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Mössbauer Spectroscopic Study of **Uranium Intermetallic Compounds** (UFe₂, U₆Fe, UGe₂, UPd₂Al₃ and URu₂Si₂)

Graduate School of Engineering Science Department of Physical Science Division of Materials Physics Toyonaka Osaka

January 1999

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Uranium Intermetallic Compounds

Abstract

Physical properties of uranium compounds depend on the characteristics of the 5f-electrons of uranium atoms. The nature of the 5f-electrons in actinide compounds is described by the characteristic properties of 3d- and 4f-electrons. Namely, the 5felectrons in the actinide compounds behave like itinerant 3d-electron and/or localized 4f-electrons.

The Mössbauer spectroscopy is one of the useful tools to investigate the local electronic states in various compounds. Since the Mössbauer effects can be observed in some isotopes of the light actinide elements, the Mössbauer measurements of actinide isotopes enable us to investigate the local electronic states of the 5f-electrons of actinide atoms directly. For the actinide intermetallic compounds, the ²³⁷Np Mössbauer spectroscopic studies of the neptunium intermetallic compounds had been extensively performed between 1960's and 1970's. However, the Mössbauer studies of uranium isotopes for the uranium intermetallic compounds have never been performed, although the uranium intermetallics have various interesting physical properties, for example, their anisotropic superconductivity.

In this work, the ²³⁸U and the ⁵⁷Fe Mössbauer measurements of the uranium intermetallics have been performed in order to investigate the physical properties of the uranium intermetallics, mainly to investigate their magnetic properties.

has been determined as 0.254 \pm 0.015 μ_N by using ^{238}U Mössbauer and ^{235}NMR measurements of UO2. Nuclear g-factor is an important coupling constant on the discussion of the physical properties of uranium compounds.

In U-Fe intermetallics, the isomer shift values obtained by ⁵⁷Fe Mössbauer spectroscopy reveal the strong hybridization between 3d-electrons of iron atoms and 5felecrons of uranium atoms. The hyperfine coupling constant of ⁵⁷Fe in UFe₂ also indicates the hybridization between 3d- and 5f-electrons. The results from the ²³⁸U Mössbauer spectroscopy of UFe₂ suggest that the spin and the orbital moments of uranium atoms in UFe2 do not cancel out each other and the magnetic moments do not exist at uranium atoms.

Firstly, the g-factor of the first excited state in the ²³⁸U Mössbauer transition

In UGe₂, the magnitude of the hyperfine magnetic field at 5.3 K is 240 ± 10 T. The hyperfine coupling constant does not depend on the temperature.

For the heavy fermion superconductors of UPd2Al3 and URu2Si2, the broadening of Mössbauer absorption spectra due to the paramagnetic relaxation is observed at the temperature where the magnitude of each magnetic susceptibility has the maximum value. Above these temperatures, the metamagnetic transitions of both compounds are reported to disappear. These phenomena are thought to be related to the appearance of the heavy fermion which plays an important role in their superconductivity.

The hyperfine coupling constants of ²³⁸U nucleus obtained in this work are obtained as 140 - 160 T / µ_B in UO₂, UGe₂ and UPd₂Al₃.

Contents

Chapter 1. Introduction

1. 1. General Introduction

- 1. 2. Characteristic Properties of Ura
- 1. 3. Previous Mössbauer Spectrosco

Chapter 2. Mössbauer Spectrosocpy

- 2. 1. Principle of the Mössbauer Effe
- 2. 2. Hyperfine Interactions
- 2. 3. Mössbauer Measurement

Chapter 3. Results and Discussion

- 3.1. Determination of the g-factor in
- 3.2. U-Fe Intermetallic Compounds,

3.3. An Itinerant Ferromagnetic Com

3.4. Heavy Fermion Superconductor

Chapter 4. Conclusion

Acknowledgment

List of Publications

	-
anium Compounds	4
opic Studies of Uranium Isotopes	7
ect	19
	24
	42
the First Excited State of ²³⁸ U	50
UFe_2 and U_6Fe	58
npounds, UGe ₂	96
rs, UPd ₂ Al ₃ and URu ₂ Si ₂	107
	137

Chapter 1. Introduction

1. 1. General Introduction

The Mössbauer spectroscopy has been applied to the various fields in physics, chemistry, biology, solid state physics and material science, after R. L. Mössbauer accomplished the first successful observation of the recoil-free nuclear gamma-ray resonance [1.1.1]. This phenomenon was named as the Mössbauer effect from his first observation. The Mössbauer spectroscopy by using various isotopes such as ⁵⁷Fe, ¹¹⁹Sn, ¹⁵¹Eu and so on, is applied to investigate the physical properties of various materials. The Mössbauer effect can be observed in 88 nuclei of about 40 elements. For the uranium isotopes as an actinide element, the Mössbauer effect has been observed for ²³⁴U, ²³⁶U and ²³⁸U nuclei. The Mössbauer spectroscopy enables us to investigate the local electronic state of the Mössbauer probe atom through the hyperfine interactions. The Mössbauer effect of the uranium isotopes was investigated for several uranium compounds like oxides, hydride and so on at the period between 1960 and 1970's [1.1.2-6]. However, the ²³⁸U Mössbauer studies of uranium intermetallic compounds have never been performed except for UFe2, whereas the 237Np Mössbauer studies of neptunium intermetallic compounds which are typical actinide intermetallics have been progressively performed in that period. The facility and the space where these experiments are permitted to perform are restricted by law since the sources and the samples used in these works are nuclear fuel materials. Moreover, there is a fatal reason, that is, the source used in the Mössbauer measurements requires the highly purified isotopes as written below.

The nuclear methods through the hyperfine interactions for the elements with felectrons have never been performed in the cerium and the uranium intermetallic compounds some of which have interesting physical properties like a typical behavior as a heavy fermion system and a coexistence or competition of the magnetic ordering and superconductivity. There are no suitable isotopes for cerium to observe the Mössbauer effect and nuclear magnetic resonance (NMR), since the nuclear spin of the ground state of ¹⁴⁰Ce is zero. On the other hand, in uranium compounds, both NMR and Mössbauer measurements can be performed. Since the natural abundance of ²³⁵U which is the only one suitable isotope to observe the NMR is as small as 0.72 %, it is difficult to perform the ²³⁵U NMR study for the uranium compounds and the reports of the study are quite less [1.1.7-8]. In the ²³⁸U Mössbauer spectroscopy, the probe isotope is ²³⁸U whose natural abundance is 99.275 % and the largest in all of the uranium isotopes. Natural uranium and depleted uranium are easier to treat than the uranium enriched with ²³⁵U, so-called uranium for the nuclear fuel. Samples made from natural or depleted uranium can be used for the ²³⁸U Mössbauer spectroscopy. The motivation of this study is to investigate the local electronic states of uranium intermetallic compounds, mainly their magnetic properties using the ²³⁸U and the ⁵⁷Fe Mössbauer spectroscopy.

In Chapter 1, we show the fundamental physical properties of uranium intermetallic compounds and the Mössbauer measurements of actinide compounds which are previously reported, in Chapter 2, the principles of the Mössbauer effect and the details of hyperfine interactions and in Chapter 3, Mössbauer spectroscopic results. Since the g-factor of the excited state of the ²³⁸U Mössbauer transition has not yet been determined, the g-factor was determined by the combination of the ²³⁸U Mössbauer spectroscopy and the ²³⁵U NMR of UO₂. The magnetic properties of U-Fe intermetallics are discussed mainly with the ⁵⁷Fe Mössbauer spectroscopy. The magnetic properties of the itinerant ferromagnet UGe₂ and the heavy fermion superconductors of UPd₂Al₃ and URu₂Si₂ are investigated with the ²³⁸U Mössbauer 4.

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3

1. 2. Characteristic Properties of Uranium Compounds [1.2.1-2]

Generally, the physical properties of uranium compounds depend on the characteristics of the 5f-electrons. The 5f-electrons in actinide compounds have a nature characterized by both specific properties of 3d- and 4f-electrons. The feature of 3d transition metals and compounds are generally itinerant electronic systems, whereas that of 4f transition metals and compounds is of a localized electronic system. The electron configuration of uranium atoms is $[Rn](5f)^3(6d)^1(7s)^2$. Generally speaking, actinide atoms could take higher valence state than lanthanide atoms which can take only the divalent and trivalent. Uranium atoms can take the valence state up to hexavalent, that is, UO3, UF6 and so on in the uranium compounds. These facts show the wave function of 5f-electrons has larger probability in distant region from the nucleus than that of 4felectrons. Therefore, it implies that the 5f-electrons could contribute to the chemical bond with the neighbor atoms. The effect of the f-p and f-d hybridization exists in 5felectron systems so that the 5f-electrons in the light actinide compounds tends to be itinerant and those of the heavy actinide compounds to be localized. Namely, as the electronic properties, some actinide compounds show itinerant behavior and some are localized behavior.

The relationships of the distance of the nearest neighbor uranium atoms to the existence of the magnetic order and the magnetic ordering temperature are given by a Hill's plot [1.2.3]. According to the Hill's plot, when the distance between uranium atoms is over 0.35 nm, the magnetic order exists. When the distance is less than 0.35 nm, the wave functions of 5f electrons are adequately overlapped and 5f-electrons are delocalized and itinerant. However, when the *f-p* and/or *f-d* hybridization with the electrons at the ligands causes the delocalization of 5f-electron, the formation of the broad 5f bands occurs and the 5f levels approach to the Fermi level. In spite of the large distance over 0.35 nm between the nearest neighbor uranium atoms, these hybridization effects enable 5f-electrons to be itinerant. The Hill's plot is the experiential index to understand the properties of 5f-electrons in uranium compounds, but the localization and delocalization of 5f-electrons cannot necessarily be determined by the distance between uranium atoms. Since the nature of 5f-electrons depends on the various factor such as the distance between the nearest neighbor uranium atoms, the

hybridization with the electrons at ligands and so on, the variety of the physical properties of uranium compounds is caused by that of 5*f*-electrons.

Electronic properties of some uranium compounds show the typical behavior as a heavy fermion system and the characteristic superconductivity which has been observed in cerium compounds. UPd₂Al₃ and URu₂Si₂ whose ²³⁸U Mössbauer effects have been measured in this work, are also heavy fermion superconductors. Some uranium compounds show the similar physical properties as those observed in cerium compounds, whereas some experimental results from a neutron scattering experiments, were reported to be different from those of cerium compounds.

Recently, the purified samples of the uranium compounds reveal interesting electronic properties as a heavy fermion system, which shows a coexistence of the magnetic ordered state and the anisotropic superconducting state. In UPt₃, superconductivity with odd parity has been firstly observed by NMR [1.2.4]. In UPd₂Al₃, a magnetic reflection in the elastic neutron scattering has an anomaly at the transition temperature of superconductivity, T_c and a excitation peak in the inelastic neutron scattering has been observed below T_c . These results show the interplay between its magnetic properties and superconductivity [1.2.5-9].

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1. 3. Previous Mössbauer Spectroscopic Studies of Uranium Isotopes

even uranium isotopes, ²³⁴U, ²³⁶U and ²³⁸U. The sources of these Mössbauer measurements are also even-even plutonium isotopes, ²³⁸Pu, ²⁴⁰Pu and ²⁴²Pu, respectively. The decay schemes of these isotopes are shown in Fig. 1.3.1. When all of the parent isotopes experience alpha-decay, the first excited state $(I = 2^{-})$ of each isotope is populated by 25 % of all transitions. The gamma-rays emitted by the transitions between the first excited state $(I = 2^{+})$ and the ground state $(I = 0^{+})$ are the Mössbauer gamma-rays of uranium isotopes. The energies of the Mössbauer gamma-rays from these uranium isotopes are around 45 keV.

The spectra obtained are very simple in shape because the ground state of all uranium isotopes is $I = 0^+$. The hyperfine interactions of even-even uranium isotopes are mentioned in detail at Section 2. 2. In all of the Mössbauer spectra obtained from these uranium isotopes, the isomer shift value which depends on the valence states of the uranium atoms cannot be observed because its magnitude is nearly zero or less than the experimental error [1.3.1]. This fact is caused by the very small difference in the nuclear radius between the ground and the excited state. This is one of the characteristic nature of the ²³⁸U isotopes. Moreover, although it is reported that the magnetic splitting is observed in UO_2 [1.3.1], the magnitude of the hyperfine field cannot be determined because of unknown g-factor of the first excited state $(I = 2^+)$ of the even-even uranium isotopes.

Table 1.3.1 shows the nuclear data of the Mössbauer transition for the actinide elements, ⁵⁷Fe, ¹¹⁹Sn, ¹⁵¹Eu and ¹⁹⁷Au nucleus [1.3.2-5]. The g-factors of even-even uranium isotopes are the theoretical values reported by Nilsson et al.[1.3.4]. As shown in Table 1.3.1, the life-time of the excited state of every even-even uranium isotopes is shorter than those of the other Mössbauer isotopes. The short life-time of the excited state implies that the spectra obtained are intrinsically broad because the life-time and full-width at half maximum (FWHM) of the spectrum have the uncertainty relationships between the time and the energy. The natural line-width of the ²³⁸U Mössbauer spectrum obtained from this uncertainty principle is 27 mm s⁻¹. This line-width is much broader than the Mössbauer spectrum of the other isotopes, for example, 0.192

The Mössbauer spectroscopy of uranium isotopes has been performed in even-

mm s⁻¹ for ⁵⁷Fe and 1.87 mm s⁻¹ for ¹⁹⁷Au.

In the case of the ²³⁸U Mössbauer effect, theoretical g-factor of the excited state is 0.25 $\mu_{\rm N}$ which is a nearly same value as the other isotopes. On the other hand, the magnitudes of their quadrupole moments are 10 times larger than those of the other isotopes, for example, + 0.2 barn for ⁵⁷Fe and - 0.08 barn for ¹¹⁹Sn. Although the natural line-width of the ²³⁸U Mössbauer spectrum is broader than the other isotopes, its hyperfine interactions can thus be discussed from the split and/or broadening of the spectrum.

The typical quadrupole split patterns show in Fig. 1.3.2. Figure 1.3.2 shows even-even uranium Mössbauer spectra of UO₂(NO₃), 6H₂O. These spectra seem to be asymmetric spectra with two peaks. The sign of the quadrupole moment is minus in each even-even uranium isotopes as shown in Table 1.3.1. The transition probabilities from the excited states, $M = \pm 2, \pm 1$ and 0, to the ground state are 2:2:1, respectively. The spectra shown in Fig. 1.3.3 are fitted by the theoretical lines whose intensities are 2:2:1, respectively, as velocity increases. Since the sign of the quadrupole moments of every even-even uranium isotopes is minus, these results show the sign of the electric field gradient is minus. These results indicate that the excited state of each uranium nuclei split three levels. As shown in Table 1.3.1, the magnitude of the quadrupole moments of every even-even uranium nuclei are nearly equal. Since the every nucleus experienced the equal electric field gradient in UO₂(NO₃)₂·6H₂O, the shapes of the quadrupole split spectra obtained from each isotope are almost identical.

A typical magnetically split pattern is shown in Fig. 1.3.3. Figure 1.3.3 shows the ²³⁸U Mössbauer spectra of UO₂ at 77 K and 4.2 K [1.3.1]. Since the Néel temperature of UO₂ is 30.8 K, the spectrum at 4.2 K can be analyzed as a magnetic pattern. The details of the results obtained in this work are discussed in Section 3.1.

Although the Mössbauer spectroscopy is one of the useful tools with which the physical properties of uranium compounds can be investigated through the hyperfine interactions at uranium nucleus, this measurement has never been performed up to now. In the case of ²³⁴U and ²³⁶U Mössbauer spectroscopy, the natural abundance of these isotopes is too small to perform the experiments. For the ²³⁸U Mössbauer spectroscopy, the natural abundance of its isotope is 99.275 % which is large enough to perform the experiments, but it is necessary to use the extremely purified ²⁴²PuO₂ source.

Isotopes separated generally with the mass separator. ²⁴²Pu cannot be separated from ²⁴¹Pu perfectly. Moreover, the life-time of ²⁴¹Pu and that of ²⁴¹Am which is the daughter nucleus of ²⁴¹Pu are much shorter than that of ²⁴²Pu. As shown in Fig. 1.3.1, 242 Pu decays to 238 U in the half-life of 3.76×10^5 years with alpha-decay and emits the ²³⁸U Mössbauer gamma-ray. On the other hand, ²⁴¹Pu decays to ²⁴¹Am in the half-life of 14.4 years with beta-decay, and ²⁴¹Am decays to ²³⁷Np in the half-life of 433 years with alpha-decay, as shown in Fig. 1.3.4. In the decay from ²⁴¹Am to ²³⁷Np, about 80 % of the transition emits the gamma-ray whose energy is 59.536 keV. The internal conversion coefficients of ²³⁸U and ²³⁷Np are 625 and 1, respectively. Therefore, the existence of the small amounts of ²⁴¹Pu isotope disturbs the detection of the ²³⁸U Mössbauer gamma-ray. This fact requires the highly purified ²⁴²PuO₂ source.

Figure 1.3.5. shows the gamma-ray energy spectrum of even-even plutonium (²³⁸Pu, ²⁴⁰Pu and ²⁴²Pu) reported previously [1.3.6]. These are the sources for ²³⁴U, ²³⁶U and ²³⁸U Mössbauer measurements, respectively. Since the half-life of ²⁴²Pu is longer than those of ²³⁸Pu and ²⁴⁰Pu, this spectrum shows the Mössbauer gamma-ray for ²³⁸U is difficult to detect. In order to take off these difficulties, Ruby et al. reported that the chemical separation of ²⁴¹Am from the source was performed every three months in order to detect the Mössbauer gamma-ray, which is essential to measure the Mössbauer spectra [1.3.1].

9

Ruby et al.[1.3.1], they investigated UO₂, UO₂(NO₃), 6H₂O and compounds as listed in Table 1.3.2. However, we want to emphasize that the ²³⁸U Mössbauer studies of its intermetallic compounds which we described in this work have never been performed except for UFen.

The source for the ²³⁸U Mössbauer measurements requires a high purity of ²⁴²Pu.

Although the ²³⁸U Mössbauer study were performed and reported previously by







Fig. 1.3.2. Mössbauer spectra of the even-even uranium isotopes in $UO_2(NO_3)_2 \cdot 6H_2O$ after R. D. Meeker et al. in 1974 [1.3.6].



Fig. 1.3.3. 238 U Mössbauer spectra of UO₂ at (a) 77 K and (b) 4.2 K after S. L. Ruby et al in 1969 [1.3.1].



separation of the souce from ²⁴¹Am.

Fig. 1.3.4. Energy spectrum of the Mössbauer gamma-ray source for every even-even uranium isotopes reported by R. D. Meeker et al. in 1974 [1.3.6]. The peaks at 59.6 keV is the one of the gamma-ray from ²⁴¹Am in which the source include as impurity. The dash line shows the effect of the chemical



Fig. 1.3.5. Decay scheme for ²⁴² Pu and ²⁴¹ Pu.

Table 1. Nuclear data for Wiossbauer Transition.											
Parameter	²³¹ Pa	²³⁴ U	²³⁶ U	²³⁸ U	²³⁷ Np	²³⁹ Pu	²⁴³ Am	⁵⁷ Fe	¹¹⁹ Sn	¹⁵¹ Eu	¹⁹⁷ Au
Eγ	84.21	43.49	45.24	44.91	59.536	57.273	84.0	14.412	23.875	21.55	77.34
$I_{\rm e}$	3/2-	2+	2+	2+	5/2+	5/2+	5/2-	3/2-	3/2+	7/2+	1/2+
$I_{\rm g}$	5/2+	0+	0+	0+	5/2-	1/2+	5/2+	1/2+	1/2+	5/2+	3/2+
μ_e [μ_N]	4.5	0.5	0.5	0.5	+1.34	-	2.86	-0.1547	+0.67	+2.587	+0.419
$\mu_g \ [\mu_N]$	2.0	0	0	0	+2.5	0.2	1.6	+0.0902	-1.041	+3.465	+0.419
Q _e [barn]	0.69	-3.0	-3.0	-3.2	4.1	-	+4.9	0.2	-0.08	+1.51	0
Q_{g} [barn]	-1.7	0	0	0	4.1	-	4.9	0	0	+1.16	+0.56
t _{1/2} [ns]	44	0.25	0.23	0.21	68	0.10	2.3	99.3	18.3	8.8	1.892
$\Gamma [\text{mm s}^{-1}]$	0.08	24	26	27	0.07	47.9	1.4	0.192	0.626	1.44	1.87
$\alpha_{\rm T}$	-	780 ± 55	607±29	625	1.06	-	0.2	8.17	5.12	29	4
σ_0 [10 ⁻¹⁸ cm ²]	-	0.008	0.01	0.01	0.33	-	0.29	2.57	1.40	0.23	0.041
ts	25.5 h	86 yr	6.58×10^3	3.79×10^5	458 yr	2.33 d	4.98 h	270 d	250 d	87 yr	18 h

Table 1. Nuclear data for Mössbauer Transition.

15

 E_{γ} : γ -ray energy; I_{g} : the ground state nuclear spin; I_{e} : the excited state nuclear spin; μ_{g} : the ground state nuclear magnetic moment;

 μ_{e} : the excited state nuclear magnetic moment ; Q_{g} : the ground state nuclear quadrupole moment ;

 $Q_{\rm e}$: the excited state nuclear quadrupole moment ; $t_{1/2}$: the half life of the excited state ; Γ : natural linewidth ;

 α_{T} : total internal conversion coefficient ; σ_{0} : resonant absorption cross-section ; t_s : the half life of the source

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Isomer Shift mm / s	2±3	1±1	1土1	0.5±1.0	3土1	-3±2	-2土2	1±1	1±1	2±2
e²qQ/4 mm / s		,			-42 ± 2	-47土3	40±2	-19土2	-21 土 1	
Magnetic Splitting mm / s	1	58土4.0	80土4				,			16土12
FWHM mm / s	48土23	45±1	45土4	55±3	47±2	50土6	60±6	48	48	48
Relative Absorption %	4.0±0.2	7.0±0.2	4.6±0.2	3.3±0.1	4.3±0.2	2.5 ± 0.2	3.0±0.2	2.7 ± 0.2	5.1 ± 0.2	2.0±0.1
Background Counts	61000	60000	86000	78000	55000	88000	128000	74000	68000	137000
Temperature K	78	4.2	4.2	4.2	4.2	4.2	4.2	78	4.2	4.2
Compounds	UO2		UF_4	UC	UO ₂ (NO ₃) ₂ •6H ₂ O	UO ₂ (NO ₃) ₂ in H ₂ O	UO3	α-U		UFe ₂

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16

Chapter 2. Mössbauer Spectroscopy

2. 1. Principle of the Mössbauer Effect [2.1-4]

2. 1. 1. Mössbauer Effect

The resonant absorption by the transition between the electronic states of atoms is proved by R. W. Wood [2.5]. Since the life-time in the excited state is generally short, the photon energy emitted from the atom by the de-excitation to the ground state is equal to the energy difference between the excited and ground state.

W. Kurn suggested that the energy levels and resonant absorption of nuclear exist such atom and molecule systems [2.6]. However, the energy differences between nuclear levels are about 1000 times larger than those of the atom and molecule systems, and their resonant absorptions have never been able to observed because the free atom experiences the recoil in the emission and absorption process by the gamma-ray.

When the gamma-ray is emitted from the nucleus, the conservation law of the energy gives the following relation,

$$E = E_{\gamma} + E_R,$$

where E is the difference of the energy between two levels in a gamma transition, E_{γ} the energy of the emitted gamma-ray, E_{R} is the recoil energy in the emission process of the gamma-ray. The conservation law of the momentum in this gamma transition gives

$$0 = \frac{E_{\gamma}}{c} - p ,$$

where p is the momentum of emitted or absorbed atoms, c the velocity of light. The recoil energy E_{R} is written using p by

$$E_R = \frac{p^2}{2M} = \frac{(E_{\gamma}/c)^2}{2M},$$

Where M is the mass of the emitting nucleus. From Eq. (2.1.1), the observed energy of the emitted gamma-ray is smaller than the transition energy by the recoil energy, $E_{\rm R}$. In the absorption process of the gamma-ray, the absorbed nucleus recoils towards incident direction of the gamma-ray. Therefore, the loss of the emission and absorption energy of the gamma-ray is just $2E_{\rm R}$.

Since the recoil energy of nuclear gamma-ray is very large in its emission and absorption processes, it is larger than the width of the gamma-ray. The energy of the Mössbauer gamma-ray, for example, is 14.4 keV in ⁵⁷Fe Mössbauer transition. Its

(2.1.1)

(2.1.2)

(2.1.3)

recoil energy is

 $E_R = 1.94 \times 10^{-3} \,\mathrm{eV}.$ (2.1.4)

On the other hand, the natural line width of its gamma-ray Γ is given by the principle of uncertainty.

$$\Gamma \tau = \hbar \,, \tag{2.1.5}$$

where τ is the life-time of the excited state, \hbar Planck constant. Since the life time of the first excited state in ⁵⁷Fe isotope is 99.3 nsec,

$$\Gamma = 6.74 \times 10^{-9} \text{ eV}. \tag{2.1.6}$$

In the case of the atoms and molecules, the loss due to the recoil energy is much smaller than the line-width and the resonant absorption can be realized.

R. L. Mössbauer studied the scattering of 129 keV gamma-ray of ¹⁹¹Ir, and observed an increase of the scattering probability as the temperature of the scatterer decreases. This phenomenon was not predicted from the classical theory [2.7], but is easily explained by Einstein model of the solid. Einstein model to explain the specific heat of the solid permits the change of the solid states whose quantum number is different by one or more than one. This change is the integral multiples of the energy of lattice vibration as the emission and absorption. Considering the case of the excitation of the phonon in the emission process of the gamma-ray, f is defined as the probability of the emission of the gamma-ray without the excitation of the phonon. The recoil energy of ⁵⁷Fe Mössbauer transition is 10⁻³ eV, comparable to the energy of the phonon. Therefore, neglecting the transition with the two or more than two quantum number change, the relation between the recoil energy $E_{\rm R}$ and the probability f is given by

$$E_{\scriptscriptstyle R} = (1 - f)\hbar\omega. \tag{2.1.7}$$

This probability f is called the recoil-free fraction. Zero phonon absorption and scattering of gamma-ray is called Mössbauer effect, and the recoil-free fraction findicates the probability of Mössbauer effect.

2.1.2. Recoil-free fraction

Since Mössbauer effect is the nuclear gamma-ray resonance without the excitation of phonon, the probability of this effect depends on three things, which are the recoil energy of a free atom, the properties of the lattice and the temperature. Therefore, recoil-free fraction, f, is greater, the smaller the probability of excitation of phonon, that is, the smaller Mössbauer gamma-ray energy, the firmer the binding of atoms in the lattice and the lower the temperature is.

The probability, W, of gamma-ray emission without the excitation of the phonon from a nucleus in a solid can be written as follows. The probability W is written by

$$W = const \langle i | H | f \rangle,$$

where $|i\rangle$ is the initial state, $|f\rangle$ the final state of the system and H the interaction Hamiltonian operator and depends on the positional coordinates of the atom and the momentum and spins of the particles within nucleus. The forces acting within the nucleus are extremely short range, whereas those holding the lattice together are much long range. Since the nuclear decay and the vibrational state are independent of each other, the matrix element can be reduced to the one term for the transition from initial vibration state L_i to the final state L_r of the lattice, and can be rewritten by

$$f = const \times \left| \left\langle L_i \middle| e^{ik \cdot x} \middle| L_f \right\rangle \right|^2,$$

where k is the wave vector for the emitted gamma-ray and x the coordinate vector of the center of mass of the decaying nucleus. Since the lattice modes are unchanged for zero phonon emission, the recoil-free fraction is rewritten by

$$f = const \times \left| \left\langle L_i \left| e^{ik \cdot x} \right| L_i \right\rangle \right|^2.$$

Since $|L_i\rangle$ is a normalized function,

$$=e^{-k^2x^2}$$

The Debye model leads to

$$k^{2}x^{2} = \frac{\hbar}{2M} \int_{0}^{\omega_{D}} \frac{N(\omega)}{\omega} \coth\left(\frac{\hbar\omega}{2k_{B}T}\right) d\omega$$

where $N(\omega) = const \times \omega^2$, $\omega_{\rm D}$ cutoff frequency, M the mass of nucleus and $k_{\rm B}$ the Boltzman constant. Therefore, the recoil-free fraction is written by

(2.1.8)

(2.1.9)

(2.1.10)

(2.1.11)

(2.1.12)

$$f = \exp\left[\frac{-6E_R}{k\theta_D}\left\{\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\frac{\theta_D}{T}} \frac{xdx}{e^x - 1}\right\}\right],$$
(2.1.13)

by using Debye model, where $E_{\rm R}$ is the recoil energy, and $\theta_{\rm D}$ the Debye temperature.

2.1.3. Mössbauer Spectrum

In the Mössbauer spectroscopy, the energy of the gamma-ray is modulated by Doppler effect and the transmission of the gamma-ray versus the Doppler velocity is a Mössbauer spectrum. The energy change, ΔE , due to the first order Doppler effect is given by

$$\Delta E = \frac{v}{c} E_{\gamma}, \qquad (2.1.14)$$

where v is the Doppler velocity.

A Mössbauer spectrum is determined by the line-width of the emitted gammaray and the scattering cross section of the absorber. The energy distribution of the gamma-ray emitted from the source is given by

$$S(E) = \frac{f_{s}\Gamma_{s}}{2\pi} \frac{1}{(E - E_{o}) + (\Gamma_{s}/2)^{2}},$$
(2.1.15)

and the scattering cross section of the absorber is given by

$$\sigma(E) = \frac{t_{eff} (\Gamma_A / 2)^2}{(E - E_0) + (\Gamma_A / 2)^2},$$
(2.1.16)

where E_{y} is the energy of the gamma-ray emitted form the source, Γ_{s} the line-width of the gamma-ray emitted from the source, E_0 the energy of the gamma-ray absorbed by the absorber, Γ_{A} the line-width of the absorption resonance, $t_{eff} (= f_a n_a \alpha_a \sigma_0 t_a)$ the effective thickness of the absorber, f_a the recoil-free fraction of the absorber, n_a the number of atoms of the element concerned per cm³ in the absorber, a_a the fractional abundance of the resonant isotope, σ_0 the cross section of the Mössbauer resonance, t_a the thickness of the absorber. Generally, the resonant absorption spectrum is expressed by

$$p(v) = N_0 + \int_{-\infty}^{+\infty} S(E - v) \exp[-\sigma(E)] dE, \qquad (2.1.17)$$

where p(v) is the count rate as a function of Doppler velocity, v, and N₀ background. When the contribution of the self-absorption in the source is small and the absorber is an ideally thin foil, the Eq. (2.1.17) can be rewritten by

$$A = \int_{0}^{+\infty} \{N_0 - p(v)\} dv \approx A' f_S \times f_A.$$

In a thin foil approximation, the resonance line is written by the combolution of two Lorentz function. The resonance line is the Lorentz function whose line-width is equal to the summation of the line-widths of source and absorber. On the other hand, when experimental condition is not treated as a thin foil approximation and/or the obtained spectra consist of the superposed lines, the line-shape p(v) is treated as the function of Eq. (2.1.17) in spectrum analyses without thin foil approximation.

2.1.4. Internal Conversion Process

As written above, the Mössbauer effect is the resonance emission and absorption of the nuclear gamma-ray. However, the de-excitation processes in the Mössbauer effect are as follows: The first one is the case where the gamma-ray is reemitted. The second one is the case where the characteristic X-ray of a probe atom without the emission of the resonance gamma-ray is emitted. The third one is the case where the bound electron of a probe atom substituted for the resonance gamma-ray is emitted. The second and third processes are called the internal conversion process. How to observe the Mössbauer effect are the detection of the emitted gamma-ray, the emitted characteristic X-ray and the emitted inner-shell electrons.

The conventional way of the Mössbauer spectroscopy is the transmission geometry how the gamma-ray through a sample is detected. In the case of measurements of too thick the bulk or single crystal for the Mössbauer gamma-ray to transmit, the measurements by using the internal conversion process is more useful way than those in the transmission geometry.

(2.1.18)

2. 2. Hyperfine interactions [2.1-4]

2. 2. 1. Isomer shift

The nucleus is surrounded by electronic charge with which it interacts electrostatically. The energy of interaction can be computed classically by considering a uniformly charged spherical nucleus imbedded in its s-electron charge cloud. Since there exists the Coulomic interaction between the electron and nucleus, a change in the s-electron density might arise from a change in valence will result as a shift of the nuclear levels. This energy shift corresponds to the monopole term of the hyperfine interaction. This is written by

$$\delta E = \frac{2\pi}{5} Z e^2 |\psi(0)|^2 R^2, \qquad (2.2.1)$$

where Z is the number of atomic number, e the charge of the electron, $|\psi(0)|^2$ the density of electron at the nucleus and R the radius of the nucleus. If two nuclei, one in source and the other in absorber, are at the same electronic state, their values of $|\psi(0)|^2$ are same. That means Mössbauer resonance is observed at zero Doppler velocity. In general, however, the chemical states are different between source and absorber so that the density of s-electrons in source is different from that in absorber. Therefore, the difference of the chemical state is observed as the difference of the nuclear energy level. In the Mössbauer spectrum, this effect is observed as the shift of the spectrum. Such a energy shift due to the chemical state is called as an isomer shift, δ . Isomer shift, δ , is written by

$$\delta = \frac{4\pi}{3} Z e^2 R^2 \left(\frac{\delta R}{R} \right) \left\{ \psi_A(0) \right|^2 - \left| \psi_S(0) \right|^2 \right\} , \qquad (2.2.2)$$

by using Eq. (2.2.1). Isomer shift depends on two factors. One is the difference between the radius of the ground state and the excited state. Another is the electronic charge density at the nucleus, which is basically an atomic or chemical parameter, since it is affected by the valence state of the atom. In the case of the application of the Mössbauer spectroscopy to the material physics, the nuclear parameter is thought to be constant. The isomer shift value is thus the important parameter from which the valence state of the probe atom can be known.

2. 2. 2. Second Ordered Doppler Shift

The existence of a relativistic temperature-dependent contribution to the isomer shift was pointed out by Pound and Rebka [2.8] and by Josephson [2.9]. The emitting or absorbing atom is vibrating on its lattice site in the crystal. The frequency of oscillation about the mean position is of the order of 1012 per second, so that the time averaged displacement during the Mössbauer event is zero. However, there is a term in the Doppler shift which depends on v^2 , so that the mean value $\langle v^2 \rangle$ is not zero.

The relativistic equation for the Doppler effect on an emitting photon gives the observed frequency ν' for the velocity, ν , in the direction from source to observer as

$$\nu' = \nu \left(1 - \frac{\nu}{c} \right) \left(1 - \frac{\nu^2}{c^2} \right)^{-\frac{1}{2}} \approx \nu \left(1 - \frac{\nu}{c} + \frac{\nu^2}{2c^2} \right)$$
(2.2.3)

where v is the frequency for a stationary system. The first-order term in velocity is a function of the velocity of the atom vibrating on its lattice site to the direction of the gamma-ray and will average to zero over the lifetime of the state. The second-order term with v^2 will not average to zero and is therefore independent to the direction of gamma-ray radiation. This term is usually referred to as a second-order Doppler shift and expressed as

$$\nu' = \nu \left(1 + \frac{\left\langle \nu^2 \right\rangle}{2c^2} \right).$$

Accordingly, there is a shift in the Mössbauer resonance line given by

$$\frac{\delta E_{\gamma}}{E_{\gamma}} = \frac{\delta v}{v} = -\frac{\langle v^2 \rangle}{2c^2}.$$

It is instructive to consider the description of $\langle v^2 \rangle$ in terms of the lattice dynamics of the solid. The following treatment is a simplification of that by Hazony [2.10]. Using a harmonic approximation, the average energy associated with each atom is

$$\frac{1}{2}M\langle v^2\rangle = 3\left(n_j + \frac{1}{2}\right)\hbar\omega_j,$$

where $n_j = 1/[\exp(\hbar\omega_j / k_B T) - 1]$ and ω_j is the oscillation frequency. We wish to sum over all possible frequencies and modes of vibration, so that

(2.2.4)

(2.2.5)

(2.2.6)

$$\frac{\delta \nu}{\nu} = -\frac{3}{2Mc^2} \sum_j A_j^2 \hbar \omega_j \left(\frac{1}{2} + n_j\right), \qquad (2.2.7)$$

where the A_j^2 terms are weighting factors such that $\sum A_j^2 = 1$. *M* is the atomic mass of the Mössbauer nucleus. From the view point of intercomparison of isomer shifts, it is useful to consider the general equation as $T \rightarrow 0$. There is a zero-point motion term by

$$\frac{\delta v}{v} = -\frac{3}{4Mc^2} \sum_j A_j^2 \hbar \omega_j . \qquad (2.2.8)$$

The magnitude of the zero-point motion will be dependent on the exact mode of vibration in the crystal, so that $\delta v / v$ will not generally be the same in all compounds.

Since the mean square of the velocity $\langle v^2 \rangle$ of nucleus, which results from thermal vibration of the lattice, depends on the temperature, the second order Doppler shift depends on the temperature. According to the Debye model of solid, the second order Doppler shift $\Delta_{S}^{D}(T)$ in the velocity unit, is written as follows,

$$\Delta_{\mathcal{S}}^{D}(T) = \frac{9k_{\mathcal{B}}\theta_{D}}{16Mc} + \frac{9k_{\mathcal{B}}\theta_{D}}{2Mc} \left(\frac{T}{\theta_{D}}\right)^{3} \int_{0}^{\frac{\theta_{D}}{T}} \frac{x^{3}dx}{e^{x}-1}.$$
(2.2.9)

The shift $\delta(T)$ observed in the spectrum contains both isomer shift $\Delta_{S}^{I,S}(T)$ and second ordered Doppler shift $\Delta_s^{\mathcal{D}}(T)$ of the source and the absorber, so that $\delta(T)$ is represented as follows,

$$\delta(T) = \left\{ \Delta_{A}^{I,S}(T) - \Delta_{A}^{D} \right\} - \left\{ \Delta_{S}^{I,S}(T) - \Delta_{S}^{D}(T) \right\}.$$
(2.2.10)

When the source or absorber is kept at a temperature, information about the lattice vibration, for example θ_{D} , can be obtained from temperature dependence of the shift of the spectrum.

2. 2. 3. Electric Quadrupole Interaction

When the nuclear spin I is 0 or 1/2, the nuclear charge is spherical symmetric and has zero quadrupole moment. When I > 1, on the other hand, the charge distribution of the nucleus is distorted from spherical symmetry, and the nucleus has non-zero quadrupole moment. The magnitude of the charge deformation of a nucleus is described as the nuclear quadrupole moment Q, given by

$$eQ = \int \rho r^2 (3\cos^2\theta - 1) d\tau \,,$$

where e is the charge of the proton, r is the charge density in a volume element $d\tau$, which is at distance r from the center of the nucleus and making an induced angle θ to the nuclear spin quantization axis. The sign of Q depends on the shape of the deformation. A negative quadrupole moment indicates that the nucleus is oblate or flattened along the spin axis, whereas for a positive moment it is prorate or elongated.

spherically symmetric. The electric field gradient at the nucleus is defined as a tensor $E_{ij} = -V_{ij} = \left(-\partial^2 V / \partial x_i \partial x_j\right) (x_i, x_j = x, y, z)$, where V is the electrostatic potential. It is customary to define the coordinate axis for the system and $V_{zz} = eq$ is the maximum value of the field gradient. The orientation of the nuclear quantized axis with respect to the principal axis, z, is quantized. There is an interaction energy between Q and eqwhich is different for each possible orientation of the nucleus.

The Laplace equation requires that the electric field gradient is traceless tensor, so that

$$V_{xx} + V_{yy} + V_{zz} = 0$$
.

Consequently, only two independent parameters are needed to specify the electric field gradient completely, and the two which are usually chosen are V_{zz} and an asymmetry parameter η defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}.$$

Using the relationships of $|V_{zz}| > |V_{yy}| \ge |V_{xx}|$ ensures that $0 \le \eta \le 1$.

The Hamiltonian of the quadrupole interaction can be written as

$$H_{Quad} = \frac{eQ}{2I(2I-1)} \left(V_{zz} \hat{I}_{z}^{2} + V_{xx} \hat{I}_{x}^{2} + V_{zx} \hat{I}_$$

where I is the nuclear spin and \hat{I}_z , \hat{I}_x and \hat{I}_y are the nuclear spin operator. Using Eq. (2.2.13), the Hamiltonian becomes

$$H_{Quad} = \frac{e^2 q Q}{2I(2I-1)} \Big[3\hat{I}_z^2 - I(I+1) +$$

or

(2.2.11)

In a chemically bonded atom, the electronic charge distribution is usually not

(2.2.12)

(2.2.13)

 $V_{yy}\hat{I}_{y}^{2}$), (2.2.14)

 $-\eta (\hat{I}_{x}^{2} - \hat{I}_{y}^{2})$ (2.2.15)

$$H_{Quad} = \frac{e^2 q Q}{2I(2I-1)} \left[3\hat{I}_z^2 - I(I+1) + \eta \left(\hat{I}_+^2 + \hat{I}_-^2 \right) \right]$$
(2.2.16)

where I_{-} and I_{-} are shift operator.

The numerical value of the principal component of the electric field gradient $(V_{-} = -E_{-})$ due to an electronic wave function is given by

$$V_{\pm} = eq = -e\left\langle\psi\left|\frac{3\cos^2\theta - 1}{r^3}\right|\psi\right\rangle$$
(2.2.17)

and

$$\eta q = \left\langle \psi \left| \frac{3\sin^2 \theta \cos 2\phi}{r^3} \right| \psi \right\rangle.$$
(2.2.18)

A table of the appropriate values for hydrogen-like wave functions is given in Table 2.2.1. The $\langle r^{-3} \rangle$ value is the expectation value of $1 / r^3$ for the appropriate hydrogenlike wave function, ψ . In the case of the rare earth and actinide elements, the electric field gradient will mainly be caused by the electronic orbital of the probe atoms themselves.

The lattice term q_{latt} can be similarly evaluated as the sum of contributions from individual changes Z, and can be written

$$q_{latt} = \sum_{i} \frac{Z_i}{r_i^3} (3\cos^2\theta_i - 1)$$
(2.2.19)

Generally the valence term is a major contribution to the electric field gradient unless the ion has the high intrinsic symmetry of an S-state ion such as high-spin Fe³⁺. In the latter case, the lattice term will be dominant.

2. 2. 4. Magnetic Hyperfine Interaction

The important part of the hyperfine interaction is the magnetic hyperfine interaction. This arises from the interaction between the nuclear magnetic moment and the magnetic field at nucleus due to the electrons of the probe atom itself. The Hamiltonian of this interaction is

$$H_{Max} = -\mu \cdot H = -g\mu_N I \cdot H \tag{2.2.20}$$

and the energy levels which are obtained are

$$E_M = -\frac{\mu_N HM}{I} = -g\mu_N HM \; ,$$

where μ_N is the nuclear magneton and g the g-factor. According to Eq. (2.2.21), every level is split with equally spaced energy.

made of transition adjacent magnetic sublevels of the ground states since its transition permits the only magnetic quantum number changes by 1 ($\Delta M = \pm 1$). In the Mössbauer effect, however, gamma-ray transitions are observed between two nucleus levels, which in generally both exhibit magnetic hyperfine structures. The gamma-ray corresponds to a transition from a particular magnetic sublevel of an excited state to a sublevel of the ground state. The selection rule depends on the multipolarity of the radiation.

Generally, a gamma transition between two nuclear levels of spin I_1 an I_2 must conserve the z-component of the angular momentum. The angular momentum, L, carried off by the gamma-ray must satisfy

$$|I_1 - I_2| \le L \le |I_1 + I_2|$$

However, L cannot be zero. For a given L, transitions between sublevels are limited to those with $|\Delta M| \leq L$. In the presence of magnetic hyperfine structure, the individual transitions between magnetic sublevels may be resolved. These probabilities are given by the square of Clebsch-Gordon coefficients, $(I_1I_2M_1M_2|I_1I_2LM_1-M_2)^2$

This magnetic interaction is caused by various sources. These are the Fermi contact interaction, the orbital current, the dipole interaction, the applied external field, and the Lorentz and demagnetizing field due to the applied field. The Fermi contact interaction is the most contributed one to the hyperfine magnetic field in all the sources of hyperfine magnetic interaction in the case of ⁵⁷Fe. As written below, the Fermi contact interaction is acting between the s-electrons at nucleus and the nuclear magnetic dipole moment. In the case of the trivalent iron, the hyperfine magnetic field is taken into account of this interaction because the quenching of the orbital angular momentum by the crystalline electric fields causes the other contribution to the magnetic fields is almost equal to zero. In the other cases, however, the contribution of the hyperfine field by the orbital current should be taken into account. The contribution of the

(2.2.21)

In nuclear magnetic resonance (NMR) measurements, direct observations are

(2.2.22)

hyperfine field to each source is explained as follows.

The Fermi contact interaction is written by

$$H_{FC} = \frac{8}{3}\pi\mu_B g \sum_n \left[\rho_{ns}^*(0) - \rho_{ns}^*(0) \right], \qquad (2.2.23)$$

where $\rho_{ns}(0)$ and $\rho_{ns}(0)$ are the contact density of s-electrons of the n-th shell having spin up and spin down, μ_B is Bohr magneton, g is Lande's g-factor. Its actual origin may be from intrinsic inpairing of the actual s-electrons, or indirectly as a result of polarization effects on filled s-orbitals. These can occur if the atom has unpaired electrons in d- or f-electrons. Since the interaction between an unpaired d- or felectron and s-electrons with parallel spin is different from that with antiparallel spin, there is a slight imbalance of spin density at the nucleus. In the case of metals, direct conduction-electron polarization as well as indirect core-polarization effects might be important.

In non-relativistic theory, $H_{\rm orb}$ produced by the total angular momentum, J, of open-shell electrons is given by

$$H_{orb} = a_{hf} \langle J \| N \| J \rangle \langle r^{-3} \rangle m_J .$$
(2.2.24)

Here a_{hf} is a hyperfine coupling constant per atomic units, $\langle J \| N \| J \rangle$ a reduced matrix element, $N = \sum \{ I_i - s_i + 3(r_i \cdot s_i)r_i / r_i^2 \}, I_i$ angular momentum, s_i spin momentum, m_j the azimuthal number connected with J_z , $\langle r^{-3} \rangle$ the expectation value of $1 / r^3$ for the wave functions of the open shell electrons [2.11]. The contribution of the orbital current to the hyperfine field is thought to be nearly proportional to the magnetic moment in the case of the lanthanide elements and neptunium of actinide.

2. 2. 5. Combined Magnetic Hyperfine Interaction and Quadrupole Interaction

When the combined magnetic and quadrupole interactions are observed in the Mössbauer spectrum, the observed spectrum is a little bit complicated. When the hyperfine magnetic field is sufficiently large, the axially symmetric field gradient causes shifts of the magnetically split absorption lines. In this case, every energy level is a pure state. The quadrupole interaction is treated as the perturbation to the hyperfine magnetic interaction.

When the quadrupole interaction is comparable or large enough to magnetic interaction, every nuclear energy level is no more pure state. In this case, the quadrupole interaction cannot be treated as the perturbation to the hyperfine magnetic interaction. The spectrum-analysis in this case is more complicated than in the former case.

2. 2. 6. Mössbauer Effect and Hyperfine Structure of 57Fe

observed in the transition from I = 3/2 to I = 1/2 and from 5/2 to 1/2. In the transition from I = 3/2 to 1/2, its Mössbauer effect can be observed even at room temperature because the transition energy of 14.4 keV is rather than small the recoil-free fraction is expected to be large. On the other hand, its Mössbauer effect in the transition from 5/2 to 1/2 can be observed only at very low temperature because the recoil energy of 133 keV gamma-ray is large. The conventional ⁵⁷Fe Mössbauer spectroscopy uses 14.4 keV gamma-ray. Typical energy spectrum of the popular gamma-ray source of ⁵⁷Co in Rh is shown in Fig. 2.2.2.

The typical level schemes and spectra are shown in Fig. 2.2.3. The transition probability between ⁵⁷Fe Mössbauer levels is shown in Table 2.2.2. In its powder pattern, the spectra when ⁵⁷Fe nuclei experience only the magnetic field are symmetric sextet, and the spectra when ⁵⁷Fe nuclei experience only the electric field gradient are symmetric doublet.

2. 2. 7. Mössbauer Effect and Hyperfine Structure of ²³⁸U

observed in the transition from $I = 2^+$ to $I = 0^+$. The energy spectrum of the source used for ²³⁸U Mössbauer spectroscopy is shown in Fig. 2.2.5. The source which contains 99.99 % 242Pu has been used in this work. The 242PuO, source in the present work does not need to perform the chemical separation from ²⁴¹Am, or the observation of ²³⁸U Mössbauer gamma-ray is not disturbed from the gamma-ray of ²⁴¹Am.

The typical level schemes and spectra are shown in Fig. 2.2.6. The transition probability of ²³⁸U Mössbauer levels is shown in Table 2.2.3. The spectra when ²³⁸U nuclei experience only the magnetic field are symmetric ones like that of UO2 at 4.2 K

The decay scheme of ⁵⁷Co is shown in Fig. 2.2.1. ⁵⁷Fe Mössbauer effect is

The decay scheme of ²⁴²Pu is shown in Fig. 2.2.4. ²³⁸U Mössbauer effect is

reported by Ruby et al.[2.12]. The spectra when 238 U nuclei experience only the electric field gradient are asymmetric ones like that of UO₂(NO₃)₂·6H₂O at 4.2 K reported by Ruby et al. Since the *g*-factor of the first excited state in even-even uranium isotopes has not yet been determined except for the theoretical value [2.13], the hyperfine magnetic field have not been able to be determined directly by the Mössbauer measurement of uranium isotopes. No isomer shift of the Mössbauer spectroscopy of even-even uranium isotopes can be observed because the difference of the nuclear radius between the ground state and first excited state is too small to observe the shift in the resonance absorption line.

Table	2.2.1	Magtitude	of a and
			O' of connes

Orbital	9	η
<i>p</i> :	$-\frac{4}{5}\langle r^{-3}\rangle$	0
p_x	$+\frac{2}{5}\langle r^{-3}\rangle$	- 3
p _y	$+\frac{2}{5}\langle r^{-3}\rangle$	+ 3
<i>d</i> _{z²}	$-\frac{4}{7}\langle r^{-3}\rangle$	0
$d_{x^2-y^2}$	$+\frac{4}{7}\langle r^{-3}\rangle$	0
d_{xy}	$+\frac{4}{7}\langle r^{-3}\rangle$	0
d_{xz}	$-\frac{2}{7}\langle r^{-3}\rangle$	+ 3
d_{yz}	$-\frac{2}{7}\langle r^{-3}\rangle$	- 3
f_{z^3}	$+\frac{8}{15}\langle r^{-3}\rangle$	0
f_{xz^2}	$-\frac{1}{10}\langle r^{-3}\rangle$	- 2
f_{yz^2}	$-\frac{1}{10}\langle r^{-3}\rangle$	+ 2
$f_{z(x^2-y^2)}$	0	0
$f_{z(x^2-y^2)}$	0	0
$f_{x(x^2-3y^2)}$	$-\frac{1}{6}\langle r^{-3}\rangle$	0
$f_{y(3x^2-y^2)}$	$-\frac{1}{c}\langle r^{-3}\rangle$	0

η for various atomic orbitals

Table. 2.2.2. Relative intensity and angular dependence of ⁵⁷Fe Mössbauer transitions for the powdered thin specimens. θ is the angle between the magnetic axis or the principle axis of the electric field gradient and the propagation direction of the gammaray.

Table. 2.2.3. Relative intensity and angular dependence of ²³⁸U Mössbauer transitions for the powdered thin specimens. θ is the angle between the magnetic axis or the principle axis of the electric field gradient and the propagation direction of the gammaray.

Transition	Relative Intensity	Angular Dependence	Transition	Relative Intensity	Angular Dependence
	in Powder Pattern			in Powder Pattern	
	Magnetic Spectra			Magnetic Spectra	
$+\frac{3}{2} \rightarrow +\frac{1}{2}$	1	$1 + \cos^2 \theta$	$+2 \rightarrow 0$	1	$\sin^2\theta + \frac{\sin^2 2\theta}{4}$
$+\frac{1}{2} \rightarrow +\frac{1}{2}$	$\frac{2}{3}$	$2\sin^2\theta$	$+1 \rightarrow 0$	1	$\cos^2\theta + \cos^2 2\theta$
$-\frac{1}{2} \rightarrow +\frac{1}{2}$	$\frac{1}{3}$	$1 + \cos^2 \theta$	$0 \rightarrow 0$	1	$\frac{3}{2}\sin^2 2\theta$
$-\frac{3}{2} \rightarrow +\frac{1}{2}$	0	0	$-1 \rightarrow 0$	1	$\cos^2\theta + \cos^2 2\theta$
$+\frac{3}{2} \rightarrow -\frac{1}{2}$	0	0	$-2 \rightarrow 0$	1	$\sin^2\theta + \frac{\sin^2 2\theta}{4}$
$+\frac{1}{2} \rightarrow -\frac{1}{2}$	$\frac{1}{3}$	$1 + \cos^2 \theta$		Quadrupole Spectra	4
$-\frac{1}{2} \rightarrow -\frac{1}{2}$	$\frac{2}{3}$	$2\sin^2\theta$	$\pm 2 \rightarrow 0$	2	$\sin^2\theta + \frac{\sin^2 2\theta}{4}$
$-\frac{3}{2} \rightarrow -\frac{1}{2}$	1	$1 + \cos^2 \theta$	$\pm 1 \rightarrow 0$	2	$\cos^2\theta + \cos^2 2\theta$
	Quadrupole Spectra	a			
$\pm \frac{1}{2} \rightarrow \pm \frac{1}{2}$	1	$2+3\sin^2\theta$	$0 \rightarrow 0$	1	$\frac{3}{2}\sin^2 2\theta$
$\pm \frac{3}{2} \rightarrow \pm \frac{1}{2}$	1	$3(1+\cos^2\theta)$			2

$$\sin^2\theta + \frac{\sin^2 2\theta}{4}$$

$$\cos^2\theta + \cos^2 2\theta$$

$$\frac{3}{2}\sin^2 2\theta$$







Fig. 2.2.2. Energy spectrum of ⁵⁷Fe Mössbauer source, ⁵⁷Co in Rh, which is measured by using a Xe gas filled proportional counter.





Fig. 2.2.3. Schmatic drawing of the hyperfine structure and corresponding spectrum of ⁵⁷Fe. (a) Electric monopole interaction. (b) Electric quadrupole interaction. (c) Magnetic dipole interaction. (d) Magnetic dipole interaction with weak electric quadrupole interaction.

Fig. 2.2.4. Decay scheme of ²⁴²Pu.

38







Fig. 2.2.6. Schematic drawing of the hyperfine structure and corresponding spectrum of ²³⁸U. (a) No hyperfine interaction. (b) Electric quadrupole interaction. (c) Magnetic dipole interaction.



2.3. Mössbauer Measurements

In conventional Mössbauer spectroscopy, gamma-ray source is mount on the driving unit which is usually electro-magnetic transducer. The gamma-ray source is moved oscillatory, so that the energy of the gamma-ray is modulated by Doppler velocity. The absorption spectrum of the specimen which contains the probe nuclei is obtained by detecting the number of the gamma-ray photons through the specimen as a function of the Doppler velocity. The block diagram of the measurement system is shown in Fig. 2.3.1. In this work, the ⁵⁷Fe and ²³⁸U Mössbauer measurements have been performed. Procedure of the each measurement is described as follows.

The ⁵⁷Fe Mössbauer effect is observed at room temperature because the transition energy of Mössbauer gamma-ray is 14.4 keV. The 57Fe Mössbauer measurement below room temperature is achieved by using He gas flow type cryostat. The schematic drawing of the gas-flow type cryostat used is shown in Fig. 2.3.2. The Mössbauer measurements under the external field was performed with cryostat containing a superconducting solenoid. The magnitude of the applied external field is up to 7 T. The direction of the applied field is parallel to the propagation direction of Mössbauer gamma-ray. Schematic drawing of the cryostat for the measurement under applied magnetic field is shown in Fig. 2.3.3. In the Mössbauer study of UFe2 and U₆Fe, the conversion electron Mössbauer spectroscopy (CEMS) has been performed by using the single crystal samples. Schematic drawing of the counter of the CEMS as shown in Fig. 2.3.4.

The ²³⁸U Mössbauer effect is observed below room temperature because the transition energy of Mössbauer gamma-ray is 44.91 keV. All the ²³⁸U Mössbauer measurements is performed with the cryostat as shown in Fig. 2.3.5. The source is PuO, gamma-ray source which contains 99.99 % 242Pu. It is prepared at the Russian Federal Nuclear Center in All-Russian Research Institute of Experimental Physics. The schematic drawing of the source used is shown in Fig. 2.3.6. Since the activity of ²⁴²PuO₂ is 72.6 MBq and rather weak for the Mössbauer gamma-ray source, a specially designed sample holder shown in Fig. 2.2.7 was used in order to eliminate the electronic absorption of the Mössbauer gamma-ray.



Fig. 2.3.1. Schematic drawing of the Mössbauer Measurements.



Fig. 2.3.2. Schematic drawing of the He gas flow type cryostat (Oxford Instruments Limited, CF500).

Fig. 2.3.3. Schematic drawing of the cryostat with superconducting magnet (Oxford Instruments Limited, ITC-4).



⁽Taiyo Toyo Sanso co Ltd, TEC-337).

Fig. 2.3.5. Schematic drawing of the cryostat for ²³⁸U Mössbauer spectroscopy







Fig. 2.3.7. Schematic drawing of the sample holder of the 238 U Mössbauer spectroscopy made of aluminum. $_{47}$

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3.1. Determination of the g-factor in the First Excited State of ²³⁸U 3.1.1. Introduction

In previous works, ²³⁸U Mössbauer spectroscopy applied to several magnetic materials [3.1.1]. However, since the g-factor of the first excited state of the ²³⁸U nucleus is unknown except for the theoretical value [3.1.2], the magnitude of the hyperfine magnetic field is determined in every magnetic material. The only energy of the magnetic Zeeman splitting had been obtained by the spectrum analysis precisely. On the other hand, the magnitude of the hyperfine magnetic field at uranium nuclei is directly determined using ²³⁵U NMR because the gamma-value is already known, 0.784 MHz / T [3.1.3]. Since the existence of the hyperfine magnetic field at uranium nuclei of UO₂ have already been known in its antiferromagnetic state [3.1.1]. In this work, the g-factor of the first excited state of ²³⁸U nuclei tried to be determined using the combination of ²³⁸U Mössbauer and ²³⁵U NMR measurements of UO₂ in the antiferromagnetic state.

The physical properties of UO₂ have been investigated very well. UO₂ has an antiferromagnetic material and ceramic nuclear fuel. Its Néel temperature and effective moment is 30.8 K and 3.1 $\mu_{\rm B}$ / U, respectively, determined by the magnetic susceptibility measurement. Its saturated moment is 1.78 $\mu_{\rm B}$ / U determined by the neutron scattering [3.1.4]. Its crystal field was also observed by neutron scattering [3.1.5]. Its ground state reveals Γ_s triplet, using several experimental results [3.1.6]. However, its magnetic properties including its antiferromagnetic transition was not understood clearly. Its phase transition is the first-order transition [3.1.4]. It is believed the first-order transition results from the competition between the exchange interaction and the Jahn-Teller distortion [3.1.7]. If so, the ground state of UO₂ is considered to be the coexistence and/or competition of the antiferromagnetic ordering and quadrupole ordering [3.1.7-9]. This phenomenon has not been explained clearly in the view point of experiments. ²³⁸U Mössbauer measurement was performed only at 77 K which is the temperature range of its paramagnetic state and 4.2 K which is of its antiferromagnetic state [3.1.1]. ²³⁵U NMR measurement have never been performed as long as I know. Fortunately, the ²³⁵U NMR signals of UO₂ have been firstly observed in the antiferromagnetic state. In order to determine the g-factor of the first excited

state of ²³⁸U nuclei, ²³⁸U Mössbauer and ²³⁵U NMR measurements of antiferromagnetic UO₂ have been thus performed in its antiferromagnetic state.

3.1.2. Experimental Procedure

Two samples were prepared. One is for ²³⁸U Mössbauer spectroscopy, and another for ²³⁵U NMR spectroscopy. As written above, the probe isotope of ²³⁸U Mössbauer measurement includes 99.275 %, whereas that of ²³⁵U NMR measurement includes 0.72 %. Therefore, the sample for the Mössbauer measurement made from the oxide of natural uranium, and that for the NMR measurement from the uranium oxide enriched to 93.01 % with ²³⁵U. Both samples prepared by sintering uranium oxide for 10 hours at 1273 K under an atmosphere of hydrogen gas. The lattice parameter of UO_{2-x} depends on the oxygen content and the detail relationships between them have been established [3.1.10]. Using the previously reported table, the stoichiometry of the specimen was confirmed by the lattice parameter obtained from Xray diffraction pattern [3.1.10-12].

²³⁸U Mössbauer spectra were measured between 5.4 K and 280 K using transmission geometry. The gamma-ray source used is ²⁴²PuO₂ which includes 99.99 % ²⁴²Pu. Doppler velocity calibrated with a laser calibrator. Zero isomer shift was adopted as ²³⁸U in PuO₂. ²³⁵U NMR spectrum was measured using pulsed NMR method at 1.5 K.

3.1.3. Results and Discussion

A ²³⁵U NMR spin-echo spectrum of UO₂ at 1.5 K was observed [3.1.13]. Seven resonance lines were obtained. The results obtained show that the magnitude of the hyperfine magnetic field of ²³⁵U nuclei is 252.3 ± 0.5 T, and that quadrupole splitting is $|e^2 q Q(3 \cos^2 \theta - 1)/h| = 392 \pm 11$ MHz [3.1.13]. The magnitudes of the nuclear quadrupole moments of ²³⁵U and ²³⁸U isotopes are Q(²³⁵U) = 4.1 barn in the ground state and Q_{ex}(²³⁸U) = -3.2 barn in the first excited state ($I = 2^{-}$), respectively [3.1.14]. The quadrupole splitting observed for ²³⁵U NMR spectrum corresponds to $|e^2 q Q(3 \cos^2 \theta - 1)| = 1.70 \pm 0.04$ mm s⁻¹ for the ²³⁸U Mössbauer spectrum. Since the natural line width of ²³⁸U Mössbauer spectra is 27 mm s⁻¹, as calculated from the short life time 0.21 ns of the first excited state ($I = 2^{-}$), the quadrupole splitting of ²³⁸U in UO₂ is, unfortunately, too small to distinguish it from the line-width.

²³⁸U Mössbauer spectra of UO₂ at various temperatures are shown in Fig. 3.1.1. The full width at half maximum (FWHM) increased appreciably with decreasing temperature. The obvious line broadening was observed at 25 K and 5.4 K below the Néel temperature, $T_{\rm N} = 30.8$ K [3.1.14]. The spectra at 25 K and 5.4 K were analyzed as a superposition of magnetically split 5 lines. The nuclear spin of ²³⁸U is $I = 0^+$ in the ground state, and $I = 2^+$ in the first excited state. In order to determine the magnitude of nuclear Zeeman splitting, we used two different methods in spectrum-analysis. Method I is to analyze the spectrum by a least-square-fit with non-constrained FWHM. Method II is a least-square-fit using a constrained FWHM. FWHM depends on the temperature because of the temperature dependence of the recoil-free fraction of UO₂ and ²⁴²PuO₂.

The Mössbauer parameters obtained by Method I are as follows: The magnetic splitting and FWHM are equal to 62.7 ± 2.1 mm s⁻¹ and 38.3 ± 6.6 mm s⁻¹ respectively at 5.4 K. The temperature dependence of FWHM had the maximum near the Néel temperature as shown in Fig. 3.1.2. The absorption area in the ²³⁸U Mössbauer spectra of UO₂, which is proportional to the recoil-free fraction, does not change appreciably below about 50 K, as also shown in Fig. 3.1.2. FWHM of the spectrum is represented as a function of the effective thickness of the specimen, which includes the recoil-free fraction of sources and absorbers and increases with decreasing temperature. When FWHM is narrower than that obtained at higher temperatures where the effective thickness is smaller, the results obtained by the analysis of superposed spectra show, in general, the overestimated quadrupole and magnetic splitting [3.1.15].

In the spectrum-analysis using Method II, we considered the temperature dependence of FWHM and recoil-free fraction. Temperature dependence of the absorption areas is related to the product of the recoil-free fractions of UO_2 and PuO_2 . FWHM of the spectrum, which is also related to the recoil-free fraction [3.1.16], could not change appreciably below 50 K and the values of FWHM between 35 K and 5.4 K should be equal to the value observed at 50 K. From the reason mentioned above, the spectra in the antiferromagnetic state at 25 K and 5.4 K were analyzed using the FWHM value at 50 K, 46.5 ± 1.57 mm s⁻¹. The results from Method II are as follows: The

magnitude of the magnetic splitting and FWHM are 59.1 ± 3.9 mm s⁻¹ and 46.5 ± 1.57 mm s⁻¹ at 5.4 K, respectively. From the relationships between FWHM and absorption area, the results from Method II is better than those from Method I.

In this study, both of the source and the absorber specimen are at the same temperature, and the temperature difference between them is less than 1 K as an experimental error. Generally, the resonant absorption is expressed by

$$p(v) = N_0 + \int_{-\infty}^{\infty} S(E - v) \exp[-\sigma(E)] dE, \qquad (3.1.1)$$

where p(v) is counts rate as a function of Doppler velocity, v, N_0 background, S(E) the distribution of gamma-ray energy from a source, $\sigma(E)$ the resonant absorption cross-section of an absorber. In thin foil approximation, the absorption area is given by

$$A = \int_{-\infty}^{\infty} \{N_v - p(v)\} dv \approx A' f_s \times f_A,$$
(3.1.2)

where f_s and f_A are the recoil-free franction of source and absorber. The recoil-free fraction f is a probability of the zero-phonon emission and absorption of gamma-ray in the lattice and is given by

$$f = \left| \left\langle \omega_q \left| e^{ik \cdot x} \right| \omega_q \right\rangle \right|^2$$

$$\approx \exp\left[-\frac{6E_R}{k\theta_D} \left\{ \frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D} \frac{x}{e^x - 1} \right\} \right].$$
(3.1.3)

The 2nd formula is expressed with the Debye model. ω_q is the phonon spectrum of the lattice, k wave vector of the gamma-ray, u is a displacement of the nucleus from its equilibrium position, E_R the recoil energy and θ_D the Debye temperature of source or absorber. The Debye temperature of UO₂ was reported to be 182 K using the specific heat measurement [3.1.7]. We adopted this value to determine the Debye temperature of ²³⁸U in PuO₂. The temperature dependence of the absorption area in a combination between UO₂ and ²⁴²PuO₂ is shown as the line calculated using the Debye temperature 182 K for UO₂ and 250 K for PuO₂, which is obtained by the least-square-fit in the temperature range above 50 K. Below 50 K, the absorption area approaches to a nearly constant value. These results suggest that the Debye temperature of uranium atoms in PuO₂ is about 250 K. Recoil-free fractions of UO₂ and/or PuO₂ do not change below 50 K and suggest the slight change in the phonon spectrum might be induced by

the antiferromagnetic ordering of UO_2 . From the consideration of the recoil-free fraction with the Debye model, we adopt the results of the spectrum-analysis using Method II rather than Method I.

The hyperfine magnetic fields obtained by ²³⁵U NMR and ²³⁸U Mössbauer effect were at the different temperatures, 1.5 K and 5.4 K, respectively. Since the magnitude of the magnetic moments of uranium atoms in UO₂ saturates at low temperature like 5.4 K [3.1.4]. The magnitude of the hyperfine magnetic field obtained by the ²³⁵U NMR spin-echo spectrum at 1.5 K should be the same as that obtained by the ²³⁸U Mössbauer effect at 5.4 K within the experimental error. We determine the g-factor of the excited state in the ²³⁸U Mössbauer transition using the results from Mössbauer effect and NMR measurements.

The energy of the hyperfine magnetic interaction is equal to $4g_{ex}\mu_N H$, where μ_N is the nuclear magneton $(e\hbar/2m_p)$, H is the hyperfine magnetic field at ²³⁸U nucleus. The energy of ²³⁸U Mössbauer gamma-ray is 44.91 keV [3.1.14]. The nuclear Zeeman splitting is equal to $(8.85 \pm 0.58) \times 10^{-6}$ eV. Therefore the g-factor of the excited state in the ²³⁸U Mössbauer transition is 0.254 ± 0.015 . This is almost equal to the theoretical value, 0.25 within the experimental error [3.1.2]. From present investigation, the conversion factor, 4.27 ± 0.28 T / mm s⁻¹, has been obtained.

The anomaly of the temperature dependence of the recoil-free fraction below 50 K was observed as written above. The observed recoil-free fraction is smaller that the calculated value in this temperature range as shown in Fig. 3.1.2. This result means the recoil-free fraction decreases below 50 K. As written below, the anomaly cannot be observed in the other compounds, UGe_2 , UPd_2Al_3 and URu_2Si_2 , whose Mössbauer effect is measured in this work. Therefore, it is suggested this anomaly is caused by the anomaly of UO_2 rather than that of PuO_2 .

Generally, when a quadrupole ordering exists at a finite temperature, the softening of the elastic constant is observed at this temperature. Since the elastic constant is relate to the recoil-free fraction, the softening of the elastic constant must be the decrease of the recoil-free fraction. For the antiferromagnetic ordering of UO_2 , it has been proposed to be the coexistence and/or competition with the quadrupole ordering [3.1.7-9]. The result obtained Indicates that the elastic constant at uranium
atoms in UO2 is softened around 50 K. This result suggests UO2 undergoes the quadrupole ordering around 50 K. This is suggested that UO2 does not undergo both of the antiferromagnetic transition and the quadrupole ordering at Néel temperature.

3.1.4. Conclusion

The combination of ²³⁸U Mössbauer and ²³⁵U NMR measurements of antiferromagnetic UO₂ has been performed in the magnetic ordered state. The g-factor of the excited state of 238 U Mössbauer transition is 0.254 ± 0.015. From the obtained g-factor, the conversion factor becomes 4.27 ± 0.28 T / mm s⁻¹.

In consideration for the obtained results of ²³⁸U Mössbauer measurement, the observed anomaly of the recoil-free fraction is thought to be due to the anomaly of the phonon spectra in UO₂. This result suggests that UO₂ does not the antiferromagnetic and the quadrupole orderings at Néel temperature, but that it experiences the quadrupole ordering at higher temperature than the antiferromagnetic ordering.







Fig. 3.1.2. Temperature dependence of the full-width at half maximum (FWHM) and the absorption area of the ²³⁸U Mössbauer spectra for UO₂. FWHM's above 35 K were obtained by spectrum analysis by using a single Lorentzian function. Below 25 K, the spectra observed were analyzed by the five magnetically split lines: The solid squares are the results of Method II, the open squares are those of Method I. The solid circles show the temperature dependence of the absorption area. The solid line is theoretical curve obtained by using the Debye model in which the Debye temperatures of UO₂ and PuO₂ were 182 K and 250 K, respectively.

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3. 2. U-Fe Intermetallic compounds

3. 2. 1. Introduction

In U-Fe system, only two intermetallic compounds have been formed in UFe₂ and U₆Fe. UFe₂ is the ferromagnetic compound whose Curie temperature is 167 K [3.2.1.1] and Laves phase whose crystal structure is C-15 (MgCu₂) type one. The Curie temperature of UFe₂ is sensitive to its stoichiometry [3.2.1.1-2]. On the other hand, U₆Fe is Pauli paramagnetic compounds and superconductor whose transition temperature is 3.96 K. U₆Fe is difficult to obtain the single phase sample because the metallic uranium and UFe₂ is easy to include as the main impurities [3.2.1.3].

In both of UFe₂ and U₆Fe, the ⁵⁷Fe Mössbauer measurements have been performed in previous works [3.2.1.4-7]. In UFe₂, the ²³⁸U Mössbauer measurement was performed by Ruby et al.[3.2.1.8]. As for the ⁵⁷Fe Mössbauer spectroscopy of UFe₂ and U₆Fe, temperature dependence of the Mössbauer parameter was discussed. In UFe₂, temperature dependence of the absorption area has the anomaly at Curie temperature. According to results of McGuire et al., this is caused by the magnetoristriction [3.2.1.5]. In U₆Fe, the second order Doppler shift, absorption area and quadrupole splitting have anomalies around 100 K. This was reported to be caused by the change of the phonon system around this temperature [3.2.1.6].

However, since single crystal samples were difficult to be obtained in those compounds, especially U_6Fe [3.2.1.3], the conversion electron Mössbauer spectroscopy (CEMS). The Mössbauer measurement under the applied magnetic field of those compounds has never been performed, either. Since UFe₂ has the magnetic ordering below 167 K, the sign of the electric field gradient and the anisotropy parameter are determined by the spectra in the ferromagnetic ordered state, but the different magnitude of the hyperfine magnetic field in the crystalographically same site are observed in the previous works. Since U₆Fe is a Pauli paramagnetic compound, those are determined with the conventional Mössbauer measurement using the powdered sample.

In this work, the conventional ⁵⁷Fe Mössbauer measurements of U-Fe intermetallic compounds and the ²³⁸U Mössbauer spectroscopy of UFe₂ has been performed. Moreover, the conversion electron Mössbauer spectroscopy and the ⁵⁷Fe

Mössbauer measurements in the applied field have also been performed.

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3. 2. 2. ⁵⁷Fe and ²³⁸U Mössbauer Spectroscopy of UFe₂

3. 2. 2. 1. Introduction

The several Laves phases (AnFe₂), UFe₂, NpFe₂, AmFe₂ and PuFe₂, which contain actinide elements (An) and iron, are known. It was reported the Curie temperature of UFe₂ is between 150 K and 200 K [3.2.2.1-7]. Its crystal structure is C-15 type (MgCu₂) structure as shown in Fig. 3.2.2.1. On the other hand, the Curie temperature of the other actinide-iron Laves phase compounds are above room temperature. As for the Curie temperature of UFe₂, it was reported to depend exactly on the stoichiometry between U and Fe [3.2.2.6-7]. UFe₂ has a lower magnetic transition temperature and smaller magnetic moment at actinide ion site than the other actinide-iron Laves phase compounds [3.2.2.5, 3.2.2.8-12]. The saturated magnetic moments at iron site are $0.6 \mu_{\rm B}$, while the magnetic moment of the uranium site is almost zero [3.2.2.13]. As for the magnetic moment at uranium site of UFe₂, neutron scattering and magnetic Compton scattering studies was suggested that the spin and the orbital moment are coupled antiparallelly and the net magnetic moment was canceled out to zero [3.2.2.13-14].

The Laves phase compounds which contain iron and rare earth elements have the very high Curie temperatures above the room temperature [3.2.2.15-21]. They have the bigger magnetic moments at both iron and rare earth sites than in UFe₂. In these Laves phase compounds except for UFe₂, 4f- or 5f- electrons are thought to be comparably localized at rare earth or actinide sites [3.2.2.22]. The highly anisotropic magnetization of these compounds is thought to be caused by the localized 4f-electrons or nearly localized 5f-electrons. In UFe₂, its magnetic moments at uranium atoms are thought to be related to the character of 5f-electrons at uranium atoms. The distance between uranium atoms is 0.3056 nm and shorter than the Hill's limit of 0.35 nm [3.2.2.23]. This fact might suggest that the uranium atoms in UFe₂ have no magnetic moment.

In order to investigate the physical properties of UFe_2 , the Mössbauer spectroscopy fortunately applies to both elements of ${}^{238}U$ and ${}^{57}Fe$ those are constituent elements of UFe_2 . The Curie temperature of UFe_2 is reported to be between 150 K and

200 K and the ²³⁸U Mössbauer gamma-ray energy of 44.91 keV is higher than that of ⁵⁷Fe Mossbauer gamma-ray energy, ²³⁸U Mössbauer effect is difficult to observe in its paramagnetic state. The ²³⁸U Mössbauer spectroscopy enables us to give the local electronic state at uranium atoms in the ferromagnetic state through the observed hyperfine magnetic field. Whereas, since the energy of the ⁵⁷Fe Mössbauer gamma-ray is 14.4 keV, the ⁵⁷Fe Mössbauer effect can be observed even in its paramagnetic states. In this work, the ⁵⁷Fe and the ²³⁸U Mössbauer measurements of UFe₂ has been performed in order to investigate the physical properties, mainly the magnetic properties.

3. 2. 2. 2. Experimental Procedure

Both of the ⁵⁷Fe and the ²³⁸U Mössbauer measurements have been performed by means of the transmission geometry. The samples used in the transmission geometry are highly purified polycrystalline powders and the specimens for the conversion electron Mössbauer spectroscopy were bulk single crystals having a specific plane surfaces. Since UFe₂ is easy to be oxidized, the measured sample is the polycrystalline one whose ingot was powdered in argon gas atmosphere. The sample for the conversion electron Mössbauer spectroscopy was the single crystal cut perpendicular to the easy axis of the magnetization, <111>.

The ⁵⁷Fe Mössbauer measurement have been performed at the temperature range between 298 K and 4.2 K. The ²³⁸U Mössbauer measurements have been performed at 200 K, 82 K and 5.2 K. The ⁵⁷Fe conversion electron Mössbauer measurements have been performed at room temperature. The Curie temperature was determined using a Mössbauer thermal scan method. The used sources are ⁵⁷Co in Rh for the the ⁵⁷Fe Mössbauer measurement and PuO₂ which contains 99.99 % ²⁴²Pu for the ²³⁸U Mössbauer measurement, respectively. The velocity calibration of the ⁵⁷Fe Mössbauer spectroscopy was referred to the α-Fe spectrum at room temperature. The Doppler velocity of the ²³⁸U Mössbauer spectroscopy was calibrated by using a laser calibrator and its zero isomer shift value was adopted to the isomer shift value of ²³⁸U in PuO₂.

3. 2. 2. 3. Results and Discussion

Figure 3.2.2.2 shows the ⁵⁷Fe Mössbauer spectra of UFe₂ at various temperatures. The spectra above 170 K are symmetric doublet, while those below 160 K are asymmetric. The spectra below 100 K seem to consist of the superposed four resonance lines. Since the Curie temperature is between 150 K and 200 K, the observed asymmetric patterns is thought to be related to the appearance of the hyperfine field due to the magnetic ordering.

The isomer shift value at room temperature is - 0.21 mm s⁻¹. The isomer shift values give us the density of *s*-electrons at probe nucleus. Since the nuclear radius of the excited state is smaller than that of the ground state, this result shows the density of electrons at ⁵⁷Fe nucleus is larger than metallic iron. In consideration for the neutrality of the charge at iron atoms, the larger density of *s*-electrons at ⁵⁷Fe nucleus is caused by the wide-spread wave function of 3*d*-electrons of iron atoms in UFe₂. Therefore, the results obtained suggest that the 3*d*-electrons of iron atoms are hybridized with 5*f*-electrons of uranium atoms.

As written above, spectra change from a symmetric doublet pattern to an asymmetric pattern between 160 K and 170 K. When the spectra change with an increase or a decrease of the temperature, the count rate is expected to change at a velocity range around the isomer shift value. In this case, since UFe_2 is a ferromagnetic compound, it is expected the magnetic pattern is observed below Curie temperature and that the paramagnetic pattern is observed above this temperature. The magnetic pattern is generally a wide-spread spectrum so that the relative absorption near the isomer shift value decreases with a decrease of the temperature. Therefore, the temperature at which the slope change of the count rate at a certain Doppler velocity versus temperature occurred is determined as the Curie temperature.

The temperature dependence of the count rate at 0 mm s⁻¹ is shown as Fig. 3.2.2.3. In both the processes of temperature increasing and decreasing, the slope change of the count rate occurred at 167.50 K and 167.04 K, respectively. At this temperature, the presence of the anomaly due to the phase transition was observed in the electrical resistivity measurement. This temperature is fairly agreed to the reported Curie temperature of UFe_{2.00} [3.2.2.6]. These results show the Curie temperature is 167 K.

Temperature dependence of the isomer shift and quadrupole splitting above the Curie temperature is shown in Fig. 3.2.2.4. The magnitude of the quadrupole splitting at room temperature is 0.45 mm s⁻¹. The quadrupole splitting does not almost change or slightly decreases above Curie temperature. On the other hand, the isomer shift increases above Curie temperature as temperature decreasing. This phenomenon corresponds to the temperature dependence caused by the second order Doppler shift.

Below the Curie temperature, the hyperfine magnetic field originated from the magnetic ordering of UFe₂ is observed. Generally, the ⁵⁷Fe Mössbauer spectrum with the hyperfine magnetic field is a sextet Lorentzian. The typical magnetic pattern such as α -FeOOH at 77 K is analyzed with the combined hyperfine magnetic and quadrupole pattern treated as the perturbation of the quarupole interaction to the hyperfine magnetic interaction. Since the saturated magnetic ordered state is thought to be too small to treat the quadrupole interaction as the perturbation [3.2.2.13]. The spectra obtained below the Curie temperature were not analyzed with the usual least-square fitting using a sextet Lorentzian function in which the quadrupole splitting was treated as the perturbation to the magnetic splitting. In the spectra obtained has been substituted for the conventional least-square fitting.

Figure 3.2.2.5 shows the arrangement of the iron atoms around a probe iron atom in UFe₂. The magnetization easy axis of UFe₂ is <111> and the principal axis of the electric field gradient expected from the atomic arrangements as shown in Fig. 3.2.2.5 is [111] directions. The angle between the magnetization easy axis and the principal axis of the electric field gradient is 0 or 109.47 degree. The site of ion atoms are called as Fe(1) and Fe(2), respectively, as shown in Fig. 3.2.2.5. The ratio of Fe(1) to Fe(2) is 1 : 3. Figure 3.2.2.6 shows the obtained Mössbauer spectra and the calculated spectra with the above consideration. The calculated spectra are compared with the experimental results. The ³⁷Fe Mössbauer parameters obtained at 4.2 K are shown in Table 1. The hyperfine magnetic field at Fe(1) and Fe(2) are 3.1 T and 4.1 T, respectively, although those locate at the same site crystallographycally. These results agreed well to the results obtained from the previous works [3.2.2.24-25].

Temperature dependence of the averaged hyperfine field in UFe2 is shown in

Fig. 3.2.2.7. It is similar to that of its magnetization [3.2.2.6]. The hyperfine coupling constants are 5.3 T / μ_B at Fe(1) and 6.9 T / μ_B at Fe(2). These values are smaller than the coupling constant of α -Fe, 15.5 T / μ_B . In the case of ⁵⁷Fe Mössbauer spectroscopy, the origin of the hyperfine field is caused mainly by Fermi contact interaction represented by

$$H_{FC} = \frac{8}{3} \pi \mu_B g \sum_{n} \left[\rho_{ns}^{\uparrow}(0) - \rho_{ns}^{\downarrow}(0) \right].$$

The small hyperfine coupling constant was obtained and its reason might be due to the hybridization of the 3d electrons of iron atoms with the 5f electrons of uranium.

Temperature dependence of the resonant absorption area is shown in Fig. 3.2.2.8. As shown in Eq. (2.1.18) of previous section, the resonance absorption area is represented by

$$A = \int_{-\infty}^{\infty} \{N_0 - p(v)\} dv = A' f_S \times f_A,$$

where N_0 is background, and f_s and f_A are the recoil-free fractions of the source and absorber. Since the temperature of the source used in this work is room temperature, the recoil-free fraction of source is constant. The resonant absorption strength is, thus, proportionate to the recoil-free fraction of UFe2. Generally, the recoil-free fraction increases continuously as a decrease of the temperature. The temperature dependence of f in UFe, has an anomaly near the Curie temperature. This phenomenon was reported already in the previous works [3.2.2.24]. Since the Mössbauer effect is the nuclear gamma-ray resonance without the excitation of phonon, the anomaly of the recoil-free fraction which corresponds to the probability of the Mössbauer effect indicates the change of the lattice system. This anomaly was reported to be caused by the magnetostriction [3.2.2.24] or the change of the phonon spectrum [3.2.2.13]. Temperature dependence of the resonant absorption area below the Curie temperature was fitted by the theoretical curve obtained by using the Debye model in which Debye temperature of UFe2 was 300 K. Resonant absorption area above Curie temperature was fitted by a theoretical curve obtained by using the Debye model in which the Debye temperature was 250 K. The difference of the Debye temperatures between the ferromagnetic and the paramagnetic states might be due to the elastic constant enhancement which appeared below Curie temperature. These results show the elastic

(3.2.2.1)

(3.2.2.2)

constant enhancement caused by the magnetoristriction, as reported by McGuire et al [3.2.2.13].

On the other hand, the enhancement of the absorption area just at the Curie temperature cannot be explained with the only difference of the Debye temperature. If the only Debye temperature changes at Curie temperature, the estimated values at 0 K of the theoretical curves are nearly equal because of the Debye temperature of 250 K and 300 K in the paramagnetic and ferromagnetic states, respectively. However, the estimated values at 0 K are very different between theoretical curves with which the temperature dependence of the absorption areas in the paramagnetic and ferromagnetic states, as shown in Fig. 3.2.2.8. This result suggests the phonon spectrum changes at Curie temperature. It corresponds to the results from neutron scattering experiments [3.2.2.13]. Therefore, these results show the enhancement by the magnetoristriction as well as the change of the phonon spectra.

In this work, the ²³⁸U Mössbauer spectroscopy has also been performed for UFe₂. Figure 3.2.2.9 shows ²³⁸U Mössbauer spectra of UFe₂ at 82 K and 5.5 K. The observation of the ²³⁸U Mössbauer effect has been tried at 200 K, above the Curie temperature of 167 K. However, since its recoil-free fraction at this temperature is very small, its spectrum at 200 K could not be obtained. The ²³⁸U Mössbauer spectrum has been successfully observed at room temperature for UO₂ whose Debye temperature is 187 K. Therefore, the Debye temperature of UFe₂ might be lower than 187 K. The magnitude of the full width at half maximum (FWHM) at 82 K and 5.5 K were 31.8 \pm 3.4 mm s⁻¹ and 43.8 \pm 2.5 mm s⁻¹, respectively. The results obtained at 5.5 K agreed with the previous works by Ruby et al. within the experimental error [3.2.2.25]. The value of the FWHM at 82 K was nearly equal to the natural line-width of ²³⁸U Mössbauer transition, 27 mm s⁻¹.

Paolasini et al. proposed that UFe_2 has a magnetic moment at uranium atoms, but that it is extremely small, comparable to the other actinide-iron Laves phase compounds, because spin and orbital moments canceled out with each other [3.2.2.13]. Lawson et al. also suggested with their magnetic Compton scattering experiment that, since the spin and orbital moments were coupled antiparallel, the net magnetic moments of uranium atoms in UFe, have a tenth of Bohr magneton [3.2.2.14]. Ruby et al. reported the ²³⁸U Mössbauer spectrum of UFe₂ at 4.2 K and analyzed the spectrum in consideration for the existence of the hyperfine magnetic field. The magnitude of its magnetic splitting at this temperature was $16 \pm 12 \text{ mm s}^{-1}$ [3.2.2.25]. This value was equal to 70 ± 20 T, using $g_{ex} = 0.254$. However, the FWHM at 82 K under the ferromagnetic ordering state was nearly equal to the natural line-width, $31.8 \pm 3.4 \text{ mm s}^{-1}$. The hyperfine magnetic field at ⁵⁷Fe nucleus in UFe₂ has been observed from the ⁵⁷Fe Mössbauer study of UFe₂ as shown in Fig. 3.2.2.2. The hyperfine field of UFe₂ was almost saturated in the range of these temperatures. These results suggest that the hyperfine magnetic field at ²³⁸U is saturated at 82 K and 5.5 K if the hyperfine magnetic field exists.

The FWHM at 5.5 K was larger than that at 82 K. The temperature dependence of FWHM can be discussed, using the temperature dependence of the recoil-free fraction, whether the hyperfine magnetic field exists or not. Generally speaking, the contribution of spin and orbital moments to the hyperfine magnetic field is different. Therefore, if uranium atoms have the magnetic moments and its spin and orbital moments were coupled antiparallelly, the hyperfine magnetic field is expected to be observed at ²³⁸U nucleus. Since the FWHM at 82 K was equal to the natural line width of the ²³⁸U Mössbauer effect, the result at 82 K shows that no hyperfine magnetic field exist at uranium nucleus. These results indicate that the magnetic moment of uranium atoms in UFe₂ was not canceled out, but that the uranium atoms in UFe₂ have no magnetic moment even in the ferrromagnetic ordered state.

In the ⁵⁷Fe Mössbauer measurement, the Mössbauer effect of the sample in the longitudinally applied magnetic field was also investigated. Figure 3.2.2.10 shows the ⁵⁷Fe Mössbauer spectra at 4.5 K under the applied field up to 7 T. The obtained spectra up to 4 T were narrower as an increase of the magnitude of the applied field. The spectra obtained under the applied field above 4 T were broadened as an increase of the magnitude of the applied field. Generally, the sign of the hyperfine magnetic field due to the magnetic ordering of the probe atoms themselves is minus because of the dominant contribution of the core-polarization. On the contrary, the sign of the field direction. These results indicate that the sign of the hyperfine magnetic field obtained in 0 T is minus. Therefore, the observed hyperfine magnetic field at ⁵⁷Fe nucleus is

mainly caused by the magnetic ordering of iron atoms, and not by transferred hyperfine field from the uranium atoms.

Finally, the result of the conversion electron Mossbauer spectroscopy (CEMS) of UFe₂ is shown in Fig. 3.2.2.11. In CEMS, the spectra are obtained by counting the conversion electron during the de-excitation of the Mössbauer resonance. According to the results from the transmission Mössbauer spectra as shown in Fig. 3.2.2.2, the principal axes of the electric field gradient at ⁵⁷Fe nucleus are in the direction of [111]. The CEMS of UFe₂ has been performed with the single crystal sample which is cut perpendicularly to the <111> direction.

The obtained spectrum seems to be a symmetric doublet. The Mössbauer spectrum of the single crystal is generally expected to be observed as an asymmetric pattern whose intensity-ratio is 1:3 when the principal axis and incident Mössbauer gamma-ray are parallel. In UFe₂, the analyses of the spectra below Curie temperature revealed that the sign of the electric field gradient was minus. In addition, the angles between the incident Mössbauer gamma-ray and the principal axis of the electric field gradient are parallel in Fe(1) site and magic angle in Fe(2) site, respectively. The components of Fe(2) are expected to show the symmetric doublet as shown in Fig. 3.2.2.2 of the spectrum of the powdered UFe₂ at room temperature. The only component of Fe(1) is expected to show the asymmetric doublet when the incident Mössbauer gamma-ray is parallel to the principal axis. The expected intensity-ratio is thus 9:7 as velocity increases. However, the obtained spectrum is symmetric so that the existence of the other component was considered in the spectrum-analysis.

U-Fe intermetallic compounds are easy to be oxidized. Generally speaking, CEMS is sensitive to the surface of the samples because the maximum struggling range of the conversion electron is about 100 nm. In uranium compounds, this range should be shorter than 100 nm because the atomic number of the uranium atom is quite large. Accordingly, the obtained spectrum was analyzed with two components; one is the component of pure UFe₂, and the other is thought to be that of oxidized UFe₂ whose isomer shift value is near 0 mm s⁻¹ that has a broad FWHM. When the component of oxidized one was taken into account of, the other components of CEMS correspond to that of the transmission spectra in the ferromagnetic state in the view-point of the sign of the quadrupole splitting.

3. 2. 2. 4. Conclusion

The isomer shift value at room temperature, - 0.21 mm s⁻¹ indicates that the 3*d*-electrons of the ion atoms and 5*f*-electrons of the uranium atoms are hybridized very well with each other. The results from the Mössbauer thermal scan method by using the ⁵⁷Fe Mössbauer effect shows that the Curie temperature is 167 K. The spectra blow the Curie temperature consists of two components. The magnitudes of the hyperfine magnetic field are 3.1 T at Fe(1) and 4.1 T at Fe(2), respectively. The obtained hyperfine coupling constants are 5.3 T / μ_B at Fe(1) and 6.9 T / μ_B at Fe(2), and smaller than that of α -Fe, 15 T / μ_B . These values also indicate that the 3*d*-electrons and 5*f*-electrons are hybridized. The results from the ²³⁸U Mössbauer measurement indicate that the uranium atoms in UFe₂ have no magnetic moments because no hyperfine magnetic field exists at the ²³⁸U nucleus.



70



Velocity, $v / \text{mm s}^{-1}$

Fig. 3.2.2.2. ⁵⁷Fe Mössbauer spectra of UFe₂ at various temperatures. 71









Fig. 3.2.2.4. Temperature dependence of (a) isomer shift (I. S.) and (b) quadrupole splitting (Q. S.) in paramagnetic state.











Fig. 3.2.2.6. The obtained and calculated spectra of UFe₂ below Curie temperature.



Fig. 3.2.2.7. Temperature dependence of the averaged hyperfine magnetic field at 57 Fe nucleus in UFe₂.

Fig. 3.2.2.8. Temperatre dependence of the absorption area. Solid lines are the theoretical curves using the Debye model whose Debye temperatures are 250 K at paramagnetic state and 300 K at ferromagnetic state, respectively.



Velocity, $v / \text{mm s}^{-1}$





79

Fig. 3.2.2.10. ⁵⁷Fe Mössbauer spectra of UFe₂ at 4.5 K under the longitudinally applied field up to 7 T.





(b) ⁵⁷Fe transmission Mössbauer spectrum of UFe₂ at room temperature.

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3. 2. 3. ⁵⁷Fe Mössbauer Spectroscopy of U₆Fe

3. 2. 3. 1. Introduction

 U_6X (X = Mn, Fe, Co and Ni) compounds are superconductors. Their transition temperatures, T_c , are in the range from 3.8 K in U_6Fe to 0.5 K in U_6Ni . The X dependence of T_c is similar to that of Slater-Pauling curve for saturation magnetization of the 3*d*-metal alloys [3.2.3.1]. However, every U_6X compounds does not have the magnetic moment but are Pauli-paramagnetic. U_6Fe has higher upper critical field, H_{c2} , than the other uranium-based superconductor whose superconductivity and magnetic properties are anisotropic [3.2.3.2]. It is 13.1 T along the [001] direction and 10.4 T along [110]. The electronic specific heat coefficient is 150 mJ / K². This result indicates the 5*f*-electrons of uranium atoms are well hybridized with the 3*d*-electrons of iron atoms. The crystal structure of U_6Fe is shown in Fig. 3.2.3.1. The arrangement of uranium atoms is a layered-like structure, whereas that of iron atoms is a dimmer-like structure.

The ⁵⁷Fe Mössbauer studies of U₆Fe were performed previously by Blow [3.2.3.3] and Kimball et al.[3.2.3.4]. In the previous experiments, the spectra obtained were doublet pattern with quadrupole splitting above 4.3 K which is observed in the paramagnetic state. However, the sign of the electric field gradient have not been determined yet. In this work, the ⁵⁷Fe Mössbauer spectroscopy under the applied field up to 7 T has been performed in order to determine the sign of the electric field gradient of the spectra. The conversion electron Mössbauer spectroscopy (CEMS) of U₆Fe has also been performed by using a single crystal.

3.2.3.2. Experimental Procedure

The sample is a single crystal grown by the Czochralski pulling method [3.2.3.2]. It was powdered in argon gas atmosphere and sealed into the polyethylenecovered sample holder for the transmission measurement. Since the mass absorption coefficient of uranium atoms is large and the natural abundance of ⁵⁷Fe is only 2 %, the sample used is enriched by ⁵⁷Fe up to 50 %. The measurement under the longitudinally applied field has been performed by using a cryostat with a superconducting magnet as shown in Fig. 2.3.3. The CEMS has been performed at room temperature, using a single crystal sample.

The gamma-ray source used is ⁵⁷Co in Rh. The Doppler velocity calibration is referred to α -Fe spectrum at room temperature.

3. 2. 3. 3. Results and Discussion

Figure 3.2.3.2 shows the ⁵⁷Fe Mössbauer spectra at various temperatures. All the spectra obtained are symmetric doublets. The isomer shift value and the magnitude of the quadrupole splitting at room temperature are - 0.36 mm s⁻¹ and 0.76 mm s⁻¹, respectively. These results agree with the previous results within the experimental error [3.2.3.3-4]. The isomer shift value obtained shows hybridization between 5f-electrons of uranium atoms and 3d-electrons of iron atoms.

The magnitude of the quadrupole splitting is bigger than that of UFe₂ which is the same as the intermetallics in the U-Fe system. In crystal structure of U₆Fe as shown in Fig. 3.2.3.1, the atomic arrangement around iron site is not a cubic symmetry. Since the strong hybridization between 5f- and 3d-electrons are well-known in this compound from the specific heat measurements, the 3d-electrons are thought to be occupied with the conduction bands of this intermetallic compound [3.2.3.5-7]. The origin of the electric field gradient is thought to be based on its crystal structure. However, the isomer shift value suggests the iron atoms are not S-state ion like an high spin state of Fe^{3+} , so that the electric field gradient can result from the 3*d*-electrons themselves at iron sites. The isomer shift value of - 0.36 mm s⁻¹ at room temperature is also suggested that the 3d-electrons of iron atoms in U₆Fe are well hybridized with the 5f-electrons of the uranium atoms like UFe. Therefore, the electric field gradient is caused by the 3d-orbital which has the existence probability near the Fermi surface.

The electric field gradient based on the orbital of the probe atoms themselves is proportionate to the expectation values of r^3 , $\langle r^3 \rangle$. In a consideration for the hybridization between 5f- and 3d-electrons, the orbital of the 3d-electrons is thought to be wide-spread. The value of $\langle r^3 \rangle$ is thus thought to be smaller in this case than in the other case such as the alloys of iron and another element. These results show the larger quadrupole splitting was based on the specified configuration of 3d-electrons. In order to determine the configuration of 3d orbital, both of the sign of the quadrupole splitting and the anisotropy parameter, η , which is defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$ are necessary. Determination of the configuration is discussed below.

The temperature dependence of the Mössbauer parameters is discussed. Figure 3.2.3.3 shows the temperature dependence of the isomer shift, quadrupole splitting and the full-width at half maximum (FWHM). Temperature dependence of the isomer shift increases with a decrease of the temperature. It tends to be saturated at lower temperature and changes continuously. These results can be intersted by the temperature dependence of the second order Doppler shift.

Kimball et al. reported that the temperature dependence of the second order Doppler shift obeys the Debye model where the Debye temperature of U6Fe is 451 K above 100 K. They insisted a deviation from Debye model below 100 K indicated either a softening in the iron vibrational modes, or a decrease in s character in the conduction electron concentration due to the increased occupation of d state in iron. The results obtained in this work did not have the anomaly around 100 K.

Moreover, temperature dependence of the absorption area has been obtained, which can be discussed with the Debye model. Figure 3.2.3.4 shows the temperature dependence of the absorption area of the 57Fe Mössbauer spectra obtained from U6Fe. Temperature dependence of the absorption area was fitted by a theoretical curve where the Debye temperature is 300 K. In this work, no anomalies can be observed

The magnitudes of quadrupole splitting increases slightly as a decrease of the temperature. Temperature dependence of FWHM has a broad peak around 150 K. Kimball et al. reported the obtained spectra of U₆Fe are asymmetric doublet patterns with the line at higher energy having larger intensity [3.2.3.4]. The spectra obtained in this work are symmetric doublet patterns. As written below, the difference of the intensities between higher and lower energy is thought to be caused by the impurity component because U-Fe intermetallic compounds are easy to be oxidized. Temperature dependence of the quadrupole splitting does not seem to have any anomalies in this work as Kimball et al reported.

In order to determine the 3d-electrons from which the electric field gradient results in U₆Fe, the ⁵⁷Fe Mössbauer spectroscopy under the applied field up to 7 T has been performed at 4.5 K. The Mössbauer spectroscopy has been performed under the

transmission geometry. The applied magnetic field is parallel to the Mössbauer gamma-ray, using a cryostat with superconducting magnet as shown in Fig. 2.3.3.

Figure 3.2.3.5 shows the ⁵⁷Fe Mössbauer spectra obtained from U₆Fe under the applied magnetic field. The magnitude of the hyperfine field is equal to the applied magnetic field for all of the spectra obtained. These results indicate no induced magnetic field exists at ⁵⁷Fe nuclei and U₆Fe is a Pauli-paramagnetic substance. The obtained sign of the quadrupole splitting is determined to be minus and the asymetry parameter is $\eta = 0$. Table 2.2.1 shows the relationships between the 3*d* orbital and the sign of the electric field gradient and the asymmetry parameter at ⁵⁷Fe nuclei. The appropriate orbital is only $3d_{32^2-r^2}$ which corresponds to both the sign of the field gradient and the asymmetry between the $3d_{32^2-r^2}$ symmetry. These results show that 3*d*-electron near the Fermi surface has a $3d_{32^2-r^2}$ symmetry. These results imply that the 3d-electrons at $3d_{32^2-r^2}$ orbital have an appreciable density at the Fermi surface.

It is also possible to determine the sign of the electric field gradient and asymmtry parameter using a single crystal sample. In this work, the conversion electron Mössbauer spectroscopy of U₆Fe single crystal has been performed in order to verify the results under the applied field. Figure 3.2.3.6 shows the conversion electron Mössbauer spectrum of U₆Fe at room temperature. As written above, the sign of the quadrupole splitting is minus and the asymmetry parameter is nearly equal to zero. The results expected ideally which are consistent to the results obtained under the applied field were the ratio of the doublet peak intensity at lower to higher velocity is 3:1. The spectrum obtained seems to be asymmetric doublet with the line at higher energy having broad FWHM and the greater intensity. These results agreed with the one reported by Kimball et al. within the experimental error [3.2.3.4]. The obtained spectrum is more unclear and weaker than the transmission spectra at room temperature, so that it is difficult to determine the exact Mössbauer parameters. Generally speaking, conversion electron Mössbauer spectroscopy is sensitive to the physical and chemical properties of the surface in the samples because of the short struggling range of the conversion electrons. U-Fe intermetallic compounds are also easy to be oxidized. When the component at 0 mm s⁻¹ with broad single line exists, the results of the

spectrum-analysis of CEMS agreed with the results obtained under the applied field. This broad component is thought to be that of the oxidized surface of U_6Fe single crystal.

3.2.3.4. Conclusion

The obtained isomer shift and the quadrupole splitting at room temperature are - 0.36 mm s⁻¹ and 0.76 mm s⁻¹, respectively. The isomer shift value shows the 3*d*-electrons of iron atoms are hybridized with 5*f*-electrons of uranium atoms. The larger quadrupole splitting is thought to be mainly based on the orbital of 3*d*-electrons themselves. From the results obtained under the applied magnetic field, the sign of the electric field gradient is minus and the asymmetry parameter is zero. These results show the orbital of $3d_{3z^2-r^2}$ has the density near the Fermi surface.



Fig. 3.2.3.1. Crystal structure of U_6 Fe.

Fig. 3.2.3.2. ⁵⁷Fe Mössbauer spectra of U_6 Fe at varios temperatures.

















at room temperature. (b) ⁵⁷Fe transmission Mössbauer spectrum of U_6 Fe at room temperature.

93

Fig. 3.2.3.6. (a) 57 Fe conversion electron Mössbauer spectrum of U₆Fe

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3. 2. 4. Conclusion

By means of the ⁵⁷Fe and the ²³⁸U Mössbauer spectroscopy, the physical properties of U-Fe intermetallic compounds have been investigated.

The isomer shift values obtained from the ⁵⁷Fe Mössbauer measurements are - 0.21 mm s⁻¹ of UFe₂ and - 0.36 mm s⁻¹ of U₆Fe relative to metallic iron. These values indicate the 3*d*-electrons of iron atoms are well hybridized with the 5*f*-electrons in U-Fe intermetallic compounds. In UFe₂, the hybridization between 3*d*- and 5*f*-electrons are suggested from the small hyperfine coupling constants whose magnitude are from 5.3 μ_B / T to 6.9 μ_B / T in the ferromagnetic ordered state. In U₆Fe, it is revealed by the ⁵⁷Fe Mössbauer spectroscopy in the applied field that the large quadrupole splitting obtained is caused by the electric field gradient due to $3d_{3x^2-x^2}$ electrons.

The results of the ²³⁸U Mössbauer measurements of UFe₂ show no hyperfine magneticfield exists at the ²³⁸U nucleus. This result suggests that the uranium atoms in UFe₂ have no magnetic moments although the spin and the orbital moments of uranium atoms were proposed to have an antiparallel coupling by the results from the neutron scattering and the magnetic Compton scattering experiments.

3.3. Itinerant Ferromagnetic Compound UGe₂

3. 3. 1. Intoroduction

In the U-Ge system, several intermetallic compounds have been formed such as UGe, U₃Ge₄, U₅Ge₃ and U₇Ge [3.3.1]. The ferromagnetic compounds in this system are UGe, and U₃Ge₄ [3.3.2, 3]. UGe, is known as a heavy fermion compound and shows highly anisotropic ferromagnetism with the Curie temperature of 52 K [3.3.3]. A saturated magnetic moment is 1.43 $\mu_{\rm B}$ / U. The crystal structure has been recently determined to be orthorhombic by means of the X-ray precession and neutron powder diffraction methods [3.3.4].

Experimental studies were extensively performed to clarify magnetic and electrical properties of UGe₂ [3.3.1, 3.3.5-10], although the local electronic state of a uranium atom has not been investigated yet. The 238U Mössbauer spectroscopy is one of the useful tools to investigate the local electronic state of the uranium atom which plays an important role of the magnetic properties in UGe2. We have performed the ²³⁸U Mössbauer spectroscopy of UGe₂ in order to investigate its magnetic property and local electronic state.

3. 3. 2. Experimental Procedure

The ²³⁸U Mössbauer spectroscopy was performed in the temperature range of 100 K to 5.3 K, using a powdered sample packed in a sample holder made of aluminum. The area density of the sample is 109.59 mg cm⁻², which is identical to 60.91 mg U cm⁻². The ²³⁸U Mössbauer measurements were performed in the transmission geometry. A disk-shaped ²⁴²PuO₂ source, which contains 99.99 % ²⁴²Pu, was used as the gamma-ray source. The Doppler velocity was calibrated by the laser calibrator, and the zero isomer shift was adopted as the isomer shift value of ²³⁸U in PuO₂.

3. 3. 3. Results and Discussion

Figure 3.3.1 shows typical ²³⁸U Mössbauer spectra measured at various temperatures between 100 K and 5.3 K. All of the spectra can be analyzed by the symmetric absorption pattern. When the electric quadrupole interaction is sufficiently large, an expected ²³⁸U Mössbauer spectrum becomes asymmetric as In an absorption spectrum of UO₂(NO₃)₂•6H₂O [3.3.11].

Here, the Hamiltonian of the electric quadrupole interaction is represented by

$$H_{\mathcal{Q}} = \frac{e^2 q Q}{4I(2I-1)} \left\{ 3M^2 - I(I+1) + \frac{\eta}{2} \left(\hat{I}_-^2 + \hat{I}_-^2 \right) \right\}, \qquad (3.3.1)$$

where q is the maximum component V_{zz} of the electric field gradient at the nucleus. O the quadrupole moment of the probe nucleus, I the nuclear spin, M the z component of Iand η an asymmetry parameter defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$. When the axially symmetric electric field gradient exists at the ²³⁸U nucleus, the excited state of the ²³⁸U nucleus is split into three levels; $e^2 qQ/4$, $-e^2 qQ/8$ and, $-e^2 qQ/4$ which depends on M^2 . The origin of the electric field gradient is generally related to the local electronic state at the probe atom.

Two fundamental mechanisms are well known for the origin of the field gradient. One is the field gradient based on the arrangement around the probe atoms, and the second is that of the electron orbitals of the probe atom, namely, ²³⁸U itself in UGe₂. Since the crystal structure of UGe₂ is anisotropic and does not have cubic symmetry around uranium atoms as shown in Fig. 3.3.2, the electric field gradient based on 5f electrons at the ²³⁸U nucleus can also be expected to exist in UGe,

The quadrupole splitting at the ²³⁸U nucleus was, however, not observed within an experimental error even in the paramagnetic state. The reason is as follows. The existence of the quadrupole interaction has been recently confirmed by the ²³⁵U NMR measurement for an antiferromagnetic compound UO₂ [3.3.12]. The spin-echo spectrum of ²³⁵U NMR shows seven resonance lines with a line-width of about 1 MHz in the antiferromagnetic state and indicates the existence of the electric quadrupole interaction with $|e^2 q Q(3 \cos^2 \theta - 1)/h| = 392 \pm 11$ MHz. The electric field gradient of 5f electrons in the Γ_5 triplet state might be an origin of the quadrupole interaction observed in NMR. This magnitude of the quadrupole interaction corresponds to $1.70 \pm$ 0.04 mm s⁻¹ in the ²³⁸U Mössbauer spectrum. The quadrupole splitting of ²³⁸U in UO₂ is too small to be detected in the Mössbauer spectrum because the natural line-width of

the ²³⁸U Mössbauer spectrum is 27 mm s⁻¹, which is a few 10 times larger than the observed electric field gradient.

In the magnetically ordered state, the effects of the quadrupole interaction on the Mössbauer spectrum are a little bit complicated. When the hyperfine magnetic field is sufficiently large, the axially symmetric field gradient causes shifts of the magnetically split absorption lines by an amount of $e^2 q Q (3 \cos^2 \theta - 1)/8$, where θ is the angle between the principle axis of the field gradient and the direction of the hyperfine magnetic field which is antiparallel to the direction of the atomic magnetic moment. A maximum value of the shift, which is expected at $\theta = 0$ or π , is $e^2 qQ/4$, which is just half of the splitting observed in the paramagnetic state.

When the quadrupole interaction is comparable or large enough to the magnetic interactions, each nuclear energy levels are no more in the pure state and the expected Mössbauer spectrum shows a broad one based on the mixed hyperfine interaction. However, one can expect an asymmetric spectrum depending on the sign of field gradient, except for the case of $\eta = 1$ where the symmetric spectrum can be expected.

For the present ²³⁸U Mössbauer measurements, the line-width is too large to resolve the small shifts of the absorption lines due to the small quadrupole interaction. However, the existence of the quadrupole interaction can be judged from the asymmetry of the absorption spectrum. Nevertheless, the spectrum observed in the paramagnetic state, for example, at 100 K is symmetric, as shown in Fig. 3.3.1. This result claims that the quadrupole splitting does not exist or its magnitude is smaller than the experimental error.

Moreover, we have to consider the contribution of the electron orbitals to the electric field gradient at the nucleus. The electric field gradient is proportional to the expectation value of $1/r^3$, $\langle r^{-3} \rangle$. The value of $\langle r^{-3} \rangle$ in UGe₂ is expected to be smaller than the one in UO_2 whose 5f electrons are well-known to be localized. The reason is as follows. The temperature dependence of the magnetic susceptibility of UGe₂ follows the Curie-Weiss law above the Curie temperature [3.3.1]. The effective magnetic moment is 3.1 μ_B / U in the paramagnetic state. On the other hand, a saturated moment of 1.43 μ_{B} / U is much smaller than the effective moment. From the experimental results of de Haas-van Alphen effect, photoemission and bremsstrahlung isochromat spectra and the temperature dependence of the electrical resistivity, the 5f electrons in UGe, are considered to be itinerant [3.3.5-7, 3.3.13]. Consequently, the quadrupole splitting in UGe, is more difficult to observe than in UO2.

With decreasing the temperature, especially below the Curie temperature of 52 K, a line broadening is clearly observed in the spectrum, as shown in Fig. 3.3.1. The temperature dependence of full-width at half maximum (FWHM) is shown in Fig. 3.3.3, where the spectra are analyzed by a single Lorentz function. The FWHM values increase steeply below 52 K. Since the Curie temperature of UGe, is 52 K, the increase of FWHM is due to the appearance of the hyperfine magnetic field at the uranium nucleus in the ferromagnetic state. The Hamiltonian of the magnetic dipole interaction or the Zeeman effect for the nuclear spin is represented by $H_{z} = g_{ex} \mu_{N} H M$,

where g_{ex} is the g-factor of the first excited state of ²³⁸U, μ_N the nuclear magneton, H the local magnetic field or hyperfine magnetic field at the 238 U nucleus and M the z component of the nuclear spin, I. The excited state of the ²³⁸U nucleus has $I = 2^+$ and is split into five levels M by the hyperfine field at the 238 U nucleus, as shown schematically in Fig. 3.3.1. The ²³⁸U Mössbauer effect is thus observed in the E2 transition from $I = 2^{-1}$ to $I = 0^{-1}$ of the ²³⁸U nucleus. The magnetic pattern of the ²³⁸U Mössbauer spectroscopy is, however, observed as a broad single peak which is an unresolved superposition of the Zeeman-split five lines, as discussed previously [3.3.11].

The line-width is related to the recoil-free fraction which depends on the temperature. In the case of the superposed spectrum such as in UGe, at 5.3 K, the usual method of least-square fitting using non-constrained FWHM is known not to give the magnitude of the 'true' hyperfine interaction parameters, as discussed by Shenoy and Ruby [3.3.14]. Namely, the obtained line-width generally tends to be smaller than the true one.

using the value of the line-width obtained at 82 K where UGe, is paramagnetic. The obtained magnetic splitting is $57.0 \pm 3.1 \text{ mm s}^{-1}$ at 5.3 K. The magnitude of the Zeeman splitting is $4g_{ex}\mu_N H = 8.53 \times 10^{-6}$ eV. By using $g_{ex} = 0.254 \pm 0.015 \mu_N$ determined from the ²³⁵U NMR and the ²³⁸U Mössbauer measurements of UO₂ in the antiferromagnetic state, the magnitude of the hyperfine field at the ²³⁸U nucleus is determined as 240 ± 10 T at 5.3 K.

(3.3.2)

In the present case, the spectra in the ferromagnetic state were analyzed by

We will discuss the present results, comparing with those of UO₂. The saturated moments of UGe₂ and UO₂ are known to be 1.43 $\mu_{\rm B}$ / U and 1.78 $\mu_{\rm B}$ / U, respectively [3.3.1, 3.3.15]. The hyperfine field at the ²³⁸U nucleus in UO₂ is 252.3 ± 1 T at 5.4 K [3.3.12]. The hyperfine coupling constants of UGe₂ and UO₂ are thus determined as 160 ± 10 T / $\mu_{\rm B}$ and 142 ± 1 T / $\mu_{\rm B}$, respectively. The contribution to the hyperfine field is due to the total angular momentum J which contains the orbital and spin moments as well as the core polarization. The hyperfine field due to the former is represented by

$$H_{orb} = a_{hf} \langle J \| N \| J \rangle \langle r^{-3} \rangle m_J, \qquad (3.3.4)$$

and to the latter by

$$H_{core} = \frac{8}{3} \pi \mu_B g \sum_{n} \left[\rho_{ns}^{\uparrow}(0) - \rho_{ns}^{\downarrow}(0) \right] , \qquad (3.3.5)$$

respectively, where a_{hf} is a hyperfine coupling constant per atomic units, $\langle J \| N \| J \rangle$ a reduced matrix element, $N = \sum \{ l_i - s_i + 3(r_i \cdot s_i)r_i / r_i^2 \}$, l_i the angular momentum, s_i the spin momentum, m_J the azimuthal number connected with $J_{z_2} \langle r^{-3} \rangle$ the expectation value of $1 / r^3$ for the wave functions of the open shell electrons [3.3.16]. $\rho_{ns}^{\uparrow}(0)$ and $\rho_{ns}^{\downarrow}(0)$ are the contact density of *s*-electrons of the *n*-th shell having spin up and spin down states. The contribution due to the orbital current is thought to be nearly proportional to the magnetic moment at uranium atoms. Moreover, since the 5f electrons of UGe₂ is thought to be itinerant, $\langle r^{-3} \rangle$ of UGe₂ is most likely smaller than that of UO₂ as mentioned above. The contribution of the orbital current to the hyperfine field of UGe₂ might be smaller than that of UO₂. Therefore, the difference of the hyperfine coupling constants between UO₂ and UGe₂ is mainly due to the difference of the contribution of both the orbital current and the core polarization.

The temperature dependence of the hyperfine magnetic field of UGe₂ is shown in Fig. 3.3.4. Its temperature dependence is the same as the one of the static magnetization shown by squares. This result indicates that the hyperfine coupling constant of ²³⁸U in UGe₂ does not depend on the temperature.

3.3.4. Conclusion

The hyperfine field at ²³⁸U nucleus in UGe₂ has been observed below the Curie temperature of 52 K. The magnitude of the hyperfine field is determined as 240 ± 10 T at 5.3 K, which is proportional to the magnetization below the Curie temperature. Therefore, the hyperfine coupling constant of 160 T / μ_B does not depend on the temperature.













atthe ²³⁸U nucleus and the magnetization of UGe₂, shown by solid circles and open squares, respectively.

Fig. 3.3.4. Temperature dependence of the hyperfine field

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3. 4. Heavy Fermion Superconductors, UPd₂Al₃ and URu₂Si₂

3. 4. 1. Introduction

Since a heavy fermion superconductor CeCu₂Si₂ was discovered by F. Steglich et al. [3.4.1.1], the other heavy fermion superconductors, UBe₁₃[3.4.1.2], UPt₃[3.4.1.3], URu₂Si₂[3.4.1.4], UNi₂Al₃[3.4.1.5] and UPd₂Al₃[3.4.1.6], were discovered in uranium The progressive studies clarified that the heavy fermion intermetallics. superconductors were the anisotropic and non-BCS-type superconductor. The common characters of the heavy fermion superconductors are the coexistence or competition of the magnetic ordering and superconductivity in their ground state, and their anisotropic superconductivity.

As for the macroscopic physical properties of heavy fermion superconductors, their temperature dependence of the electrical resistivity and magnetic susceptibility have a broad peak at the characteristic temperature of Kondo effect. Below this temperature, every electrical resistivity shows a metallic behavior. And then, it become zero at the superconducting transition temperature.

resistivity and the magnetic susceptibility is shown in Fig. 3.4.1.1 and Fig. 3.4.1.2 [3.4.1.6-8]. The electrical resistivity and magnetic susceptibility of UPd₂Al₃ have the maximums around 80 K and 30 K, respectively. Those of URu₂Si, have the maximums around 100 K and 50 K, respectively. Both of the maximums of electric resistivity and magnetic susceptibility is thought to be characteristics of the Kondo effect. The origins of the difference in those temperature dependence observed for the uranium-based heavy fermion superconductors, UPd₂Al₃, URu₂Si₂ and so on, have not yet been understood.

On the other hand, the results from microscopic studies are as follows: The NMR studies revealed CeCu₂Si₂[3.4.1.9] and UPd₂Al₃[3.4.1.10-15] were an even parity and d-wave type superconductors, and that UPt₃ was an odd parity superconductor [3.4.1.16]. The neutron studies clarified the interplay between their magnetic ordering and superconductivity from the anomalies of the magnetic reflection in the elastic scattering at the superconducting transition temperature [3.4.1.17-24]. Although the ²³⁸U Mössbauer measurement is also the microscopic experiments,

For UPd₂Al₃ and URu₂Si₂, the temperature dependence of the electrical

it has never been performed since the discovery of its Mössbauer effect because of the reason as written in Chapter 1. The motivation of this work is mainly to investigate their magnetic properties by using the ²³⁸U Mössbauer spectroscopy. The ²³⁸U Mössbauer spectroscopy might clarified the local electronic states of 5f-electrons of uranium atoms which attribute to the physical properties of the uranium-based heavy fermion superconductor. In this work, ^{238}U Mössbauer measurements of UPd_2Al_3 and URu_2Si_2 have been performed in order to investigate their magnetic properties and the origin of the appearance of a heavy fermion which plays an important role for the superconductivity.



and electrical resistivity, ρ , of UPd₂Al₃ [3.4.1.6].



Fig. 3.4.1.2. Temperature dependence of (a) the electrical resistivity, ρ , and (b) magnetic susceptibility, χ , of URu₂Si₂ [3.4.1.6-8].

109

Fig. 3.4.1.1. Temperature dependence of the magnetic susceptibility, χ ,



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3. 4. 2. ²³⁸U Mössbauer Spectroscopy of UPd₂Al₃

3. 4. 2. 1. Introduction

A heavy fermion superconductor UPd₂Al₃ has the Néel temperature of 14 K and shows the superconducting ordered state below 2 K [3.4.2.1]. The saturated magnetic moment is $0.85 \mu_B / U$. The electronic specific-heat coefficient is 145 mJ / K². This compound is a typical heavy fermion superconductor whose magnetic ordering coexists with superconductivity. Figure 3.4.2.1. shows the crystal and magnetic structure of UPd₂Al₃. The results of NMR spectroscopy suggest the parity of its superconducting is the *d*-wave type [3.4.2.2-7]. From the report of the results for neutron scattering experiments, the magnetic peak has an anomaly at the onset temperature of its superconducting transition [3.4.2.8-12]. This phenomenon was observed in the other heavy fermion superconductor, UPt₃[3.4.2.13], URu₂Si₂[3.4.2.14] and UNi₂Al₃ [3.4.2.15]. In the neutron inelastic spectrum of UPd₂Al₃, a scattering excitation appears below the transition temperature which is due to the energy gap of its superconductivity. These results suggest that their superconductivity has the relation to their magnetic properties.

On the other hand, the electronic resistivity and magnetic susceptibility measurements have the broader peak at 80 K and 30 K, respectively [3.4.2.1]. The magnetic susceptibility obeyed the Curie-Weiss law above 100 K. The Weiss temperature and magnitude of the effective moment are - 47 K and 3.2 μ_B / U. The metamagnetic transition was observed at 18 T below the Néel temperature [3.4.2.16]. Even above Néel temperature, the metamagnetic transition was observed. It was observed up to the temperature where the magnetic susceptibility has a maximum value [3.4.2.17].

The Mössbauer spectroscopy has been performed in order to investigate the physical properties, mainly magnetic properties of UPd₂Al₃.

3. 4. 2. 2. Experimental Procedure

A single crystal of UPd_2Al_3 was grown by the Czochralski pulling method in a tetra-arc farce and annealed using the solid-state electrotransport method under vacuum of 10^{-10} torr [3.4.2.18]. It was powdered in argon gas atmosphere and sealed into the

sample holder made of aluminum. The gamma-ray source used for the ²³⁸U Mössbauer spectroscopy was a PuO₂ source which contains 99.99 % ²⁴²Pu. The ²³⁸U Mössbauer measurement was performed in a transmission geometry. The Doppler velocity of the gamma-ray source was given with the sinusoidal motion. The Doppler velocity was calibrated with a laser calibrator. The isomer shift of ²³⁸U in PuO₂ was adopted to the zero isomer shift value.

3. 4. 2. 3. Results and Discussion

Figure 3.4.2.2 shows the ²³⁸U Mössbauer spectra obtained from the UPd₂Al₃ specimen at various temperatures. The line-width observed is obviously broad below 10 K and all of the spectra obtained are symmetric. These results show the obtained spectra do not include the quadrupole interaction or its magnitude is too small to be detected by ²³⁸U Mössbauer spectroscopy, as discussed in Section 3.3. Since the Néel temperature of UPd₂Al₃ is 14 K, this line broadening is thought to be due to the appearence of the hyperfine magnetic field with the magnetic ordering. In order to determine the temperature dependence of the Mössbauer parameters in more detail, the results from the analysis of the spectra with a single peak is discussed.

Figure 3.4.2.3 shows the temperature dependence of the full width at half maximum (FWHM) and resonance absorption area of the ²³⁸U Mössbauer spectra where the spectra are analyzed with a single Lorentzian function. The absorption area increases monotonously with decreasing the temperature. The results obtained are fitted by the Debye model as shown in Fig. 3.4.2.3.

The values of FWHM do not show simple temperature dependence. As written above, the obvious broadening below Néel temperature is thought to be caused by the appearance of the hyperfine magnetic field. Moreover, the temperature dependence of FWHM seems to have the maximum around 50 K. Firstly, the temperature dependence around 50 K is discussed.

The thickness of the used source was about 50 μ m and the fractional abundance of ²³⁸U was adequately small because of the very long half-life of ²⁴²Pu, 3.76 \times 10⁵ years. Since the effective thickness of ²³⁸U Mössbauer resonance is small, the self-absorption in the source can be neglected. As shown in Eq.(2.1.17), transmission spectrum by the combination of gamma-ray source and the absorber is thus expressed

by

$$p(v) = N_0 + \int_{-\infty}^{+\infty} \frac{f_s \Gamma_s}{2\pi} \frac{1}{(E - E_0) + (\Gamma_s / 2)^2} \exp\left[-\frac{t_{eff} (\Gamma_A / 2)^2}{(E - E_0)^2 + (\Gamma_A / 2)^2}\right] dE$$
(3.4.2.1)

Since the recoil-free fraction f depends on the temperature and is proportionate to the strength of the resonant absorption, the temperature dependence of the observed FWHM in the single peak spectrum, which include neither magnetic splitting nor quadrupole splitting, depends on the change in recoil-free fraction [3.4.2.19]. FWHM is thus related to the absorption area if the spectra above Néel temperature consist of single peak without any hyperfine interactions. In this case, the temperature dependence of the FWHM observed above Néel temperature must increase monotonously as a decrease of temperature such as that of absorption area from Eq. (3.4.2.1). In fact, temperature dependence of FWHM seems to possess a maximum around 30 K. Therefore, it is not appropriate to analyze each spectrum with a single Lorentazian, but with a magnetic splitting or quadrupole splitting pattern. However, all the spectra observed in UPd₂Al₃ are symmetric patterns so that the quadrupole splitting is treated as the negligibly small contribution to the line broadening as discussed in Section 3.3.

The recoil-free fraction is related to the absorption area. When the effective thickness t_{eff} (= $f_a n_a a_a \sigma_0 t_a$) is small, Eq. (2.1.18) can be abbreviated and the absorption area is given by

$$A = \int \{N_0 - p(v)\} dv \approx A' f_s \times f_A, \qquad (3.4.2.2)$$

where N_0 is the background. The recoil-free fraction is the probability of zero-phonon emission and absorption of the gamma-ray from the lattice and is given by

$$f = \exp\left[\frac{-6E_R}{k\theta_D}\left\{\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\frac{\theta_D}{T}} \frac{xdx}{e^x - 1}\right\}\right],$$
(3.4.2.3)

as written above Eq. (2.1.13). The Debye temperature of ²³⁸U in PuO₂ is determined as 250 K as discussed in Section 3.1. By using this Debye temperature of PuO₂, we determined the Debye temperature of UPd₂Al₃ as 200 ± 25 K by fitting the data of the absorption area with Eq. (3.4.2.3) and the results obtained is shown by the solid line in

Fig. 3.4.2.3.

Since the Néel temperature of UPd_2Al_3 is 14 K, it is difficult to consider the hyperfine magnetic field due to the magnetic ordering exists above Néel temperature. As discussed above, the line-broadening around 30 K must be thought to be caused by some hyperfine interactions.

Since the spectra obtained are symmetric patterns as written above, the linebroadening results from the magnetic hyperfine interaction. Above the Néel temperature of 14 K, UPd₂Al₃ is paramagnetic. Therefore, the hyperfine magnetic field observed around 30 K is thought to be caused by the paramagnetic relaxation phenomenon.

The temperature of 30 K where the magnitude of FWHM has a maximum above Néel temperature, corresponds to the one that the temperature dependence of the magnetic susceptibility has a peak [3.4.2.20]. In the elastic neutron scattering, however, the magnetic ordering was not observed in this temperature range. These results might be explained as follows: A Mössbauer effect can detect phenomena in the time scale more than the life-time of the excited state in the Mössbauer transition. In the ²³⁸U Mössbauer effect, the life-time of the excited state is very short one, 0.21 ns, so that the change of the state can be detected as a static state in several times more than the life time. The temperature with the maximum value of the magnetic susceptibility might mean the line-broadening observed around 30 K is due to paramagnetic relaxation phenomenon. The line broadening observed might be caused by the appearance of the hyperfine magnetic field. The observation of the hyperfine magnetic field around 30 K suggests some magnetic fluctuation exists and the static magnetic ordering does not.

The reason why the observation phenomenon is due to a paramagnetic relaxation is as follows: The Mössbauer spectra observed as relaxation spectra, which are reported in the case of many ²³⁷Np Mössbauer spectra in actinide [3.4.2.21], cannot determine both the relaxation time and the magnitude of the hyperfine magnetic field in this case [3.4.2.22]. It is the reason the exchange energy due to the magnetic interaction and relaxation time between each state have the uncertainty relation each other [3.4.2.23-24]. Moreover, the poor energy resolution of ²³⁸U Mössbauer spectroscopy is prevented from detection of the exact physical value. These results are

thought to indicate the fluctuation of the magnetic interaction in this temperature range, but cannot give the exact relaxation time and magnitude of the hyperfine magnetic fields.

The origin of the line broadening above Néel temperature is discussed. The temperature dependence of the apparent FWHM is the same as that of the magnetic susceptibility, as written above. In the 4*f*-electron systems such as cerium compounds, the maximum of the magnetic susceptibility is explained with the relation to the Kondo effect. In the case of uranium compounds, the maximum of the magnetic susceptibility does not necessarily indicate the direct relation to the Kondo effect, but this phenomenon is characteristic of the Kondo effect. Namely, the temperature where the temperature dependence of the magnetic susceptibility has maximum value is related to the one of the appearance of the heavy fermion which plays an important role of the superconductivity. In another approach, the temperature of this line-broadening corresponds to the upper-limit temperature of the observation of the metamagnetic transition [3.4.2.17]. The temperature where the metamagnetic transition vanishes and the temperature dependence of the magnetic susceptibility has maximum is thought to be related to appearance of the heavy fermion. Therefore, the temperature of 30 K might be related to the appearance of the heavy fermion.

Secondary, the hyperfine magnetic field below the Néel temperature is discussed. Since the magnitude of the magnetic splitting obtained by the spectrumanalysis with the non-constrained FWHM is larger than that of the 'true' magnetic splitting, as written in Section 3.3. The FWHM are related to the absorption area. The temperature dependence of the area ratio does not almost change below 20 K. These results mean that the recoil-free fraction does not change below 20 K. In this temperature, UPd₂Al₃ is paramagnetic. The spectra obtained at 20 K is a single peak spectrum because the apparent FWHM does not almost change between 15 K and 20 K within the experimental error. The spectra below the Néel temperature were thus analyzed with the least-square fit using the value of FWHM at 20 K, 50.0 ± 2.8 mm s⁻¹. The magnitude of the hyperfine magnetic field at 5.1 K is 140 ± 10 T obtained with the spectrum analysis of the constrained FWHM using that of 20 K. Figure 3.4.2.3 shows the temperature dependence of the hyperfine magnetic field of UPd₂Al₃ below the Néel temperature dependence of the hyperfine magnetic field of UPd₂Al₃ below the Néel temperature dependence of the hyperfine magnetic field increases steeply with decreasing temperature. This temperature dependence of the hyperfine magnetic field is same as that of the magnetic moment obtained by the neutron elastic scattering [3.4.2.25]. These results show the hyperfine coupling constant of ²³⁸U nucleus might be constant in UPd₂Al₃. Since the magnitude of the saturated magnetic moment of UPd₂Al₃ at uranium atoms is 0.85 μ_B , that of the hyperfine coupling constant is 160 ± 10 T / μ_B . This result obtained in UPd₂Al₃ is nearly equal to in UGe₂.

3.4.2.4. Conclusion

The results from the ²³⁸U Mössbauer spectroscopy of UPd₂Al₃ indicate the broadened spectra have the magnetic splitting around 50 K and below 14 K. The magnetic splitting around 50 K is thought to be the appearance of the magnetic fluctuation. The temperature where the temperature dependence of FWHM has maximum almost corresponds to the maximum of the magnetic susceptibility and the upper limit temperature of the observation of the metamagnetic transition of UPd₂Al₃. These phenomena are thought to be related to the appearance of the heavy fermion.

The magnetic splitting below 14 K was due to the antiferromagnetic ordered state whose the Néel temperature is 14 K. The magnitude of the hyperfine magnetic field at ²³⁸U in UPd₂Al₃ at 5.1 K is 140 ± 10 T. The hyperfine coupling constant of UPd₂Al₃ is 160 ± 10 T / μ_B and nearly equal to that of UGe₂.







Fig. 3.4.2.2. ²³⁸U Mössbauer spectra of UPd₂Al₃ at various temperatures. 119





Fig. 3.4.2.3. Temperature dependence of the full width at half maximum (FWHM) and absorption area when 238 U Mössbauer spectra of UPd₂Al₃ were analyzed with a single Lorentzian function. The solid line is the theoretical curve using Debye model in which the Debye temperature of PuO_2 and UPd_2Al_3 are 250 K and 225 K, respectively.



Fig. 3.4.2.4. Temperature dependence of the hyperfine field at ²³⁸U

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3. 4. 3. ²³⁸U Mössbauer Spectroscopy of URu₂Si₂

3. 4. 3. 1. Introduction

URu₂Si₂ is known as a heavy fermion superconductor which has the antiferromagnetic order below $T_{\rm N} = 17.5$ K and show the superconductivity below $T_{\rm C} =$ 1.3 K. Its electric specific-heat coefficient and the Debye temperature were determined previously and reported to be 180 mJ / K² mol and 312 K, respectively [3.4.3.2.1]. At the transition temperature of 17.5 K, some anomalies were obviously observed in the electrical resistivity and specific heat measurements, claiming that a spin density wave is formed below T_N like as in Cr [3.4.3.1-4]. The magnetic moment of URu₂Si₂ in the antiferromagnetic state is very small and is reported to be 0.03 μ_B / U [3.4.3.5]. In order to explain this small magnetic moment in the antiferromagnetic state, it has been discussed whether this transition is due to the antiferromagnetic ordering or quadrupole ordering transition which induces the antiferromagnetic ordered state. The crystal and magnetic structures have been determined as shown in Fig. 3.4.3.1.

The uranium atoms in an itinerant ferromagnet UFe, have also been reported to have a small magnetic moment of 0.01 $\mu_{\rm B}$ / U in its magnetic ordered state as written in Section 3.2 [3.4.3.6]. In the case of UFe, it has been proposed that uranium atom's spin and orbital moments cancel each other [3.4.3.6-8]. However, there is no direct evidence to explain the origin of the small moment experimentally. For example, the hyperfine magnetic field at U nuclei in UFe, has not been observed in the ferromagnetic ordered state by using the ²³⁸U Mössbauer spectroscopy as discussed in Section 3.2, although the contribution to the hyperfine magnetic field are different for the orbital current and the core polarization.

The ²³⁸U Mössbauer spectroscopy may enable to know whether the small magnetic moment of URu, Si, is intrinsically small or not, by considering the hyperfine coupling constants for the core polarization and for the orbital current. In this work, the ²³⁸U Mössbauer spectroscopy of URu₂Si₂ has been performed for the first time in order to investigate its magnetic properties and local electronic state of uranium atoms.

3. 4. 3. 2. Experimental Procedure

been performed in the same way of UPd, Al, as follows. A single crystal of URu, Si, was grown by the Czochralski pulling method in a tetra arc furnace and was annealed using a solid-state electrotransport method under the high vacuum of 10⁻¹⁰ Torr [3.4.3.9-10]. It was powdered in argon gas atmosphere and sealed into the sample holder made of aluminum. The gamma-ray source used for the ²³⁸U Mössbauer spectroscopy was a PuO2 source which contains 99.99 % 242Pu. The gamma-ray source was driven with sinusoidal motion. The Doppler velocity was calibrated with a laser calibrator. The zero isomer shift value is adopted to that of ²³⁸U in PuO₂.

3. 4. 3. 3. Results and Discussion

Figure 3.4.3.2 shows ²³⁸U Mössbauer spectra at various temperatures. Each spectrum seems to be a single and symmetric peak pattern. The observation of the symmetric spectra indicates the quadrupole splitting is small enough to be neglected, as discussed in previous sections. The obtained spectra seem to be independent on the temperature. In order to investigate the temperature dependence of the spectra in detail, the spectrum-analysis has been performed in the same way of UPd₂Al₃ as follows.

Figure 3.4.3.3 shows the temperature dependence of the full-width at half maximum (FWHM) and the absorption area of the ²³⁸U Mossbauer spectra where all the spectra were analyzed with a single Lorentzian function. The absorption area increases monotonously with a decrease of the temperature. On the other hand, FWHM does not show the simple temperature dependence like that of the absorption area. The temperature dependence of FWHM has the maximum around 50 K.

As discussed in previous section, the thickness of the source used was thin enough to neglect the self-absorption in the source; in this case, the transmission absorption spectrum is expressed by

$$p(v) = N_0 + \int_{-\infty}^{-\infty} \frac{f_s \Gamma_s}{2\pi} \frac{1}{(E - E_0) + (\Gamma_s / 2)^2} \exp\left[-\frac{t_{eff} (\Gamma_A / 2)^2}{(E - E_0)^2 + (\Gamma_A / 2)^2}\right] dE.$$

The sample preparation and ²³⁸U Mössbauer measurements of URu₂Si₂ have

(3.4.3.1)
The recoil-free fraction f_s , depends on the temperature, and the effective thickness of the absorber, t_{eff} (= $f_a n_a a_a \sigma_0 t_a$) also depends on the temperature because of its including the recoil free fraction of absorber. The observed FWHM thus depends on the recoilfree fraction, that is, the strength of the resonance absorption. Therefore, the temperature dependence of FWHM without any hyperfine interaction may have proportionality to the temperature dependence of the absorption area. Since the observed FWHM's does not show monotonous the increase of FWHM might be due to the temperature induced hyperfine interaction like a slow relaxation of the magnetic fluctuation with a decrease of the temperature, the spectra obtained include the paramagnetic relaxation phenomena. Moreover, since all of the observed spectra are the symmetric pattern, the hyperfine interaction detected by ²³⁸U Mössbauer spectroscopy is mainly the magnetic one as discussed in Section 3.3 and 3.4.2. The temperature dependence of FWHM has a maximum around 50 K and increase a little below 10 K. Therefore, the spectra around 50 K and below 10 K were analyzed with a magnetically split pattern.

The recoil-free fraction is related to the absorption area. When the effective thickness t_{eff} is small, Eq. (2.1.18) can be abbreviated and the absorption area is given by

$$A = \int \{N_0 - p(v)\} dv \approx A' f_s \times f_A, \qquad (3.4.3.2)$$

where N_0 is background. The recoil-free fraction is the probability of zero-phonon emission and absorption in the lattice and given by

$$f = \exp\left[\frac{-6E_R}{k\theta_D}\left\{\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\frac{\theta_D}{T}} \frac{xdx}{e^x - 1}\right\}\right],$$
(3.4.3.3)

as written previously as Eq. (2.1.13). The Debye temperature of ²³⁸U in PuO₂ is determined to be 250 K as discussed in Section 3.1. By using this Debye temperature of PuO₂, we determined the Debye temperature of ²³⁸U in URu₂Si₂ as 225 ± 25 K from fit with Eq. (3.4.2.3) to the data of the absorption area, as shown in Fig. 3.4.2.3. The Debye temperature obtained with the Mössbauer measurements is smaller than the one by the specific heat measurement [3.4.3.1]. The former is the local Debye temperature at uranium atoms, and the latter is the whole lattice of a URu₂Si₂ bulk. The difference between them is thought to depend on whether the Debye temperature was obtained in the local site or not.

Anyhow, the temperature dependence of the absorption area can be interpreted by using a single value of the Debye temperature. This result indicates that the phonon spectrum of URu₂Si₂ does not change in the temperature range between 5.1 K and 200 K. If the quadrupole ordering exist in this temperature range, the softening of the elastic constant can be observed. The elastic constant is generally related to the recoil-free fraction. This phenomenon can thus be observed in the change of the strength of the absorption area. However, since the temperature dependence of the absorption area was described as the only Debye temperature, the quadrupole ordering is not thought to exist in the temperature range where ²³⁸U Mössbauer spectroscopy has been performed.

Since the temperature dependence of the absorption area changes continuously, the behaviors of FWHM around 50 K and below 10 K are thought to be caused by the appearance of the hyperfine magnetic field due to the paramagnetic relaxation. Firstly, the behavior of FWHM around 50 K is discussed.

As written above, the Néel temperature of URu_2Si_2 is 17.5 K. The observed hyperfine magnetic field is thus not related to the magnetic ordering. On the other hand, the temperature dependence of the magnetic susceptibility has a maximum around this temperature [3.4.3.1], the same as UPd_2Al_3 [3.4.3.11]. Its metamagnetic transition was also observed up to this temperature [3.4.3.12]. As discussed above, this phenomenon is the same as the one observed in UPd_2Al_3 around 30 K. Therefore, its behavior around 50 K is also thought to be related to the appearance of the heavy fermion, and to be the common phenomenon for the heavy fermion superconductor.

Secondary, the behavior of FWHM below 10 K is discussed. The results from the temperature dependence of the recoil-free fraction in URu₂Si₂ suggest the quadrupole ordering does not induce antiferromagnetic ordering. The FWHM and absorption area do not change between 10 K and 30 K exceeding the experimental error, but the FWHM increases and the absorption area decreases slightly below 10 K. These results indicate FWHM is broadened intrinsically, and that the decrease of the absorption area might be caused by the spectrum analysis with the substitution of a single Lorentzian function from the magnetic pattern. Since the obtained spectra were symmetric ones, the line broadening below 10 K are thought to be the well overlapped magnetic pattern.

Since the magnetic pattern below 10 K consists of superposed five resonance lines, in spectrum analysis of these spectra the least-square fitting could not be available using non-constrained FWHM [3.4.3.13]. We analyzed the spectra below the Néel temperature, 17.5 K, with the magnetic pattern although the obvious broadened spectra were not observed at 10 K and 15 K. The recoil-free fraction is nearly equal at 10 K and 25 K. URu₂Si₂ is a paramagnetic at 25 K. The spectrum at 25 K is thought to be a single line one because of its symmetry. The spectra below the Néel temperature were thus analyzed by the least-square fit using the value of FWHM at 25 K, 50.6 ± 1.8 mm s⁻¹. The spectrum at 5.2 K has the magnitude of the hyperfine field at ²³⁸U are 90 ± 20 T, using g = 0.25 determined in this work.

Figure 4 shows the temperature dependence of the hyperfine fields obtained for URu₂Si₂. The magnitudes of the hyperfine field at 10 K and 15 K were thought to be comparable to the lower limit of the hyperfine field detected by 238U Mössbauer spectroscopy, because the lower limited value of the hyperfine field in ²³⁸U Mössbauer spectroscopy is about 30 T [3.4.3.14]. The magnitude of the saturated hyperfine field at 0 K is estimated at about 100 ± 30 T.

The obtained values of the hyperfine magnetic field below Néel temperature was extremely large compared with the value which was expected from the magnitude of the magnetic moment of URu₂Si₂, 0.03 $\mu_{\rm B}$. The hyperfine coupling constants of ²³⁸U nuclei obtained in his work are 142 ± 1 T / μ_B in UO₂ and 160 ± 10 T / μ_B in UGe₂ and UPd2Al3, respectively. If the hyperfine coupling constant of URu2Si2 is equal to the other uranium compounds measured in this work, UO2, UGe2 and UPd2Al3, the magnitude of the expected hyperfine magnetic field is between 4 T and 5 T. The lower limited value of the hyperfine magnetic field is about 30 T in ²³⁸U Mössbauer spectroscopy. [3.4.3.13] In the consideration for the lower limited value of the hyperfine field observed with ²³⁸U Mössbauer spectroscopy, such small hyperfine field was not detectable. Therefore, the origin of the observed hyperfine field of URu₂Si₂ must be thought to be different from the other uranium compounds.

Generally the contributions to the magnetic hyperfine field from core polarization and orbital current were different. In non-relativistic theory as shown in Chapter II, the contribution of the orbital current, B_{orb} , is represented by

$$\boldsymbol{B}_{orb} = \boldsymbol{a}_{hf} \left\langle \boldsymbol{J} \| \boldsymbol{N} \| \boldsymbol{J} \right\rangle \left\langle \boldsymbol{r}^{-3} \right\rangle \boldsymbol{m}_{J},$$

where $\langle J \| N \| J \rangle$ is a reduced matrix element angular magnetic momentum, s_i the spin m connected with J_z , $\langle r^{-3} \rangle$ the quantum mech functions of the open shell electrons. B_{orb} is the other hand the core polarization field, B_{core}

$$B_{core} = \frac{8}{3} \pi \mu_B g \sum_{n} \left[\hat{\rho_{ns}}(0) - \hat{\rho_{ns}}(0) \right],$$

where $\rho_{ns}(0)$ or $\rho_{ns}(0)$ are the contact density of s-electrons of the n-th shell having spin up or spin down and S the net spin of the open-shell electrons. Therefore the contribution of the orbital current depends on the quantum number J, approximately.

Although the hyperfine coupling constants of UO₂, UGe₂ and UPd₂Al₃ corresponds to each other, that of URu₂Si₂ is extremely different. This result suggest that the configuration of uranium atoms might be different from that of the other compounds whose hyperfine fields are proportionate to their magnetic moment. In this case, it can be proposed that the contribution of the core polarization or Fermi contact interaction to the hyperfine magnetic field is larger than that of the orbital current. Therefore, the results of ²³⁸U Mössbauer spectroscopy might indicate that the orbital and spin moments of URu, Si, whose magnitude is large enough cancel each other. This result corresponds to the proposal of the band calculation [3.4.3.15], and can explain the anomaly of the electrical resistivity and specific heat measurement at 17.5 K.

3.4.3.4. Conclusion

The results from ²³⁸U Mössbauer spectroscopy of URu₂Si₂ indicate that the obtained broadened spectra have the magnetic splitting around 50 K and below 10 K. The magnetic splitting observed around 100 K might be caused by the appearance of

ent,
$$N = \sum_{n} \{ l_i - s_i + 3(r_i \cdot s_i)r_i / r_i^2 \}$$
, l_i the
momentum, m_j is the azimuthal number
manical average of 1 / r^3 using the wave
is thus proportionate to $\langle r^{-3} \rangle$ and m_j . On
, in non-relativistic theory is given by

the heavy fermions, in the consideration for the results of the metamagnetic transition and magnetic susceptibility measurement.

The magnetic splitting observed below 10 K was due to the antiferromagnetic ordering. The magnitude of the hyperfine field of URu_2Si_2 at 5.2 K is 90 ± 20 T. The hyperfine coupling constant of URu₂Si₂ is thus about 20 times lager than the one of UO₂. The origin of the hyperfine field is thought to be different from that of the other compounds in this work, UO₂, UGe₂ and UPd₂Al₃. The temperature dependence of the absorption area between 5.1 K and 200 K is fitted by the Debye model of the only Debye temperature and cannot show the anomaly at 17.5 K. These result suggests the phase transition at 17.5 K is the simple antiferromagnetic ordering temperature, and the anomalies of the electrical resistivity and specific heat measurement at that temperature are related to the adequate large spin and orbital moments.





Fig. 3.4.3.1. Crystal and Magnetic Structure of URu₂Si₂.









Fig. 3.4.3.3. Temperature dependence of the full width at half maximum (FWHM) and absorption area when 238 U Mössbauer spectra were analyzed with a single Lorentzian function. The Solid line is the theoretical curve using Debye model in which the Debye temperature of PuO₂ and URu₂Si₂ are 250 K and 225 K, respectively.

133

Temperature, T / K





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135

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3. 4. 4. Conclusion

From the results of the ²³⁸U Mössbauer measurements of heavy fermion superconductors, UPd2Al3 and URu2Si2, their physical properties were revealed as follows.

The hyperfine magnetic fields in a paramagnetic state of both UPd₂Al₃ and URu₂Si₂ were observed. It is suggested that the observed hyperfine field is caused by the paramagnetic relaxation at uranium nucleus. They appeared around the temperature where the magnetic susceptibility has a maximum value each other. These temperatures to show the maximum values are agreed also with the upper-limits temperature to show the metamagnetic transition by the externally applied magnetic field. This common phenomenon observed for UPd2Al3 and URu2Si2 is thought to be the characteristic property of the heavy fermion superconductor. This phenomenon is related to the appearance of a heavy fermion which plays an important role for their superconductivity.

In UPd₂Al₃, the hyperfine magnetic field is observed below Néel temperature of 14 K. The magnitude of the hyperfine magnetic field is 140 ± 10 T at 5.1 K. The hyperfine coupling constant obtained for UPd₂Al₃ is 160 ± 10 T which agrees with that of UGen.

In URu₂Si₂, the hyperfine magnetic field is also observed below Néel temperature of 17.5 K, although the magnitude of the saturated magnetic moment is quite small as 0.03 μ_B . The magnitude of the hyperfine magnetic field obtained at 5.2 K is 90 \pm 20 T. The observation of the hyperfine magnetic field is thought to be reflected by the difference of hyperfine coupling constants between the orbital current and the core polarization. This result suggests that the small saturated moment is caused by the antiparallel coupling between the spin and the orbital moments. The spin and the orbital moments are thought to have finite magnitudes, respectively. The obvious anomalies observed in the specific heat and the electrical resistivity measurements of URu₂Si₂ might be explained using this model.

Chapter 4. Conclusion

The ²³⁸U and ⁵⁷Fe Mössbauer measurements have been performed for the uranium intermetallic compounds in order to investigate their local electronic states, mainly their magnetic properties. The materials, which were studied by the Mössbauer effect, are an antiferromagnetic compound of UO₂, itinerant ferromagnetic compounds of UFe₂ and UGe₂, a Pauli-paramagnetic compound showing superconductivity of U₆Fe, and heavy fermion superconductors of UPd2Al3 and URu2Si2.

In order to determine the g-factor of the first excited state of ²³⁸U, ²³⁸U Mössbauer and ²³⁵U NMR measurements have been performed for UO₂. ⁵⁷Fe Mössbauer measurements have been performed for U-Fe intermetallic compounds of UFe₂ and U₆Fe. ²³⁸U Mössbauer measurements have been performed for itinerant ferromagnetic compounds of UFe2 and UGe2, and for heavy fermion superconductors of UPd2Al3 and URu2Si2.

reported except for the theoretical value, which is an important parameter as a coupling constant to determine the hyperfine magnetic field at ²³⁸U nucleus. The hyperfine magnetic field is important to discuss the magnetic properties by using the Mössbauer and NMR measurement. In this work, the ²³⁸U Mössbauer and the ²³⁵U NMR measurements of UO₂ in its antiferromagnetic ordered state have been performed. The magnitude of the hyperfine magnetic field has been already determined as 252.3 ± 0.5 T by the ²³⁵U NMR measurements. The magnitude of the nuclear Zeeman splitting of 238 U Mössbauer spectrum is determined as $(8.85 \pm 0.58) \times 10^{-6}$ eV. From these results, the nuclear magnetic moment of the first excited state of 238 U is determined as 0.254 ± 0.015 µN.

In U-Fe intermetallic compounds, the isomer shift values obtained by the ⁵⁷Fe Mössbauer spectroscopy are smaller than 0 mm s⁻¹ relative to α -Fe at room temperature. These results show the hybridization between 3d- and 5f-electrons exists in UFe2 and $U_{c}Fe$. The hyperfine coupling constant of UFe₂ is much smaller than that of α -Fe. It shows the strong hybridization exists between 3d- and 5f-electrons. The origin of the electric field gradient of ⁵⁷Fe in U₆Fe was determined as the orbital of $3d_{3r^2-r^2}$ electrons from the ⁵⁷Fe Mössbauer measurements under the externally applied field. The results from the ²³⁸U Mössbauer measurements of UFe, show no hyperfine

The nuclear magnetic moment of the first excited state of ²³⁸U has been not yet

Acknowledgment

magnetic field exists at 238 U nucleus. This suggests that the uranium atoms in UFe₂ have no magnetic moments although the spin and orbital moments of uranium atoms were proposed to be coupled antiparallel by the neutron scattering and the magnetic Compton scattering experiments.

The hyperfine magnetic field at 238 U nucleus in the itinerant ferromagnet UGe₂ has been observed below the Curie temperature. The magnitude of the hyperfine magnetic field is determined as 240 ± 10 T at 5.3 K. Temperature dependence of the hyperfine magnetic field is proportionate to the magnetization below the Curie temperature.

In heavy fermion superconductors of UPd₂Al₃ and URu₂Si₂, spectral broadening due to the magnetic fluctuation was observed even in the paramagnetic states. The observed hyperfine fields in both the compounds are caused by the paramagnetic relaxation at uranium atoms. They appeared around the temperature where the temperature dependence of the magnetic susceptibility has a maximum value. In consideration for the temperature range of the observation of the metamagnetic transition, the common phenomena in UPd₂Al₃ and URu₂Si₂ are thought to be related to the appearance of a heavy fermion which plays an important role for their superconductivity.

In UPd₂Al₃, the hyperfine magnetic field is observed below Néel temperature of 14 K. The magnitude of the hyperfine magnetic field at 5.1 K is 140 ± 10 T. Even in URu₂Si₂, the hyperfine magnetic field is also observed below Néel temperature, 17.5 K, although the magnitude of the saturated magnetic moment is quite small as 0.03 μ_{B} . The magnitude of the hyperfine magnetic field at 5.2 K is 90 \pm 20 T. This result suggests that the small net moment is caused by the antiparallel coupling between the spin and orbital moments whose magnitudes are finite. The obvious anomalies observed in the specific heat and electrical resistivity measurements for URu₂Si₂ might be explained by using this model.

In this work, the obtained hyperfine coupling constants are $142 \pm 1 \text{ T} / \mu_B$ of UO₂ and $160 \pm 10 \text{ T} / \mu_B$ of UGe₂ and UPd₂Al₃. As for these compounds except for UFe₂ and URu₂Si₂, the magnitude of the hyperfine magnetic field at ²³⁸U nucleus is proportionate to the magnetic moment at a uranium atom.

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List of Publications

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