²³⁸U Mössbauer Spectroscopic Study of UX_2 (X = Ga, As, Sb)

Satoshi TSUTSUI¹, Masami NAKADA², Saburo NASU³, Yoshinori HAGA¹, Tetsuo HONMA⁴, Etsuji YAMAMOTO¹, Yoshihumi TOKIWA^{1,5}, Dai AOKI⁵, Piotr WIŚNIEWSKI⁵ and Yoshichika ŌNUKI^{1,5}

¹Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan ²Department of Materials Science, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan ³Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

⁴ Japan Synchrotron Radiation Institute, Mikazuki, Hyogo 679-5143, Japan

⁵ Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

We have measured the 238 U Mössbauer effect of a ferromagnetic UGa₂ and antiferromagnetic UAs₂ and USb₂. Rather large nuclear quadrupole interactions at 238 U nuclei have been observed in these compounds at their magnetic ordered-states. The nuclear quadrupole interaction in UGa₂ has been visible in the ferromagnetic state, whereas not in the paramagnetic state. This is most likely due to the induced nuclear quadrupole interaction in the ferromagnetic state. Since the sign of the nuclear quadrupole interaction is positive from the point of the symmetrical view of UGa₂, it suggests that 5f-orbital is elongated along [1120] direction. In UAs₂ and USb₂, the hyperfine interactions, combined with magnetic dipole and electric quadrupole interactions, have been observed in the antiferromagnetic states. Since the sign the nuclear quadrupole interactions of both samples is negative, 5f-orbitals are spread in tetragonal (001) plane.

KEYWORDS: UGa₂, UAs₂, USb₂, ²³⁸U Mössbauer spectroscopy, combined hyperfine interaction

§1. Introduction

The uranium compounds indicate a variety of physical properties including magnetic and quadrupole ordering, heavy fermions and anisotropic superconductivity. We have studied UGa₂, UAs₂ and USb₂ with ²³⁸U Mössbauer spectroscopy.

UGa₂ has the hexagonal structure, while UAs₂ and USb₂ have the tetragonal one. The former compound is the ferromagnet whose Curie temperature is 125 K and a saturated moment is 3.0 $\mu_{\rm B}$ / U,¹) whereas the latters are antiferromagnets whose Néel temperatures are close to room temperature and their ordered moments are 1.6 and 1.9 $\mu_{\rm B}$ / U, respectively.^{2–5}) In UAs₂ and USb₂, cylindrical Fermi surfaces were observed with the de Haas-van Alphen (dHvA) experiments.^{6–8} On the other hand, UGa₂ has the usual three dimensional Fermi surfaces.^{9,10}

 238 U Mössbauer spectroscopy is one of the useful tools to investigate the physical properties of uranium compounds. Although the atomic arrangements are twodimensional (2D) in these compounds, the Fermi surfaces observed are three-dimensional (3D) in UGa₂ and 2D in UAs₂ and USb₂. Aoki *et al* pointed out that the cylindrical Fermi surfaces were related to their magnetic structure.⁸⁾ 3D Fermi surfaces in UGa₂ have not been able to understood yet. Since the magnetic structures of these compounds have already been known, the 238 U Mössbauer spectroscopy enables us to discuss the 5f-orbitals in their ground states. We have performed the Mössbauer measurements in order to investigate the 5f-orbitals in their magnetic ordered states.

§2. Experimental

The single crystal sample of UGa₂ was prepared by the Czochralski pulling method, that of USb₂ by the self-flux method and that of UAs₂ by the chemical transport method with iodine. The samples were crushed into powder in order to perform the transmission Mössbauer measurements. In usual cases, ²³⁸U Mössbauer effects in uranium intermetallics can be observed below 200 K. Since the Curie temperature is about 125 K,¹⁾ we have measured the Mössbauer spectra at 150 and 5.1 K. Since the Néel temperatures are above 200 K in UAs₂ and USb₂,^{2,3)} we have measured at 5.3 K, in their antiferromagnetic states. The source used was ²⁴²PuO₂.¹¹⁾ The velocity calibration was referred to the laser calibrator.

§3. Results and Discussion

Figure 1 shows the 238 U Mössbauer spectra of UGa₂ at 150 K and 5.1 K. A symmetric singlet resonance line is observed in the paramagnetic state of 150 K, whereas the spectrum becomes asymmetric and broad in the ferromagnetic state of 5.1 K. The hyperfine interaction cannot be observed at 150 K within an experimental error. Since the Curie temperature of UGa₂ is about 125 K,¹⁾ the combined hyperfine interaction can be observed at 5.1 K.

The obtained spectrum at 5.1 K suggests the two possible relationships between the hyperfine field and electric field gradient (EFG) tensor as follows; either (a) the main axis of the EFG tensor is perpendicular to the hyperfine field, parallel to the [0001] direction or (b) the main axis of EFG tensor is parallel to the hyperfine field, namely [11 $\overline{2}$ 0]. In the case of (a), the direction of



Fig.1. ²³⁸U Mössbauer spectra of UGa₂ at 150 and 5.1 K.

the main axis of the EFG tensor is certainly appropriate from the point of the crystallographical view, but the relation between the magnetic moment and the quadrupole moment is inappropriate from the point of the symmetrical view. In the case of (b), the relation between the quadrupole moment and magnetic moment is appropriate at least from the point of symmetrical view. Anyway, since the nuclear quadrupole interaction, which is too small to be observed in the paramagnetic state, can be clearly observed in the ferromagnetic state, this result suggests that the nuclear quadrupole interaction has been surely induced by the ferromagnetic ordering. The spectral analysis at 5.1 K was performed with the calculated eigenvectors and eigenvalues obtained from the Hamiltonian without using the perturbation. In the case of (b), the obtained Mössbauer parameters are shown in Table I. In the case of (a), only the magnitude of the quadrupole splitting (QS) is by a factor - 0.5 as much as that obtained in the former case. The hyperfine coupling constant at 5.1 K is 150 \pm 20 T / $\mu_{\rm B}$. This value

Table I. The ²³⁸U Mössbauer parameters of UGa₂ at 150 and 5.1 K.

is almost consistent with other uranium intermetallics other than URu_2Si_2 .^{12,13} The QS values are generally represented by

$$QS = e^2 qQ.$$

where e is the charge of the proton, Q the quadrupole moment of the ²³⁸U Mössbauer level and q the value of the main axis of the EFG tensor. It is represented by

$$eq = -b\langle J ||\alpha||J\rangle O_2^0 \langle r^{-3} \rangle$$

where b is the coupling constant equal to 0.975×10^{18} V $/\operatorname{cm}^2$, $\langle J || \alpha || J \rangle$ the Stevens factor,¹⁴) O_2^0 the quadrupole tensor in the electronic system, and $\langle r^{-3} \rangle$ the expectation value of r^{-3} . $\langle J || \alpha || J \rangle$ is negative when the valence of uranium atoms is either trivalent or tetravalent.¹⁴⁾ The sign of the EFG tensor is positive. This suggests that the 5f-orbital is elongated along the magnetic easy axis. Figure 2 shows the ²³⁸U Mössbauer spectra of UAs₂ and USb₂ at 5.3 K. Since the Néel temperatures of these compounds are 274 K of UAs_2 and 203 K of USb_2 , both of the observed spectra also include the combined hyperfine interaction.⁷⁾ The magnetic structures were already known and the main axis of the EFG tensor is suggested by the crystal structure.^{4,5} The direction of the hyperfine field is most likely to be parallel to that of the main axis of the EFG tensor. When the Mössbauer parameters are determined with the same way as in the case of UGa₂, the obtained ones are shown in Table 2.

Since the sign of QS values are negative, these results indicate that the quadrupole tensor is oblate in the tetragonal (001) plane as mentioned above. In other words, the 5f-orbitals in these compounds are spread within the basal plane. These are probably related to the 2D Fermi surfaces in UAs₂ and USb₂. The hyperfine coupling constants of these compounds are 170 ± 10 T / $\mu_{\rm B}$ in UAs₂ and 140 ± 10 T / $\mu_{\rm B}$ in USb₂, respectively. These values fairly agree with that of UGa₂ as mentioned above. The induced nuclear quadrupole interaction in UAs₂ and USb₂ could not be discussed with the present results.

Summary

We have observed the induced nuclear quadrupole interaction in the ferromagnetic state of UGa₂. Judging from the point of the symmetrical view, the sign of the nuclear quadrupole interaction is positive. It suggests that 5f-orbital is elongated from $[11\bar{2}0]$ direction. In the antiferromagnetic states of UAs₂ and USb₂, We have also observed the combined hyperfine interactions. Considering the crystal and magnetic structures, it suggests that 5f-orbitals is oblate within (001) plane in these com-

Table II. The $^{238}\mathrm{U}$ Mössbauer parameters of UAs2 and USb2 at 5.3 K.

N.						
Temperature	$H_{ m hf}$ T	$QS \ (= e^2 q Q)$ $mm \ s^{-1}$	Compounds	$H_{\rm hf}$ T	$QS (= e^2 qQ)$ mm s ⁻¹	
150	440 + 60	0 ± 9.2 44.6 + 14.2	$\begin{array}{c} UAs_2\\ USb_2 \end{array}$	$270 \pm 20 \\ 270 \pm 20$	-31.3 ± 6.3 -35.4 ± 9.3	
0.1	110 ± 00	1110 LL 1111				



Fig.2. ²³⁸U Mössbauer spectra of UAs₂ and USb₂ at 5.3 K.

pounds. The present results indicate that the states of the 5f-orbitals are determined with $^{238}\rm U$ Mössbauer spectroscopy in UGa₂, UAs₂ and USb₂. The hyperfine coupling constants of these compounds are nearly equal to about 160 T / $\mu_{\rm B}.$

Acknowledgments

The present work is partially supported by the Grantin-Aid for COE Research (10CE2004) of Ministry of Education, Science, Sports and Culture.

- A. V. Andreev, K. P. Belov, A.V. Deriagin, R. Z. Levitin and A. Menovsky: J. Physique suppl. 49 (1979) C4-82.
- Z. Henkie and Z. Kletowski: Acta Phys. Polon. A42 (1972) 405.
- A. Blaize, J. M. Fournier, R. Kangnier, M. J. Mortimer, R. Schnkel, Z. Henkie and A. Wojakowski: Inst. Phys. Conf. Ser. 37 (1978) 184.
- R. Troć, J. Leciejewicz and R. Ciszewski: Phys. Stat. Sol. 15 (1966) 515.
- 5) A. Oles: J. Physique **26** (1965) 561.
- 6) D. Aoki, P. Wiśniewski, K. Miyake, N. Watanabe, Y. Inada, R. Settai, E. Yamamoto, Y. Haga and Y. Ōnuki: J. Phys. Soc. Jpn., 68 (1999) 2182.
- P. Wiśniewski, D. Aoki, N. Watanabe, K. Miyake, R. Settai, Y. Ōnuki, Y. Haga, E. Yamamoto and Z. Henkie: J. Phys.: Condensed Matter 12 (2000) 1971.
- D. Aoki, P. Wiśniewski and Y. Onuki: Kotai Butsuri (Solid State Physics), 35 (2000) 355 [in Japanese].
- 9) I. Sakamoto, S. Ohara, I. Oguro, E. Yamamoto, Y. Haga, Y. Ōnuki and S. Murano: J. Alloy. Compounds 275-277 (1998) 505.
- 10) T. Honma, Y. Inada, R. Settai, S. Araki, Y. Tokiwa, H. Sugawara, H. Sato, K. Kuwahara, M. Yokoyama, H. Amitsuka, T. Sakakibara, E. Yamamoto, Y. Haga, A. Nakamura, H. Harima, H. Yamagami and Y. Ōnuki: J. Soc. Jpn. 69 (2000) 2647.
- S. Tsutsui, S. Nasu, M. Nakada, N. M. Masaki, M. Saeki, K. Ikushima, H. Yasuoka and A. Nakamura: J. Phys. Soc. Jpn. 67 (1998) 2641.
- 12) S. Tsutsui, M. Nakada, S. Nasu, Y. Haga, T. Honma, E. Yamamoto, H. Ohkuni and Y. Ōnuki: Hyperfine Interactions 126 (2000) 335-340.
- 13) S. Tsutsui, M. Nakada, S. Nasu, Y. Haga, T. Honma, E. Yamamoto, H. Ohkuni and Y. Ōnuki: Physica B281&282 (2000) 242.
- 14) R. Elliot and K. W. H. Stevens: Proc. Roy. Soc., A218 (1953) 553.