Review Article

Evolution of Nuclear Resonant Scattering Research at SPring-8

Spectroscopy using the nuclear resonant scattering of synchrotron radiation has been used effectively in a wide range of research areas, taking advantage of its excellent features. Since only one nuclide (isotope) is resonantly excited with the undulator radiation, it enables the measurement of element (isotope)-specific electronic states through hyperfine interactions between the nucleus and the surrounding electrons. Moreover, the measurement of element (isotope)-specific phonons (lattice vibrations) is possible using nuclear resonant inelastic scattering. In addition, by using the ultranarrow width of the nuclear excited states (for example, the width of the first nuclear excited state of ^{57}Fe is 4.7 neV), quasi-elastic scattering measurement is possible, allowing the study of the slow dynamics of macromolecules and glass transitions. Since the nuclear resonant scattering method enables a wide range of measurements from the electronic state to quasi-elastic and inelastic scattering with an element (isotope)-specific feature, the range of areas of application is very wide such as materials science, earth science, physics, chemistry, and biology. Measurement methods employing these unique features of nuclear resonant scattering have progressively been advanced at SPring-8. Here, recent nuclear resonant scattering studies using these features are reviewed.

1. Nuclear Resonant Elastic Scattering of Synchrotron Radiation (Mössbauer Spectroscopy)

Mössbauer spectroscopy, which uses the recoilless nuclear resonant absorption effect known as the Mössbauer effect, is a powerful and well-established method used in a wide variety of research areas. One of the most important tasks of Mössbauer spectroscopy is to elucidate the electronic states of a specific element, and this can be achieved via the measurement of nuclear energy levels. This is because nuclear energy levels are affected by the surrounding electrons; if a resonant atom has a magnetic moment and/or an anisotropic electronic structure, the nuclear energy levels are split. A schematic of the nuclear energy levels of ^{57}Fe with (and without) magnetic field splitting and corresponding typical Mössbauer spectra are shown in Fig. 1. The density of electrons at the nucleus affects the nuclear energy levels and induces an energy shift, which is directly due to *s*-electrons and indirectly due to other electrons. Therefore, the measurement of the nuclear energy levels provides information on the electronic states. To determine the electronic state, this method seems to be indirect, but the identification of the observed element is obvious and the disturbance for the electronic states usually can be ignored. Table 1 shows the elements for which the Mössbauer effect has been observed.

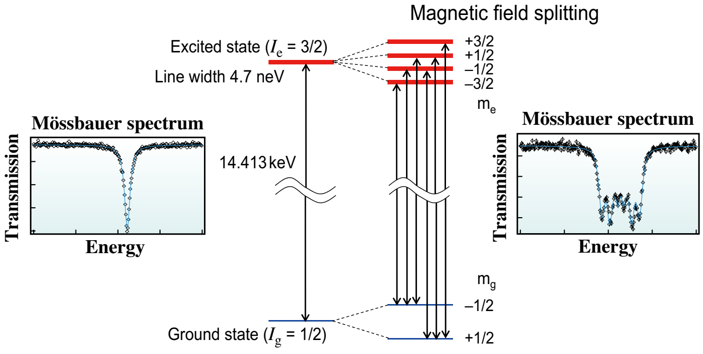
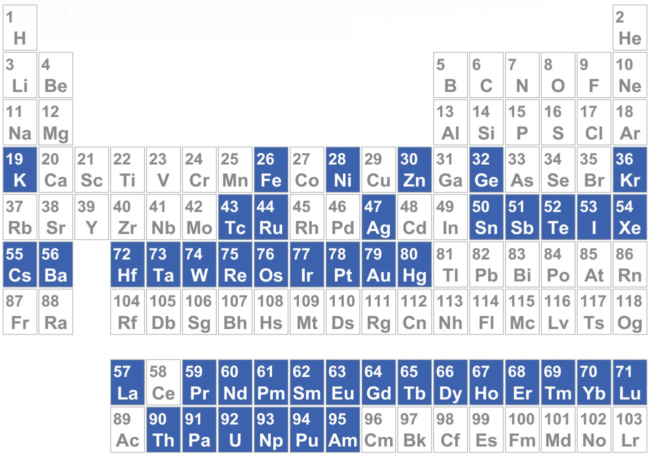


Fig. 1. Nuclear energy levels of ^{57}Fe with (right) and without (left) magnetic field splitting and corresponding typical Mössbauer spectra.

Synchrotron Mössbauer Sources

The ability to measure element (isotope)-specific electronic states is one of the unique features of nuclear resonant scattering; by combining this feature and high brilliance synchrotron radiation as an excitation source, novel studies that are difficult with radioactive isotope (RI) sources such as measurement under extreme conditions are possible. Synchrotron radiation, however, cannot be used as a simple alternative Mössbauer γ-ray source because the bandwidth of the incident synchrotron radiation is much broader than the line width of the nuclear levels usually used and even hyperfine splitting (typically below μeV). One method of generation an ultranarrow-width X-ray is to use electronically forbidden but nuclear-allowed Bragg reflections called synchrotron Mössbauer source (SMS). In this method, the obtained Mössbauer radiation is collimated, polarized, and 100% recoilless, and the spectrum obtained using an SMS is essentially identical to that obtained using conventional RI sources, although an SMS has only been realized for ^{57}Fe using iron borate ($FeBO_3$) single crystals set under diffraction conditions at the Néel temperature (75.3°C). The measurement of iron-enriched dense silicate glasses, as laboratory analogues for dense magmas, up to a pressure of 85 GPa was performed using an SMS at SPring-8 BL11XU [1]. Although the possible presence of dense magmas at Earth's core-mantle boundary is expected to substantially affect the dynamics and thermal evolution of Earth's interior, the thermal transport properties of silicate melts under relevant high-pressure conditions are not understood fully. Combined with the result of *in situ* high-pressure optical absorption measurement, it was suggested that the radiative thermal conductivity of dense silicate melts may decrease with increasing pressure and, therefore, may be significantly smaller than previously expected under core-mantle boundary conditions.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	**26 Fe**	27 Co	**28 Ni**	29 Cu	**30 Zn**	31 Ga	**32 Ge**	33 As	34 Se	35 Br	**36 Kr**
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	**43 Tc**	**44 Ru**	45 Rh	46 Pd	**47 Ag**	48 Cd	49 In	**50 Sn**	**51 Sb**	**52 Te**	**53 I**	**54 Xe**
55 Cs	**56 Ba**		**72 Hf**	**73 Ta**	**74 W**	**75 Re**	**76 Os**	**77 Ir**	**78 Pt**	**79 Au**	**80 Hg**	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			57 La	58 Ce	**59 Pr**	**60 Nd**	**61 Pm**	**62 Sm**	**63 Eu**	**64 Gd**	**65 Tb**	**66 Dy**	**67 Ho**	**68 Er**	**69 Tm**	**70 Yb**	**71 Lu**
			89 Ac	**90 Th**	**91 Pa**	**92 U**	**93 Np**	**94 Pu**	**95 Am**	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Table I. Periodic table of the elements for which the Mössbauer effect has been observed (elements on blue backgrounds).

Synchrotron-radiation-based Mössbauer absorption spectroscopy

To utilize the element (isotope)-specific feature, we should use other methods. Previously, nuclear resonant forward scattering (NFS) measurement in the time domain has been used. Recently synchrotron-radiation-based Mössbauer spectroscopy in the energy domain was developed at BL09XU and BL11XU; this method yields absorption spectra that are similar to Mössbauer spectra measured with radioactive sources [2]. The high brilliance of the radiation enables the measurement of tiny samples, such as samples held in diamond anvil cells. In fact, a ^{151}Eu Mössbauer study has already been performed under high pressure with this method [3]. It, however, took a long time for the measurement and, therefore, a detection system using a windowless avalanche photodiode (APD) X-ray detector in a cryostat chamber was developed to enhance the measurement efficiency [4]. In the previous measurement, γ-rays and/or fluorescent X-rays accompanied with internal conversion (IC) electron emissions from the resonantly excited nuclei were detected, but the IC electrons themselves were not detected because the electrons were shielded by the X-ray windows of the cryostat and the detector used. A schematic drawing of the experimental setup and a photograph of the detection system are shown in Fig. 2. The developed system was applied to SR-based Mössbauer spectroscopy for the 76.5 keV-excited state of ^{174}Yb. Moreover, although the natural abundance of ^{61}Ni is only 1.14%, it made the measurement of Ni samples without isotope enrichment possible. This method has been applied to studies on the electronic state of Ni nanoparticles [5], Ni-substituted proteins [6], and so forth.

2. Nuclear Resonant Inelastic Scattering

Nuclear resonant inelastic scattering spectroscopy is a method for investigating the vibrational states in substances. This method utilizes the nuclear resonance excitation accompanied by the creation and/or annihilation of phonons. The recoilless excitation of atomic nuclei is known as the Mössbauer effect, while resonance excitation of the nuclei and phonon generation can occur when the energy of the incident synchrotron radiation is larger than the resonant excitation energy and the difference is equal to the energy of a phonon. Also, when the incident energy is lower than the resonant excitation energy and the difference is equal to the energy of a phonon, annihilation of the phonon and resonant excitation occur. These are nuclear resonance inelastic excitations. In this method, phonon energy spectra are measured by counting the scattering from the excited nuclei as a function of the incident photon energy as shown in Fig. 3. The typical resolution of the spectra is around 1 meV for ^{57}Fe measurement.

Nuclear resonant inelastic scattering has many interesting features and, owing to the high brilliance of the synchrotron radiation, samples under extreme conditions such as high pressures can be measured. One of the most important features is that it is possible to excite specific isotopes as in electronic state measurement. Therefore, for compounds composed of many elements, phonon information concerning only the excited nuclide is obtained; more precisely, partial phonon densities of states (PDOSs) are obtained. This feature is very advantageous when there is interest

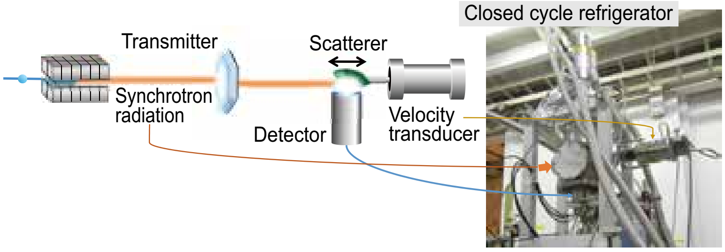


Fig. 2. Schematic drawing of the experimental setup and photograph of the detection system using a windowless avalanche photodiode (APD) X-ray detector in a cryostat chamber.

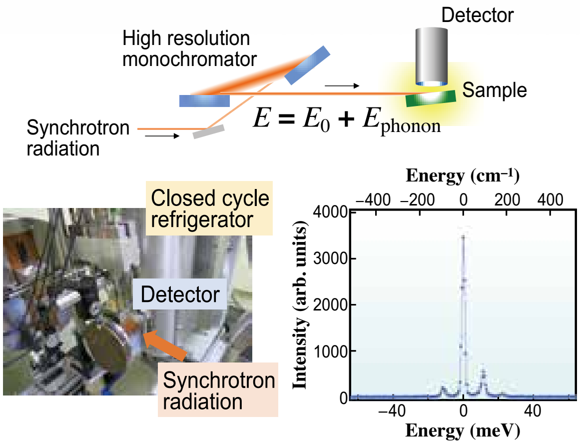


Fig. 3. Schematic for the measurement of nuclear resonant excitation accompanied by phonon creation (upper). Photograph of the detector and the cryostat with a closed-cycle refrigerator (lower left) and typical phonon energy spectrum (lower right).

in the function and/or local structure of a specific element (isotope) in a complex compound. From a spectroscopic viewpoint, this method is similar to resonant Raman spectroscopy, which provides valuable information on the vibrational properties of samples such as metalloprotein samples. Resonant Raman spectroscopy is very useful and has been used effectively. However, the selection rule sometimes hampers the observation of vibrational modes of interest while the nuclear resonant inelastic scattering method gives all modes that involve the motion of resonant nuclides.

Recently, this method has been actively performed in studies on the specific sites in large molecules such as metalloprotein samples involving thousands of other atoms. In these studies, the structure around a specific site of interest is investigated by comparing the obtained phonon energy spectrum with the vibrational spectrum obtained from density functional theory (DFT) calculations under the assumption of a feasible structural model. Using this methodology, which is sometimes called nuclear resonance vibrational spectroscopy (NRVS), many interesting studies have been performed at SPring-8 [e.g., 7-12]. This method is particularly effective for samples that cannot be crystallized, such as the intermediates in the catalytic cycles of enzymes, and a study on the structural characterization of the reactive Fe(IV)=O intermediate in the catalytic cycles of a mononuclear non-haem iron (NHFe) enzyme (the halogenase SyrB2 from the bacterium *Pseudomonas syringae* pv. *syringae*) has been performed [7]. This intermediate reacts through an initial hydrogen-atom abstraction step and performs subsequent halogenation of the native substrate or hydroxylation of non-native substrates and, therefore, it is essential and important to reveal the local structure and the mechanism. In this study, it was found that the orientation of the Fe(IV)=O intermediate depends on the substrate, presenting specific frontier molecular orbitals responsible for hydrogen-atom abstraction that can selectively lead to halogenation or hydroxylation.

Moreover, NRVS was applied to study the catalytic mechanism of hydrogenases, which catalyze the reversible conversion of molecular hydrogen to protons and electrons. Understanding the mechanism is significant because it is expected to lead to the development of clean energy sources producing hydrogen. NRVS was applied to an [FeFe]-hydrogenase variant lacking the amine proton shuttle, which stabilizes a putative hydride state [11]; [FeFe]-hydrogenases are metalloenzymes that reversibly reduce protons to molecular hydrogen with extremely high efficiency. NRVS spectra clearly showed the bending modes of the terminal Fe–H species, which were consistent with widely accepted models of the catalytic cycle.

3. Quasi-elastic Scattering Measurement Using Nuclear Resonant Scattering

The topics discussed thus far take full advantage of the properties of nuclear resonance excitation and, therefore, they are isotope-specific. Another important property is the ultranarrow bandwidth of the excited states (for example, a width of 4.7 neV for the first excited state of ^{57}Fe with an excited state energy of 14.4 keV). This unique property sheds light on the small energy shift of the microscopic region induced by quasi-elastic scattering measurement. Studies on the slow dynamics of glass-forming molecular liquids, alloys, ionic liquids, liquid crystal polymers, and biological molecules are possible using the property, and experimental studies have been performed at SPring-8 [e.g., 13,14].

In this method, the small energy broadening of a scattered γ-ray due to the motion of the atoms (molecules) is analyzed using reference absorbers containing the resonant nuclide. This method is known as the Rayleigh scattering of Mössbauer radiation (RSMR) method. Note that, in contrast to the previously discussed method, this method does not require a sample containing the resonant nuclide. A time-domain interferometry (TDI) method that uses the nuclear resonant scattering of synchrotron radiation is the time-domain analogue of the RSMR method. In the TDI method, the quasi-elastic broadening of nuclear resonant scattering in the energy domain can be observed as a relaxation in the time domain. A schematic of the experimental method of TDI measurement is shown in Fig. 4. To observe the relaxation, an interference pattern in the time domain is used; the pattern is formed by the interference between the nuclear resonant scattering of pulsed synchrotron radiation from the upstream nuclear absorber and that from the downstream nuclear absorber with resonance energy different from that of the upstream one. As shown in Fig. 5, if a suitable sample is placed between the absorbers, the interference pattern is perturbed by the energy broadening of the radiation from the upstream nuclear absorber caused by the

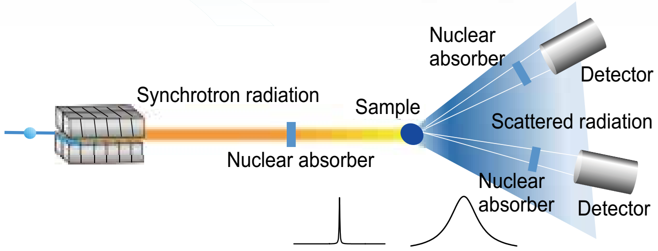


Fig. 4. Schematic of the TDI method. A sample is illuminated by synchrotron radiation transmitted through an upstream nuclear absorber, and the scattered radiation from the sample is transmitted through a downstream nuclear absorber. The nuclear absorbers contain the resonant nuclide such as ^{57}Fe. The time evolution of the transmitted radiation, reflecting the relaxation of molecules (ions) in the sample, is measured by a detector.

motion of the atoms in the sample. To analyze the change in the pattern from the non-perturbed one, we can obtain the relaxation of the atoms in the sample. The resolution of this method is typically on the order of neV; however, the line width of synchrotron radiation is on the order of eV and, therefore, most of the synchrotron radiation is not used even considering the energy broadening of μeV order. Although the efficiency of this method using synchrotron radiation is considerably higher than that with RI sources, it is not sufficient for measurement under special conditions such as at small angles. Recently, a multi-line TDI system was developed to improve the efficiency by increasing the number of nuclear absorbers with different resonance energies in order to use the unused part of the synchrotron radiation [15]. The developed multi-line TDI method allows us to obtain microscopic relaxation pictures much more rapidly and accurately than conventional single-line TDI.

Recently, using this method, a study on the slow dynamics of liquids with a mesoscopic structure and its relation to the shear viscosity was performed [13]. In this work, quasi-elastic scattering measurements were performed on a liquid higher alcohol, 3,7-dimethyl-1-octanol; the properties of liquids with mesoscopic structures have been attracting many researchers. The intermolecular correlation in simple liquids appears at the wavenumber corresponding to the contact distance as a peak of the static structure factor called the "main peak" and, in some liquids, an additional peak, called a "prepeak", is observed at a wavenumber lower than that of the main peak. The prepeak exhibits the presence of a characteristic mesoscopic structure with a spatial dimension much larger than the intermolecular contact distance. Using the developed method, the structural relaxation at the two wavenumbers of the prepeak and the main peak of the static structure factor was determined. This result indicates that the dynamics of a mesoscopic structure represented as the prepeak contributes to the shear viscosity through the slowest mode of the viscoelastic relaxation by comparison with the viscoelastic spectrum exhibiting bimodal relaxation.

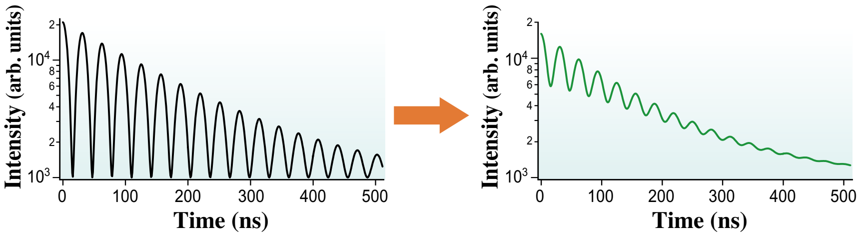


Fig. 5. The interference pattern without a sample (left) is perturbed by the energy broadening of the radiation from the upstream nuclear absorber caused by the motion of the atoms in the sample. A typical perturbed spectrum is shown on the right.

Summary

Recent nuclear resonant scattering studies at SPring-8 using advanced features such as element (isotope)-specific electronic states and an ultranarrow width were reviewed. The efficiency of the methods has been improved and will be further improved as a result of development. Moreover, more advanced methods such as depth-selective Mössbauer spectroscopy are expected to be realized. In addition to the reviewed work, many interesting studies have been performed and, in particular, important studies on fundamental physics have been performed [16,17]. The range of areas in which nuclear resonant scattering methods can be used is very wide, as discussed, and further important results are expected.

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