MS25-P03

X-ray Absorption spectroscopy options for crystallographic research at BESSY II

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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 µm. µ-EXAFS and µ-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:

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[4] Sample Environment available at BESSY-II, https://www.helmholtz-berlin.de/user/experimental-infrastructures/sample-environment/se-at-bessy/specifications_en.html

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Electron diffraction tomography of modulated minerals: the crystal structure of daliranite

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Daliranite is a mineral originally discovered in 2003 at Zarshouran, northwest Iran, and approved by IMA in 2007 with the formula $PbHgAs_2S_6$. 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 Å x 4 Å x 23 Å and b =115°, with possible space groups *P*2, *Pm* or *P*2/*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 ~~is~~ exhibits a modulated structure with the main reflections that can be indexed with an orthorhombic cell having a = 9.5 Å b = 4.3 Å c = 21 Å and extinction symbol *Pc_n*. The modulation is along a (**q** = α 0 0) with α 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 *Pcmn*. The resulting structure shows a chemical formula that differs from that originally reported: $PbHgAs_2S_5$, which does not require the presence of $(S_2)^{2-}$ in the structure. The average structure is formed by zig-zag chains of PbS_8 bicapped trigonal prisms running along *a,* laterally connected by linear HgS_2 and As_2S_6 dimers. In order to discover the mechanism behind the modulation we integrated the superstructure reflections from a crystal with **q** = 0.25 0 0 and analyzed them with a superpace approach using JANA2006. The modulated structural model obtained in the 4D space group *Pcmn* (α00)0*s*0 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.