High-resolution hard-X-ray fluorescence spectrometer

Evgueni Kleimenov¹, Anna Bergamaschi¹, Jeroen van Bokhoven², Markus Janousch¹, Bernd Schmitt¹ and Maarten Nachtegaal¹

¹Paul Scherrer Institut, CH-5232 Villigen, Switzerland
²ETH Zurich, Institute for Chemical and Bioengineering, 8093 Zurich, Switzerland
E-mail: evgueni.kleimenov@psi.ch, maarten.nachtegaal@psi.ch

Abstract. A Johann-type X-ray fluorescence spectrometer for XES, RXES/RIXS, HERFD XAS and RXS experiments was designed, constructed and commissioned at the X10DA-SuperXAS beamline of the Swiss Light Source. The spectrometer consists of three key elements: a sample manipulator, an X-ray dispersive element (spherically bent silicon or germanium crystal), and an one-dimensional-array X-ray detector. The detected X-ray fluorescence energy is scanned by changing the angle between the sample, crystal and detector. The energy resolution of the spectrometer ranges from sub-eV to several eV. Thanks to the use of a one-dimensional array detector the spectrometer is easy to align and operate.

1. Introduction

We present the design of an X-ray fluorescence spectrometer for synchrotron-based hard-X-ray photon-in-photon-out experiments [1], such as X-ray emission spectroscopy (XES), resonant X-ray emission spectroscopy (RXES) / resonant inelastic X-ray scattering (RIXS), high-energy-resolution fluorescence-detected X-ray absorption spectroscopy (HERFD XAS), and X-ray Raman spectroscopy (XRS). The spectrometer is noticeable for its simple design, alignment, and operation. The spectrometer is constructed, commissioned, and operated at the X10DA-SuperXAS beamline of the Swiss Light Source (SLS). The photon-in-photon-out techniques require the resolution of the spectrometer to be below the lifetime broadening of the fluorescence line (several eV). A high collection efficiency of the instrument is an essential requirement for the experiments with diluted samples, such as catalysts, which have a concentration of the active element of few weight percent. To fulfill these two requirements the Johann geometry of the spectrometer was chosen.

2. Principles of high-resolution X-ray emission spectroscopy and factors influencing the performance of the spectrometer

The detection of an X-ray emission spectrum is based on the phenomenon of X-ray diffraction on the crystal lattice. For an ideal crystal lattice, the dependence of the wavelength $\lambda$ of the diffracted beam on the incident angle $\theta_I$ is given by the Bragg law

$$2d \sin(\theta_I) = n \lambda,$$

where $n$ is a positive integer called order of diffraction, and $d$ is the crystal lattice spacing. The photon energy is inversely proportional to the wavelength: $E = h\nu/\lambda$, where $h$ is the Planck
constant and \( c \) is the speed of light. In case of a real crystal, the X-ray radiation of wavelength \( \lambda \) will be dispersed to some range of angles close to \( \theta_B \). The angular width of the dispersed radiation is called Darwin width. Its value depends on the quality of the crystal lattice, stress in the lattice, thickness of the crystal and some other parameters. The contribution of the angular width \( d\theta \) to the energy resolution \( dE \) is given by the derivative of the Bragg law

\[
dE/E = d\theta \cot(\theta_B),
\]

and vanishes for \( \theta_B = 90^\circ \), which is so-called backscattering geometry.

There are two types of widely used XES spectrometer designs: spectrometers for instant recording of an emission spectrum in an energy region of several dozen eV and spectrometers, which require scanning of the Bragg angle. The first type includes flat-crystal spectrometers [2, 3] and cylindrically-bent-crystal (von-Hamos-type) spectrometers [4, 5]. Spherically-bent crystals are normally used in the spectrometers of the second type [6, 7, 8], which are Johann- and Johansson-type spectrometers. A spherically-bent-crystal spectrometer design has been chosen aiming for the high collection efficiency to maximize photon counts.

A sketch of a spectrometer with a spherically-bent crystal is shown in Figure 1. This type of spectrometer was first presented by Johann in 1931 [6]. The elements of the spectrometer are located on a Rowland circle of radius \( R \). The incident X-ray beam causes the sample to emit fluorescence radiation. The crystal diffracts the fluorescence radiation, thus selecting only the wavelengths satisfying the Bragg law (1). The crystal is produced by bending a flat crystal-wafer to a radius of curvature (ROC) of \( 2R \). This geometry ensures the approximate focusing of the diffracted fluorescence onto the detector, while the exact focusing can be achieved only in backscattering geometry. Another type of the spectrometer called after its inventor Johansson [10] has improved focusing as compared to the Johann spectrometer. The radius of curvature of the reflecting surface of a Johansson crystal is equal to the radius \( R \) of the Rowland circle, but the radius of curvature of the crystal lattice planes is \( 2R \). Because Johansson-type crystals require a complicated production procedure, no experiments were performed using these crystals.

The resolution of a Johann-type spectrometer is influenced by the intrinsic resolution of the crystal (Darwin width), quality of the crystal surface, Rowland-geometry aberrations (non-exact

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Johann-type spectrometer. Objects not to scale}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2.png}
\caption{Reflectivity curves simulated with the cryst_mrl routine of XOP package [9] for Si(733), thickness=0.3 mm, \( \theta_B=81.7^\circ \)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.png}
\caption{Estimated resolution of the Johann-type spectrometer}
\end{figure}
focusing), and deviations from the Rowland geometry (misalignment, size of the X-ray spot on the sample). The intrinsic resolution of the crystal mainly depends on the ratio of the crystal-wafer thickness to its radius of curvature. The thinner the wafer, the smaller the radius of curvature that can be achieved without deteriorating the overall resolution of the spectrometer, and thus, the better the collection efficiency can be achieved. Simulated reflectivity curves for different radii of curvature are shown in Figure 2. The simulations were performed for a wafer thickness of 0.3 mm and only elastic bending effects were taken into account, while other types of lattice distortion were neglected. A radius of curvature of 1000 mm leads to an angular width of 0.2 mrad, which results in a contribution to the energy resolution of 0.3 eV at the Pt L0\textsubscript{1} line. The contributions to the instrumental resolution of aberrations, source size and deviation from Rowland geometry are plotted in Figure 3. They were calculated according to reference [8],

![Figure 4. 3D-view of the XES spectrometer installed at the SuperXAS beamline](image)

![Figure 5. Translation and rotation of the spectrometer parts. Dash-dot lines indicate the movements of the crystal and detector](image)

using a source size $dx=dy=dz=0.5$ mm, a deviation of the crystal position from the Rowland circle $dX=5$ mm, a radius of curvature $ROC=1000$ mm, and a crystal diameter $d=100$ mm. The main contributions result from the horizontal spot size along the beam $dz$, deviation from Rowland geometry $dX$, and spherical aberrations in the vertical plane. The contribution of the source size $dy$ is negligible. For the spectrometer located in the horizontal plane (Figure 1) the spot sizes $dz$ and $dy$ are defined by the focus size of the beamline. The spot size $dz$ is defined by the penetration depth of X-rays or by the thickness of the sample and can be much bigger than the focus size. If the spectrometer is located in the vertical plane (perpendicular to the X-ray beam), $dx$ and $dz$ are defined by the focal size, and $dy$ depends on the penetration depth or spot size, which slightly improves the resolution but requires a more complex technical design.

3. Spectrometer design
The spectrometer is designed in the Johann geometry and located in the horizontal plane (Figure 4). A crystal with $ROC=1$ m and $d=10$ cm is fixed in a standard 4-inch optical-mirror mount, which makes it easily exchangeable and enables a manual adjustment of the crystal orientation. The crystal is mounted on an XYZ stage driven by stepper motors with encoders. The Bragg
angle is scanned by moving the crystal position in the horizontal plane as shown in Figure 5. The center of the reflecting surface of the crystal is always located on a circle of a radius $R$, which is equal to the radius of the Rowland circle (50 cm). The scanning range is limited by the movement range of the Z-motor, which is 5 cm. The position of the crystal-stage assembly on the optical table can be changed manually with a step of 2.5 cm along X or Z axis. The X-ray fluorescence is registered by a MYTHEN-II detector developed at the Paul Scherrer Institute [11]. The X-ray sensor of the detector is a one-dimensional array of 1280 silicon strips, which ensure a spatial resolution of 0.05 mm. The size of the sensor is 8 mm x 6.4 cm. The detector consists of a sensor module and a minicomputer acquisition board, which transmits the acquired data to the main computer over a computer network. The detector is suitable for registration of X-ray radiation in the energy range between 4.5 and 40 keV. The detector operates in single photon counting mode. The electronic noise and low-energy background are discriminated by applying a threshold. The threshold can be set with a resolution of about 200 eV on the whole detector [12]. The minimum achievable value of the threshold is limited by the electronic noise to 3 keV. Mismatches between channels are corrected by means of a flat field normalization. The detector dynamic range of $2^{24}$ is not affected by non-linearities at the counting rate used for this kind of measurements. The use of an one-dimensional-array detector allows an easier adjustment of the spectrometer compared to a conventional photodiode. No slit in front of the detector is required to set the energy resolution because a pixel range for detection can be selected. The detector is mounted on a translation-rotation stage which allows translations along the X, Y and Z axes and rotation in the horizontal plane. In a Bragg-angle scan the z position of the detector is scanned simultaneously with the crystal position and the detector is rotated to keep the sensor plane on the Rowland circle as shown in Figure 5. To decrease the absorption of X-ray by air, a rubber party-balloons of a nominal diameter of 110 cm filled with helium can be placed between the sample, crystal, and detector. A silicon photodiode was placed between the sample and the detector to record the transmission of the sample simultaneously with the fluorescence. The intensity of the incident beam was recorded with an ionization chamber placed in front of the sample.

**Figure 6.** Distribution of the platinum-foil fluorescence signal on the detector at a beamline energy of 11565 eV and spectrometer energy of 9442 eV

**Figure 7.** Instrumental resolution derived from the size of the X-ray spot on the detector and linear dispersion of the spectrometer

**Figure 8.** Pt L$_{\alpha 1}$ fluorescence line of a platinum foil and elastically scattered X-rays
14th International Conference on X-Ray Absorption Fine Structure (XAFS14) IOP Publishing
Journal of Physics: Conference Series 190 (2009) 012035 doi:10.1088/1742-6596/190/1/012035

Figure 9. Fluorescence-detected and transmission-detected L₃-edge XAS spectra of platinum foil. RIXS spectrum integrated along the fluorescence-energy axis is shown for comparison.

Figure 10. 1s2p RIXS plane of platinum foil. Two horizontal lines denote the fluorescence energy range selected by the spectrometer in the HERFD XAS experiment.

4. Spectrometer operation and performance
The spectrometer is operated at the X10DA-SuperXAS beamline of the Swiss Light Source. The resolution of the beamline dE/E at energies below 12 keV is better than 2 × 10⁻⁴. The beamline equipped with a Si(111) monochromator crystal provides a flux of 6 × 10¹¹ photon/s at E=9442 eV (Pt Lα₁) and 8 × 10¹¹ photon/s at the E=11564 eV (Pt L₃ edge) measured with a silicon photodiode at the sample position. The spot size on the sample can be varied between 10 mm (horizontal) x 0.5 mm (vertical) and 0.1 mm x 0.1 mm. The spectra shown here were taken with a spot size of 0.2 mm x 0.2 mm. The beamline energy was calibrated by the inflection point of the transmission-detected XAS spectra of platinum (11564 eV) and zinc (9659 eV) foils. A Si(733) crystal with a wafer thickness of 0.3 mm was used in the spectrometer for the detection of the Pt Lα₁ fluorescence line. The spectrometer was aligned using the following procedure: All elements were put in their position on the Rowland circle, the crystal orientation was aligned using a laser pointer focused on an aperture placed at the sample position, after which the optimization of the crystal and detector positions was performed with the X-ray fluorescence of a metal foil. A slight miscut of the crystal surface resulted in a shift of the fluorescence spot position on the detector with respect to the position of the laser beam, which complicated the alignment procedure. Using the 1D-array detector allowed a fast alignment of the spectrometer, which takes typically one hour. The energy scale of the fluorescence spectrometer was calibrated by the energy of elastically scattered X-rays with an uncertainty of less than 1 eV. A typical distribution of the intensity on the detector is shown in Figure 6. The spectrum was accumulated over 10 s without using the helium balloon. Introducing the balloon lead to an increase of the count rate by a factor of 2.5 at the Pt L₃ edge. For recording a XES, XAS or RIXS spectrum, the counts were integrated over a selected pixel range. The resolution of the spectrometer was estimated by the width of the intensity distribution on the detector multiplied by the linear dispersion of the spectrometer. The experimentally measured resolution is shown in Figure 7 and varied between one and three eV. The resolution at Pt Lα₁ (E=9442 eV, θ=81.7°) was 1.0 eV. A measured Pt Lα₁ fluorescence line is shown in Figure 8. A comparison of the fluorescence spectrum with a spectrum of the elastically scattered beam demonstrates the suitability of the spectrometer for recording a fluorescence spectrum with a resolution, which is several times smaller than the core-hole-lifetime broadening. An L₃-edge XAS spectrum of a platinum foil
is shown in Figure 9. The spectrum was recorded by detecting the fluorescence signal at the maximum of the fluorescence line shown in Figure 8. The high-energy-resolution fluorescence-detected XAS spectrum has a more pronounced structure compared to that of the transmission-detected spectrum because of the line sharpening effect. The nature of the line sharpening can be understood by looking at the RIXS spectrum of the platinum foil (Figure 10). The spectrum consists of two main contributions: a diagonal rib, which results from the resonant X-ray Raman process and a horizontal rib, which is the normal fluorescence. The X-ray Raman process is similar to the well-known Raman process for the visible light. The net transition of the Raman process is $3d_{5/2}$ to an unoccupied state. The transition energy corresponds to the difference between the incident photon energy and the fluorescence photon energy, which leads to the linear dependence of the fluorescence energy on the incident energy. The normal fluorescence is formed by the transition of the $3d_{5/2}$ electron to the $2p_{3/2}$ core hole left after the excitation of the electron by the incident photon. Its energy is independent of the incident energy. Selecting a narrow range of fluorescence energies, as shown in Figure 10 by two horizontal lines, allows to cut off the tails formed by the Raman process, while both components are registered in a low-resolution fluorescence-detected XAS spectrum. The RIXS signal, integrated along the fluorescence-energy axis, is also shown in Figure 9. The shape of the spectrum is very similar to that of the transmission-detected XAS spectrum. The difference between the integrated and transmission-detected spectra can be explained by the self-absorption and contribution of other processes, such as Auger decay, in the transmission-detected absorption. The line-broadening in Figure 9 is similar to previously reported HERFD XAS on platinum-containing catalysts [13, 14].

The spectrometer is installed, commissioned and ready for user operation.

Acknowledgments
The authors would like to thank Pieter Glatzel and György Vankó for valuable discussions on X-ray optics and practical advise on the construction of the X-ray spectrometer. E. Kleimenov, J.A. van Bokhoven, M. Janousch and M. Nachtegaal thank SNF for the granted research fund.

References
[1] Glatzel P, de Groot F M F and Bergmann U 2009 Synchrotron Radiation News 22 12 – 16
[2] Hayakawa S, Goto S, Shoji T, Yamada E and Godshik Y 1998 Journal of Synchrotron Radiation 5 1114–1116
[3] Dickinson B, Seider G T, Webb Z W, Bradley J A, Nagle K P, Heald S M, Gordon R A and Chou I M 2008 Rev. Sci. Instrum. 79 123112 (pages 8)
[4] von Hamos L V 1938 Journal of Scientific Instruments 15 87–94
[5] Hayashi H, Kawata M, Tskoda R, Udagawa Y, Watanabe Y, Takeo T, Nanao S and Kawamura N 2004 Journal of Electron Spectroscopy and Related Phenomena 136 191 – 197
[6] Johann H 1931 Z. Phys. 69 185–206
[7] Stojanoff V, Hamalainen K, Siddons D, Hastings J, Berman L, Cramer S and Smith G 1992 Rev. Sci. Instrum. 63 1125–1127
[8] Bergmann U and Cramer S 1998 Proceedings of SPIE 3448 198–209
[9] Sanchez del Rio M and Decus R J 1997 Proceedings of SPIE 3152 148–157
[10] Johansson T 1933 Zeitschrift für Physik A Hadrons and Nuclei 82 507–528
[11] Mazzanica A, Bergamaschi A, Dinapoli R, Gozzo F, Henrich B, Kraft P, Patterson B and Schmitt B 2009 Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 607 250–252
[12] Bergamaschi A, Cervellino A, Dinapoli R, Gozzo F, Henrich B, Johanson I, Kraft P, Mazzanica A, Schmitt B and Shi X 2009 Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 604 136 – 139
[13] Sazonova O V, Tromp M, van Bokhoven J A, de Groot F M F, Evans J and Glatzel P 2006 The Journal of Physical Chemistry B 110 16162–16164
[14] Singh J, Aroyan E M C, Tromp M, Sazonova O V, Glatzel P, Nachtegaal M, Frahm R and van Bokhoven J A 2008 Angew. Chem.-Int. Edit. 47 9260–9264