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Design concept of the high-resolution end-station PEAXIS at BESSY II: Wide-*Q*-range RIXS and XPS measurements on solids, solutions, and interfaces

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ABSTRACT

The design of a soft X-ray end-station for the Berlin Electron Synchrotron BESSY II is presented. It will be used for Resonant Inelastic X-ray Scattering (RIXS) and Angle-dependent X-ray Photoelectron Spectroscopy (AdXPS) studies for energy material science. In RIXS-mode the instrument operates with two spherical Variable Line Space (VLS) gratings for energy resolving measurements in two overlapping energy ranges from 200 to 1200 eV. The end-station will allow measurements of solid samples, solutions and interfaces in a wide range of experimental conditions with high energy resolution covering a large *Q*-range realized by a continuous rotation of the RIXS detector arm by 120°.

Besides the description of this end-station, a systematic way is shown for the design of a RIXS instrument assessing the grating parameters based on existing theories and for the calculation of optimal instrument settings as a function of photon energy. Different grating inclinations, line densities, groove shapes and RIXS instrument lengths were investigated. Possible parameter combinations were calculated analytically and the resulting instrument performance was determined by ray-tracing simulations using the simulation package RAY. The performance of the RIXS instrument was evaluated by choosing the product of the intensity at the detector and the square of the resolving power as figure of merit to optimize the spectrometer. The robustness of the optimized parameters has been checked in order to define tolerance parameters for the engineering design of the spectrometer.

1. Introduction

1.1. Motivation

The global need for sustainable sources of energy is an important driving force for materials science. This social challenge is a strong motivation to build a new end-station at the Berlin Electron Synchrotron BESSY II that is suitable for the growing energy material research program conducted at the HZB. Materials to be studied include solids, solutions, and their interfaces.

Soft X-ray spectroscopy methods are able to probe the local electronic structure through the K-edge of biologically relevant elements (e.g. oxygen, carbon, nitrogen) and the L-edge of transition metals. This makes it a very attractive technique for investigations of biological and chemical processes. While most of the modern applications of soft X-ray spectroscopy are already well established [1], the synchrotron radiation community recognizes the most recent trend to apply soft X-ray techniques in the field of

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spectroscopy of energy materials [2–4] driven by the rapid progress in X-ray photon-in/photon-out spectroscopy [5,6] and photon-in/electron-out spectroscopy [2,7]. In the new end-station, we will use Resonant Inelastic X-ray Scattering (RIXS) as the photon-in/photon-out method and Angle-dependent X-ray Photoelectron Spectroscopy (AdXPS) as the photon-in/electron-out method in the soft X-ray regime.

For solid state materials, RIXS, as a synchrotron-based technique, can provide information about elementary excitations in solids through the energy, momentum and polarization dependence of the emitted photon spectra, because the scattered photons couple to plasmonic, charge-transfer, crystal-field and magnetic excitations [8]. Moreover, during the last decade RIXS has also been successfully applied to liquids and established as a tool capable of providing information on dynamics in solutions and the electronic structure of organic molecules [5], liquid water [9], liquid solutions in closed cells [10] and open micro-jets [11].

AdXPS, a refinement of the X-ray Photoelectron Spectroscopy (XPS), provides information about the composition of elements on the surface of a sample, their chemical state and the binding energies of the electrons by measuring the kinetic energy of the photoelectrons generated on the sample surface. Usually, this is applied to dry solids [7], but can also be applied to biological samples [12] and liquids [2,13].

The combination of X-ray absorption spectroscopy (XAS), RIXS and XPS techniques at the ligand and metal sites of all the systems mentioned can give an atom-specific, chemical-state-selective, crystal-field-symmetry and orbital-symmetry-resolved description of the electronic structure of catalysts.

In the permanently evolving field of RIXS and XPS applications, the PEAXIS (Photo Electron Analysis and X-ray resonant Inelastic Spectroscopy) end-station will focus on the investigation of electronic and elementary excitations in thermoelectric and catalytic materials. PEAXIS will help in understanding and further developing the role these material classes can play in the global quest for sustainable energy sources.

1.2. Objective

The envisioned PEAXIS end-station is based on the idea of applying soft X-ray spectroscopic methods such as photon and photoelectron emission to materials in solid and liquid states and their interfaces. The primary goal is to achieve the best resolution at an acceptable intensity. The primary technique to be applied is angle-resolved Resonant Inelastic X-ray Scattering (RIXS). Although it is possible to match the information measured by means of neutrons and soft X-ray photons even with limited angular variation [14,15], RIXS experiments benefit from an increased flexibility in accessing a large range in momentum space Q (0.052–0.196 $Å^{-1}$ for 200 eV and 0.315–1.175 $Å^{-1}$ for 1200 eV photon energy). This will be realized by the PEAXIS spectrometer through continuous rotation of the RIXS arm by 120°, which makes it different from instruments using discrete sets of angles, currently available at the SLS [16]. The second technique that will be implemented in the PEAXIS instrument is Angle-dependent Photoelectron Spectroscopy (AdXPS), with a focus on both liquid state and solid state materials.

Investigating the angular dependence of photoelectrons emitted under different angles between the photoelectron analyzer and the direction of the jet, it is possible to distinguish surface from bulk contributions to the energy spectrum [17]. Chemical bond phenomena can be observed and local electronic structures, density and depth profiles, along with molecular orientation and relaxation processes in aqueous solution [18] can be investigated, e.g. for metal ions or biological molecules [11].

In the following section, the PEAXIS end-station is described presenting especially the conceptual design of the RIXS spectrometer, its individual spectrometer components and practical boundary conditions which have to be taken into account. Section 3 shows the assessment and optimization of the relevant parameters of the RIXS instrument based on analytical calculations and ray-tracing simulations as well as the expected performance. A particular emphasis is given to the robustness of the optimization with respect to misalignment or optical device imperfections. Finally, key results will be summarized and an outlook is given on potential extensions and upgrade paths for the spectrometer.

2. Design of the spectrometer

2.1. Concept

A number of photon spectrometers dedicated to the solution of a variety of scientific problems have been built ([19] and references therein). However, the configuration of the end-stations do not allow continuous rotation of these spectrometers. Therefore, *Q*-resolved measurements were not possible for most single crystals or limited to a discrete number of *Q*-values enabled by a number of available directions for the outgoing beam. However, the new PEAXIS spectrometer to be built at BESSY II will allow continuous angular motion by 120° using a unique measurement chamber design as the core of the end-station. This concept is also planned for the VERITAS instrument [20] at MAX IV; and the idea for a technical realization was communicated to us by Markus Agåker. To facilitate the alignment of RIXS spectrometer optical elements, we chose a conservative optical design that uses only one optical element following the simple scheme: source – variable line space grating – detector [21,22]. The wavelength dependent diffraction by the grating results in a spatial separation of photons with different energies on the detector. The goal is to achieve the best possible resolving power E/δE and a high detector count rate. The arm length, i.e. the distance from the sample to the detector, is limited to 4.9 m due to space restrictions in the instrument hall.

In the soft X-ray regime, the RIXS process involves both core and valence photoelectrons. As shown in Ref. [8], the $L_{3,2}$ edges of transition metals are preferable for studies of solid state samples. Elements of particular interest for the foreseen research areas are Fe, Co, Cu, Zn which have $L\alpha_{1,2}$ lines between 705.0 eV and 1011.7 eV. The K edges of oxygen, carbon and nitrogen, especially important for organic compounds, have $K\alpha_{1,2}$ lines between 277 eV (carbon) and 524.9 eV (oxygen). These boundary conditions define the energy ranges of the low energy (200–600 eV) and the high energy grating (400–1200 eV). The parameters have to be optimized for both, high efficiency of the gratings and high resolution of the spectrometer.

Spatial focusing on the detector is achieved by one spherical variable line space (VLS) grating in each set-up that focuses all photons of the same energy to the same vertical position on the detector (horizontal strip). Horizontal focusing is not foreseen. The spectrometer operates in 1st diffraction order ($m = 1$), in which the angle β of the outgoing beam is smaller than the angle α of the incoming beam (see Fig. 1b). The used area of the grating can be reduced by slits behind and in front of the grating to improve resolution (at the cost of intensity). Masks are also foreseen to reduce the illuminated sample area, and thus, the size of the virtual source, which also improves resolution.

A photoelectron analyzer is positioned opposite to the RIXS arm. It can be freely rotated when the RIXS arm is decoupled, thereby allowing for Angle-dependent X-ray Photoelectron Spectroscopy (AdXPS) of the same sample under identical conditions as used for RIXS measurements. If the RIXS arm is connected to the chamber, rotation of the photoelectron analyzer is restricted.

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