BL11XU
QST Quantum Dynamics I

1. Introduction

BL11XU is an in-vacuum undulator beamline operated by the National Institutes for Quantum Science and Technology (QST). It is designed to provide scientists and engineers with a wide range of options on advanced synchrotron radiation and quantum functional material research. In BL11XU, switchable Si(111) and Si(311) double-crystal monochromators cooled by liquid nitrogen are installed in the optical hutch. Highly brilliant and well-collimated synchrotron X-rays are available in the energy range of 6–70 keV. There are three experimental hutches; each one contains specialized measurement instruments for studies using Mössbauer spectroscopy (EH1), inelastic X-ray scattering and X-ray magnetic circularly polarized emission (EH2), and surface X-ray diffraction (EH3).

2. Mössbauer spectroscopy

The first experimental hutch is equipped with a nuclear resonance spectrometer that generates highly brilliant γ-rays from synchrotron radiation, the so-called synchrotron Mössbauer source (SMS). The SMS enables the local analysis of magnetic interactions, electronic states, and spin configurations of various functional materials. Recently, with the introduction of a new focusing mirror, the SMS has been used to measure small samples and thin-film samples using a beam that can focus the SMS down to 20 μm [1].

Mössbauer spectroscopy is usually performed in the transmission geometry. However, conversion electron Mössbauer spectroscopy (CEMS) is often used in the backscattering geometry to measure an opaque sample. The probe beam is incident normal to the sample surface, and the ^{57}Fe atoms contributing to the spectra are limited to those within the conversion electron escape depth from the surface, typically approximately 100 nm from the sample surface. The surface sensitivity of CEMS can be improved by analyzing the energy of the electrons. This method is known as depth-selective CEMS (DCEMS) and is based on the principle that electrons emitted near the surface lose less energy upon escaping from a solid.

Recently, we have developed a 3D Mössbauer surface analysis system consisting of focused SMS radiation, a precision stage, a gas-flow proportional counter, and multiple multichannel scalers for the first time. As a demonstrative experiment, a 3D Mössbauer surface analysis of laser ablated α-^{57}Fe foil was performed [2].

The DCEMS spectra were measured in three different energy regions: low energy (2–6.5 keV), medium energy (6.5–11 keV), and high energy (>11 keV). Scanning measurements of DCEMS were performed by changing the γ-ray irradiation position on the surface of the iron foil. A magnetic sextet and a nonmagnetic doublet were clearly observed in the DCEMS spectra. The α-Fe magnetic phase showed the hyperfine parameters of H_{int} = 330 kOe, QS = 0 mm/s, and IS = 0 mm/s, while the hyperfine parameters of the nonmagnetic phase were QS = 0.68 mm/s and IS ~ 0.85 mm/s. In the latter case, the large IS and QS values strongly suggest that this phase is iron monoxide (wustite).

Significant changes were observed in the area ratio of nonmagnetic phases determined from the DCEMS measured in the high (H), medium (M), and low (L) energy regions and their dependence on the beam irradiation position. The mapping diagrams of the area ratio of the nonmagnetic phases determined by DCEMS (H, M, L) are displayed at the four corners of Fig. 1.

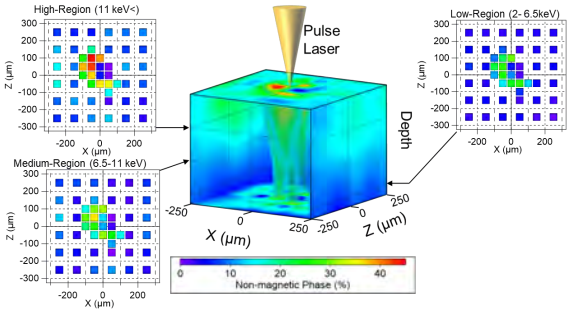

Fig. 1. Mapping diagram of area ratio for nonmagnetic phase determined by DCEMS spectra with energy discrimination measurement in high (H), medium (M), and low (L) regions. The 3-D distribution of the nonmagnetic phase was calculated using spline interpolation [2].

To facilitate an intuitive understanding of the oxidation state penetrating from the surface to the interior of the iron foil, the spatial distribution of the area ratio of the nonmagnetic phase was visualized by the 3D quadratic spline interpolation method. The results are shown in the center of Fig. 1. The visualized data clearly show that there are three prominent regions of compositional changes in columnar form, indicating that heterogeneous oxide formation occurs inside the iron foil. So far, we infer that the origin of the heterogeneous spatial distribution of the nonmagnetic phase is the complicated detachment and scattering of molten fragments from the iron surface, caused by the pulsed laser ablation. In this case, the scattered molten fragments may fall at irregular positions near the laser irradiation position and form iron oxides during resolidification. This surface oxidation would also be highly dependent on the laser heat density, cooling rate, and sample environment.

In the near future, this method will be a powerful analytical tool in the field of steel science, such as for corrosion, welding, and surface modification by laser ablation and peening.

3. Inelastic X-ray scattering

An inelastic X-ray scattering (IXS) spectrometer for hard X-rays installed in EH2 is used for resonant inelastic X-ray scattering (RIXS) at the K-edge of 3*d* transition metals and the L-edge of 5*d* transition metals. The optics of EH2 provides an energy resolution of 0.1–1 eV for both incident and scattered (emitted) X-rays. High-energy-resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) and X-ray emission spectroscopy (XES) are also possible using this spectrometer. In FY2022, we implemented a vertical scattering configuration of the analyzer by installing a rotating device for analyzer crystals and three stages mimicking a 2θ-arm for scattering from the analyzers [3]. This configuration enables the use of a grazing-incidence condition without compromising the energy resolution, and we examined measurements under this condition. Figures 2(a) and 2(b) show Kβ main lines and satellite lines of X-ray emission spectra of a bulk $LaMnO_3$ crystal, respectively. The spectra obtained under grazing-incidence (θ = 2°) and specular (θ = 45°) conditions are almost identical. Note that the scattering angle of the sample (2θ) is kept at 90°.

The ability to use the grazing-incidence condition allows us to measure thin samples efficiently.

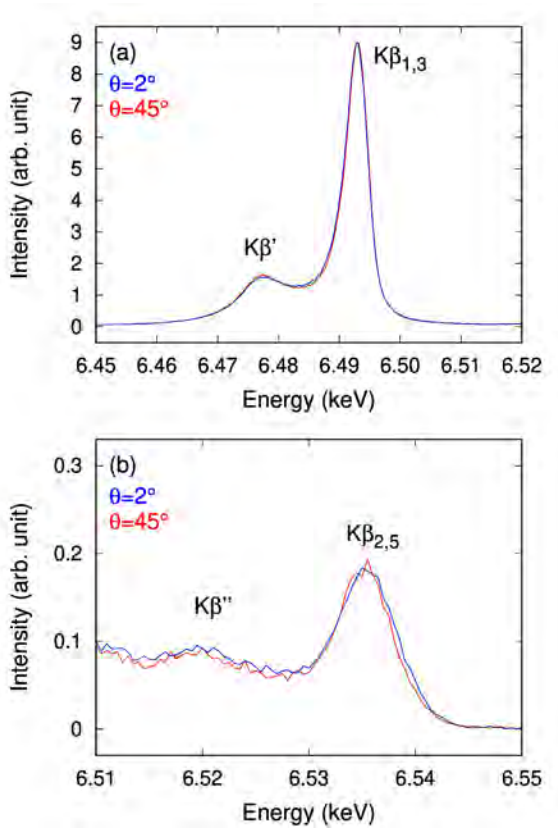

Fig. 2. X-ray emission spectra of a bulk $LaMnO_3$ crystal. (a) Kbeta main lines and (b) Kbeta satellite lines are shown for grazing-incidence (θ = 2°) and specular (θ = 45°) conditions.

4. Surface X-ray diffraction

The third experimental hutch is equipped with a surface X-ray diffractometer connected to a molecular beam epitaxy (MBE) chamber [4]. This instrument is designed for *in situ* studies on III–V group semiconductor surfaces, especially surface crystallography under MBE conditions and growth dynamics of multilayer and nanostructures. The III–V group semiconductors are nitrides such as GaN and InN and arsenides such as GaAs and InAs, which can be grown by exchanging the two types of MBE chamber.

Our recent activity on nitrides focuses on observing the interfacial atomic structure between liquid Ga and the GaN surface during MBE growth [5,6]. Extensive theoretical studies have been performed to elucidate the interfacial structure of liquid Ga/GaN, employing first-principles calculations to predict the interfacial structure at the atomic scale and establish structural models of Ga ordering. However, despite the theoretical efforts, the precise interfacial atomic ordering under MBE conditions remains unclear, primarily because of the lack of accessible analytical data. X-ray crystal truncation rod (CTR) measurements are commonly used to analyze surface or interfacial atomic structures quantitatively. However, it is difficult to expand the measurement range to determine three-dimensional atomic structures in real time. We developed a method for CTR measurements, which involves simultaneous intensity measurements of X-rays and electron diffraction under MBE conditions. By fitting the experimental CTR spectra of the 00 and 01 rods, we successfully determined the three-dimensional atomic structures (lattice distances, coverages, and B-factors for each layer) and observed the formation of Ga ordering on the GaN surface. This method has the potential for broader applications, including the study of other nitride semiconductors such as AlN, InN, and their mixed crystals.

MITSUI Takaya[*1], FUJIWARA Kosuke[*1], ISHII Kenji[*2], and SASAKI Takuo[*3]

[*1]Magnetism Research Group, National Institutes for Quantum Science and Technology (QST)

[*2]Advanced Spectroscopy Research Group, National Institutes for Quantum Science and

Technology (QST)

[*3]Coherent X-ray Research Group, National Institutes for Quantum Science and Technology (QST)

References:

[1] Fujiwara, K. Nakamura, S. Shimomura, S. & Mitsui, T. (2024). *JPS Conf. Proc*. **41**, 011002.

[2] Fujiwara, K. et al. (2024). *Appl. Phys. Express* [In press].

[3] Mitsui, T. Inami, T. Ishii, K. & Sasaki T. (2022). *SPring-8/SACLA Annual Report FY2022*, 138–141.

[4] Sasaki, T. et al. (2016). *Jpn. J. Appl. Phys.* **55**, 05FB05.

[5] Sasaki, T. et al. (2024). *Jpn. J. Appl. Phys.* **63**, 020901.

[6] Sasaki, T. et al. (2024). *Appl. Phys. Express* **17**, 025502.