Hyperfine Interact (2017) 238:100
https://doi.org/10.1007/s10751-017-1473-z

Sm valence states and magnetic properties in $SmBe_{13}$ and $SmTi_2Al_{20}$ investigated by Sm synchrotron-radiation-based Mössbauer spectroscopy

Satoshi Tsutsui[1] · Yoshio Kobayashi[2] · Jin Nakamura[2] · Michael K. Kubo[3] · Shota Amagasa[4] · Yasuhiro Yamada[4] · Yoshitaka Yoda[1] · Yusei Shimizu[5,7] · Hiroyuki Hidaka[5] · Tatsuya Yanagisawa[5] · Hiroshi Amitsuka[5] · Akira Yamada[6] · Ryuji Higashinaka[6] · Tatsuma D. Matsuda[6] · Yuji Aoki[6]

Abstract Synchrotron-Radiation-based ^{149}Sm Mössbauer spectroscopy was applied to Sm intermetallics, $SmBe_{13}$ and $SmTi_2Al_{20}$. Temperature dependence of the Mössbauer parameters in $SmBe_{13}$ indicate the Sm valence state is purely trivalent. $SmBe_{13}$ also showed second-order Doppler shift in synchrotron-radiation-based ^{149}Sm Mössbauer spectroscopy. The Mössbauer parameters obtained in $SmTi_2Al_{20}$ suggest that the Sm valence is fluctuating and the magnitude of the magnetic moment is reduced by hybridization between 4f and conduction electrons and/or effect of crystal electric field.

Keywords Synchrotron-radiation-based Mössbauer spectroscopy · Hyperfine interaction · Sm intermetallic compounds · Valence fluctuation · Magnetism

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2017), Saint-Petersburg, Russia, 3-8 September 2017*
Edited by Valentin Semenov

✉ Satoshi Tsutsui
satoshi@spring8.or.jp

[1] Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Sayo, Hyogo 679-5198, Japan

[2] The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

[3] International Christian University, Mitaka, Tokyo 181-8585, Japan

[4] Tokyo University of Science, Shinjuku, Tokyo 162-8601, Japan

[5] Graduate School of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan

[6] Department of Physics, Tokyo Metropolitan University, Hachioji, 192-0397, Japan

[7] Present address: Institute for Materials Research, Tohoku University, Oarai, Ibaraki, 311-1313, Japan

Published online: 27 November 2017

1 Introduction

Sm intermetallics have been more attractive in solid state physics since the discovery of heavy fermion behavior in $SmOs_4Sb_{12}$ [1]. This compound exhibits a ferromagnetic ordering with a large Sommerfeld coefficient of ∼800 mJ / mol K^2. The heavy fermion behavior in this compounds is robust to applied magnetic field. A number of heavy fermion Sm intermetallics are known. $SmTi_2Al_{20}$ is a heavy fermion compound accompanied with a possibly field-insensitive ordering [2, 3]. Its heavy fermion behavior is also robust to applied magnetic fields [2]. To consider the mechanism of such heavy fermion behaviors, it is important to investigate low energy fluctuations associated with heavy fermion behavior. Judging from previous macroscopic measurements [2, 3], magnetic or valence fluctuation is expected to play an essential role in such heavy fermion behaviors. Although neutron scattering is a powerful tool to investigate magnetism, it is difficult to apply this to Sm compounds as Sm is a good neutron absorber. However, since Mössbauer spectroscopy can detect valence states as well as magnetic properties, this technique is useful to investigate physical properties in Sm compounds because several Sm isotopes are available for Mössbauer spectroscopy.

Among the Sm Mössbauer isotopes, ^{149}Sm is one of the best for material science investigations. The transition energy of ^{149}Sm Mössbauer resonance is 22.502 keV [4, 5]. This permits observation of the Mössbauer effect in a wide range of above ambient temperatures. Although the difference of the nuclear radii between the excited and ground states and nuclear quadrupole moments in both excited and ground states are small, hyperfine interactions of isomer shift and nuclear quadrupole interaction as well as nuclear Zeeman splitting due to hyperfine magnetic field is observable in the ^{149}Sm Mössbauer effect. ^{149}Sm Mössbauer spectroscopy using a radioactive source was established a long time ago as a probe of valence states and magnetic properties [6–9]. In contrast to conventional Mössbauer spectroscopy using radio-active sources, ^{149}Sm nuclear resonant forward scattering experiments using synchrotron radiation, which are time-domain measurements, have been used to investigate the magnetic properties of Sm intermetallics [10–13]. Recently, synchrotron-radiation-based (SR-based) Mössbauer spectroscopy, in which the horizontal axis is Doppler velocity, as for conventional Mössbauer spectroscopy using radioactive sources, was established [14]. In addition, improvement of detectors permits the measurement of a Mössbauer spectrum over several hours in nuclei having a relatively high conversion factor [15].

In this paper, we describe the application of ^{149}Sm SR-based Mössbauer spectroscopy to some Sm intermetallics to elucidate their valence states and magnetic properties. We successfully determined center shift values and hyperfine magnetic fields at ^{149}Sm nuclei to discuss electronic states in $SmBe_{13}$ and $SmTi_2Al_{20}$. The results demonstrate that $SmBe_{13}$ is a typically trivalent Sm intermetallic. On the other hand, results for $SmTi_2Al_{20}$ suggest that it is a valence fluctuating system, which exhibits a magnetic ordering at low temperature. Additionaly, a linear temperature dependence of center shift values was observed in both compounds, the origin of which, we conclude, is a second-order Doppler shift, based on a comparison with the calculated.

2 Experimental procedure

SR-based Mössbauer spectroscopy was carried out at BL09XU in SPring-8 [16, 17]. The experimental setup used in the present work was the same as that reported in Ref. [18]: a

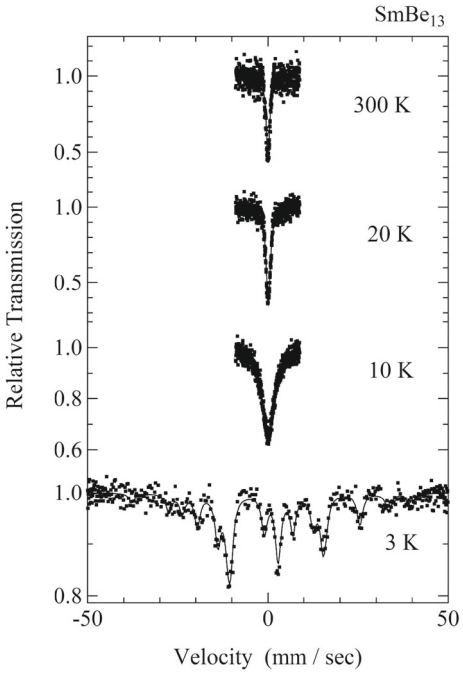

Fig. 1 Synchrotron-radiation-based ^{149}Sm Mössbauer spectra of $SmBe_{13}$ at various temperatures

nested-type Si(4 2 2) and Si(16 8 8) high-resolution monochromator was used to reduce background intensity; the analyzer mounted onto the velocity transducer was $^{149}Sm_2O_3$; the detector was a multi-element avalanche photodiode detector (APD) located over the $^{149}Sm_2O_3$ analyzer. The operation mode chosen in the present work was the 4 bunch-train $\times$ 84 mode in SPring-8 [19], where 4 bunches with a 1.97 nsec interval were separated by a 51.1 nsec interval.

Single crystalline $SmBe_{13}$ and $SmTi_2Al_{20}$ were synthesized using Al flux method [2, 20]. Many small pieces of single crystalline $SmBe_{13}$ were chosen for the Mössbauer measurements. Single crystalline $SmTi_2Al_{20}$ was crushed into powder for the Mössbauer measurements. Both samples packed with Al foil were mounted onto a He-flow cryostat. For measurements with a narrow velocity range of $\pm\sim$10 mm / sec and a "high"-energy resolution setup, the detector time window was opened 20 nsec after the last electron bunch. For measurements with a wide velocity range of $\pm\sim$50 mm / sec and "low"-energy resolution setup, the detector time window was opened 7 nsec after the last electron bunch. The Doppler velocity was calibrated with a laser calibrator.

3 Experimental results and discussion

3.1 ^{149}Sm synchrotron-radiation-based Mössbauer spectroscopy of $SmBe_{13}$

Figure 1 shows ^{149}Sm SR-based Mössbauer spectra of $SmBe_{13}$ at various temperatures. Spectra above 20 K show a pure singlet, suggesting the absence of any nuclear magnetic and quadrupole interactions. The value of the center shift at 300 K is 0 mm / sec, indicating that the Sm valence state is purely trivalent. The spectrum at 10 K is much broader than that

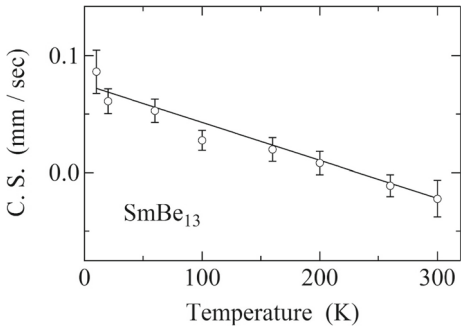

Fig. 2 Temperature dependence of center shift value in $SmBe_{13}$

above 20 K. A spectrum taken at 3.1 K exhibits magnetic splitting combined with nuclear quadrupole interaction. Since the magnetic transition temperature determined by a magnetic susceptibility measurement was reported to be T_M ~8 K [20] and 9 K [21], broadened spectra at 10 K might be caused by short-range magnetic ordering.

Mössbauer parameters at 3.1 K obtained by spectral analysis are a hyperfine magnetic field of $H_{int} = 329 \pm 3$ T and nuclear quadrupole interaction $e^2qQ_{ex} = 15.1 \pm 0.6$ mm / sec. The linewidth of the spectrum is 1.9 ± 0.2 mm / sec, close to the natural linewidth of the ^{149}Sm Mössbauer transition. The hyperfine magnetic field of 330 T observed at 3.1 K is close to the calculated value based on a free Sm^{3+} ion, indicating that Sm ions in $SmBe_{13}$ are a purely trivalent state. Meanwhile, the linewidth demonstrates that the magnitude of the ordered magnetic moment is a finite value, suggesting magnetic ordering accompanied by finite magnetic moments in $SmBe_{13}$. Some of the RBe_{13} compounds (R: rare-earth or actinide elements) exhibit helical and/or modulated magnetic structure at low temperatures. The magnetic structure of $NpBe_{13}$ exhibits a modulation of magnetic moments [22], for example: the spectrum at 1.3 K consists of two sets of magnetic patterns, suggesting modulated magnetic ordering of Np atoms like a spin density wave structure. Since such is not the case in the spectrum of $SmBe_{13}$ at 3.1 K is not the case, magnitude of Sm magnetic ordered moment in $SmBe_{13}$ is not modulated.

Figure 2 shows the temperature dependence of the center shift of the Mössbauer spectra. This exhibits a linear temperature dependence. Isomer shift values are in general determined by electronic density at probe nuclei, and are strongly connected with valence states. Since the obtained hyperfine magnetic field at 3.1 K and isomer shift value at 300 K demonstrate that the Sm valence state in $SmBe_{13}$ is purely trivalent, it is difficult to explain that such temperature dependence of the center shift is caused by change of Sm valence state. Origin of changing center shift values include the effect of the second-order Doppler shift. Linear temperature dependence of center shifts is a typical behavior in the high temperature limit of the second-order Doppler shift. As shown in Fig. 3, the calculated second order Doppler shift in ^{149}Sm nuclei exhibits a linear temperature dependence except in the low temperature region. The slope of the center shift against temperature line for $SmBe_{13}$ is $(3.2 \pm 0.3) \times 10^{-4}$ mm / sec / K, close to that in the high temperature limit, $\sim 2.7 \times 10^{-4}$ mm / sec / K. According to the Einstein or Debye temperature at the Sm site obtained by X-ray diffraction [23] and the phonon dispersion relation obtained by inelastic X-ray scattering [24], the Einstein (Debye) temperature at the Sm site is ~160 (~200) K and a nearly dispersionless mode is observed around ~16 meV. It is thus reasonable that the temperature dependence of the center shift observed in $SmBe_{13}$ is caused by the second-order Doppler shift.

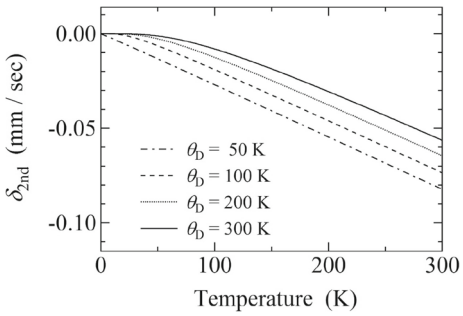

Fig. 3 Temperature dependence of calculated second-order Doppler shift in ^{149}Sm Mössbauer transition of 22.502 keV

3.2 ^{149}Sm synchrotron-radiation-based Mössbauer spectroscopy of $SmTi_2Al_{20}$

Figure 4 shows ^{149}Sm SR Mössbauer spectra of $SmTi_2Al_{20}$ at various temperatures. Spectra above 10 K show pure singlets, which demonstrates the absence of any magnetic and quadrupole interactions. The center shift value at 300 K is - 0.10 ±0.03 mm / sec, corresponding to a valence state of $Sm^{2.8-2.9+}$. These means that the Sm valence state in $SmTi_2Al_{20}$ occupy an intermediate state. The spectrum at 3.1 K exhibits magnetic splitting combined with quadrupole interaction, which can be interpreted as a polycrystalline sample. This spectrum proves that the phase transition at ∼6.5 K is caused by magnetic ordering.

Judging from Ref. [2], the present results above 10 K provide evidence that the Sm valence state in $SmTi_2Al_{20}$ is an intermediate state arising from valence fluctuation. The magnetic susceptibility in $SmTi_2Al_{20}$ differs from that in $SmBe_{13}$, exhibiting a nearly constant temperature dependence of the van Vleck term above its magnetic transition temperature [2, 3], whereas that in $SmBe_{13}$ exhibits temperature dependence approximating the Curie-Weiss law [20], suggesting that in the latter material, Sm is purely trivalent. Since the magnetic susceptibility in $SmTi_2Al_{20}$ exhibits temperature dependence in Sm valence fluctuating compounds, the results are consistent with Sm valence fluctuation between divalent and trivalent states. X-ray absorption spectroscopy (XAS) provides further evidence that the Sm valence state is intermediate between divalent and trivalent states [25]: the XAS spectra consist of two components, suggesting the presence of Sm divalent and trivalent states. The average Sm valence state qualitatively agrees with the valence state suggested by the center shift value in the present work.

There seems to be inconsistency between the results of Mössbauer spectroscopy and the XAS experiments. Such a discrepancy was already reported for some rare-earth intermetallic compounds such as SmB_6 and $Eu_3Pd_{20}Ge_6$ [8, 18, 26–28]. This difference is caused by valence fluctuation at rare-earth sites. In fact, time scales of Mössbauer spectroscopy and XAS are different: that of the former is in the MHz or GHz region, depending on the magnitude of hyperfine interactions at nuclei, while that of the latter is in the PHz region, corresponding to the life time of core holes in the optical transition process [29, 30]. This means that the results of the present Mössbauer spectroscopy combined with those of the XAS experiments reported previously [25] can prove whether Sm valence is fluctuating in $SmTi_2Al_{20}$. Since the Mössbauer spectra consist of a single component and the XAS spectra consist of two components above 10 K, it can be concluded that the Sm valence is fluctuating in $SmTi_2Al_{20}$. Considering the difference between typical isomer shift values for divalent and trivalent states, the rate of the Sm valence fluctuation is of the order of several tens of MHz in $SmTi_2Al_{20}$ as was discussed for SmB_6 [18].

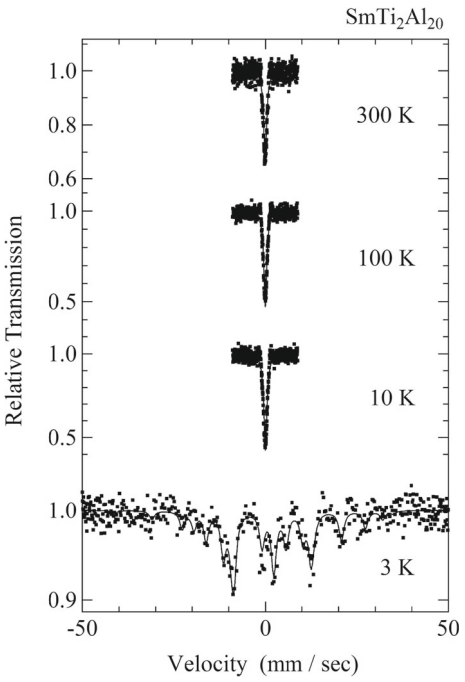

Fig. 4 Synchrotron-radiation-based ^{149}Sm Mössbauer spectra of $SmTi_2Al_{20}$ at various temperatures

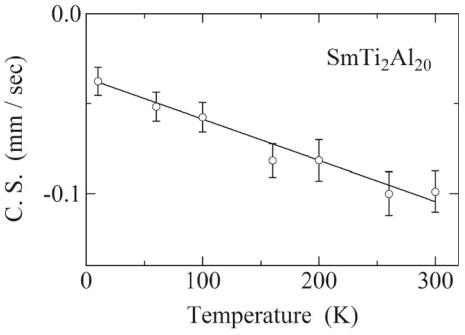

Fig. 5 Temperature dependence of center shift value in $SmTi_2Al_{20}$

Figure 5 shows the temperature dependence of the center shift in $SmTi_2Al_{20}$. Similarly to the results for $SmBe_{13}$, the center shift exhibits a linear temperature dependence. Since the slope of the center shift against temperature is $(2.3 \pm 0.6) \times 10^{-4}$ mm / sec / K, close to that in the high temperature limit, it is likely that this linear temperature dependence is caused by the second-order Doppler shift as was discussed in the previous section. If this is the case, the temperature dependence of the center shift would indicate that the Sm valence state is nearly independent of temperature, which agrees with the $SmTi_2Al_{20}$ XAS results [25]. Considering both the present work and the previous XAS results, we conclude that the Sm in $SmTi_2Al_{20}$ does not exist in static mixed valence states but rather is fluctuating without change of average valence state.

Spectral analysis indicates that the hyperfine magnetic field observed at 3.1 K is 270 ± 3 T in $SmTi_2Al_{20}$. This value is smaller than that in $SmBe_{13}$ at 3.1 K. Assuming that

the hyperfine coupling constant is independent of crystal electric field (CEF) levels, the magnitude of the ordered magnetic moment in $SmTi_2Al_{20}$ is $\sim$0.67 μ_B / Sm. This value implies hybridization between 4f and conduction electrons and/or reduction of the ordered magnetic moment by CEF effects, but a few magnetic degrees of freedom due to reduced ordered magnetic moment might be available for enhancement of conduction electron mass. In other words, valence degrees of freedom helps enhancement of conduction electron mass at least in $SmTi_2Al_{20}$ due to the Sm valence degrees of freedom arising from Sm valence fluctuation.

4 Summary

We have investigated the valence states and magnetic properties of Sm in the intermetallics, $SmBe_{13}$ and $SmTi_2Al_{20}$ by SR-based Mössbauer spectroscopy. Center shift values from 300 K to 3.1 K and magnitude of the hyperfine magnetic field at 3.1 K were precisely determined in both compounds and revealed that SR-based ^{149}Sm Mössbauer spectra show a contribution due to a second-order Doppler shift, affording a linear temperature dependence, as well as allowing precise determination of isomer shift values. These findings may be helped by the good collimation of the incident X-rays provided by synchrotron radiation. Meanwhile, observation of the hyperfine magnetic field afforded information on the magnetic properties of $SmBe_{13}$ and $SmTi_2Al_{20}$. The magnitude of the hyperfine magnetic field in $SmBe_{13}$ at 3.1 K demonstrates that Sm in the valence ground state is purely trivalent with fully ordered magnetic moments. The magnitude of the hyperfine magnetic field in $SmTi_2Al_{20}$ at 3.1 K, however, suggests that the ordered magnetic moments are reduced by hybridization between 4f and conduction electrons and/or CEF effects because the center shift values at 300 K indicates that the Sm valence state is an intermediate one. Taken together with the results of the XAS experiments [25], the spectra above 10 K indicates that the Sm valence is fluctuating.

Acknowledgements The authors thank Dr. M. Mizumaki for fruitful discussion with him and Dr. Y. Kobayashi and Dr. R. R. Masuda, Prof. H. Kobayashi for their experimental assistance, and Prof. Julian R. Koe for his kind English correction. The present work was carried out under approval of JASRI (Proposal Nos. 2015A2036, 2015B1947, 2016A1281, 2016B1057, 2016B1967, 2017A1060). This work is partially supported by Grant-in-Aid for the Scientific Research on Innovative Area of J-Physics (Grant Nos. 15H05882, 15H05884, 15H05885) from the MEXT and Grant-in-Aids for Scientific Research S (Grant No. 20224015), Scientific Research B (Grants Nos. 15H03693, 15H0397), Scientific C (Grant Nos. 25400346, 26400342, 15K05178, 16K05454) and Challenging Exploratory Research (Grants No. 15K14170). One of the authors (AY) was supported by Grant-in-Aid for JSPS Research Fellow (Grants No. 15J07600).

References

1. Sanada, S., Aoki, Y., Aoki, H., Tsuchiya, A., Kikuchi, D., Sugawara, H., Sato, H.: Exotic heavy-fermion state in filled skutterudite $SmOs_4Sb_{12}$. J. Phys. Soc. Jpn. **74**, 246 (2005)
2. Higashinaka, R., Maruyama, T., Nakama, A., Miyazaki, R., Aoki, Y., Sato, H.: Unusual field-insensitive phase transition and Kondo behavior in $SmTi_2Al_{20}$. J. Phys. Soc. Jpn. **80**, 093703 (2011)
3. Sakai, A., Nakatsuji, S.: Strong valence fluctuation effects in $SmTr_2Al_{20}$ (Tr = Ti, V, Cr). Phys. Rev. B **84**, 201106 (2011)
4. Sergueev, I., Wille, H.C., Hermann, R.P., Bessas, D., Shvyd'ko, Y.V., Zajac, M., Rüffer, R.: Milli-electronvolt monochromatization of hard X-rays with a sapphire backscattering monochromator. J. Synchrotron Rad. **18**, 802 (2011)

5. Inoyatov, A.K.h., Filosofov, D.V., Gorozhankin, V.M., Kovalik, A., Adam, I., Perevishchikov, L.L., Rysavy, M.: Improved characteristics of the 22.5 keV (M1 + E2) nuclear transition in ^{149}Sm. Eur. Phys. J. A **47**, 64 (2011)
6. Ofer, S., Segal, E., Nowik, I., Bauminger, E.R., Grodzins, L., Freeman, A.J., Schieber, M.: Hyperfine interactions in the ground state and 22-keV state of Sm^{149} in ferromagnetic compounds of samarium. Phys. Rev. **137**, A627 (1965)
7. Ofer, S., Nowik, I.: Magnetic and quadrupole moments of the 22 keV state of ^{149}Sm. Nucl. Phys. **A93**, 689 (1967)
8. Cohen, R.L., Eibschütz, M., West, K.W.: Electronic and magnetic structure of SmB_6. Phys. Rev. Lett. **24**, 283 (1970)
9. Eibschütz, M., Cohen, R.L., Buehler, E., Wernick, J.H.: Mössbauer isomer shifts in Sm^{149} compounds. Phys. Rev. B **6**, 18 (1972)
10. Barla, A., Sanchez, J.P., Haga, Y., Lapertot, G., Doyle, B.P., Leupold, O., Rüffer, R., Abd-Elmeguid, M.M., Lengsdoft, R., Flouquet, J.: Pressure-induced magnetic order in golden SmS. Phys. Rev. Lett. **92**, 066401 (2004)
11. Barla, A., Derr, J., Sanchez, J.P., Salce, B., Lapertot, G., Doyle, B.P., Rüffer, R., Lengsdort, R., Abd-Elmeguid, M.M., Flouquet, J.: High-pressure ground state of SmB_6: electronic conduction and long range magnetic order. Phys. Rev. Lett. **94**, 166401 (2005)
12. Tsutsui, S., Kobayashi, Y., Seto, M., Indoh, K., Onodera, H.: ^{149}Sm nuclear resonant scattering of SmB_2C_2. J. Magn. Magn. Mater. **199**, 272–276 (2004)
13. Tsutsui, S., Kobayashi, Y., Okada, T., Haba, H., Onodera, H., Yoda, Y., Mizumaki, M., Tanida, H., Uruga, T., Sekine, C., Shirotani, I., Kikuchi, D., Sugawara, H., Sato, H.: A possible novel magnetic ordering in $SmRu_4P_{12}$. J. Phys. Soc. Jpn. **75**, 093703 (2006)
14. Seto, M., Masuda, R., Higashitaniguchi, S., Kitao, S., Kobayashi, Y., Inaba, C., Mitsui, T., Yoda, Y.: Synchrotron-radiation-based Mössbauer spectroscopy. Phys. Rev. Let. **102**, 217602 (2009)
15. Masuda, R., Kobayashi, Y., Kitao, S., Kurokuzu, M., Saito, M., Yoda, Y., Mitsui, T., Iga, F., Seto, M.: Synchrotron radiation-based Mössbauer spectra of ^{174}Yb meauired with internal conversion electrons. Appl. Phys. Lett. **104**, 082411 (2014)
16. Yoda, Y., Yabashi, M., Izumi, K., Zhang, X.W., Kishimoto, S., Kitao, S., Seto, M., Mitsui, T., Harami, T., Imai, Y., Kikuta, S.: Nuclear resonant scattering beamline at SPring-8. Nucl. Instrum. Methods A **467**, 715 (2001)
17. Yoda, Y., Imai, Y., Kobayashi, H., Goto, S., Takeshita, K., Seto, M.: Upgrade of the nuclear resonant scattering beamline, BL09XU in SPring-8. Hyperfine Int. **379**, 204–208 (2012)
18. Tsutsui, S., Masuda, R., Kobayashi, Y., Yoda, Y., Mizuuchi, K., Shimizu, Y., Hidaka, H., Yanagisawa, T., Amitsuka, H., Iga, F., Seto, M.: Synchrotron radiation Mössbauer spectroscopy using ^{149}Sm nuclei. J. Phys. Soc. Jpn. **85**, 083704 (2016)
19. http://www.spring8.or.jp/en/users/operationstatus/schedule/bunchmodes
20. Hidaka, H., Yamazaki, S., Shimizu, Y., Miura, N., Tabata, C., Yanagisawa, T., Amitsuka, H.: Magnetically ordered state and crystalline-electric field effects in $SmBe_{13}$. J. Phys. Soc. Jpn. **86**, 074703 (2017)
21. Bucher, E., Maita, J.P., Hull, G.W., Fulton, R.C., Cooper, A.S.: Electronic properties of beryllides of the rare-earth and some actinides. Phys. Rev. B **11**, 440 (1975)
22. Hiess, A., Bonnet, M., Burlet, P., Ressouche, E., Sanchez, J.-P., Warenbourge, J.C., Zwirner, S., Wastin, F., Rebizant, J., Lander, G.H., Smith, J.L.: On the magnetic interactions in metal-Be_{13} compounds. Phys. Rev. Lett. **77**, 3917 (1996)
23. Hidaka, H., Nagata, R., Tabata, C., Shimizu, Y., Miura, N., Yanagisawa, T., Amitsuka, H.: unpublished
24. Tsutsui, S., et al.: unpublished
25. Higashinaka, R., Yamada, A., Miyazaki, R., Aoki, Y., Mizumaki, M., Tsutsui, S., Nitta, K., Uruga, T., Sato, H.: Mixed valence states in $SmTr_2Al_{20}$ (Tr = Ti, V, Cr, and Ta). J. Phys. Soc. Conf. Proc. **3**, 011079 (2014)
26. Tsutsui, S., Mizumaki, M., Kobayashi, Y., Kitagawa, J., Takabatake, T.: Site-specific valence fluctuations in $Eu_3Pd_{20}Ge_6$ studied via Mössbauer and x-ray absorption spectroscopies. Phys. Rev. B **80**, 235115 (2009)
27. Tarascon, J.M., Ishikawa, Y., Chevalier, B., Etourneau, B., Hagenmuller, P., Kasaya, M.: Temperature dependence of the samarium oxidation state in SmB_6 and $Sm_{1-x}La_xB_6$. J. Phys. (Paris) **41**, 1141 (1980)
28. Mizumaki, M., Tsutsui, S., Iga, F.: Temperature dependence of Sm valence in SmB_6 studied by X-ray absorption spectroscopy. J. Phys.: Conf. Ser. **176**, 012034 (2009)
29. Teo, B.K.: EXAFS: Basic Principles and Data Analysis. Springer-Verlag, Berlin (1986)
30. Keski-Rahkonen, O., Krause, M.O.: Total and partial atomic-level width. At. Data Nucl. Data Tables **14**, 139 (1974)