Mössbauer spectroscopy in the energy domain using synchrotron radiation

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Abstract. We have developed a Mössbauer spectroscopic method that yields absorption-type spectra by using synchrotron radiation. Owing to the energy selectivity of synchrotron radiation, this method can be applied to almost all Mössbauer nuclides including those that are difficult to prepare their parent radioactive sources. This method offers the flexibility of measuring the sample in a transmission or in a scattering configuration depending on the sample condition. We have investigated the modulation and narrowing of the spectral shapes caused by the time-window effect, and we have confirmed that the previously developed theory reproduces the measured spectra well.

1. Introduction
The use of synchrotron radiation as an alternative source for Mössbauer spectroscopy was proposed in 1974 [1]. Energy-tunable, highly bright, well-collimated, pulsed, and polarized synchrotron radiation is distinct, and it affords unique opportunities to perform measurements of the hyperfine interactions in very small samples, samples under high pressures, and ultrathin films, which are difficult using conventional radioactive sources. The first conclusive result of nuclear resonant Bragg scattering of synchrotron radiation was published in 1985 [2] after some pioneering experiments. This result opened new possibilities for Mössbauer spectroscopy using synchrotron radiation. Time-differential nuclear resonant forward scattering of synchrotron radiation, a time analogue of Mössbauer spectroscopy that was developed in 1991 [3], is a standard method, and it has been employed in many scientific researches because it does not require single-crystal samples. The applicability of this method is as extensive as that of Mössbauer spectroscopy using radioactive sources. Furthermore, it was recently shown that the nuclear resonant forward scattering method is applicable to the high-energy nuclide $^{61}$Ni (67.41 keV) using multielement (stacked) avalanche photodiodes (APDs) [4]. In addition, a method that uses the nuclear lighthouse effect was developed [5]. In this method, the time evolution of the decaying nuclei in a rotating sample is translated into an angular deviation. This method is
effective for high-energy short-lifetime excited states, although the sample environment in this method is restricted. Furthermore, a heterodyne (stroboscopic) detection method for nuclear resonant forward scattering of synchrotron radiation [6][7] has also been developed. This method is effective for nuclides with very long lifetimes. Mössbauer spectroscopy can be carried out in a straightforward manner by using synchrotron Mössbauer sources obtained using pure nuclear Bragg scattering. In fact, single-line Mössbauer sources for $^{57}$Fe were obtained [8][9], and the successful results of a high-pressure study were reported [10]. Because the spectrum obtained using synchrotron Mössbauer sources is basically identical to that obtained using conventional radioactive sources, this approach may be easily applicable and beneficial for a wide range of Mössbauer research; however, thus far, $^{57}$Fe is the only available nuclide. Furthermore, the use of synchrotron radiation enables us to measure nuclear resonant inelastic scattering, which provides element-specific phonon energy spectra [11]. Recently, we developed a method that yields Mössbauer absorption spectra using synchrotron radiation and that is applicable to many Mössbauer nuclides [12]. This method enabled us to carry out unique Mössbauer spectroscopy with the excellent features of synchrotron radiation. We discuss the theoretical framework of this method and the spectra obtained using it.

2. Conceptualization and theoretical framework of developed method
The concept behind the developed method and its theoretical framework have been described previously [12]. We repeat only those details that are required here and use the same abbreviated notations as used previously.

We use two samples containing the same resonant Mössbauer nuclides; one is used as a transmitter and the other as a scatterer. The scatterer is placed behind the transmitter in the path of the synchrotron radiation. A schematic of the typical experimental setup is shown in figure 1. In order to measure the energy-domain Mössbauer spectra, we use a silicon APD detector placed above or below the scatterer to detect delayed $4\pi$ scattering containing internal conversion electrons and fluorescent X-rays following the de-excitation in addition to the emitted $\gamma$-rays, as a function of the Doppler velocity. It is easier to detect fluorescent X-rays than $\gamma$-rays using a silicon APD detector; this is because the energies of fluorescent X-rays are lower than those of $\gamma$-rays. Moreover, the detection of electrons is not difficult using APD detectors.

When the resonance energies of the scatterer and the transmitter are equal, there is a decrease in the nuclear resonance scattering from the scatterer; this is because of the strong nuclear resonance absorption of the resonance energy radiation in the transmitter. Therefore, by measuring the scattering from the scatterer as a function of the relative energy (velocity), we can observe a local minimum when the relative energy is zero. This velocity-dependent scattering intensity yields a spectrum in the energy domain. This description is simple and purely conceptual; however, an actual reproduction of the measured spectra will be more complex. In the scatterer, there exist two processes that depend on the relative resonance energy shift $w_s$ in units of the natural width of the nuclear excited state between the transmitter and the scatterer—the nuclear resonant recoilless absorption of radiation (A-channel)
and the scattering of the radiation owing to photoelectron absorption (C-channel). The dependence of other processes such as nuclear resonant absorption of radiation with recoil (B-channel) on the relative energy shift is small and can be ignored. Using the corresponding intensities ($I_A$, $I_B$, and $I_C$), the absorption spectrum intensity $I(w_s)$ can be expressed as follows:

$$I(w_s) = I_A(w_s) + I_C(w_s) + I_B,$$

(1)

$$I_A(w_s) = C_A \int_0^{r_s} \int_0^{r_t} dz \left[ \frac{dw}{2\pi} \frac{\exp(-iw_\tau)}{w-w_s+i/2} E_i(w)E_s(w,w_s,z) \right]^2,$$

(2)

$$I_C(w_s) = C_C \int_0^{r_s} \int_0^{r_t} dz \left[ \frac{dw}{2\pi} \frac{\exp(-iw_\tau)(E_i(w)E_s(w,w_s,z) - 1)}{2} \right]^2,$$

(3)

$$E_i(w) = E_{0i} \exp \left(-\frac{\mu_{nt}Z}{2} \exp \left(-i \frac{\mu_{nt}Z}{2(2w+i)} \right) \right),$$

(4)

$$E_s(w,w_s,z) = E_{0s} \exp \left(-\frac{\mu_{es}Z}{2} \exp \left(-i \frac{\mu_{es}Z}{2(2w-w_s+i)} \right) \right).$$

(5)

Here, $z_t$ ($z_s$) denotes the thickness of the transmitter (scatterer); $\mu_{nt}$ ($\mu_{ns}$), the linear absorption coefficient of radiation by the nuclei at resonance in the transmitter (scatterer); $\mu_{nt}$ ($\mu_{es}$), the electronic absorption coefficient of the transmitter (scatterer); $E_i$ ($E_s$), the propagating coherent field amplitudes of the transmitter (scatterer); and $E_{0i}$ ($E_{0s}$), the amplitude of the radiation field at the entrance of the transmitter (scatterer). $C_A$ and $C_C$ are constants, and $r_t$ and $r_s$ are the starting and ending times, respectively, of the measured time window in units of the lifetime of the nuclear excited state. In order to calculate the measured spectra correctly, we must take into account the exact experimental conditions because of the absorption of fluorescent X-rays, internal conversion electrons, and $\gamma$-rays in the scatterer.

It is known that exact line shapes can be obtained in the Mössbauer spectrum by the transmission integral method [13], and that the Lorentzian line shape is observed only in the case of an ideally thin sample. Furthermore, the time-window effect, which is known in delayed coincidence Mössbauer spectroscopy [14],[15], yields a narrower and modified line shape of Mössbauer spectra obtained using radioactive sources. These attributes can be clearly seen in the developed method because of the pulsed nature of synchrotron radiation. If the measured time range can be approximated to the time range from $r_1 = 0$ to $r_2 = \infty$, then a Lorentzian line shape can be obtained using thin-sample approximation by ignoring the contribution of $I_C$ [16].

3. Experiments
Experiments were performed at the nuclear resonant scattering beamline (BL09XU) at SPring-8. The storage ring was operated in the 203-bunch mode, yielding a bunch distance of 23.6 ns. We used a powder sample of EuF$_3$ (not enriched, 40-µm thick) as the transmitter. A disk of enriched EuF$_3$ powder (not enriched, 30-µm thick) was used as the scatterer. Delayed emission from the irradiated surface of the scatterer was measured using a multielement Si-APD detector ($4 \times 2$ APDs, each with a detection area of $3 \times 5$ mm$^2$).

4. Results and discussion
We studied the time-window effect in the Mössbauer spectra of the 21.54 keV excited state of $^{151}$Eu; the measured spectra are shown in figure 2. In this measurement, we used EuF$_3$ samples, which are
single-line materials, for both the transmitter and the scatterer. In figure 2, the values of $\tau_1$ for the three measured spectra are (a) 5.7 ns, (b) 8.1 ns, and (c) 10.5 ns, and $\tau_2 = 17.0$ ns is common to all the measurements. The changes in the spectral lineshape can be clearly seen as being dependent on $\tau_1$. Because the half-life of the first excited state of $^{151}$Eu is 9.6 ns, the used values of $\tau_1$ cannot be approximated as zero. We observe that as $\tau_1$ increases, the linewidth becomes narrower, the background becomes more distinctly wavy, and the cycle becomes larger. As discussed, these effects were observed in the Mössbauer spectra measured by the delayed coincidence method [14],[15]. Moreover, similar spectral changes were observed in the Mössbauer spectra obtained by the nuclear resonant Bragg scattering of synchrotron radiation [17]. We have calculated the spectral lines using the previously developed theory for corresponding time windows; the results are shown in figure 2. It was confirmed that the developed method reproduced the measured spectra well. This result shows that the theoretical and experimental results are consistent with each other.

In conclusion, we have successfully measured the time-window effect and demonstrated that the developed theory works well. In our method, we use two samples as the transmitter and the scatterer. By using only one single-line reference material with a sufficient recoilless fraction, we can carry out good-quality measurements for the samples under investigation. This situation is similar to the selection of a Mössbauer RI source; however, this method does not require radioactive material. Moreover, one of the features of this method is the flexibility of the experimental setup in that the measured sample can be used as a transmitter or as a scatterer, depending on the sample conditions.
The transmission experiments are suitable for high-pressure measurements, measurements of small samples, measurements of natural (not-enriched) samples, etc. On the other hand, scattering experiments are suitable for surface measurements, films on a substrate, measurements of very thick samples, etc. Mössbauer nuclides are widely available; therefore, this method offers the potential for unique measurement capabilities for various scientific requirements such as microscopic measurements, measurements under extreme conditions for ultrasmall samples, and measurements of complex nanostructured materials.

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References

[1] Ruby S L 1974 J. Phys. (Paris). Colloq. 35 C6-209
[2] Gerdau E, Rüffer R, Winkler R H, Tolksdorf W, Klages C P and Hannon J P 1985 Phys. Rev. Lett. 54 835
[3] Hastings J B, Siddons D P, van Bürck U, Hollatz R and Bergmann U 1991 Phys. Rev. Lett. 66 770
[4] Sergueev I, Chumakov A I, Deschaux Beaume-Dang T H, Rüffer R, Strohm C and van Bürck U 2007 Phys. Rev. Lett. 99 097601
[5] Röhlsberger R, Toellner T S, Sturhahn W, Quast K W, Alp E E, Bernhard A, Burkel E, Leupold O and Gerdau E 2000 Phys. Rev. Lett. 84, 1007
[6] Coussement R, Cottenier S and L’abbé C 1996 Phys. Rev. B 54 16003
[7] Callens R, Coussement R, Kawakami T, Ladrière J, Nasu S, Ono T, Serdons I, Vyvey K, Yamada T, Yoda Y and Odeurs J 2003 Phys. Rev. B 67 104423
[8] Smirnov G V, Van Bürck U, Chumakov A I, Baron A Q R and Rüffer R 1997 Phys. Rev. B 55 5811
[9] Smirnov G V, Sklyarevskii V V, Voskanyan R A and Artem’ev A N 1969 Pis’ma Zh. Eksp. Teor. Fiz. 9 123
[10] Mitsui T, Seto M, Masuda R, Kiriyama K and Kobayashi Y 2007 Jpn. J. Appl. Phys. 46 L703
[11] Seto M, Yoda Y, Kikuta S, Zhang X W and Ando M 1995 Phys. Rev. Lett. 74 3828
[12] Seto M, Masuda R, Higashitani-guchi S, Kitao S, Kobayashi Y, Inaba C, Mitsui T and Yoda Y 2009 Phys. Rev. Lett. 102 217602
[13] Margulies S and Ehrman J R 1963 Nucl. Instrum. Methods 21 217
[14] Lynch F J, Holland R E and Hamermesh M 1960 Phys. Rev. 120 513
[15] Hamill D W and Hoy G R 1968 Phys. Rev. Lett. 21 724
[16] Smirnov G V, van Bürck U, Arthur J, Brown G S, Chumakov A I, Baron A Q R, Petry W and Ruby S L 2007 Phys. Rev. A 76 043811
[17] Tischler J Z, Larson B C, Boatner L A, Alp E E and Mooney T 1996 J. Appl. Phys. 79 3686