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To cite this article: Y Kobayashi 2010 J. Phys.: Conf. Ser. 217 012023

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99\textsuperscript{Ru} and 61\textsuperscript{Ni Mössbauer Spectroscopic Studies Using the Accelerator at RIKEN

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Abstract. Ruthenium and nickel are important constituent elements of a wide variety of compounds, including oxides, catalysts, and functional and industrial materials for solar batteries and shape-memory alloys. 99\textsuperscript{Ru} and 61\textsuperscript{Ni Mössbauer spectroscopy can reveal significant information about the physical and chemical properties of these compounds. However, there have not been many studies that use Mössbauer spectroscopy to investigate Ru and Ni compounds. This paper discusses Mössbauer source preparation methods using the RIKEN accelerator for conventional Mössbauer absorption spectra in addition to our recent results.

1. Introduction
The Mössbauer effect has been observed for nearly 100 nuclear transitions in about 80 nuclides distributed over 43 elements [1]. Of these elements, about 20 have yet to be investigated by Mössbauer spectroscopy, since not all transitions are amenable to normal experimental conditions. Mössbauer elements of Fe, Ni, Zn, Ru, Sn, Sb, Te, I, Xe, Eu, Hf, Ta, W, Os, Ir, Pt, Au, Hg, U are used in chemistry, solid-state physics, biology, metallurgy, and earth science. Some Mössbauer nuclides including 57\textsuperscript{Fe}, 119\textsuperscript{Sn} and 151\textsuperscript{Eu} have been extensively investigated in a wide variety of fields, whereas other nuclides have not been studied greatly by Mössbauer spectroscopy despite being significant elements for materials science. There are several reasons for this state of affairs: the half-lives of Mössbauer mother nuclides are too short, inappropriate lifetimes of the first excited levels, few Mössbauer transitions, and complicated preparation procedures or their chemical treatments to produce appropriate Mössbauer mother nuclides.

In addition to Fe and Sn, Ru and Ni are important iron-group elements. Ruthenium is a major element of important oxides, catalysts utilized in organic synthesis, and solar energy technologies. An interesting feature of Ru chemistry is that Ru has a large variety of oxidation states ranging from 0 to 8+. For example, Ru ions have an oxidation state of 4+ (4d\textsuperscript{4} configuration) in superconducting Sr\textsubscript{2}RuO\textsubscript{4} (T\textsubscript{c}=1.5 K) [2], and an oxidation state of 8+ (4d\textsuperscript{0}) in RuO\textsubscript{4}. On the other hand, Ni is ferromagnetic near room temperature. It is used in many industrial and electrical devices including magnets, rechargeable batteries, shape-memory alloys, and catalysts. In addition, several enzymes and microorganisms contain nickel.

It is important to study the physicochemical properties of many Ru and Ni compounds using 99\textsuperscript{Ru} and 61\textsuperscript{Ni Mössbauer spectroscopy. However, there have not been many Mössbauer spectroscopic studies of Ru and Ni compounds because of experimental difficulties. Specifically, 99\textsuperscript{Ru} and 61\textsuperscript{Ni do not have long-lived nuclides that can be used as Mössbauer sources, and both the source and the
absorber should be cooled to low temperatures because of the low Debye–Waller factors caused by the relatively high energies of the γ-ray transitions (see Fig. 1). Table 1 compares typical precursors, the nuclear reactions for source preparation, and nuclear data of $^{99}$Ru and $^{61}$Ni Mössbauer spectroscopy with those of $^{57}$Fe Mössbauer spectroscopy. Facilities for the source preparation, including a heavy-ion accelerator and the liquid helium supply are necessary for continuous spectroscopic measurement. In this paper, the experimental procedures for $^{99}$Ru and $^{61}$Ni Mössbauer spectroscopy using the accelerator at RIKEN are introduced and recent results for CaRuO$_3$ [3], Hg$_2$Ru$_2$O$_7$ [4,5] and Ru-containing skutterudites [6,7] are presented.

![Figure 1](image_url). Simplified decay schemes of $^{99}$Ru and $^{61}$Ni. Only transitions relevant to Mössbauer studies are shown.

**Table 1.** Mössbauer precursor nuclides and simplified nuclear data of $^{57}$Fe, $^{61}$Ni, and $^{99}$Ru.

| nuclide | abundance | precursor (reaction) | $T_{1/2}$ | $E_\gamma$ (keV) | $t_{1/2}$ (ns) | $\Gamma_0$ (mm/s) |
|---------|-----------|---------------------|----------|-----------------|---------------|----------------|
| $^{57}$Fe | 2.1 % | $^{57}$Co | 270 d | 14.4 | 97.8 | 0.1946 |
| $^{61}$Ni | 1.1 % | $^{61}$Co ($^{62}$Ni($\gamma$,p)$^{61}$Co) | 99 m | 67.4 | 5.27 | 0.7805 |
| $^{61}$Ni | 1.1 % | $^{61}$Cu ($^{59}$Ni(α,p)$^{61}$Cu) | 3.3 h | 67.4 | 5.27 | 0.7805 |
| $^{99}$Ru | 12.8 % | $^{99}$Rh ($^{99}$Ru(p,n)$^{99}$Rh) | 16 d | 89.8 | 20.5 | 0.1468 |

$T_{1/2}$: half-life of Mössbauer precursor nuclide, $E_\gamma$: energy of Mössbauer γ-ray transition, $t_{1/2}$: lifetime of excited nuclear state, $\Gamma_0$: natural linewidth (FWHM).

2. $^{99}$Ru Mössbauer spectroscopic studies at RIKEN

2. 1. Source preparation and $^{99}$Ru Mössbauer measurement

First, the source nuclide, $^{99}$Rh ($T_{1/2}$=15.0 d) of $^{99}$Ru Mössbauer spectroscopy must be produced by the $^{99}$Ru(p,n)$^{99}$Rh reaction. Figure 2 shows a schematic of the experimental layout at a beam-line connected with the AVF cyclotron (K70-MeV) in RIKEN Nishina Center (RNC) [8]. The AVF cyclotron typically provides protons with energies up to 14 MeV [9]. The proton beam for the (p,n) reactions was extracted from the AVF cyclotron and used to bombard the target of 96 %-$^{99}$Ru metallic powder. The energy and intensity of the p-beam were 12 MeV and 10 µA, respectively. The $^{99}$Ru-enriched powder was pressed and packed into an Al holder. The holder was tightly fixed to the irradiation equipment and the target was cooled by He gas flow and water flow during the p-irradiation. The active area (i.e., the spot size of the p-beam) was 8×8 mm$^2$. After p-irradiation for
about 24 hours, the $^{99}$Rh Mössbauer source was estimated to have an activity of 10 MBq. The Al holder was removed from the beam-line, and immediately transported to the Mössbauer laboratory in RNC for off-line measurement without being subjected to annealing or chemical treatment. The obtained $^{99}$Rh Mössbauer source could be used for measurements up to about 7–8 weeks after p-irradiation.

$^{99}$Ru Mössbauer spectra were obtained using a Mössbauer spectrometer (Wissel, MVT-1000) and a multichannel analyzer (EG&G, ORTEC MCS-plus). Due to the relatively high energy of the Mössbauer $\gamma$-ray (89.8 keV), both the source and the absorbers were maintained at low temperatures in a liquid-helium cryostat during the measurements. The Mössbauer $\gamma$-rays were detected by a 2-mm-thick NaI(Tl) scintillator. Velocity calibration of the system was performed by measuring the Mössbauer absorption lines of $^{57}$Fe in an iron foil against a $^{57}$Co/Rh source. In our experimental setup, the linewidth (FWHM) and the area intensity of the resonance singlet were 0.25(2) mm/s and 1.56(5) %, respectively, against an absorber of natural ruthenium metal.

We analyzed the $^{99}$Ru Mössbauer spectrum by least-squares fitting, adopting the following values for the electric quadrupole ($Q$) and magnetic dipole moments ($\mu$) of the $^{99}$Ru nucleus: $Q_e = 0.22$ b and $\mu_e = -0.285$ nm for the excited level ($I_e = 3/2$), and $Q_g = 0.076$ b and $\mu_g = -0.623$ nm for the ground level ($I_g = 5/2$). The E2/M1 mixing ratio, $\delta^2$, for the $\gamma$-transition was assumed to be 2.7 [10]. When the nuclei of $^{99}$Ru are in a pure magnetic field with no electric field gradient, 18 absorption lines appear symmetrically in the spectrum. An asymmetric doublet, each branch consisting of three unresolved lines, appears in the presence of an electric field gradient of ordinary magnitude [11]. The chemical valence state dependence of the isomer shift of $^{99}$Ru is similar to that of $^{57}$Fe, although the sign is reversed because $\Delta R/R$ is positive for $^{99}$Ru.

2. 2. Applications of $^{99}$Ru Mössbauer spectroscopy
Since the 1990s, we have used $^{99}$Ru Mössbauer spectroscopy to investigate ruthenium trichlorides [11], Fe$_3$Si-based Heusler alloys [12] and to perform nuclear probe studies in iron oxides [13,14]. We summarize our recent results below.

2. 2. 1. Perovskite CaRuO$_3$: Orthorhombic ruthenates M$\text{RuO}_3$ (M = Sr or Ca) have attracted renewed interest as a result of the superconductivity found in Sr$_2$RuO$_4$ [2]. Sr$\text{RuO}_3$ and Ca$\text{RuO}_3$ have orthorhombically distorted GdFeO$_3$-type structures and exhibit metallic conductivity. However, despite having similar crystallographic and electrical properties, they exhibit quite different magnetic properties. Sr$\text{RuO}_3$ is ferromagnetic with a $T_c$ of 165 K [15,16], whereas the magnetic ground state of Ca$\text{RuO}_3$ has yet to be determined (possibilities include antiferromagnetic [17], weak ferromagnetic [18–20], a spin-glass-like state [21], exchange-enhanced paramagnetic [22]). We have studied the magnetism of Ca$\text{RuO}_3$ by magnetization measurements and Mössbauer spectroscopy. Our previous
studies revealed that no spin glass-like state exists in CaRuO$_3$ and that its magnetism strongly depends on its purities. Single crystals of CaRuO$_3$ were prepared by a self-flux method using CaCl$_2$ as the flux. An off-stoichiometric mixture of CaCO$_3$, RuO$_3$, and CaCl$_2$ was charged into a Pt crucible and heated to 1350 °C in an electric furnace. It was then carefully cooled to 900 °C, and quenched to room temperature to prevent other phases from growing. A small-crystal sample of CaRuO$_3$ was found to be mostly composed of rough cubes of 0.5 mm$^3$. These crystals were characterized by XRD, EPMA, magnetization and electrical resistivity measurements [3]. $^{99}$Ru Mössbauer spectroscopy, and $\mu$SR method.

![Figure 3. $^{99}$Ru Mössbauer spectrum of the single crystals of CaRuO$_3$ at 4.2 K.](image)

From the measurements of the temperature dependence of the magnetic susceptibility between 2 and 300 K, it was found that the magnetic susceptibility, $\chi(T)$, exhibited paramagnetic behavior and obeyed the Curie-Weiss law. The effective magnetic moment in the temperature range 90 K $< T < 300$ K was estimated to be $P_{\text{eff}} = 2.92 \mu_B$. Figure 3 shows the $^{99}$Ru Mössbauer spectrum obtained from single crystals of CaRuO$_3$ at 4.2 K. This spectrum could be satisfactorily analyzed by assuming an axially symmetric electric field gradient. The isomer shift was $-0.31$ mm/s and the quadrupole splitting was $0.22$ mm/s. Based on these Mössbauer parameters, the Ru ion was assigned to be in a low-spin state of Ru$^{4+}$. The Mössbauer measurement results indicate that CaRuO$_3$ has no long-range magnetic order down to 4.2 K. In addition, the $\mu$SR measurements were performed down to 0.3 K at RIKEN RAL muon facility. The results obtained for the temperature dependences of ZF-$\chi$, TF-$\chi$, and LF-$\mu$SR measurements agree with those described above.

2. 2. 2. **Pyrochlore Hg$_2$Ru$_2$O$_7$**: Hg$_2$Ru$_2$O$_7$ is a new ruthenium oxide with pyrochlore structure, $A_2B_2O_7$, which was recently synthesized by Yamamoto et al. [4,5]. Of the wide variety of 4$d$- and 5$d$-pyrochlore oxides, pyrochlores with tetravalent ruthenium Ru$^{4+}$ occupying the B-site, $A_2^{3+}$Ru$_2^{4+}$O$_7$, have been intensively studied. In contrast to Ru$^{4+}$ pyrochlores, only two Ru$^{5+}$ pyrochlores, Cd$_2$Ru$_2$O$_7$ and Ca$_2$Ru$_2$O$_7$, has been reported, partly due to the difficulty of oxidizing Ru to make it pentavalent. Hg$_2$Ru$_2$O$_7$ is a new pyrochlore oxide and it is the third Ru$^{5+}$ compound to be synthesized. The properties of Cd and Ca analogues have not been completely explored. However, both have a relatively low resistivity ($\rho$) of the order of milliohm-centimeters but neither exhibits a metallic $T$ dependence (i.e., $d\rho/dT > 0$) [23,24]. In contrast to Cd and Ca analogues, Yamamoto et al. found a well defined a metal–insulator transition (MIT) at $\sim$107 K in Hg$_2$Ru$_2$O$_7$. $^{99}$Ru Mössbauer spectroscopy was used to determine the oxidation state of Ru ions in Hg$_2$Ru$_2$O$_7$. The Hg$_2$Ru$_2$O$_7$ sample was prepared in a small Au cell under 6 GPa using a cubic-anvil-type high-temperature and high-pressure apparatus. Consequently, it was very difficult to produce an adequate amount for $^{99}$Ru Mössbauer measurements. Although the quality of the $^{99}$Ru Mössbauer spectrum was low, preliminary analysis suggests that the oxidation state of Ru ions in Hg$_2$Ru$_2$O$_7$ is Ru$^{5+}$; however, further studies are needed to confirm this.
2. 2. 3. **Skutterudite SmRu₄P₁₂**: SmRu₄P₁₂ is an attractive compound among filled skutterudites. Its electric resistivity shows MIT at $T_{MI} = 16$ K. Specific heat measurements with an applied magnetic field suggest that successive transitions occur around $T_{MI}$. The magnetic susceptibility of SmRu₄P₁₂ has a cusp around 14 K, implying an antiferromagnetic ordering. The successive transitions were initially ascribed to antiferroquadrupole and antiferromagnetic orderings, since the entropy at $T_{MI}$ reaches $R \log 4$. The possibility of an octupole ordering has been proposed in SmRu₄P₁₂ based on a macroscopic point of view. The clear jump in the specific heat and antiferromagnetic-like temperature dependence of the magnetic susceptibility in SmRu₄P₁₂ resemble those in NpO₂, which is a typical system with octupole ordering. If the ordering in SmRu₄P₁₂ is caused by an octupole similar to NpO₂, the absence of the hyperfine field and/or magnetic moment should be clarified at the Sm site in addition to the observation of the hyperfine field at ligand sites.

Figure 4 shows $^{99}$Ru Mössbauer spectra of SmRu₄P₁₂ at 77 K and 5 K [7].

Figure 4 shows $^{99}$Ru Mössbauer spectra of SmRu₄P₁₂. The spectra obtained at 77 and 5K could be satisfactorily analyzed using typical doublets with no obvious magnetic field. These doublets are caused by a sufficiently large electric field gradient near the $^{99}$Ru nuclei that possess small asymmetries. The value of the isomer shift ($I.S. = -0.24(2)$ mm/s at 5 K) suggests that the Ru ions are in the tetravalent state.

The Debye temperature at the Ru site in SmRu₄P₁₂ was estimated to be high because the relative area intensity of the spectrum exhibited little variation with increasing temperature. The Mössbauer spectroscopic results support the presence of a dipole moment, which was demonstrated by X-ray absorption spectroscopy and $^{149}$Sm nuclear resonant forward scattering at low temperatures performed by Tsutsui et al. [7]. The presence of the magnetic dipole moments at the Sm ions is in a sharp contrast with their absence in NpO₂. The experimental results reported thus far suggest that a possible primary order parameter is a $T^{\alpha}$-type octupole.

3. $^{61}$Ni Mössbauer spectroscopic studies at RIKEN

Two parent nuclides of $^{61}$Co and $^{61}$Cu are used for $^{61}$Ni Mössbauer spectroscopy (see Fig. 1). Although the half-life of $^{61}$Co ($T_{1/2} = 99$ m) is considerably shorter than that of $^{61}$Cu ($T_{1/2} = 3.4$ h), $^{61}$Co is more suitable for Mössbauer measurements because it undergoes $\beta^-$ decay direct to 67.4-keV Mössbauer levels. The Mainz group in Germany has performed extensive $^{61}$Ni Mössbauer spectroscopic investigations using the $^{61}$Co source. $^{61}$Co source are typically produced by $^{62}$Ni($\gamma,p$)$^{61}$Co using bremsstrahlung (100 MeV) from an electron accelerator or by $^{64}$Ni($p,\alpha$)$^{61}$Co with proton bombardment. These nuclear reactions require enriched $^{62}$Ni or $^{64}$Ni, but both isotopes have very low isotopic abundances (3.6 % for $^{62}$Ni and 0.9 % for $^{64}$Ni). On the other hand, we adopted $^{64}$Cu as the source at RNC, although it decays in a complex manner with only 2.4 % populating the Mössbauer level. The
nuclear reactions of $^{58}\text{Ni}(\alpha,p)^{61}\text{Cu}$ and $^{58}\text{Ni}(\alpha,n)^{61}\text{Zn}\rightarrow EC \beta^+ \rightarrow ^{61}\text{Cu}$ are utilized to produced the source nuclide in the AVF cyclotron. When a paramagnetic $\text{Ni}_{0.84}\text{V}_{0.16}$ alloy was irradiated for 3 hours with 25 MeV $\alpha$-particles, a $^{61}\text{Cu}$ Mössbauer source with an activity of 10 MBq was obtained. This preparation method has an advantage that it does not require an enriched isotope because $^{58}\text{Ni}$ has a high natural abundance of 68.1%. The Mössbauer source preparation procedure was the same as that for $^{99}\text{Rh}$. Recently, we have used $^{61}\text{Ni}$ Mössbauer spectroscopy to evaluate the catalytic performance of NiO samples; detailed results of this study will soon be published elsewhere.

4. Conclusion

Ru and Ni are important constituent elements of a wide variety of compounds, including oxides, catalysts, and functional materials in solar butters and shape-memory alloys. $^{99}\text{Ru}$ and $^{61}\text{Ni}$ Mössbauer spectroscopy can reveal important information about the physicochemical properties of these compounds. We have developed irradiation equipment for these Mössbauer sources and an off-line measurement system at low temperatures at RNC. In addition, $^{61}\text{Ni}$ Mössbauer spectra have been obtained by a new technique using synchrotron radiation at SPring-8 and ESRF. Moreover, short-lived radioisotope-beam implantation methods will be available for studying of these elements. Conventional methods that use Mössbauer sources produced by nuclear reactions play a complementary role to these sophisticated Mössbauer techniques, but they remain the most basic Mössbauer measurement technique.

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