

Overview of the NRS Programs at SPring-8

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There are multiple avenues for doing nuclear resonant scattering (NRS) at SPring-8, including proposals to the Japan Synchrotron Radiation Research Institute (JASRI) for one of several beamlines, proposals to the National Institutes for Quantum and Radiological Science and Technology (QST –formerly associated with JAEA/JAERI) for BL11XU and proposals to RIKEN and proposals to SACLA. The majority of work has been done through JASRI at BL09XU, which has been the main home for NRS experiments at SPring-8 over the past 2 decades (talk by Yoshitaka YODA). Additional programs have developed at BL11XU/QST (talk by Takaya MITSUI) and at BL19LXU (a RIKEN beamline accessible for NRS via proposals through JASRI). There is also a specific program using a synchrotron Mossbauer source (SMS) at BL10XU for high-pressure work with diamond anvil cells (talk by Naohisa HIRAO) accessible via proposals to JASRI. The JASRI program has been largely aided and driven by collaborations with external groups, including members of KEK, JAEA/QST, the lab of Makoto SETO at KURRI and, recently, by visiting scientists (Ryo MASUDA and Makina SAITO). Presently, the main JASRI NRS activity is being moved from BL09XU to BL35XU (see the next talk by Yoshitaka YODA). There is also the potential to do work at BL29XUL and at the SACLA Free-electron laser.

Beamline ^{Contact}	Accessibility	Comment
BL09XU ¹ (through 2020)	JASRI Proposals	Main JASRI NRS program through 2020 Program moving to BL35XU in 2021
BL11XU ²	QST Proposals	Mainly SMS and EDMS/Resonant Detector work
BL19LXU ^{1,3}	JASRI Proposals (RIKEN Proposals)	25m ID with high flux Biological samples and specific experiments (e.g. ²²⁹ Th)
BL35XU (early)	JASRI Proposals	Specific experiments (e.g. ¹⁸¹ Dy)
BL35XU ¹ (From 2021)	JASRI Proposals	Main JASRI NRS program from 2021. Strong source 14.4 - 27 keV & >43 keV
BL10XU ⁴	JASRI Proposals	High Pressure DAC Work – SMS only
BL29XUL ^{1,5}	JASRI Proposals (RIKEN Proposals)	General purpose beamline (1 km) <i>Possibly</i> for E<14. keV, 28<E<43 keV
SACLA ^{1,6}	Proposals to SACLA	Short Pulse Free Electron Laser

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TIME-DOMAIN INTERFEROMETRY FOR DYNAMICS STUDY

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Inelastic/quasi-elastic scattering methods allow us to measure the microscopic dynamics of condensed matter systems in various time and spatial scales as shown in Fig. 1. Quasi-elastic scattering experiments using Mössbauer gamma-rays from RI sources have been performed soon after the discovery of the Mössbauer effect in 1960s [1,2]. However, because gamma rays from RI sources do not have enough brilliance as a parallel beam required for quasi-elastic scattering experiments, the method requires much measuring time.

Synchrotron-radiation (SR)-based quasi-elastic scattering experiment has been attempted using Mössbauer gamma rays from ⁵⁷Fe-nuclear Bragg monochromator [3,4]. Additionally, SR-based gamma-ray time-domain interferometry (TDI) has been used for quasi-elastic scattering experiments. [5-8] It has been demonstrated that SR-based experiment allows for much quicker measurement. In the presentation, we talk the quasi-elastic scattering technique using TDI which covers unique time and spatial scales as shown in Fig. 1.

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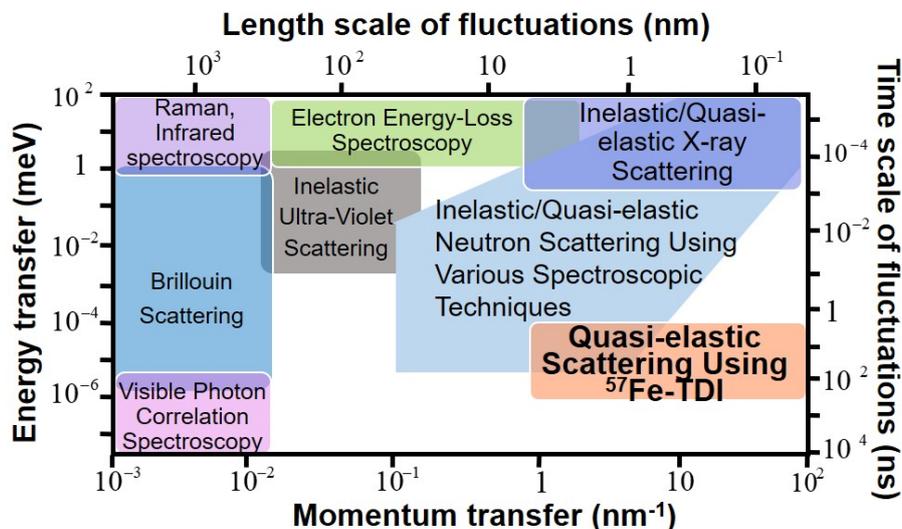


Fig. 1 Time and spatial scales of fluctuations studied by various inelastic/quasi-elastic scattering systems.

Application of time-domain interferometry to study dynamics of lipid membranes

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Lipid molecules are basic building block of cell membranes, which are thought of two-dimensional fluid and are dynamic platform of various biological functions. The time scale of the dynamics spans from atomic and molecular motions in ps scales up to fusion of cell membranes in second scales or longer. We have used neutron spin echo spectroscopy, one of quasi-elastic neutron scattering techniques that covers ps to 100 ns scales, in order to study lipid membrane dynamics, and we describe thermal fluctuations of membranes are dictated by the membrane's elastic and viscous properties. Membrane viscosity is a fundamental property that controls the molecular transport and structural rearrangement in lipid membranes. Given the importance of cell membranes to a variety of biological functions, various techniques have developed to determine the values, while the observed values differ from one method to another and vary by many orders of magnitude. In order to understand the nature of the membrane viscosity, we have used time-domain interferometry as well as neutron spin echo spectroscopy to access nanoscale dynamics of lipid alkyl chains. Lipid alkyl chain correlation peak appears around 1.5 \AA^{-1} (or the correlation length of approximately 4.5 \AA), and the temperature dependence of the relaxation time of the structural correlation was measured in different phases. Above the lipid melting temperature, where the lipid membranes are in fluid phase, the relaxation time is of the order of 1 ns, and the estimated membrane viscosity is $\sim 10^{-9} \text{ Pa s m}$, which is in the middle of the variety of membrane viscosities measured by various techniques. The time-domain interferometry technique is suited to measure relaxation dynamics in the gel phase (at lower temperatures), where the relaxation time of the alkyl tail correlations is estimated on the order of 10 ns and the membrane viscosity is calculated on the order of 10^{-8} Pa s m , which is about an order of magnitude larger than those in the fluid phase. These results are consistent to a general understanding in the difference in the time scale of the dynamics between the fluid and gel phases. The present experiment is the first of this kind, and the results suggest that the structural relaxation of lipid alkyl chains characterize the membrane viscosity.

INSTRUMENTATION FOR ENERGY DOMAIN SYNCHROTRON-RADIATION-BASED MÖSSBAUER ABSORPTION SPECTROSCOPY USING VARIOUS NUCLIDES

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Synchrotron radiation (SR) is a highly brilliant X-ray source with energies below typically 100 keV. In this energy region, there are many nuclides available for Mössbauer spectroscopy as its probe. SR-based Mössbauer absorption spectroscopy is a method for Mössbauer spectroscopy using these nuclides and we can obtain the absorption-type energy-domain Mössbauer spectra by this method.^{1,2)} Recent improvement on the detection efficiency by means of the detection of internal conversion electrons³⁾ extends its applicability; Mössbauer spectroscopy of ⁴⁰K, ⁶¹Ni, ⁷³Ge, ⁹⁹Ru, ¹¹⁹Sn, ¹²⁵Te, ¹²⁷I, ¹⁴⁹Sm, ¹⁵¹Eu, ¹⁵⁸Gd, ¹⁷⁴Yb and ¹⁸⁹Os was performed until now and further nuclides are promising.

The measurement system for the SR-based Mössbauer absorption spectroscopy mainly includes the monochromator(s), transmitter, analyzer, and detector, as shown in Fig. 1. We summarize the current system and present its details, including the combination of the monochromators in addition to the standard monochromator, the chemical specimen of the energy reference for each nuclide, and detector for the nuclear resonance.

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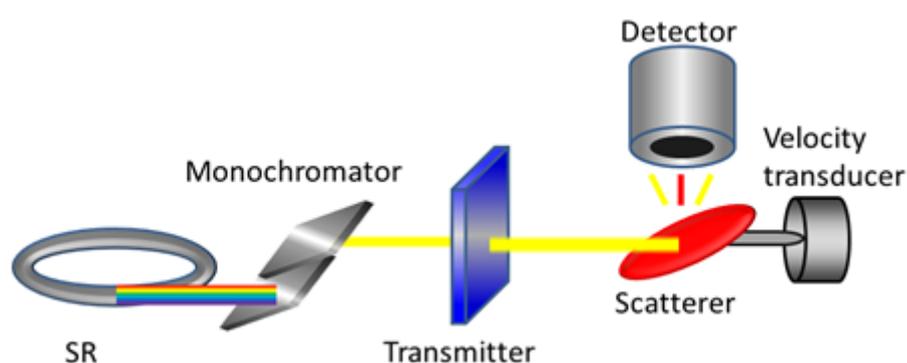


Fig. 1 A schematic drawing of the measurement system for the SR-based Mössbauer absorption spectroscopy. One of the transmitter and the scatterer is the sample under study and the other is the energy reference for the isomer shift.

Dynamical valence fluctuations in YbAlB_4 observed by ^{174}Yb SR-based Mössbauer Spectroscopy

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Synchrotron-radiation-(SR)-based ^{174}Yb Mössbauer spectroscopy is new state-of-the-art technique to investigate electronic states of Yb ions in compounds. The energy resolution of this technique is much higher than that of the conventional Yb Mössbauer spectroscopies. Valence fluctuating compounds YbAlB_4 have two crystal structures, $\alpha\text{-YbAlB}_4$ (*Pbam*) and $\beta\text{-YbAlB}_4$ (*Cmmm*). These form in the orthorhombic layered Yb, Al layers and B layers in turn and Yb ions have one crystallographic site. Although $\alpha\text{-YbAlB}_4$ is a heavy fermion compound behaved like Fermi-liquid below $T^* \sim 8$ K, $\beta\text{-YbAlB}_4$ exhibits anomalous quantum criticalities without tuning. We have applied this new technique to investigate electronic states of Yb ions in $\beta\text{-YbAlB}_4$ at low temperatures.

The SR-based ^{174}Yb Mössbauer experiments were performed using the single-crystalline samples of $\beta\text{-YbAlB}_4$ at ambient pressure and under pressure up to ~ 3 GPa on BL09XU and BL19LXU at SPring-8. We observed two absorption components related to the Yb^{2+} and Yb^{3+} ions in the ^{174}Yb SR-based Mössbauer spectra of $\beta\text{-YbAlB}_4$ below 5 K. This characteristic feature in the spectra disappears above $\sim T^*$ and then almost one absorption component was observed in the spectra. The widths of the absorption components are much wider than that expected in the present experimental conditions. We evaluated the averaged relaxation time of the Yb ions between the Yb^{2+} and Yb^{3+} ionic states via the analyses of ^{174}Yb SR-based Mössbauer spectra using a stochastic model. It is clarified that this refined relaxation time correlates closely with non-Fermi liquid behaviors observed in $\beta\text{-YbAlB}_4$.

In the presentation, I will show the pressure dependence of ^{174}Yb Mössbauer spectra of $\beta\text{-YbAlB}_4$ at 2 K and discuss the dynamics of valence fluctuation of Yb ions in $\beta\text{-YbAlB}_4$.

Present state of synchrotron Mössbauer spectroscopy in BL11XU of SPring-8

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Abstract

Energy domain Mössbauer spectroscopy has been performing at the QST dedicated beamline (BL11XU) of SPring-8. In this presentation, I will introduce the present state of beamline operation, device performance including the nuclear Bragg monochromator, a brief introduction of applied research, future upgrade plans and research directions.

Brief Report on the SMS Setup for High Pressure at BL10XU

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In recent high-pressure studies, it becomes important to elucidate various physical properties and phenomena comprehensively under high-pressure conditions using multiple analytical methods. High-pressure experiments using a complementary method to X-ray diffraction, a fundamental technique used to determine the crystal structure, are required for enhanced understanding of a variety of physical and chemical properties.

Iron (Fe) is by far the most abundant transition-metal element in the composition of the Earth and is a crucial element in deep Earth studies. The valence or magnetic state of iron cannot be determined using X-ray diffraction, but ^{57}Fe -Mössbauer spectroscopy is a well-established probe for studying the behavior of iron in a crystal structure and its electronic and magnetic properties. The combination of X-ray diffraction and ^{57}Fe -Mössbauer spectroscopy becomes a powerful technique to understand the complicated high-pressure behavior of iron compounds, such as deep Earth materials.

An energy-domain synchrotron ^{57}Fe -Mössbauer spectroscopy system was designed for combinatorial studies at BL10XU beamline of SPring-8, dedicated to high-pressure X-ray diffraction measurements in a diamond anvil cell. The system has been installed on the downstream side of the X-ray diffractometer in an experimental hutch (Fig. 1), and this equipment arrangement allows to perform the X-ray diffraction experiment. The Mössbauer system has all the components for ^{57}Fe -Mössbauer spectroscopy, including a nested high-resolution monochromator with asymmetric Si(511) and symmetric Si(975) channel-cut crystals, a variable-frequency nuclear monochromator crystal unit, and an NaI scintillation detector. As the nuclear monochromator, a pure nuclear Bragg reflection (333) of iron borate, FeBO_3 , single crystal is utilized. Here, we will introduce the ^{57}Fe -Mössbauer spectroscopy system and some typical results.

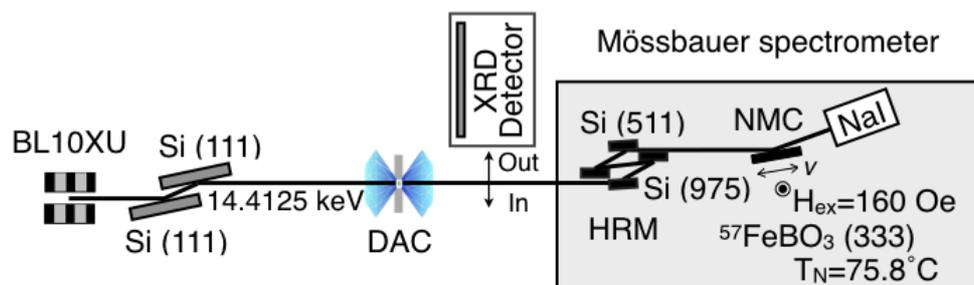


Fig. 1. The setup of energy-domain ^{57}Fe -Mössbauer spectroscopy at the BL10XU beamline

Towards the spectroscopy of ^{229}Th nuclear isomeric transition using nuclear resonant scattering at SPring-8

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The first excited nuclear state of ^{229}Th is known to be an only laser-accessible nuclear excited state; the excitation energy is around 8 eV [1,2] (wavelength $\lambda \sim 150$ nm; VUV-region). If fact, it is the lowest nuclear excited state found in Nature so far. This level energy is so low that the radiative lifetime of the level is expected to be relatively long, called *isomer state* (estimated $10^3 \sim 10^4$ s.). The quantum state of nucleus is quite insensitive to outer environment compared to electronic states in atomic shell. Therefore, the optically controllable nuclear state of ^{229}Th is not only a valuable exception in nuclear physics, but also expected to be useful for ultra-precise measurement of time and space. Such optical "nuclear clock" is expected to be superior to currently most precise atomic clock where atomic transition is exploited in the isolated atom [3, 4]. More precise determination of its energy and measurement of the radiative lifetime of the state is strongly motivated as an important step to expand the related researches.

We successfully populated into the ^{229}Th isomer state by using nuclear resonant scattering (NRS) through the second-excited state (29.19 keV), performed at SPring-8 [5]. This is the first active excitation into the isomer state, and expected to be an important step to conduct a spectroscopy of the optical transition from the isomer state. Now we are trying to detect the VUV-photon from the NRS-assisted isomer state using the ^{229}Th -doped VUV-transparent crystal; $^{229}\text{Th}:\text{CaF}_2$. We will report the present status of our project in this talk.

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Si-APD linear-array detector system and High-Z loaded plastic scintillators

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We have developed an X-ray detector system using silicon avalanche photodiode (Si-APD) linear array and fast pulse-counting electronics for multichannel scaling (MCS) [Fig. 1]. The Si-APD linear array consists of 64 or 128 pixels, which have 100×200 or $100 \times 400 \mu\text{m}^2$ in size, pixel pitch of $150 \mu\text{m}$, and depletion depth of 10 or $30 \mu\text{m}$. Ultrafast Amplifier-Shaper-Discriminator (ASD) ASICs and FPGAs can record timing of X-rays arriving at each pixel with 0.5 ns interval at minimum. The detector was used for nuclear resonant forward scattering on ^{57}Fe , which spatial resolution and detection efficiency were improved by inclining the detector up to 12° from the incident beam. We will show the present status on the Si-APD linear array detector system, including some problems.

One more topic is high-Z loaded plastic scintillators. We fabricated fast plastic scintillators (PLSs) by loading HfO_2 nanoparticles. Such a heavy metal loaded PLS will be useful for measurements of high-energy X-rays with up to a high count-rate $> 10^7 \text{ s}^{-1}$. A 40 and 60 wt% HfO_2 nanoparticle-loaded plastic scintillators (Hf-PLS) were successfully polymerized by mixing with polystyrene and (2-(4-tert-butylphenyl)-5-(4-biphenyl))-1,3,4-oxadiazole (b-PBD) as fluorophore [Fig. 2]. We tested the 40 wt% Hf-PLS (8 mm in diameter, 3 mm in thickness) mounted on a photomultiplier tube (PMT) using synchrotron X-ray beam at beamline BL-14A of the Photon Factory (PF). The detection efficiency at 50.0 keV reached $44.3 \pm 0.2\%$. Counting rates of up to $2.8 \times 10^7 \text{ s}^{-1}$ were recorded in the multibunch-mode operation of the PF ring. A superior time resolution (FWHM) of $0.29 \pm 0.06 \text{ ns}$ was obtained but with a time resolution of 0.46 ns at best using a commercially available 5 wt% lead loaded PLS, EJ-256. A $\sim 3 \text{ mm}$ cube 40 wt% Hf-PLS on a Si-APD (Geiger-mode or proportional-mode) was also investigated as a new fast scintillation detector for high-energy X-rays.

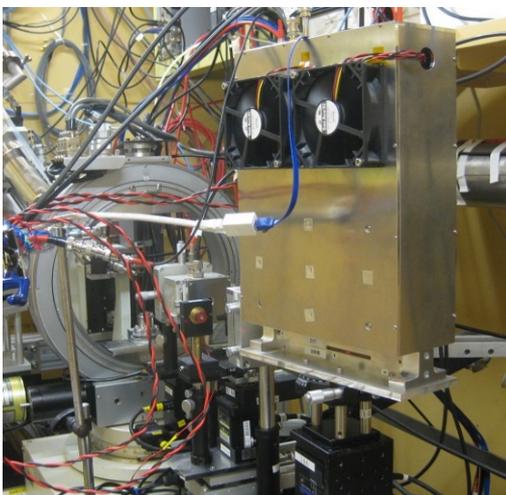


Fig. 1: Photograph of the 128 channel Si-APD linear-array detector (front).



Fig. 2: Photograph of 40 wt% (left) and 60 wt% (right) HfO_2 nanoparticle-loaded plastic scintillators, approximately 8 mm in diameter and 3 mm in thickness.

High Flux ^{57}Fe Nuclear Spectroscopy with a 25m ID

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We have been using the high flux available at BL19LXU for NRVS measurements on Fe-H and Fe-(H₂) complexes. Our goal has been to observe Fe-H and Fe-H₂ vibrational modes, some of which occur in the 1700-2000 cm⁻¹ region. These are relevant to future studies on [NiFe] and [FeFe] hydrogenase enzymes, which catalyze: $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$. Iron hydrogen chemistry is also relevant in its own right, since many Fe complexes and materials are being developed for fuel cell catalysts.

We observed Fe-H stretching modes at 1915 and 1957 cm⁻¹, along with an asymmetric Fe-H₂ stretch at 1773 cm⁻¹. Calculations suggest that even D-D stretching modes in Fe(D₂) should be observable above 2000 cm⁻¹. These are often hard to see in other spectroscopies. The rich information content in NRVS spectra continues to surprise.

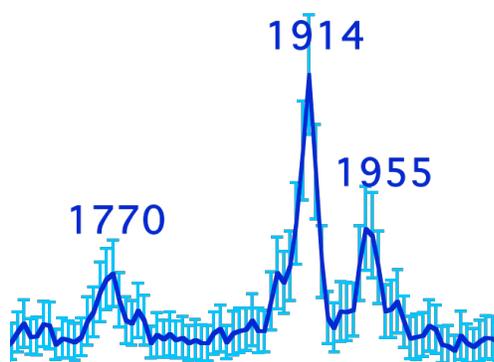


Figure. NRVS in the high frequency region for the classic complex *trans*-[⁵⁷Fe(η^2 -H₂)(H)(dppe)₂][BPh₄].