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Nuclear Forward Scattering of Synchrotron Radiation by $^{99}$Ru


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Nuclear Forward Scattering by $^{99}$Ru

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We have measured nuclear forward scattering spectra utilizing the $^{99}$Ru transition, 89.571(3) keV, with a notably mixed E2/M1 multipolarity. The extension of the standard evaluation routines to include mixed multipolarity allows us to extract electric and magnetic hyperfine interactions from $^{99}$Ru containing compounds. This paves the way for several other high energy Mössbauer transitions, $E \sim 90$ keV. The high energy of such transitions allows for operando nuclear forward scattering studies in real devices.

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Nuclear forward scattering of synchrotron radiation [1, 2] is nowadays a standard technique for obtaining information similar to that extracted from Mössbauer spectroscopy [3]. This technique is particularly useful when preparation of the radioactive source for Mössbauer spectroscopy is difficult, when the lifetime of the radioactive source is short, or when the experimental setup requires a collimated or a small-size beam.

Synchrotron radiation matching the energy difference between the nuclear ground state and an excited state impinges on the sample and leads to nuclear excitation. The excited state has a finite lifetime and the resonantly scattered photons are delayed with respect to non-resonantly scattered (prompt) photons. Both coherent nuclear forward scattering [4] and incoherent fluorescence are observed. The typical lifetime of excited states ranges between 0.2 and 200 ns and matches the bunch structure of the current synchrotron radiation facilities. Hence, the nuclear forward scattering can, in principle, be measured for any of the Mössbauer isotopes.

The typical bandwidth of conventional X-ray optics is in the eV range. As a result, every photon resonantly scattered is accompanied by between $10^6$ and $10^9$ photons that are not nuclearily scattered, often overloading the detection scheme [5, 6]. In order to circumvent detection overload from non resonant quanta, monochromatization of the X-ray beam by high resolution monochromators with meV band-pass [7] is typically used. Such monochromators are usually made out of silicon. Efficient high resolution monochromatization for energies above 30 keV is restricted because of the physical properties of silicon, see Ref. [8], thus seriously limiting the number of high energy Mössbauer transitions studied using synchrotron radiation. Other approaches were suggested to circumvent the pitfalls of silicon monochromators and thus the problem of non resonant detection overload, such as sapphire backsicattering monochromatization [9–12], and nuclear lighthouse effect [13]. However, these approaches seriously limit the sample environment.

It was previously shown that nuclear forward scattering around 70 keV can be carried out with medium resolution monochromatization of 30 [14] or even 100 meV [12]. The extension of this concept to higher energies in combination with an optimized detector system and the lower flux of synchrotron radiation above 80 keV highly reduces the need for sophisticated approaches to circumvent non resonant detection overload. In addition the high energy allows for operando measurements in real devices.

Although conventional Mössbauer spectroscopy can be applied to high energy Mössbauer transitions such as $^{155}$Gd (60.0106(6) keV) and $^{166}$Er (80.577(2) keV), Nuclear Forward Scattering with a collimated of small-size beam by $^{156}$Gd (88.970(1) keV) and $^{164}$Er (91.38(2) keV) may provide superior information related to hyperfine interactions on nanostructures and under extreme conditions, e.g., study of magnetic anisotropies in Gd nanostructures [15] and studies of partial amorphization of Er$_2$O$_3$ under applied pressure [16]. Moreover, a study of a yet unexplored chemistry related to the novel electronic properties of hafnium compounds such as two dimensional hafnium honeycombs - similar to graphene - structure [17], hafnium carbides for use in extreme environments [18], and studies related to the applications of hafnium hydride in nuclear power plants [19] are now feasible by nuclear forward scattering on $^{176}$Hf (88.349(24) keV).

In this letter, we report on nuclear forward scattering, NFS, of synchrotron radiation at energy as high as 90 keV using a conventional double crystal monochromator and a multielement Avalance Photo Diode, APD, detector. Using such a setup we measured (in two hours each) nuclear forward scattering spectra for $^{99}$Ru-metal and $^{99}$RuO$_2$ 99% enriched to $^{99}$Ru and (in ten hours) spectra for SrRuO$_3$ [20, 21] with 12.7% $^{99}$Ru natural abundance [22]. The related information, i.e., absolute values of recoil-free fraction ($f_{LM}$), its temperature dependence and the related Debye temperature in $^{99}$Ru-metal and the quadrupole splitting in $^{99}$RuO$_2$ as well as the
The double crystal monochromator allows transmission for radiation related both to the third harmonic - Si (3 3 3) - with energy of 89.6 keV, and the first harmonic - Si (1 1 1) - with energy of 29.8 keV. The coexistence of the first and third harmonic gave us the opportunity to calibrate the energy scale using the Sn K-edge (29.2004(2) keV [38]). The resonance energy for the $^{99}$Ru first excited state was found to be 89.571(3) keV, in excellent agreement with the tabulated value, 89.57(6) keV [39]. In order to avoid detector overload in the forward direction, the 29.8 keV radiation was filtered out by a 200 µm Sn foil [40]. The small fraction of low energy radiation passing through the Sn foil is further absorbed by the ruthenium containing sample, 3.5 mg/mm² of $^{99}$Ru.

The recorded time distribution of the delayed Ru $K_{\alpha}$ fluorescence reveals an exponential decay; see Fig. 2a. Fitting the data with a simple exponential function, $I(t) = I_0e^{-t/\tau} + c$, yields a lifetime, $\tau$, of the excited state of 28.8(3) ns. The lifetime extracted herein is in agreement with the reported value of 29(1) ns [41] measured using the delayed coinci-
In order to extract the recoil-free fraction from the obtained spectrum the unitless effective thickness, $\xi$, of the sample is used:

$$\xi = \frac{1}{4} L \sigma_0 f_{LM} \frac{\beta}{V_{Ru}}$$

where $L$ is the geometric sample thickness, $\sigma_0$ is the nuclear resonant absorption cross section, $f_{LM}$ is the recoil free fraction, known as Lamb-Mössbauer factor, $\beta$ is the isotopic enrichment, $V_{Ru}$ is the volume per Ru atom. Pronounced beating, i.e., dynamical beats, is observed when $\xi$ is large. The spectra for $^{99}$Ru-metal shown in Fig.2b were fitted between 5 and 150 ns and the obtained $\xi$ is 10.01(9) and 7.35(6) at 5 and 80 K, respectively. The $f_{LM}$ and the Debye temperature is extracted by fitting a Debye model to the obtained values of the effective thickness [12]. The obtained $f_{LM}$ are 0.19(1) and 0.14(1) at 5 and 80 K, respectively and the obtained Debye temperature is 466(50) K. The Debye temperature extracted herein is in good agreement with the Debye temperature, 495(24) K, extracted from X-ray diffraction on Ru [44, 45].

The mixing of electric quadrupole and magnetic dipole multipolarity of the nuclear transition is not included in the available fitting routines [46, 47] and, as a result, they cannot be used to analyse our measurements on $^{99}$RuO$_2$ and SrRuO$_3$. Thus, we had to modify [48] the available routines for extracting the quadrupole splitting and the magnetic hyperfine field in paramagnetic $^{99}$RuO$_2$ and ferromagnetic SrRuO$_3$, respectively. The fit of the data was performed with an algorithm [14] developed on the basis of the Fourier transformation of the energy spectrum to nuclear forward scattering [43] and extended for the case of large effective thickness. The mixing of E2 and M1 multipolarities was included with a fixed ratio $\delta^2$ E2/M1 = 2.7 [23]. The ratio of the nuclear quadrupole moments of the ground, $Q_g$, and excited state, $Q_e$, were fixed to $Q_e/Q_g = 2.93$ [49]. The nuclear magnetic moments of the ground state, $\mu_g = -0.641 \mu_n$, and of the excited state, $\mu_e = -0.284 \mu_n$, were also fixed. The spectra were treated using an isotropic distribution of the hyperfine interactions.

The beats in the NFS spectra of $^{99}$RuO$_2$ are due to a combination of the dynamical beats related to the large effective thickness and the quantum beats related to the quadrupole interaction which merge into hybrid beats [50]. By using the routine we developed we fitted the data with only two free parameters the quadrupole splitting, $eQV_{zz}/2$, and the effective thickness. The obtained quadrupole splitting, 5.93(15) $\Gamma_0$ or 0.44(1) mm/s, agrees with that obtained by Mössbauer spectroscopy, 0.5(1) mm/s [42]. The $f_{LM}$ and the Debye temperature are extracted similarly to the $^{99}$Ru-metal case. The obtained Lamb-Mössbauer factor is 0.24(1) and 0.22(1) at 5 and 60 K, respectively, and the extracted Debye temperature is 535(60) K. This value is slightly lower than the Debye temperature measured previously using calorimetry [51], 610(10) K at 10 K.
The shape of the nuclear forward scattering spectrum of SrRuO$_3$ is defined by the magnetic hyperfine splitting. The obtained countrate was low, 0.04 Hz, and comparable with the background countrate. The low countrate is due to the low $^{99}$Ru natural isotopic abundance. Magnetic splitting of the excited and the ground state for the E2/M1 mixed multipolarity allows for 18 transitions. Due to the numerous transitions distinct peaks appear in the nuclear forward spectrum. A similar effect was observed for the $^{181}$Ta nuclear transition [52]. In the case of SrRuO$_3$, the clearly seen peak at 60 ns; see Fig. 2b; allows us to precisely extract a hyperfine magnetic field of 33.9(5) T at 5 K. This value is in agreement with the result, 33.0(4) T at 4 K, determined by Mössbauer spectroscopy measurements [53, 54].

In conclusion, we have studied the nuclear forward scattering by the 89.571(3) keV in several $^{99}$Ru containing reference materials, i.e., $^{99}$Ru-metal, $^{99}$RuO$_2$ and SrRuO$_3$. Moreover, we have modified the available fitting routines for extracting electric and magnetic hyperfine interaction in mixed multipolarity transitions. The typical countrate observed on $^{99}$Ru enriched sample is $\sim$ 0.5 Hz and allows us to acquire reasonable statistics in two hours. Measurements on non-$^{99}$Ru enriched samples are currently challenging. The observed countrate can be increased in the future by at least an order of magnitude by optimization and upgrading the optics and the detector. Under such conditions measurements on non enriched samples will be feasible. By taking advantage of the high penetration depth of the radiation at 89 keV [55] as well as of the simplicity of the experimental setup operando hyperfine interaction studies on real devices are now feasible. Our study opens a new field of research not only on ruthenium compounds with a variety of application, i.e., photocontrolled DNA binding in life sciences [30], energy harvesting using photovoltaic cells [31], energy storage in lithium-ion batteries [32], and ruthenium catalyst systems [56], but also on isotopes which have similar nuclear transition energies, $^{170}$Hf (88.349(24) keV), $^{156}$Gd (88.970(1) keV), and $^{164}$Er (91.38(2) keV). Despite the expectedly low $f_{LM}$ in organometallic compounds, feasibility measurements on ruthenium nitrosyls already exist in literature [57] using conventional Mössbauer spectroscopy.
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[22] SrRuO$_3$ was synthesized by heating a mixture of SrCO$_3$ and Ru powders at 1000°C. X-ray diffraction confirmed that the product was single phase SrRuO$_3$ (space group Pnma), and magnetization measurements showed the expected Curie temperature near 160 K.
[40] The transmission of the 29.8 and the 89.6 kev radiation is 0.2% and 72%, respectively.
[48] Supplementary material is available, which includes Refs. [43, 58–60].


[55] At 89 keV, 2 mm of steel has 50% transmission.


