovered and understood. Anomalous scattering at the appropriate x-ray absorption edge for the oxidation states of interest is a powerful method to study charge ordering.

Commonly, developments in materials science arise from synthesis and subsequent characterization of materials with certain properties of interest (conductivity, thermal expansion, magnetoresistance, catalytic effect, etc.). Understanding of these materials originates from precision structure determinations coupled with parametric studies (T, pO_2, composition, etc.). As most of these materials rarely come as single crystals, high-resolution powder diffraction is essential for structural work. A recent example comes from the field of dielectric ceramics, in which complex phase equilibria in the $LaCa_{0.5}Zr_{0.5}O_3$—$SrTiO_3$ pseudobinary have been studied. Phase diagrams and structure-property relationships were determined for several samples quenched from synthesis

conditions. The proposed instrument would dramatically increase the rate at which the phase space in such systems can be mapped, as well as offering *in situ* monitoring of reactivity and phase transformations at elevated temperatures.

High resolution powder diffraction likewise is a key research tool in many other fields, including structural biology, geosciences, catalysis, pharmaceuticals, and many others. For exploration of new pharmaceuticals materials, powder diffraction is vital for exploring polymorphic forms – now required by the FDA, since crystalline form affects bioavailability. Likewise it holds promise as a high throughput screening tool for drug binding studies using macromolecular powder diffraction crystallography. The applications in other fields are too numerous to list. It comes as no surprise that all new 3rd+ generation sources have new powder diffraction capabilities.

Powder Diffraction Instrumentation

To obtain ideal resolution in powder diffraction a highly monochromatic beam is used. Detection typically is done with an analyzer crystal, which serves to limit the acceptance of the detector to parallel rays originating from the sample, while rejecting fluorescence and Compton scattering that deviates in energy. These pseudo-parallel beam optics allow resolution to be decoupled from the sample size.

Linear and area detection offers potentially many orders of magnitude greater efficiency. However, pixelated detectors have higher background, since collimation and energy analysis is not possible. Further, in a typical instrument, resolution is limited both by the pixel size of the detector and the finite size of the sample. Decreasing the sample size diminishes the number crystallites that scatter, which decreases the accuracy of the measurement. New instrument designs, which introduce focusing optics close to the sample, coupled with new designs for detectors have promise for overcoming this problem as this allows a large beam on the sample which is focused to match the detector point spead function. New generations of detectors may also offer energy discrimination, giving further favor to use of pixilated detectors. The development work for new powder instruments at Diamond and NSLS-II is also prompting new designs for analyzer-based detection.

The APS is fortunate that our bending magnets have a spectrum and brightness very well matched to the needs of powder diffraction. However, use of focusing to subtend the large divergence of the source causes minor degradation of resolution. A bending magnet instrument will suit most experimental needs, but there will be a small number of experiments that can only be performed with an insertion-device source.

XOR currently has three beamlines that are used for high-resolution powder diffraction, 33-BM, 1-BM and 11-BM. 33-BM is a general purpose diffraction station that is migrating towards surface-interface scattering applications. 1-BM is a highly versatile instrument that currently is deployed in specialized diffraction measurements and fuel-spray imaging. 11-BM is a recently commissioned high-throughput and high-resolution instrument. It has a best-in-world 12-analyzer detection system that provides the alignment flexibility of a discrete detector system but with better than an order of

magnitude improvement in throughput. The current scope of the 11-BM instrument is limited to samples of a specific mounting geometry and measurements in the temperature range from 80 K to 500 K.

Development Plan

This proposal seeks to expand the utility of the 1-BM instrumentation through modernizing it. It seeks to expand the capabilities of 11-BM and develop an instrument along a similar design to 11-BM that would share beam on an insertion device station.

1-BM needs an upgrade of optics, since the components are now over 10 years old and well below the state of the art. The relevant optics to be improved are a water-cooled flat white-beam mirror, a flat vertically focusing mirror, and a sagittal bending second monochromator crystal. The mirror tanks and mirror supports (including the bending mechanisms) will be kept and reused. The monochromator at present requires very high level of training to tune. A more advanced design has the potential to be more user friendly and allow automation. It can also extend the energy range of the station. With this upgrade, 1-BM will again be among the highest flux bending magnet beamlines in the world. Many experiments would benefit from an advanced detector system, for example a tiled array of amorphous silicon detectors. Others would benefit from a multiplexed analyzer system, such as the 12-crystal system in use at 11-BM or perhaps the 64-detector system that is has been discussed for Diamond.

11-BM optics are limited by the poorly designed mirror mounts, which make beamline alignment difficult and will prevent easy access to the planned energy range. While the initial proposal for 11-BM envisioned a wide range of sample environmental support, only the Oxford 700+ cryostream device remained in the final program scope. In contrast, note below the planned suite of ancillary equipment that will be available on the Diamond I11 powder diffraction station when it begins operation in August 2008:

- Stoe capillary furnace (T = 300 – 1700 K)
- MRI flat plate furnace, (T=300 - 2000 K)
- Bruker Humidity chamber (-5°C up to 75°C dew-point, T= 25 – 90°C)
- Linkam DSC (T = 77 – 870 K)
- Cyberstar Hot air blower (T = RT-1300 K)
- PheniX He Cryostat (T = 11 – 300 K)
- ASI cryostat (T= 4 -300 K)
- Oxford Cryosystem 700+ cryostream (T = 80 – 500 K)

All of these capabilities are vitally needed by US scientists. Additional engineering will be required to adapt the goniometer to support such equipment and to allow it to be shared with 1-BM.

With the envisioned improvements to 1-BM and 11-BM, we envision that most

beamtime on 11-BM will be dedicated to high-throughput diffraction measurements. A large fraction will be mail-in samples that are run under routine conditions. In general, experiments that require considerable setup time will be run on 1-BM, which is a more flexible station. As mentioned, however, there are some experiments that require the best possible resolution and sensitivity. These measurements can only be performed on an ID line. Since the demands of such an instrument are modest both with respect to beamtime shifts and physical space, this is can share with any number of beamlines and does not need a dedicated source. Such an ID line may also prove to be much better for automating resonant scattering experiments, since focusing is not required and the 11-BM analyzer design has proven to be easy to align when changing energy.

User Community and Partnerships

The user community for synchrotron powder diffraction at the APS can be expected to grow to well over a hundred academic groups. It will certainly include a number of industrial laboratories, including UOP, Chevron and General Electric, who are already active in the brief time since 11-BM became operational. Government researchers in military and the DOE can also be expected to major users. Key partners may be:

- John Mitchell (MSD)
- Angus P. Wilkinson, Chemistry, Georgia Institute of Technology
- Yan Gao, General Electric
- James Kaduk, INEOS technology
- Ken Poeppelmeier, Chemistry Department, Northwestern University
- Clare Grey, Chemistry, Stony Brook
- David Bish, Geology, Indiana University

Estimated Budget

The budget for this project will be on the order of $400 K for 1-BM, $500 K for 11-BM and $2M for a new ID instrument. A total of additional 6-10 FTEs will be needed to properly staff the instruments, depending on the scope of the intended user program.