

**MS25-P03****X-ray Absorption spectroscopy options for crystallographic research at BESSY II**Daniel Többens<sup>1</sup>, Götz Schuck<sup>1</sup>, Ivo Zizak<sup>1</sup>, Susan Schorr<sup>1</sup>

1. Department Structure and Dynamics of Energy Materials, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany

email: [daniel.toebbens@helmholtz-berlin.de](mailto:daniel.toebbens@helmholtz-berlin.de)

X-ray absorption spectroscopy (XAS) is increasingly used to study crystallographic problems in a wide range of scientific fields. Its element specificity and sensitivity to the local structure provide high complementarity to X-ray diffraction. Due to the need for radiation with tunable energy it is yet restricted to synchrotron sources. The Berlin Electron Synchrotron BESSY II operates multiple XAS stations for user service, some of which are particularly optimized for crystallographic problems:

mySpot [1] is optimized for mapping experiments with focus spot sizes as low as 1.5  $\mu\text{m}$ .  $\mu$ -EXAFS and  $\mu$ -XANES in the energy range 5 - 25 keV can be combined simultaneously with small or wide angle scattering (SAXS & WAXS), X-ray fluorescence analysis (XRF), and Raman Scattering. Lateral focusing lenses with long focal length of 4-7 mm allows scanning of areas and volumes. The experiment is especially designed (but not limited to) for the study of hierarchically structured biological samples.

CryoEXAFS at KMC-3 beamline, developed in cooperation with Freie Universität Berlin [3], allows sample temperatures as low as 20 K, with convenient sample change at cold temperatures. Due to the absence of absorption in air, low radiation energies (3.6 - 14 keV) can be used, extending the range of observable light elements.

KMC-2 XANES [3] provides a stable beam in the energy range 4 - 15 keV, microfocus option and a selection of detectors, allowing transmission and fluorescence geometries. The open concept of the station allows the use of a wide range of sample environments, both in-house and user-provided, and flexible movement of the sample. A particular strong point is the suit of atmosphere control systems [4], which allows for continuous flow or volumetric control, high and low temperatures and pressures, precarious gases and, added most recently, humidity control.

## References:

- [1] Helmholtz-Zentrum Berlin für Materialien und Energie. (2016). mySpot: a versatile microfocussing station for scanning methods at BESSY II. *Journal of large-scale research facilities*, 2, A101. doi 10.17815/jlsrf-2-115
- [2] Helmholtz-Zentrum Berlin für Materialien und Energie. (2016). KMC-2: an X-ray beamline with dedicated diffraction and XAS endstations at BESSY II. *Journal of large-scale research facilities*, 2, A49. doi 10.17815/jlsrf-2-65
- [3] H. Dau, Institut für Experimentalphysik, Freie Universität Berlin
- [4] Sample Environment available at BESSY-II, [https://www.helmholtz-berlin.de/user/experimental-infrastructures/sample-environment/se-at-bessy/specifications\\_en.html](https://www.helmholtz-berlin.de/user/experimental-infrastructures/sample-environment/se-at-bessy/specifications_en.html)

**Keywords:** EXAFS, XAS, Synchrotron

**MS25-P04****Electron diffraction tomography of modulated minerals: the crystal structure of daliranite**Mauro Gemmi<sup>1</sup>, Arianna Lanza<sup>1</sup>, Enrico Mugnaioli<sup>1</sup>, Luca Bindi<sup>2</sup>, Werner H. Paar<sup>3</sup>

1. Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia, Pisa, Italy
2. Dipartimento di Scienze della Terra, Università di Firenze, Firenze, Italy
3. Department of Chemistry and Physics of Materials, University of Salzburg, Salzburg, Austria

email: [mauro.gemmi@iit.it](mailto:mauro.gemmi@iit.it)

Daliranite is a mineral originally discovered in 2003 at Zarshouran, northwest Iran, and approved by IMA in 2007 with the formula  $\text{PbHgAs}_2\text{S}_6$ . It occurs as matted nests of acicular crystals usually associated with quartz and orpiment. Single-crystal needles are just several hundreds of nanometers in size. On the basis of zone-axis electron diffraction patterns, daliranite was recognized as monoclinic,  $19 \text{ \AA} \times 4 \text{ \AA} \times 23 \text{ \AA}$  and  $b = 115^\circ$ , with possible space groups  $P2$ ,  $Pm$  or  $P2/m$ . The unit cell was confirmed by powder X-ray diffraction, however no structure solution was achieved and its crystal structure remained unknown [1].

The daliranite structure problem is a perfect candidate to be tackled using electron diffraction tomography (EDT). This method allows collecting 3D electron diffraction data on coherent domains having size of few hundreds of nanometers, like a single crystal X-ray diffractometer equipped with an area detector [2].

EDT data collected on isolated squared pieces of 200 nm of broken acicular crystals reveals that daliranite exhibits a modulated structure with the main reflections that can be indexed with an orthorhombic cell having  $a = 9.5 \text{ \AA}$   $b = 4.3 \text{ \AA}$   $c = 21 \text{ \AA}$  and extinction symbol  $Pc_n$ . The modulation is along  $a$  ( $\mathbf{q} = \alpha 0 0$ ) with  $\alpha$  varying from crystal to crystal in the range between 0.33 and 0.25. The average structure of daliranite can be solved in space group  $Pcmm$ . The resulting structure shows a chemical formula that differs from that originally reported:  $\text{PbHgAs}_2\text{S}_5$ , which does not require the presence of  $(\text{S}_2)^{2-}$  in the structure. The average structure is formed by zig-zag chains of  $\text{PbS}_8$  bicapped trigonal prisms running along  $a$ , laterally connected by linear  $\text{HgS}_2$  and  $\text{As}_2\text{S}_6$  dimers. In order to discover the mechanism behind the modulation we integrated the superstructure reflections from a crystal with  $\mathbf{q} = 0.25 0 0$  and analyzed them with a superpace approach using JANA2006. The modulated structural model obtained in the 4D space group  $Pcmm(\alpha 00)0s0$  can be refined and indicates that the modulation is due to shifts of the As atoms of the dimers along  $b$ , forming alternatively dimers parallel or inclined with respect to the  $ac$  plane. It is highly remarkable that EDT can furnish data reliable for structure investigation of modulated structures on such small crystal grains, where in fact zone-axis electron diffraction and powder X-ray diffraction even failed in the unit cell determination.

## References:

- [1] Paar W. H., Pring A., Stanley C. J., Putz H., Topa D., Roberts A. C., & Braithwaite R. S. W. (2009) *Mineralogical Magazine*, 73, 871-881.
- [2] Mugnaioli E. & Gemmi M. (2018) *Z. Kristallogr.* 233, 163-178.

**Keywords:** Electron diffraction, modulated structure, daliranite

## MS25-P05

### Application of laboratory X-ray diffraction equipment for Pair Distribution Function (PDF) analysis

Milen Gateshki<sup>1</sup>, Marco Sommariva<sup>1</sup>, Detlef Beckers<sup>1</sup>, Stjepan Prugovecki<sup>1</sup>, Martijn Fransen<sup>1</sup>

1. Malvern Panalytical B.V., Almelo, Netherlands (Holland, Europe)

**email:** [milen.gateshki@panalytical.com](mailto:milen.gateshki@panalytical.com)

The increased interest in recent years regarding the properties and applications of nanomaterials has also created the need to characterize the structures of these materials. One of the most promising techniques to study nanostructures using X-ray diffraction is by using the total scattering (Bragg peaks and diffuse scattering) from the samples and the pair distribution function (PDF) analysis. The pair distribution function provides the probability of finding atoms separated by a certain distance. From experimental point of view a typical PDF analysis requires the use of intense high-energy X-ray radiation ( $E \geq 15$  KeV) and a wide  $2\theta$  range. At present, synchrotron and neutron sources are the preferred choice for PDF analysis, but there is clearly an increasing need for a PDF solution based on laboratory diffraction equipment. Such a solution, though limited, will benefit areas where quick feedback about the materials properties is important and will allow the routine application of PDF analysis for materials characterization in university laboratories as well as industrial R&D departments.

After the initial feasibility studies regarding the use of standard laboratory diffraction equipment for PDF analysis [1,2] this application has been further developed to achieve improved data quality and to extend the range of materials, environmental conditions and geometrical configurations that can be used for PDF experiments. The recent introduction of detectors with improved efficiency for high-energy X-rays [3] has further enhanced the capabilities of laboratory diffractometers for total scattering experiments. This contribution presents several examples of laboratory PDF studies performed on different nanocrystalline and amorphous materials of scientific and technological interest (organic substances, oxides, metallic alloys, materials for battery applications, etc.) and demonstrates that PDF analysis with a laboratory diffractometer can be a valuable tool for structural characterization of nanomaterials.