Abstract. The hard X-ray beamline BL 8 at the 1.5 GeV electron storage ring DELTA is described, and experimental data of different fields of research are presented. Making use of the intense X-ray beam emitted by a superconducting wiggler, the beamline is dedicated to X-ray absorption experiments. Three different monochromator crystal pairs are permanently available for experiments in the spectral range from about 1 keV to ca. 25 keV photon energy. Results of reference materials show that high quality EXAFS data can be obtained using Si(111) and Si(311) monochromators. First measurements in the energy range between 1.2 and 5 keV have been accomplished using YB66(400) monochromator crystals. The experimental hutch accommodates a unique 6-axis diffractometer which is well suited for all kinds of diffraction and absorption experiments, including the grazing incidence geometry. The diffractometer can carry heavy loads related to non-ambient sample environments such as e.g. ultrahigh vacuum sample stages or cryostats. Here we present typical results obtained at BL8 in different areas of materials science including investigations of dilute alloys by fluorescence mode EXAFS and the study of the structural changes associated with temperature induced spin transitions of metallo-supramolecular polyelectrolyte-amphiphile-complexes.

1. Beamline layout and performance

The beamline is installed at the superconducting asymmetric wiggler (SAW) at the electron storage ring DELTA in Dortmund (Germany). The storage ring operates with 1.5 GeV electrons, injection currents of 130 mA and offers beam lifetimes of 8-10 h. The beamline is designed for X-ray absorption spectroscopy, diffraction measurements and surface sensitive X-ray reflectivity experiments in the energy range from ca. 1 to 25 keV (12.4 – 0.49 Å) making use of the intense radiation emitted by the insertion device. In its asymmetric mode, with a maximum magnetic field of 5.3 T and a magnetic gap of 18 mm, the wiggler parameter amounts to 149, yielding a critical energy of about 8 keV. Three different pairs of monochromator crystals – namely Si(311), Si(111) and YB66(400) – are mounted in a complex triple monochromator. Each of the first crystals is indirectly water cooled, with the cooling being designed for heat loads of up to 500 W. For the Si(111) and the Si(311) crystals, the cooling is combined with a bending mechanism to compensate the thermal bump induced by the high heat load of the wiggler [1], resulting in an energy resolution very close to that predicted by the Darwin theory [2]. Typical absorption data measured in transmission mode are presented in figure 1, where the room temperature absorption spectrum of a Pt metal foil measured at
the L$_3$-edge using ionization chambers is shown. A sharp white line feature and detailed EXAFS oscillations are visible up to more than 1 keV above the edge. The first derivative of the absorption spectrum is presented in the lower inset of figure 1, where the energy resolution can be estimated to be about 1.8 eV from the full width of the first peak at about 11.564 keV. Furthermore, the $k^3$-weighted extracted fine structure oscillations $\chi(k) * k^3$ are depicted in the upper inset of figure 1. Almost noise-free data are visible even for $k > 16$ Å$^{-1}$, which allow obtaining detailed and precise short range order structural information.

Figure 1. Room temperature transmission mode spectrum of a Pt metal foil at the Pt L$_3$-edge measured within ca. 35 minutes of acquisition time. In the lower inset, the first derivative spectrum is shown. The upper inset shows the extracted $k^3$-weighted EXAFS oscillations.

Up to now, there are only few beamlines worldwide that offer the technologically important spectral range between 1 and 2 keV using e.g. YB$_{66}$ crystals [3,4] with the possibility to switch to hard X-ray beams on the same sample. While a much more detailed description of the beamline and its performance can be found in ref. [2], we will focus here on first scientific XAS projects performed at the beamline in order to demonstrate its capabilities in different research areas.

2. Experimental results

2.1. Fluorescence EXAFS investigations of reactor pressure vessel steels

Alloyed elements in steels are important for their elastic properties. During alloy fabrication, small nm-sized precipitates may form. Those precipitates can pin dislocations and thus hinder dislocation gliding, leading to a less ductile behaviour compared to a homogeneous dispersion in the steel matrix. Therefore, the local atomic environment, valence and the location of the alloyed elements in the Fe host matrix are of crucial interest in order to derive relations between the microstructure and the mechanical behaviour of such steels. In figure 2, fluorescence spectra of an iron based steel containing ca. 1 at.% Mn are shown for excitation energies in the vicinity of the Mn K-edge at 6.539 keV. A Peltier cooled Si-pin diode served as detector for the present experiments, and thus the fluorescence spectra suffer from the limited energy resolution of this equipment.

Figure 2. Fluorescence spectra of an iron based alloy containing 1 at.% Mn in the vicinity of the Mn K-edge (6.539 keV) for the indicated excitation energies. EXAFS data were collected in the region of interest indicated by vertical dotted lines. In the inset, raw EXAFS data collected within ca. 1 h of total integration time are depicted.
However clearly separated fluorescence signatures of Mn (5.90 keV), Cr (5.39 keV) and Ti (4.46 keV) are detectable. The abundant iron already becomes detectable for the highest photon energy of 7.09 keV, which is slightly below the Fe K-edge at 7.112 keV, and furthermore, also elastically scattered photons are detectable. The EXAFS spectrum shown in the inset of figure 2 was obtained by using the Mn Kα-peak in the energy range between 5.66 keV and 6.25 keV. The increase of the fluorescence intensity for E > 6.7 keV is related to the onset of the Fe Kα excitation in the pre-edge region of the Fe host. The low energy tail of this intense Fe-peak overlaps with the Mn Kα signals here, and prevents the complete separation of the Mn- from the Fe-contributions - however a detailed fitting of the two peaks with two Gaussians or Lorentzian peak function would solve this problem. Despite the low Mn concentration within the alloy and a total integration time of only 1 h for the photon energy range from 6.4 to 7.1 keV, the quality of the spectrum allows a more detailed and quantitative EXAFS analysis. From the EXAFS spectrum we can conclude that the alloyed Mn atoms are located on bcc-lattice sites; this is obvious from a comparison to a bcc metal such as pure iron or alloyed metal elements on bcc iron positions [5].

2.2. Spin transitions in metallo-supramolecular polyelectrolyte-amphiphile-complexes
Polyelectrolyte-amphiphile-complexes (PACs) are of particular interest because the spin state of the metal ions and thus the magnetization of the system can be switched by temperature, light or pressure. This behaviour could lead to future applications in molecular memory and switching devices [6]. It is well known that the low-spin (LS) to high-spin (HS) transition can be initiated by illumination with visible light, and it has been demonstrated by EXAFS that this photo-induced spin transition is associated with a deformation of the octahedral coordination symmetry around the metal cations [7]. Here we want to address the structural changes in a supramolecular arrangement induced by a variation of temperature from liquid helium (ca. 4 K) to room temperature (300 K) in an ultrahigh vacuum chamber (p<10^-8 mbar) using the well known spin crossover compound Fe(phen)2(NCS)2 (phen=1,10-phenanthroline), revealing S=0 and S=2 in the LS and HS states, respectively. The diffractometer at DELTA BL8 is well suited for such kind of experiments, because it can handle non-ambient sample environments such as cryostats or vacuum chambers of up to 120 kg without any counterbalances, making a precise sample alignment possible. In figure 3, spectra obtained at low and high temperature are compared with each other together with fits of the corresponding Fourier transforms.

![Figure 3. Iron K-edge transmission mode EXAFS spectra of the spin-crossover compound Fe(phen)2(NCS)2 in the LS state at 10 K and in the HS state at 300 K. In the insets, fits (dashed lines) of the Fourier-transformed experimental data (full lines) are presented (k -range for the FT: 2.4 Å⁻¹ < k < 15 Å⁻¹). The data are not corrected for phase shifts. Note the shift of the nearest neighbor peak to lower bond distances in the FT of the low-spin state spectrum.](image)

The obtained fit results are consistent with a deformation of the Fe-N octahedra in the course of the spin transition, leading to an overall increase of all Fe-N distances with temperature as expected from previous X-ray diffraction [8] and EXAFS [9] studies. More specific, we determined Fe-N distances of 1.93 and 1.98 Å for the two iron-nitrogen bonds with phenanthroline-ligands, and Fe-NCS bonds at 1.99 Å in the LS-state at 10 K. For the HS-state (300 K), the corresponding values are 2.06, 2.20 and 2.22 Å, respectively. The overall increase of the bond lengths is consistent with literature data [8, 9].
2.3. Aging of amorphous titania at room temperature

Nanomaterials are becoming important for the use in Li-ion batteries as these can deliver an increased capacity and improved power performance. Also amorphous materials are of interest due to their promising electrochemical properties [10]. However, there are problems with the stability of such materials, which leads to reduced capacity and lifetime of batteries. Therefore, the aging of amorphous TiO$_2$ phases which were prepared by the hydrolysis of titanium(IV)isopropoxide and the subsequent condensation and aggregation to titania agglomerates (see e.g. [11]) is investigated. Crystalization and degradation effects are well investigated at elevated temperatures, but little is known about changes at room temperature. Freshly precipitated TiO$_2$-samples as well as samples aged at room temperature for about one year were investigated by transmission EXAFS. Figure 4 shows a fit of the XANES region of the aged sample with TiO$_2$ reference compounds, yielding a composition of about 54.5 wt.% amorphous TiO$_2$, ca. 41.3 wt.% anatase, no brookite and only 4.2 wt.% rutile. This suggests that about half of the initial amorphous precipitate is transformed into a nanocrystalline anatase modification after storage in air at room temperature for one year.

The selected results show the advanced possibilities of beamline BL 8 for XAS spectroscopy, which will be further extended when the low energy region below 2 keV becomes accessible for spectroscopy of e.g. the Al and Si K-edges.

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