

Spectrochemical Analysis

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1. Introduction

As described in the previous report [1] BL39XU will be equipped with the SPring-8 in-vacuum type undulator, a rotated-inclined double crystal monochromator, a Pt coated plane deflection mirror and a phase retarder. Monochromatized linear polarized x-rays of 5 keV to 25 keV will be produced by utilizing fundamental to the third harmonics of the undulator radiation. Spectrochemical analysis group is preparing x-ray focusing optics and two chambers inside the experimental hutch for the initial stage of beamline operation. One chamber for x-ray fluorescence (XRF) analysis and imaging is under construction and the design of the other chamber (grazing incidence reflecto-spectrometer) has been finished. Utilizing these two chambers following research subjects are being prepared.

2. Proposed research subjects

2.1. Chemical state analysis of trace elements with a scanning x-ray microprobe

As we have demonstrated at Photon Factory, an aspherical total reflection mirror is advantageous when designing an energy tunable x-ray microbeam [2]. A Wolter type focusing mirror [L3] or a glass capillary will be used to obtain small x-ray beam on the sample. Spatial resolution of less than 5 μm will be realized with the glass capillary and the spatial resolution of less than 1 μm is expected with the focusing mirror.

XRF analysis is one of most promising method to detect trace elements without significant damage to a sample and the combination of XRF and the x-ray microprobe can be a powerful tool for studies in materials sciences and biology [4]. To realize trace sensitivity of less than 100 ppb a wavelength dispersive spectrometer was designed which is composed of a flat

analyzing crystal and a position sensitive proportional counter (PSPC). It covers K lines from Cl to Te by utilizing 6 analyzer crystals which will be mounted on the revolver and will be remotely controlled

Various kinds of x-ray images will be obtained simultaneously by collecting transmitted x-rays, XRF, diffracted x-rays and x-ray excited optical luminescence (XEOL). Qualitative and quantitative XRF analysis and near edge x-ray absorption fine structure (NEXAFS) measurements can be carried out at the position of interest on the sample. (S.H.)

2.2 High resolution X-ray fluorescence spectroscopy and spin selective XAFS

It is well known that various types of chemical effects can be observed when XRF spectra are measured with sufficient energy resolution [5]. Fig.1. shows Fe K-M ($K\beta$) spectra of iron compounds measured with a double crystal spectrometer [6] using a conventional x-ray source. Fe $K\beta'$ is sensitive to the unpaired electron and preliminary results of the $K\beta'$ detection for the spin-selective XAFS measurements were reported [7]. It is promising to combine the high resolution XRF measurement and energy tunable x-ray source and we are now designing a high resolution spectrometer. (S.H.)

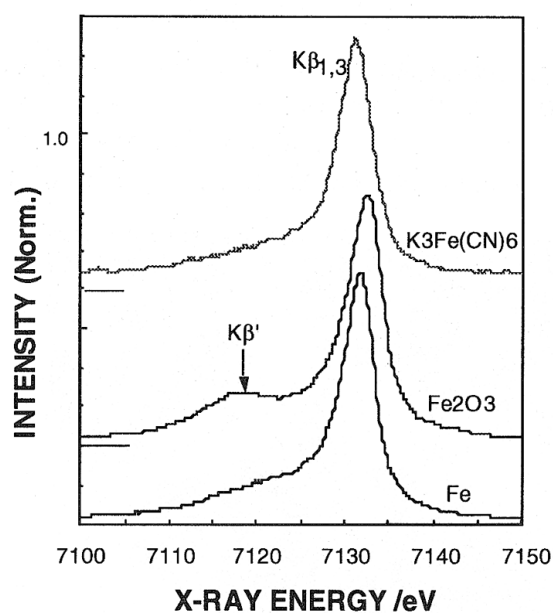


Fig. 1. Fe K-M($K\beta$) spectra of Fe, Fe_2O_3 and $\text{K}_3\text{Fe}(\text{CN})_6$. W target x-ray source and Si(111) double crystal spectrometer [6] were used.

2.3. Analysis of interfaces of thin films by X-ray fluorescence and scattering using total reflection

Controlling thin films interfaces is a key technology in realizing some new physical/chemical characteristics which are unlikely obtained from bulk materials. Grazing incidence X-ray experiments are powerful tools for analyzing the surface and interface because of the high sensitivity due to the shallow penetration of X-rays around the critical angle [8]. Use of interference effect caused by multiple reflection at each interface is promising to enhance information on specific interface [9]. In the present research, some combined measurements of the diffuse scattering and fluorescent X-rays are planned in order to evaluate the shape of the interface, the degree of the gradation of interfaces and the segregation of trace elements. The grazing incidence reflecto-spectrometer has been designed for BL39XU. The schematics are shown in Fig.2, and the prototype had been fabricated (Fig. 3). Since recent experiments shows that it works well with the laboratory source, the beamline reflecto-spectrometer will become almost the same design with minor improvement. (K. S.)

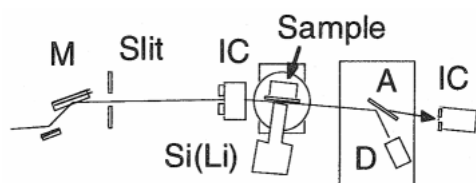


Fig. 2. Experimental layout of grazing incidence spectroscopy with vertical rotational axis. M: Monochromator, A: Analyzer crystal, IC: ionization chamber, D: Detector(YAP: Ce or APD)

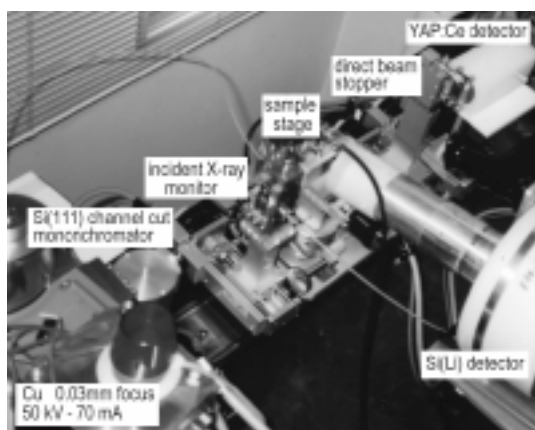


Fig. 3. The grazing incidence reflecto-spectrometer prototype.

2.4. Chemical characterization of ultra trace metals in small liquid drop

Investigation of trace metals has become quite significant in materials as well as in biomedical sciences [10]. Not only the identification/determination of metals but also information on the chemical state is essential to clarify their role in the phenomena taking place. However, when the quantity of the sample is limited, and the sample is only a liquid drop or fine particles, it becomes extremely difficult to analyze its trace components by conventional techniques like chromatography based on chemical separation. X-ray fluorescence detection of the absorption edge shifts is highly sensitive and is a powerful technique for characterizing trace metals in the order of ppm ($\mu\text{g/g}$) in a bulk sample [11], and also can be applied to the small quantity sample by employing a mirror-polished substrate as a sample support [12]. In the present research, the reflecto-spectrometer (Fig.2) will be used to gain the signal to background ratio by means of the total reflection of X-rays. Our target is trace metals in the order of μM in a small quantity of liquid drop of μl or smaller. (K. S.)

2.5. Development of high energy resolution detectors for trace chemical characterization

Detector technologies are important as well as a brilliant source to enable the chemical characterization of trace metals by means of X-ray spectroscopic techniques.

In the present research, chemical state analysis of trace metals in the order of ppb ($\mu\text{g/g}$) is planned by improving the detector system. We need to measure a signal which exhibits inherently enough detectable and systematic variance as the chemical state changes, with an excellent signal to background ratio. Chemical shifts of absorption edges, which varies around 10 eV at K edges for 3d transition metals, can be used for trace chemical characterization if the measurement was carried out by X-ray fluorescence detection [11]. However, Largely speaking, the average limit of detection has remained in ppm ($\mu\text{g/g}$) Level so far. This is principally because of a rather poor energy-resolving-power of the detector to separate the tail of the scattering background of the

incident X-rays and the $K\alpha$ fluorescent signal. When the scattering background dominates the detector, the detection limit cannot be improved any more just by employing a further brilliant source.

After all, it is indispensable to develop a detector which possesses better energy resolution than a Si(Li) detector as well as much higher efficiency than a crystal analyzing spectrometer. A super-conducting tunneling junction (STJ) detector [13] is a promising candidate. A He3 cryostat has been developed for the detector and some cooling tests as well as fabricating an STJ device are now under way. (K.S.)

2.6. Fluorescent x-ray holography of single crystals

Diffraction methods for crystallographic structure determination suffer from the so-called "phase problem". A diffraction pattern provides intensity but not phase information for scattered beams, and therefore cannot be uniquely inverted to obtain the crystal structure of a sample. Holographic methods offer means of extracting both intensity and phase information. Electron emission holography is powerful tool for studying surface structure; but it cannot image the internal structure of solids because of complications arising from the highly anisotropic nature of electron scattering process. On the other hand, x-rays scatter more isotropically than electrons. Fluorescent X-ray holography, whose possibility was theoretically shown by Len[14], was first performed by Tegze et al. [15]. But, this method has some technical difficulties such as long measuring time and effect of sample shape because the scattering efficiencies are 10^{-4} order. When the synchrotron radiation lights are applied to fluorescent x-ray holography method, these problems are expected to be resolved. Furthermore, since the x-ray energy is changeable, it is suitable for fluorescent x-ray holography using resonant excitation and multi-energy x-ray holography [16], which utilize the interference fields generated by incident x-ray and scattered one. In BL-39XU, capillaries or focusing mirrors will be equipped for micro beam, and therefore we will be able to apply

this method to a crystalline substance composing thin film materials in future. (K. H.)

References

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