Synchrotron radiation Mössbauer spectroscopy for ^{61}Ni nanoparticles

Mössbauer spectroscopy is a well-established and effective method in physics, chemistry, biology and Earth science. It provides element-specific information on the electronic states of each constituent in complex materials, such as valence and magnetism. Most Mössbauer studies have been performed using ^{57}Fe and ^{119}Sn with γ-rays from radioactive isotope (RI) sources, although the Mössbauer effect has been observed in approximately 100 nuclides of nearly 50 elements (Fig. 1). One major difficulty in Mössbauer spectroscopy using nuclides other than ^{57}Fe and ^{119}Sn is the preparation of RI sources. With the exception of ^{57}Fe and ^{119}Sn (purchasable), we should synthesize the RI using a reactor or an accelerator, as is also the case with ^{61}Ni Mössbauer spectroscopy. This difficulty is avoided by using synchrotron radiation (SR); we can extract X-rays with an appropriate energy for Mössbauer spectroscopy from SR. Furthermore, the high brilliance of SR facilitates Mössbauer measurement for materials under extreme conditions, such as high pressures. SR-based Mössbauer absorption spectroscopy is one such method in the energy domain [1], and measurement using the many nuclides shown in Fig. 1 is promising. Recently, the measurement efficiency of this method was drastically improved [2]. Thus, although the natural abundance of ^{61}Ni is only 1.14%, it has become realistic to perform the SR-based Mössbauer absorption spectroscopy of Ni samples including nanoparticles without expensive isotope enrichment.

The hexagonal close-packed (hcp) structure is known to be the metastable state for Ni metal. Recently, hcp-Ni nanoparticles have been synthesized by many groups using chemical reduction methods because hcp-Ni nanoparticles are expected to show novel functionality different from that of typical face-centered cubic (fcc) Ni, such as catalytic action. However, it has been suspected that the nanoparticles formed nickel carbide (Ni_3C) in which the Ni arrangement is the same as that in hcp-Ni; hcp-Ni and Ni_3C can hardly be distinguished by X-ray diffraction (XRD). Furthermore, the magnetism of hcp-Ni is still debated. Theoretical calculations predicted the ferromagnetism of hcp-Ni with an atomic magnetic moment similar to that of fcc-Ni of approximately 0.6 μ_B (μ_B: Bohr magneton). In contrast, the experimentally observed magnetization of hcp-Ni nanoparticles is at most one-fifth of that of fcc-Ni. Since Ni_3C is non-magnetic, this discrepancy also casts doubts. Still, other possible factors should be considered: surface oxidization, magnetic impurities, and so forth. To study hcp-Ni nanoparticles in detail, we performed measurements using ^{61}Ni SR-based Mössbauer absorption spectra.

The experimental setup for ^{61}Ni SR-based Mössbauer absorption spectroscopy is shown in Fig. 2. The experiments were performed at SPring-8 **BL09XU** and **BL11XU**. The operating mode of the electron-storage ring was the "203 bunch" mode, where SR with the energy of ^{61}Ni nuclear resonance is transmitted by a sample in a cryostat. The samples were Ni metal (1 mm thickness at 20 K) or hcp-Ni nanoparticles (0.9 g (component Ni)/cm^2 at 4 K). The nanoparticles were synthesized by a chemical reduction method and coated with polyvinylpyrrolidone. Their crystallite size was around 40 nm as determined by XRD. Both samples were without ^{61}Ni enrichment. Then, the SR was scattered by $^{61}Ni_{0.86}V_{0.14}$ (enrichment: 86.2%) foil at typically 30 K in another vacuum cryostat. The nuclear resonance energy of the foil was scanned using the Doppler effect by controlling its velocity. An eight-element Si avalanche photodiode (APD) detector was built in the vacuum cryostat of the Ni-V foil, and

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	104~														

Elements including nuclides where Mössbauer effect has been observed

Elements without nuclides where Mössbauer effect has been observed

*Lanthanide	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**Actinide	Ac	Th	Pa	U	Np	Pu	Am	Cm		Cf	Es	Fm	Md	No	Lr

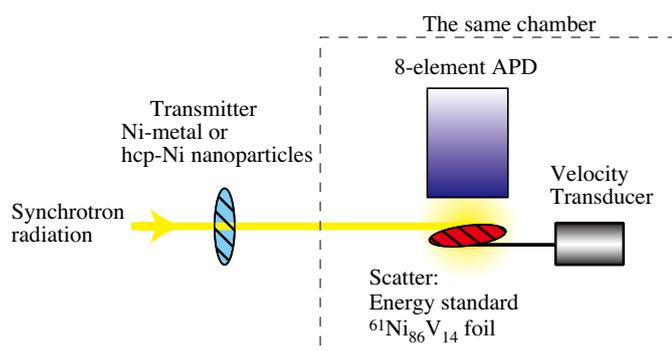Fig. 1. Table of elements exhibiting Mössbauer effect.

Fig. 2. Schematic drawing of the developed X-ray windowless system for ^{61}Ni SR-based Mössbauer absorption spectroscopy.

thus there was no X-ray window between the foil and detector, whereas such a window was used in the previous measurement system reported in Ref. 1. This X-ray windowless system [2] drastically improves the detection rate of signals, because both X-rays and electrons can be detected as the emission from the foil, and the distance between the foil and detector can be short, giving a large solid angle for the detector subtended at the foil. Since nuclear resonant scattering (NRS) by ^{61}Ni is emitted with a delay (half-life 5.34 ns), the NRS was separated from the strong immediate electronic scattering by setting a time window of 3 ns to 20 ns after the SR incidence. The detail of the measurement system is given in Ref. 3.

The ^{61}Ni Mössbauer spectra of bulk fcc-Ni metal and hcp-Ni nanoparticles are shown in Fig. 3. We successfully obtained the spectra within 20 h. The spectrum of the bulk shows a magnetic hyperfine field of 7.7 ± 0.2 T, which agrees well with previous results. The spectrum of the hcp-Ni nanoparticles was reasonably analyzed by assuming one component with a magnetic hyperfine field of 3.4 ± 0.9 T. It does not show a secondary component, such as a 7.7 T (fcc-Ni) or 10 T (nickel oxide NiO) component, and thus the contamination of fcc-Ni and NiO due to surface oxidization of the nanoparticles was below the statistical error of the spectrum. The 3.4 T field also disagrees with that of non-magnetic Ni_3C. One likely substance for this magnetic hyperfine field is the presence of nickel carbide with less carbon than Ni_3C. In fact, carbon might be supplied during the synthesis. Fang *et al.* [4] calculated the decrease in the atomic magnetic moment of Ni in NiC_x as x increases in the framework of ferromagnetic order. In the framework, the 3.4 T field corresponds to an atomic magnetic moment of 0.3 μ_B under a proportionality assumption similar to that for fcc-Ni, where 7.7 T corresponds to 0.6 μ_B. From the value of 0.3 μ_B, the chemical composition of the nanoparticles is $NiC_{0.1}$ using the calculation in Ref. 4.

In summary, we observed ^{61}Ni SR-based Mössbauer absorption spectra of hcp-Ni nanoparticles using an X-ray windowless system. Although the nanoparticles were not enriched, we successfully obtained the spectrum within 20 h. The Mössbauer spectrum of hcp-Ni revealed that the impurity levels of fcc-Ni and NiO were below the detectable limit, and the nanoparticles consisted of a single component. The spectrum shows the magnetic hyperfine field of 3.4 ± 0.9 T at 4 K, corresponding to an atomic magnetic moment of 0.3 μ_B. This can be understood as corresponding to nickel carbide ($NiC_{0.1}$). Note that this method is also effective for the detailed study of many materials containing Ni. In fact, ^{61}Ni Mössbauer spectroscopy of the cathode material of a Li-ion battery and a Ni-substituted protein has already been measured using this system [5].
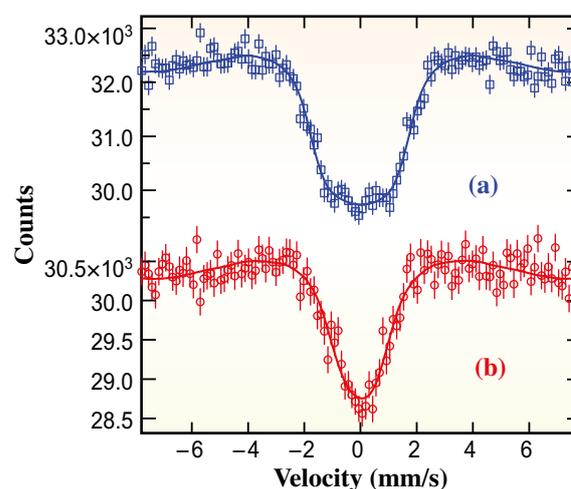

Fig. 3. ^{61}Ni SR-based Mössbauer absorption spectra of **(a)** Ni metal and **(b)** hcp-Ni nanoparticles. The open circles and squares are experimental data and the lines were fitted by the formulas discussed in Ref. 1.

Ryo Masuda and Makoto Seto*

Research Reactor Institute of Kyoto University

*Email: seto@rri.kyoto-u.ac.jp

References
[1] M. Seto *et al.*: Phys. Rev. Lett. **102** (2009) 217602.
[2] R. Masuda *et al.*: Appl. Phys. Lett. **104** (2014) 082411.
[3] *R. Masuda, Y. Kobayashi, S. Kitao, M. Kurokuzu, M. Saito, Y. Yoda, T. Mitsui, K. Hosoi, H. Kobayashi, H. Kitagawa and M. Seto: Sci. Rep. **6** (2016) 20861.*
[4] C.M. Fang *et al.*: Phys. Rev. B **86** (2012) 134114.
[5] T. Segi *et al.*: Hyperfine Interact. **237** (2016) 7; L.B. Gee *et al.*: Inorg. Chem. **55** (2016) 6866.