Energy Domain Mössbauer Spectroscopy Using Synchrotron Radiation

Mössbauer spectroscopy is a powerful and well-established method for a wide range of research fields, including physics, chemistry, biology, and earth science [1]. Information about magnetism, valence, electronic state anisotropy, and electron densitiy can be obtained through hyperfine interactions between the nucleus and surrounding electrons. Since the hyperfine interactions induce the split and/or shift in nuclear energy level, a precise measurement of nuclear energy level gives information regarding electronic states. The Mössbauer effect occurs when the nucleus absorbs γ-rays resonantly without recoil, thereby allowing the precise measurement of nuclear energy level without the effect of recoil. In Mössbauer spectroscopy, energy level is measured by an energy scan using a narrow single line of a radioisotope source; the energy scan is performed by the Doppler effect. The information regarding the electronic states obtained by Mössbauer spectroscopy is concentrated on the electrons surrounding the nucleus that cause the Mössbauer effect. The element-specific information, which is obtained by Mössbauer spectroscopy, is important and is required for modern precise materials science and complex systems, such as biological substances. As an alternative Mössbauer source, third-generation synchrotron radiation has many superior features, such as high brilliance, high directionality, and energy selectivity. It affords unique opportunities to measure hyperfine interactions in very small samples, samples at high pressures, and ultrathin films, all of which are difficult to measure using conventional radioactive sources. However, since the bandwidth of synchrotron radiation is much wider than those of Mössbauer radioactive sources, other measuring methods must be adopted. The most frequently used method involves the detection of the time-differential nuclear resonant forward scattering of synchrotron radiation, which is a time analogue of Mössbauer spectroscopy [2]. This method is effective and efficient for nuclides with long-lifetime and relatively low-energy excited states; however, nuclides with short-lifetime and high-energy excited states may be difficult to measure. Moreover, in the case of contaminated or complex samples, it is sometimes difficult to carry out spectrum analysis by the time differential method.

We have developed a method that yields Mössbauer absorption-type spectra using synchrotron radiation and is applicable to many Mössbauer nuclides, including those with short-lifetime and high-energy excited levels [3]. This method enables us to carry out a unique Mössbauer spectroscopy, retaining the excellent features of synchrotron radiation. Figure 1 shows the schematic of the measuring concept. In this method, in addition to a measurement sample, a reference sample is used; these samples are used as a transmitter and a scatterer, respectively. The Mössbauer spectrum is measured by determining the intensity of delayed scattering from the excited Mössbauer nuclei in the scatter as a function of Doppler velocity. Since part of the incident radiation with an energy the same as the excitation energy of the nuclides in the transmitter is absorbed and therefore decreases after passing through the transmitter, the intensity of nuclear resonant scattering in the scatterer decreases, provided that the nuclear excitation energy of the scatterer is the same as that of the transmitter. Usually, nuclear resonant excitation energies in different electronic states differ from each other. Therefore, by scanning the relative nuclear resonant energy using the Doppler effect, the relative energy shift of the sample being measured from the reference sample is found as the local minimum of scattering intensity. It should be noted that we can use the
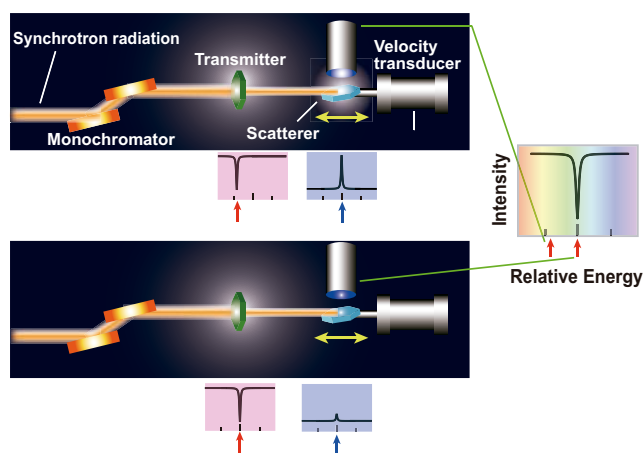

Fig. 1. Schematic of concept of energy domain in Mössbauer spectroscopy. A component of synchrotron radiation with the same energy as the resonant excited states of the Mössbauer nucleus in a transmitter is absorbed by the transmitter. Therefore, the transmitted radiation induces nuclear resonant scattering in a scatterer if the relative resonant excited state energy of the scatterer is different from that of the transmitter (upper part of the figure) but not if they are the same (lower part). Consequently, by counting the scattering intensity with the Si-APD detector as a function of their relative energy, the Mössbauer absorption-type spectrum is obtained. The relative energy shift is obtained using the velocity transducer.

measurement sample as either the transmitter or the scatterer, depending on the sample conditions and/or experimental purposes. This flexibility broadens the experimental possibilities. We can set the sample as a transmitter for measurement under extreme conditions, such as high pressures, strong magnetic fields, and high temperatures. For the study of very thick samples and samples kept in a special holder through which X-rays cannot penetrate and for the study of surface states, such as nanostructured materials, the sample can be set as the scatterer.

To confirm the validity of this method, we have measured a well-known ^{57}Fe Mössbauer spectrum using an α-Fe$_2$O$_3$ (unenriched) powder sample as the transmitter and a Pd metal foil containing ^{57}Fe (2%) as a single-line reference scatterer. The measurement was performed at the JAEA beamline **BL11XU** at 298 K. The scattered γ-rays at de-excitation from a resonantly excited nucleus were measured using a multi-element (4 × 2) Si-APD detector. The measured Mössbauer spectrum is shown in Fig. 2. The hyperfine split sextet can be clearly seen, and the peak positions of the spectrum are in agreement with previous observations using an RI source [4]. This result provides evidence that the developed system functions well. We have also measured the ^{73}Ge Mössbauer spectrum at a high resonance energy of 68.752 keV and a short lifetime of 2.51 ns in the third excited state, which is difficult to measure with a radioactive source. The measurement was carried out at beamline **BL09XU** using a Li$_2$GeO$_3$ (unenriched) powder sample as the transmitter and an enriched GeO$_2$ powder sample (96.4% ^{73}Ge enriched, a rutile structure with a tetragonal unit cell) as the scatterer.
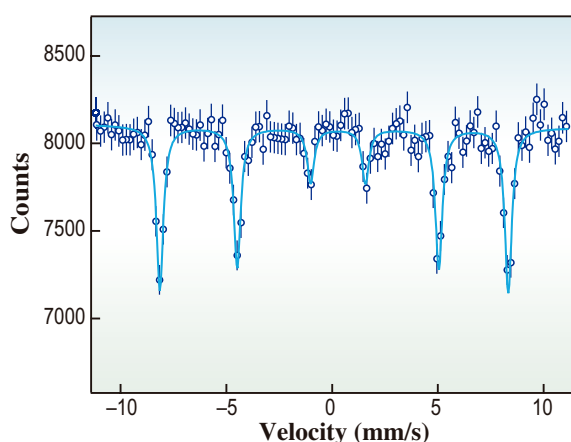
The scatterer and the transmitter were cooled to 77 K and 20 K, respectively. The Mössbauer spectrum of ^{73}Ge is shown in Fig. 3. The exact line shape of the measured spectrum can be obtained theoretically [5]. The isomer shift of Li$_2$GeO$_3$ relative to tetragonal GeO$_2$ was obtained as $-0.21(12)$ mm/s; isomer shifts depend directly on the s-electron densities and indirectly on p-, d-, and f-electrons through shielding effects and give the difference between the electronic state of the transmitter and that of the scatterer.

Since Mössbauer nuclides are widely available for use with synchrotron radiation, this method offers the potential for unique measurement capabilities for various scientific requirements including microscopic measurements, measurements under extreme conditions for ultrasmall samples, and measurements of complex nanostructured materials.
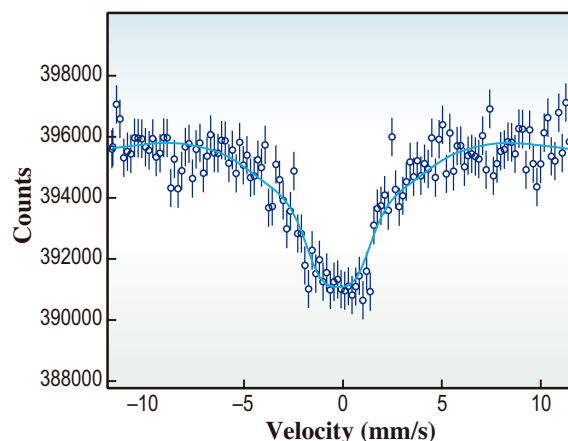

Fig. 3. Mössbauer spectrum of ^{73}Ge measured by nuclear resonant scattering of synchrotron radiation [3]. A powder sample of Li$_2$GeO$_3$ (unenriched, 20 K) was used as the transmitter, and a powder sample of GeO$_2$ (95% enriched, 77 K) was used as the scatterer. The solid line shows the fitted spectrum obtained using the developed theory [5].

Fig. 2. Mössbauer spectrum of ^{57}Fe observed by nuclear resonant scattering of synchrotron radiation [3]. A powder sample of α-Fe$_2$O$_3$ (unenriched) was used as the transmitter, and a Pd metal foil containing ^{57}Fe (2%) was used as the scatterer. The solid line shows the fitted spectrum with Lorentz line shapes.

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