Development of a quasi-elastic gamma-ray scattering technique to reveal nanosecond atomic dynamics

Atomic and molecular structures and dynamics are the fundamental origins of various macroscopic properties, such as viscoelasticity. Inelastic and quasi-elastic scattering techniques enable the study of microscopic dynamics in wavenumber vector $\boldsymbol{q}$ space. Inelastic X-ray scattering (IXS) and neutron-based techniques have been widely used to measure the dynamic structure factor $S(\boldsymbol{q},E)$ as a function of energy E, which reflects the two-body space-time density correlation in a system.

Directive Mössbauer gamma rays generated by synchrotron radiation (SR) can be used in quasi-elastic gamma-ray scattering (QEGS) experiments. The energy resolution of Mössbauer gamma rays Γ_0 from ^{57}Fe nuclei is on the order of neV, allowing the measurement of microscopic dynamics on time scales of approximately $\hbar/\Gamma_0$ ~100 ns. Time-domain interferometry (TDI) [1] is a technique used to measure QEGS. Using TDI, the intermediate scattering function (ISF; $F(\boldsymbol{q},t)$), $\boldsymbol{q}$ and time t representations of the two-body space-time correlation function were observed [1]. The time and length scales of the dynamics covered by inelastic and quasi-elastic scattering techniques, including TDI-QEGS, are shown in Fig. 1. However, TDI cannot access timescales in the nanosecond range due to the time resolution limit of the avalanche photodiode detector of ~1 ns. In contrast, the nanosecond time scale is important for many applications, particularly in soft matter studies. Although energy-domain measurement techniques of QEGS have been demonstrated to access nanosecond dynamics [2], their widespread use has been limited due to low measurement efficiency.

Recently, we developed a novel energy-domain quasi-elastic *multiline gamma-ray* scattering technique [3] at SPring-8 **BL35XU**. Figure 2 shows the schematic of the experimental setup. Gamma rays emitted from a $^{57}Fe_2O_3$ nuclear Bragg monochromator (NBM) were introduced into the sample. The multiline energy profile of the gamma rays contained several peaks with a line width of 10 neV. The energy spectrum of the scattered gamma-rays was measured by Mössbauer spectroscopy using a $^{57}Fe_2O_3$ analyzer, which also had a multiline absorption profile, as shown in Fig. 2. These multiline energy profiles of gamma rays emitted by the NBM and absorbed by the analyzer significantly enhanced the incident gamma-ray flux and spectroscopy efficiency. A high-speed two-dimensional X-ray detector, CITIUS, with 840 kpixels, capable of performing quasi-elastic scattering measurements in a two-dimensional $\boldsymbol{q}$ space [4], was introduced. In the following, we present the new system, multiline spectroscopy (MLS) of QEGS, which effectively spans the time scales of dynamics from 100 ps to several tens of nanoseconds, as shown in Fig. 1.

Figure 3(a) shows the obtained energy spectra (absorption profile of the transition-type spectrum) of the forward-scattering gamma-rays (green line). The energy profile remained unaffected by sample dynamics and was used as the resolution function to analyze the quasi-elastic scattering data. The resolution function exhibited multiple energy widths on the order of 10 neV (Γ_1) and 1 μeV (Γ_2), which are sensitive to dynamics in the time scales of $\hbar/\Gamma_1$ ~ several tens of nanoseconds and $\hbar/\Gamma_2$ ~ sub nanoseconds, respectively. The quasi-elastic scattering spectrum obtained for polybutadiene at 235 K at q = 14 nm^{-1}, reflecting interchain correlations, is shown as red dots. The data were well fitted using standard quasi-elastic scattering analysis procedures. Here, we assume a stretched exponential form for the relaxation form of the ISF. Figure 3(b) shows the ISF obtained from the quasi-elastic scattering spectrum via Fourier transformation-based analysis. The ISF follows a stretched exponential function, whose parameters were determined by fitting to the energy spectrum, indicating that the ISF, which has direct information on microscopic dynamics, can be accurately visualized.

Figure 3(c) displays the temperature T dependence of relaxation times obtained by MLS-QEGS (blue circles), as well as those obtained by TDI-QEGS (red squares). All data followed the Vogel-Fulcher-Tammann law (solid curve) with previously reported parameters, indicating the accuracy of the obtained

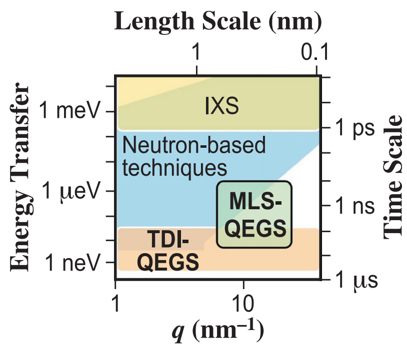

Fig. 1. Time and length scales of dynamics covered by various inelastic/quasi-elastic scattering techniques. The MLS-QEGS technique uniquely covers a specific time and length scale.

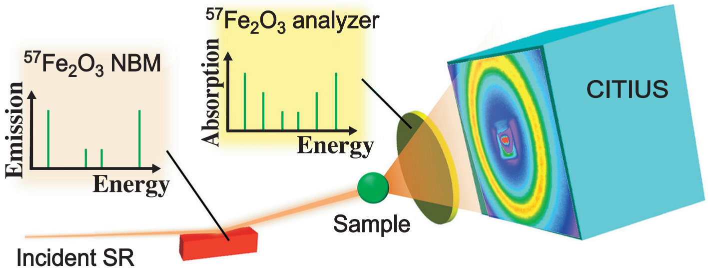

Fig. 2. Schematic of the experimental setup of MLS-QEGS measurement system using the $^{57}Fe_2O_3$ multiline monochromator/analyzer and CITIUS 840k. The energy spectra of the emitted gamma rays from NBM and the absorption profile of analyzer are also shown.

relaxation time over a wide time scale from 100 ps to several tens of nanoseconds. Further analysis revealed that multiple energy resolutions contributed to the broadband nature of the MLS system. Notably, the measurement efficiency was more than 100 times higher than that of previous systems due to the high flux of multiline gamma rays, the high efficiency of multiline spectroscopy, and the efficient two-dimensional *q* space observation of the quasi-elastic scattering by introducing CITIUS. Recently, we further improved efficiency by developing a high-efficiency multiline energy analyzer system [5].

In conclusion, we successfully developed a novel SR-based energy-domain quasi-elastic scattering technique using multiline Mössbauer gamma-rays. The developed system effectively covers a relatively wide timescale, ranging from 100 ps to several tens of nanoseconds, a part of which has not been fully covered by any other technique. The MLS-QEGS system accelerates the microscopic understanding of various materials such as liquids, glasses, and soft matter systems.

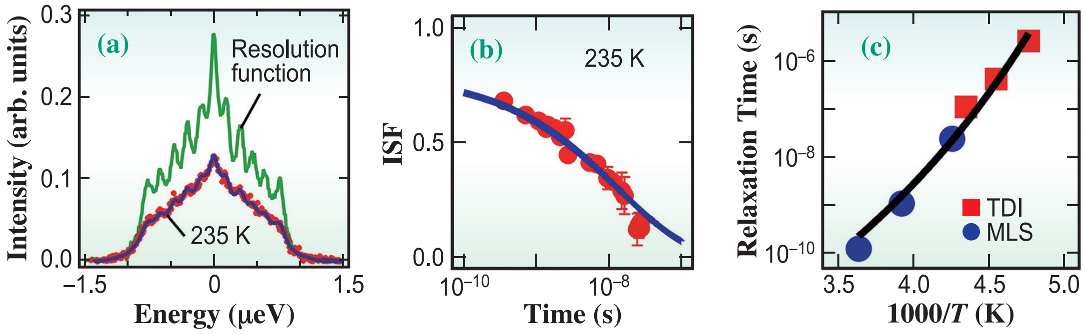

Fig. 3. **(a)** Energy spectra of the resolution function and quasi-elastic scattering spectrum obtained for polybutadiene at q = 14 nm^{-1} at 235 K. **(b)** Intermediate scattering function obtained from the quasi-elastic scattering spectrum via Fourier-transformation-based analysis. **(c)** Temperature dependence of relaxation time obtained by MLS-QEGS (blue circles) and TDI-QEGS (red squares). The solid line represents the fitting curve using the Vogel-Fulcher-Tammann law.

Makina Saito

Department of Physics, Tohoku University

Email: makina.saito.d6@tohoku.ac.jp

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