1. 主論文

Ferroquadrupolar ordering in UCu₂Sn
(UCu₂Snにおける強四重極子秩序)

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2. 公表論文

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(4) Elastic quantum oscillation of LuB₁₂
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主論文
Abstract

The ternary uranium compound UCu₂Sn with a hexagonal ZrPt₂Al-type structure shows a phase transition at 16 K. We reported previously that huge lattice-softening is accompanied by the phase transition, which originates from ferroquadrupolar ordering of the ground state non-Kramers doublet Γ₅. However, the electronic entropy in UCu₂Sn was not reproduced by the entropy calculated from that CEF level scheme. We measured the elastic modulus $C_{66}$ in the magnetic field parallel to [100], [001] and [110] by the phase-comparison type pulse-echo method and made out the $H - T$ phase diagram of UCu₂Sn. So, we optimized the CEF parameters so as to reproduce the data of entropy, magnetic susceptibility, elastic moduli and $C_{66}$ in the magnetic field parallel to [100], [001] and [110]. The proposed level scheme is the ground state doublet Γ₅, the first excited state Γ₄ at 109 K and · · ·. The $H - T$ phase diagram is well reproduced. A macroscopic strain, which is expected to emerge spontaneously, was not detected by powder X-ray diffraction in the temperature range between 4.2 and 300 K. To search the spontaneous strain, we have manufactured the capacitance cell and carried out thermal expansion measurements on a single-crystalline sample along the $a$, $b$ and $c$ axes using a capacitance technique with the resolution of $10^{-8}$. We found the spontaneous $\varepsilon_{xx} - \varepsilon_{yy}$ strain which couples to the ground state doublet Γ₅. The effect of uniaxial pressure along the $a$, $b$ and $c$ axes on the transition temperature is also discussed.
Chapter 1

Introduction

1.1 Orbital flexibility

The electron on each orbit moves in an electric charge distribution depended on the orbit. A wave function of $s$, $p$, $d$ and $f$ orbits are shown in Fig. 1. $s$ orbit which is a orbital angular momentum $L = 0$ is expressed as scalar, that is the monopole. $p$ orbit which is $L = 1$ is expressed as vector, that is the dipole, and $d$ orbit which is $L = 2$ is expressed as second-order tensor, that is the quadrupole. $f$ orbit which is $L = 3$ is expressed as third-order tensor, that is the octopole. The orbit which has a multipole higher than a quadrupole is $d$ and $f$ orbits. A symmetry of electron on the orbit is lowered by a crystal electric field (CEF) from other ligands depended on the crystal structure. In $f$ electron systems, few high symmetry compounds, such as a cubic, have an octopole. In a hexagonal symmetry, thereto, some compounds have a quadrupole at the highest. Multipoles which have such an electric charge distribution arranged in parallel and anti-parallel with each other are called as ferromultipolar and anti-ferromultipolar ordering. In ferroquadrupolar ordering, quadrupole couples to strain which is the second-order tensor and the crystal symmetry lowers.

A flexibility of an electric charge and a spin, which are related to the electric conduction and the magnetism for instance, respectively, are considered mainly so far in solid state properties. Recently, a orbital flexibility is attracted in addition to the electric charge flexibility and the spin flexibility. Extensive searches have been carried out for the interaction between the spin flexibility and the orbital flexibility and among the orbital flexibility. In $d$ electron systems, many compounds, such as a
perovskite-type Mn oxides, are reported to show the order of orbital flexibility. The perovskite-type Mn oxides have been applied to a magnetic device by using a colossal magnetoresistance derived from the orbital flexibility. The orbital angular momentum $L$ is quenched in the $d$ electron systems which have the itinerant property. CEF effect is relatively stronger than a spin-orbital interaction. The Jahn-Teller interaction which is a interaction between a strain and multipole is mainly affected to order in $d$ electron systems. In $4f$ electron systems, many compounds, such as CeB$_6$, are reported to show the order of orbital flexibility [1]. In case of a localized $f$ electron state in $4f$ electron systems, the total angular momentum $J$ is good quantum number according to the spin-orbit interaction which is relatively stronger than CEF. The multipole-multipole interaction is mainly affected to order in $4f$ electron systems. In $5f$ electron systems, a few compounds, including NpO$_2$ [2], UPd$_3$ [3], URu$_2$Si$_2$ [4], UNiSn [5] and UCu$_2$Sn [6], are reported to show the multipolar ordering. $5f$ electrons have an intermediate property between the strongly localized property of $4f$ electrons and the itinerant property of $d$ electrons. Shown in Fig. 2 [7], $5f$ electrons mainly exist in the inside of $6s$ and $6p$ orbits as for spatial spread of the U wave function. However, $5f$ electrons have a certain probability of existence also in the outside of these orbits. Studies of the multipolar ordering in $5f$ electron systems which connect between $d$ and $4f$ electron systems are useful to an understanding of the multipolar ordering as whole the strongly correlated electron system.

1.2 UCu$_2$Sn

The ternary uranium compound UCu$_2$Sn has a hexagonal ZrPt$_2$Al-type structure (space group $P6_3/mmc$) shown in Fig. 3. U, Cu and Sn atoms are located in $(1/3, 2/3, 1/4)$, $(1/3, 2/3, 0.58)$ and $(0, 0, 0)$ atomic site, respectively. Lattice parameters are $a = 4.457$ Å and $c = 8.713$ Å at room temperature. All constituent atoms are stacked in layers perpendicular to the hexagonal $c$-axis with a sequence of $\cdots$Sn, Cu, U and Cu$\cdots$. U atoms in UCu$_2$Sn which have a single U site form a triangular lattice. A distance between U layer and Cu layers of upper and lower sides is unequal though a distance between U layer and Sn layers is equivalent. The
nearest interatomic distance between U and U, Cu and Sn are $d_{u-u} = 4.46 \, \text{Å}$, $d_{u-cu} = 2.87 \, \text{Å}$ and $d_{u-sn} = 3.37 \, \text{Å}$, respectively [8]. It is thought that an influence by the overlap between $5f$ electron wave functions of U is small since $d_{u-u} >$ Hill limit [9].

Takabatake et al. found that UCu$_2$Sn underwent a phase transition around 16 K [10]. Figure 4 shows the temperature dependence of specific heat for instance. At first, the transition was considered as an antiferromagnetic ordering because cusp-like behavior was seen at 16 K in the magnetic susceptibility shown in Fig.5 and spin-flop-like change in the magnetization curve was also observed at 23.5 T in the ordered state shown in Fig.6 [11]. As for the electrical resistivity shown in Fig. 7, a rapid increase below 16 K was considered as an influence caused by development of the superzone gap [11]. However, the transition was estimated to be a non-magnetic one since Mössbauer [12] and NMR [13] (Fig. 8) spectroscopies inferred the absence of a hyperfine field at Sn and Cu sites and neutron diffraction detected no magnetic reflection [11] in the ordered state. In Muon Spin Resonance (μSR) measurement, furthermore, no change was detected in muon spin relaxation between above and below 16 K [14].

We estimated a entropy derived from electrons in UCu$_2$Sn, which subtracted the specific heat caused by a lattice contribution of reference compound ThCu$_2$Sn from the data of UCu$_2$Sn, shown by solid circles in inset of Fig. 4. The electronic entropy in UCu$_2$Sn is about $R \ln 2$ at 16 K, where $R$ is gas constant. The ground state of CEF in non-ordered state is considered as a doublet. The magnetic susceptibility of UCu$_2$Sn above 150 K shows the Curie-Weiss behavior with an effective magnetic moment of $\mu_{\text{eff}} = 3.0 - 3.6 \mu_B/\text{U}$ corresponding to $5f^2$ or $5f^3$ configurations, which suggests the localized property of $5f$ electrons above 150 K. If $5f$ electrons in UCu$_2$Sn have the $5f^2$ configuration with the total angular momentum $J = 4$ and nearly localized property through to low temperatures, a ground multiplet of $5f$ electrons in hexagonal CEF splits into seven eigen-states; three singlets $\Gamma_1$, $\Gamma_3$ and $\Gamma_4$, and three non-Kramers doublets $2\Gamma_5$ and $\Gamma_6$ with degenerate quadrupoles, where $\Gamma_i$ denotes the irreducible representation for the 6/mmm point group. Therefore, we expected that the ground state of UCu$_2$Sn is non-Kramers doublet which have a
quadrupole degeneracy.

If \( f \) electrons have a quadrupole moment, a strain induced by the ultrasonic linearly couples to these quadrupole moment and the elastic modulus corresponding to a symmetry of quadrupole moment shows a softening. We measured elastic moduli which are a good probe for observation of a lattice change. In Fig. 9, a large softening with more than 56 % reduction at 16 K was observed in the temperature dependence of elastic modulus \( C_{66} \) [6], which is an evidence for the quadrupolar ordering of the ground state \( \Gamma_5 \). Taking account of both the strain-quadrupole coupling and the quadrupole-quadrupole (q-q) coupling, we analyzed \( C_{66} \) and then obtained the positive sign for the q-q coupling coefficient \( g_{12} \), that is, ferroquadrupolar coupling in the ground state. To distinguish the quadrupolar ordering from the cooperative Jahn-Teller transition, we employed a non-dimensional parameter \( D \equiv |g'C_0/g^2 N_0| \) [15], where \( g \) is the strain-quadrupole coupling constant, \( C_0 \) is the background stiffness and \( N_0 \) is the number density of U ions per unit volume at room temperature. The obtained result \( D \gg 1 \) clearly indicated that the q-q coupling \( g' \) predominates over the strain-quadrupole coupling \( g \) in \( UCu_2Sn \) and consequently the transition is classified as the ferroquadrupolar ordering. The prominent result of above work was finding of the phase transition in \( UCu_2Sn \) caused by quadrupole degeneracy of the ground state doublet \( \Gamma_5 \). The level scheme of CEF which is most reproducible for elastic moduli is shown in inset of Fig. 9. However, the electronic entropy in \( UCu_2Sn \) was not reproduced by the entropy calculated from the CEF level scheme shown in inset of Fig. 4.
Chapter 2

Purpose

To investigate the ordered state in UCu$_2$Sn and make out the $H - T$ phase diagram, we have measured the elastic modulus $C_{66}$ in the magnetic field parallel to [100], [001], and [110]. We have also optimized the CEF parameters so as to reproduce the data of entropy, magnetic susceptibility, elastic moduli and $C_{66}$ in the magnetic field parallel to [100], [001] and [110].

The ferroquadrupolar ordering must be accompanied by a macroscopic strain or distortion below $T_Q$. To observe the spontaneous strain, we have carried out the X-ray diffraction experiment on a polycrystalline sample. Thereto, we have manufactured the capacitance cell and carried out thermal expansion measurements on a single-crystalline sample along the $a$, $b$ and $c$ axes using the sensitive three-terminal capacitance method with higher resolution $\sim 10^{-8}$. 
Chapter 3
Experimental

3.1 Samples

A single crystal of UCu$_2$Sn was grown by a Bridgman method. The details of sample preparation was described elsewhere [11]. Electron Probe Micro Analysis for our single-crystalline sample of UCu$_2$Sn detected the impurity phase of UCuSn at $\sim 4\%$ of the host crystal. The dimensions of the sample is $2.824 \times 2.908 \times 3.288$ mm$^3$. Each plane was polished by number 800, 3000 carborundum and $\phi 0.05$ $\mu$m alumina powder so as to shape into a rectangular parallelepiped. A powdered sample of UCu$_2$Sn for X-ray diffraction experiments was prepared from the polycrystal of UCu$_2$Sn. These samples were provided by Takabatake laboratory, Department of Quantum Matter, ADSM, Hiroshima University.

3.2 Ultrasonic measurements

3.2.1 Phase-comparison type pulse-echo method

The elastic modulus is given by the following relation:

$$C = \rho v^2$$

where $\rho$ is a mass density and $v$ is a propagation velocity. We disregarded a temperature dependence of $\rho$ and applied the value of $\rho = 10.72$ (g / cm$^3$) at room temperature because the temperature dependence of $\rho$ is negligibly small as against the temperature dependence of $v$. 
We measured the elastic modulus using a phase-comparison type pulse-echo method. Figure 10 shows a diagram of the pulse-echo method. Transducer which is the electric-acoustic translation device is bonded on both ends of a sample perpendicular to the propagation direction of ultrasound. If a pulse voltage is impressed to one transducer, ultrasound occurs from the transducer. The generated ultrasound repeats reflection at both ends of a sample, then, a pulse-echo sequence is outputted from other transducer. A propagation velocity $v$ is given by following relation:

$$v = \frac{2l}{T}$$  
(3.2)

where $l$ is a distance between two transducer, that is a sample length, and $T$ is a time interval of pulse-echo.

A block diagram of the phase-comparison method is shown in Fig. 11. The carrier wave of frequency $f$ outputted from the oscillator is divided into a sample and reference side. The signal of sample side is formed into a drive pulse by a diode switch. The drive pulse is changed into the ultrasound by the transducer. Since the generated ultrasound repeats reflection at both ends of a sample, the phase of ultrasound delays in proportion to propagation time in a sample. The $n$-th pulse-echo is propagated in a sample for distance of $l(2n-1)$, that is time of $(2n-1)t/l$. Thus, a phase contrast $\Delta \phi_n$ between the phase of pulse-echo and reference signal is given by following equation:

$$\Delta \phi_n = 2\pi f \frac{(2n-1)t}{v}.$$  
(3.3)

$\Delta \phi_n$ is detected by the phase detector. When the ultrasonic velocity $v$ in a sample changes $\Delta v$, $\Delta \phi_n$ also changes with temperature change of a sample. Frequency $f$ is changed $\Delta f$ so as to take 0 for $\Delta \phi_n$. This process is presented as

$$\Delta \phi_n = 2\pi f \frac{(2n-1)t}{v} = 2\pi (f + \Delta f) \frac{(2n-1)t}{v + \Delta v}.$$  
(3.4)

Thus, a relative change of ultrasonic velocity, $\Delta v/v$, is given by following equation:

$$\frac{\Delta v}{v} = \frac{\Delta f}{f}.$$  
(3.5)

By measuring a relative change of frequency, the relative change of ultrasonic velocity in a sample is measured. Here, a temperature change of sample length $l$ is negligibly
small. A block diagram of the equipment for ultrasonic measurement is shown in Fig 12. The details of device development was described elsewhere [16].

3.2.2 Measurements

We used the transducer made from LiNbO$_3$ which is fundamental frequency of $\sim$ 9MHz. RTV rubber was used as a bond between sample and transducer. Measurements were performed by putting the sample rod, which is attached the angle rotation cell, to a Variable Temperature Insert (VTI) with a 16 T superconducting magnet. Temperature was downed to 4.2 K using liquid $^4$He and then downed to about 2 K by pumping liquid $^4$He with the Alcatel pump. Intelligent Temperature Controller (ITC4) was used for temperature control with a heater. Temperature of sample was measured by a Carbon Glass Resistor (CGR) thermometer with the AC resistance bridge (AVS-46). The thermometer was calibrated from 1.3 K to 300 K in a zero magnetic field and from 1.3 to 150 K in H = 2.5, 5, 10 and 14 T. We measured the temperature dependence of elastic modulus $C_{66}$ from 3 to 30 K in H = 2.5, 5, 7.5, 10, 12 and 14 T parallel to [100], [001] and [110] by the phase-comparison type pulse-echo method.

3.3 X-ray diffraction experiments

When the monochrome X-ray of wavelength $\lambda$ is radiated to a powder polycrystal sample, $\lambda$ is given by the Bragg equation:

$$\lambda = 2d_{hkl} \sin \theta$$

(3.6)

where $\theta$ is a incident angle of X-ray to a sample, $d$ is a interval of lattice plane and $hkl$ is the Miller index. Then, a diffraction peak of X-ray is observed in the direction of $2\theta$ for the incident direction of X-ray.

We carried out the X-ray diffraction measurement in the cryogenic center of Hiroshima university. The intensity of X-ray diffraction was detected by the scintillation counter. Helium flow type cryostat which has the optical window for X-ray is connected with $^4$He vessel by the transfer tube. The cryostat is cooled down by decompressed circulation of $^4$He with a pump. Since a sample space, which is
sealed with the radiation shield, is changed into a vacuum state in advance and then a circulating decompressed state of $^4$He, the sample space is maintained at nearly vacuum state. Temperature control was carried out by ITC4 with a heater. Powder polycrystal sample was taken on a Cu plate and fixed by Apiezon-N-grease which was melted and diluted with toluene. X-ray diffraction was measured as a function of $2\theta/\theta$ from 20 to 76° with a step width of 0.012° and a counting time of 2 s at 4.2, 10, 12, 20, 77, 296 K. Figure 13 shows a calculation result of diffraction peak position and intensity for UCu$_2$Sn by the Rietveld analysis. Numerical characters in parenthesis show the Miller index.

3.4 Thermal expansion measurements

3.4.1 Capacitance method

A capacitance method, which measures a change of capacitance between two electrodes as minute expansion and contraction of a sample, is one of techniques for thermal expansion measurement. Figure 14 shows a diagram of capacitance method. Sample is located between the inside of capacitance cell and the movable plate electrode. The movable plate electrode moves smoothly parallel to the fixed plate electrode in response to minute change of a sample length.

When only sample temperature is changed, minute change of parallel plate electrodes interval, that is minute change of the sample length, is detected as the change of capacitance. The capacitance $C$ between parallel plate electrodes in Fig. 14 is given by the following equation:

$$C = \varepsilon_d \frac{S}{d}$$  \hspace{1cm} (3.7)

where $S$ is a area of parallel plate electrodes, $d$ is the parallel plate electrodes interval and $\varepsilon_d$ is the dielectric constant between parallel plate electrodes. If minute change of capacitance, $\Delta C$, varies in response to minute change of $d$, $\Delta d$, $\Delta d$ is represented as

$$\frac{\Delta d}{d} = -\frac{\Delta C}{C}.$$  \hspace{1cm} (3.8)
Here, minute change of the sample length, \( \Delta l \), is equal to \(-\Delta d\). If \( \Delta l = -\Delta d \) is substituted to formula 3.8, a thermal expansion \( \Delta l/l \) is given by the following equation:

\[
\frac{\Delta l}{l} = \frac{d \Delta C}{C}.
\]  

(3.9)

The resolution of our experiments, which is \( d = 0.1 \) mm, \( C \approx 12 \) pF, \( \Delta C = 5 \times 10^{-6} \), is \( \sim 10^{-8} \) for our \( \sim 3 \) mm sample.

So far, only a change of the sample length by temperature change is considered. However, it is difficult to measure only a change of the sample length by temperature change in actual measurement because the capacitance cell itself expands and contracts depending on temperature change. A change of the sample length by temperature change is obtained by subtracting a change of the capacitance cell from a measured total change when temperature of the capacitance cell keeps sample temperature. The parallel plate electrodes interval \( d \) increases in case that a sample is shrunk. Meanwhile, \( d \) decreases if the capacitance cell is shrunk. A change of parallel plate electrodes interval, \( (\Delta d)^{\text{sample}}_{\text{meas.}} \), is given by following relation:

\[
(\Delta d)^{\text{sample}}_{\text{meas.}} = - (\Delta l)^{\text{sample}} + (\Delta l)^{\text{cell}}.
\]  

(3.10)

where \( (\Delta l)^{\text{sample}} \) is a change of the sample length and \( (\Delta l)^{\text{cell}} \) is a change of the capacitance cell. Temperature change of the capacitance cell is obtained to measure a standard sample that the thermal expansion is exactly decided. We measured the thermal expansion of copper as the standard sample [17]. Temperature change of capacitance cell is given by following relation:

\[
(\Delta l)^{\text{cell}} = (\Delta d)^{\text{Cu}}_{\text{meas.}} + (\Delta l)^{\text{Cu}}_{\text{lit.}}.
\]  

(3.11)

where \( (\Delta l)^{\text{sample}} \) is equal to \( (\Delta l)^{\text{Cu}}_{\text{lit.}} \) in case of copper as the standard sample. Thus, temperature change of the sample length is decided by following relation, using formulas 3.10 and 3.11:

\[
(\Delta l)^{\text{sample}} = - (\Delta d)^{\text{sample}}_{\text{meas.}} + (\Delta d)^{\text{Cu}}_{\text{meas.}} + (\Delta l)^{\text{Cu}}_{\text{lit.}}.
\]  

(3.12)
3.4.2 Three-terminal method

The capacitance between parallel plate electrodes is exactly decided in case that these are covered by earthed conductor. Figures 15 and 16 show a diagram of the three-terminal method and an equivalent circuit of the three-terminal method, respectively. The capacitance between parallel plate electrodes, $C_X$, and a capacitance between parallel plate electrodes and earthed conductor, $C_{HG}$ and $C_{LG}$, are called as the direct capacitance and the terminal capacitance, respectively. Figure 17 shows a diagram of bridge circuit to remove the terminal capacitance, where $C_S$ is a standard capacitance, $C_{HG}$, $C'_{HG}$, $C_{LG}$ and $C'_{LG}$ are terminal capacitance and $G$ is the earth. Only direct capacitance is detected as $C_X$ by well balanced $V_X$ with $V_S$. The bridge circuit is balanced without current flow in the detector D by adjusting the ratio of $V_X$ and $V_S$. Then, a difference of voltages between G and E becomes zero and all current which flowed on $C_X$ flow into $C_S$. Thus, a balance condition is given by following relation:

$$V_S Y_S = V_X Y_X$$  \hspace{1cm} (3.13)

where $Y_X$ and $Y_S$ are the admittance of measured capacitance and standard capacitance, respectively.

In actual measurements, a parallel constituent impedance $R_P$ caused by dielectric loss and insulating resistance and a serial constituent impedance $R_S$ caused by contact resistance and resistance of lead wire exist in addition to the admittance. A influence of $R_P$ rather than a influence of $R_S$ is important in low frequency. The admittance $Y$ is given by following equation:

$$Y = \frac{1}{R_S + \frac{1}{j\omega C}} + \frac{1}{R_P} .$$  \hspace{1cm} (3.14)

Here, $\omega CR_S$ is much less than 1 because of $f = 1$ kHz, $R_S \sim 1\Omega$, $C = 12$ pF. The admittance $Y$ is expanded as follows:

$$Y \sim j\omega C \left[ 1 - \left( \frac{\omega CR_S + \frac{1}{\omega CR_P}}{\omega CR_P} \right) \right].$$  \hspace{1cm} (3.15)

$R_S$ is negligible because of $R_P \sim 10^7$, that is $\omega CR_P \sim 1$. Therefore, formula 3.15 is represented as

$$Y = j\omega C + \frac{1}{R_P} .$$  \hspace{1cm} (3.16)
It assumes that $R^p$ component and admittance corresponding to the capacitance $C_X$, $C_S$ are $R_X$, $R_S$ and $Y_X$, $Y_S$, respectively. Formula 3.16 is rewrote as follows:

$$Y_S = j\omega C_S + \frac{1}{R_S}$$  \hspace{1cm} (3.17) 

$$Y_X = j\omega C_X + \frac{1}{R_X}.$$  \hspace{1cm} (3.18)

Using formulas 3.13, 3.17 and 3.18, the balance condition is given by following equation:

$$V_S \left( j\omega C_S + \frac{1}{R_S} \right) = V_X \left( j\omega C_X + \frac{1}{R_X} \right).$$  \hspace{1cm} (3.19)

If formula 3.19 is divided into a real part and an imaginary part, formula 3.19 is rewrote as follows:

$$C_X = C_S \frac{V_S}{V_X}$$ \hspace{1cm} (3.20) 

$$R_X = R_S \frac{V_X}{V_S}.$$  \hspace{1cm} (3.21)

Thus, if a real part and an imaginary part are balanced independently, capacitance $C_X$ can be measured exactly.

### 3.4.3 Measurements

We have manufactured the capacitance cell based on the three-terminal capacitance method [18]. Figure 18 shows the structure of our capacitance cell. Our capacitance cell becomes uniform temperature quickly without local distortion in response to a temperature change since components of capacitance cell, which are made from copper, are wholly column-shaped. Both plane of the plate electrode was polished so as to be parallel. The movable plate electrode always moves in parallel to the fixed plate electrode because the movable plate electrode is supported by three rods and a sample is fixed with spring. We used a flexible Be-Cu spring in fear of the influence of tension from a spring to a sample as possible. Since a sample space is fixation, we needed to prepare one spacer about one axis. It is a possibility that the present experimental setup may disregard the $\varepsilon_{xy}$ strain technically even though it emerges. As depicted in Fig.19(a), a change in the sample length along
the x direction, consequently the strain $\varepsilon_{xx} - \varepsilon_{yy}$, can be directly measured since we capacitively detect the change in spacing between the parallel plate electrodes. In the case of the strain $\varepsilon_{xy}$, the sample will rotate so as to fit the two surfaces of the sample onto the parallel plates as shown in Fig.19(b). The change $\Delta d$ in the parallel plate electrodes interval will be negligibly small because $\Delta d$ is proportional to $(1 - \frac{3}{2} \varepsilon_{xy}^2 + \cdots)$. Temperature of sample was measured by a cernox thermometer, which was calibrated from 1.5 K to 280 K, with the AC resistance bridge (AVS-47). The thermometer thermally contacts with the capacitance cell by Apiezon-N-grease. To avoid a earth loop, only one coaxial cable, which is made from stainless to prevent a heat influx from outside, was earthed. Thermal expansion was measured as a function of temperature $T$ from 4.2 to 40 K with a temperature interval of 0.1 K along the $a$, $b$ and $c$ axes using the capacitance bridge (ANDEEN HAGERING 2500A). The $b$ axis is defined as perpendicular to the $a$ axis in the hexagonal $c$ plane. The value of $\Delta l/l$ for each axis was defined as $(l(T) - l(40K)) / l(40K)$.
Chapter 4

Results & Discussion

4.1 CEF parameters

4.1.1 Elastic modulus $C_{66}$ in magnetic field

Figures 20, 21 and 22 show the temperature dependence of $C_{66}$ in the magnetic field parallel to [100], [001] and [110], respectively. We made out the $H - T$ phase diagram of UCu$_2$Sn shown in Fig. 23, assuming that $T_Q$ is the minimum point of data. In $H \parallel [100]$, a softening of elastic modulus at $T_Q$ is strongly suppressed with increasing $H$. $T_Q$ shows a bending in low magnetic field and then decreases monotonically with increasing $H$. The softening of elastic modulus at $T_Q$ is suppressed gradually and $T_Q$ decreases with increasing $H$ in $H \parallel [001]$. In $H \parallel [110]$, the softening of elastic modulus at $T_Q$ is strongly suppressed and $T_Q$ increases monotonically with increasing $H$.

4.1.2 Strain susceptibility

In our compound, a elastic strain induced by the ultrasound linearly couples to the quadrupole moment derived from 5$f$ electrons and affects 5$f$ electron state as a perturbation. The perturbation Hamiltonian $H_{ME}$ is given by following equation:

$$H_{ME} = \sum_i g_i \mathcal{O}_i \varepsilon_i .$$  \hspace{1cm} (4.1)

The calculation of strain susceptibility is performed by the Wigner-Brillouin perturbation method. When the elastic strain is induced, each energy eigenvalue divided
by CEF, which is took a perturbation to the second-order into consideration, is presented as

\[ E_i(\varepsilon_\Gamma) = E_i^0 + g_\Gamma \langle i|O_\Gamma|i \rangle \varepsilon_\Gamma + g_\Gamma^2 \sum_{i \neq j} \frac{|\langle i|O_\Gamma|j \rangle|^2}{E_i^0 - E_j^0 - \varepsilon_\Gamma^2} \]  \hspace{1cm} (4.2)

where \( E_i^0 \) is an energy eigenvalue in non-perturbation state. A free energy of Helmholtz contributed from 5f electrons, \( F_{\text{ion}} \), is given by following equation:

\[ F_{\text{ion}}(\varepsilon_\Gamma, T) = -N_0 k_B T \ln Z(\varepsilon_\Gamma, T) \]

\[ = -N_0 k_B T \ln \left[ \sum_i \exp \left( -\frac{E_i(\varepsilon_\Gamma)}{k_B T} \right) \right] \]  \hspace{1cm} (4.3)

where \( Z \) is the partition function and \( k_B \) is the Boltzmann constant. Meanwhile, a free energy originated from a kinetic energy and a potential energy of electrons other than 5f electrons, \( F_{\text{lattice}} \), is presented as

\[ F_{\text{lattice}} = \frac{1}{2} C_{\Gamma,\text{ME}}^{0} \varepsilon_\Gamma^2 \]  \hspace{1cm} (4.4)

The total free energy \( F_{\text{total}} \) is accordingly given by following equation:

\[ F_{\text{total}} = F_{\text{ion}} + F_{\text{lattice}} \]  \hspace{1cm} (4.5)

The elastic modulus \( C_{\Gamma,\text{ME}} \) is defined by the second-order differentiation of total free energy with respect to \( \varepsilon_\Gamma \) and given by following equation:

\[ C_{\Gamma,\text{ME}} = \left( \frac{\partial^2 F_{\text{total}}(\varepsilon_\Gamma, T)}{\partial \varepsilon_\Gamma^2} \right)_{\varepsilon_\Gamma \rightarrow 0} \equiv C_{\Gamma,0} - N_0 g_\Gamma^2 \chi_\Gamma^r(T) \]  \hspace{1cm} (4.6)

where \( \chi_\Gamma^r \) is the strain susceptibility. \( \chi_\Gamma^r \) with \( E_i \) in formula 4.2 is presented as

\[ -g_\Gamma^2 \chi_\Gamma^r(T) = -\sum_i \left[ \left( -\frac{\partial^2 E_i}{\partial \varepsilon_\Gamma^2} \right) + \frac{1}{k_B T} \left\{ \left( \frac{\langle \partial E_i \rangle}{\partial \varepsilon_\Gamma} \right)^2 - \left( \frac{\langle \partial E_i \rangle}{\partial \varepsilon_\Gamma} \right)^2 \right\} \right] \]  \hspace{1cm} (4.7)

where \( \langle \rangle \) denotes a heat statistics average of the Boltzmann distribution. First and second term in formula 4.7 are called as Van-Vleck and Curie term, respectively, as is the case with the magnetic susceptibility. Van-Vleck and Curie term are contributed from off-diagonal and diagonal element of the quadrupole operator, respectively.
In addition to the interaction of strain-quadrupole coupling, the interaction of q-q coupling also occurs. The Hamiltonian originated from q-q coupling, $H_{Q-Q}$, using the molecular field approximation, is given by the following equation:

$$H_{Q-Q} = -g'_{\Gamma_1} \sum_{\Gamma_i} \sum_j \langle O_{\Gamma_i} \rangle O_{\Gamma_i} (j).$$  (4.8)

Thus, the temperature dependence of elastic modulus $C_T(T)$ is given by the following equation:

$$C_T(T) = -\frac{N_0 g_{\Gamma_1}^2 \chi_{\Gamma_1}(T)}{1 - g_{\Gamma_1}^2 \chi_{\Gamma_1}(T)} + C_0$$  (4.9)

where $C_0$ is the linear $T$ dependence of the background stiffness assumed as

$$C_0 = a + bT.$$  (4.10)

### 4.1.3 CEF parameters

We consider an effective Hamiltonian $H_{\text{eff}}$ in zero magnetic field:

$$H_{\text{eff}} = H_{\text{CEF}} - H_{\text{ME}} + H_{Q-Q}$$  (4.11)

$$H_{\text{CEF}} = B^0_2 O^0_2 + B^4_4 O^4_4 + B^6_6 O^6_6 + B^8_6 O^8_6$$  (4.12)

$$H_{\text{ME}} = g_{\Gamma_1} (O_{xy} \varepsilon_{xy} + O_{yz} \varepsilon_{yz}) + g_{\Gamma_6} (O_{yz} \varepsilon_{yz} + O_{xz} \varepsilon_{xz})$$

$$+ g_{\Gamma_4} O^0_2 + g_{\Gamma_6} O^4_2 + g_{\Gamma_8} O^8_2 + g_{\Gamma_6} O^6_6$$  (4.13)

$$H_{Q-Q} = -g'_{\Gamma_1} \langle O_{\Gamma_1} \rangle O_{\Gamma_1}$$  (4.14)

where $B^m_n$ is CEF parameter. In a magnetic field, the Zeeman term:

$$H_{\text{Zeeman}} = -gJ \mu_B J \cdot H$$  (4.15)

is added to the formula 4.11.

We have optimized the CEF parameters in order to reproduce the data of entropy, magnetic susceptibility, elastic moduli, and $C_{66}$ in the magnetic field. Figures 24, 25, and 26 show the fitting result of $C_{66}$ in case of $H = 5, 14$ T along [100], [001], and [110], respectively. Theoretical curves by solid line good reproduce all data with the parameters listed in Tables 1 and 2. Figure 27 shows the fitting result of
magnetic susceptibility in case of $a$ and $b$ axes. Theoretical curves good reproduce all data above $T_Q$ with CEF. The data below $T_Q$ is reproduced by 60 degree domain structure. Theoretical curve assumed for 60 degree domain structure is smaller than the data above $T_Q$ because of equally probability 60 degree domain structure. The calculated entropy by CEF parameters is shown in Fig. 28. The data of entropy is almost reproduced by CEF parameters though a little deviance is seen between the data and theoretical curve. The CEF level scheme corresponding to CEF parameters in Table 1 is shown in Fig. 29. The analysis of data proposed the level scheme in which the first excited state $\Gamma_4$ is situated at 109 K, the second excited state $\Gamma_6$ at 332 K and ··· above the ground state doublet $\Gamma_5$. Figure 30 shows the $H-T$ phase diagram of UCu$_2$Sn, assuming that $T_Q$ is the minimum point of the data and theoretical curve. Theoretical curves well reproduce $H-T$ phase diagram in all $H // [100], [001]$- and $[110]$. $T_Q$ increases monotonically with increasing $H // [110]$. It is estimated that quadrupole moment is strongly induced because of a mixing between the ground state and exited state in $H // [110]$.

4.2 X-ray diffraction

Figure 31 shows a X-ray diffraction peak of UCu$_2$Sn at 20 K and 4.2 K, that is above and below $T_Q$. Experimental results show almost same diffraction peak as the calculation result in Rietveld analysis shown in Fig. 13. Diffraction peak at 43.3, 50.5 and 74.3° in experimental results are caused by Cu which is a basal plate of the sample. The difference was not found in the position of diffraction peak between above and below $T_Q$. Therefore, we did not succeed in detecting any indication for the spontaneous occurrence of macroscopic strain.

We numerically calculated the magnitude of strain taking account of the strain-quadrupole coupling constant of $\Gamma_5$, $g_{\Gamma_5}$, in the analysis of elastic modulus by using the relation [19]

$$|\varepsilon_{\Gamma_5}| = \frac{N_0k_Bg_{\Gamma_5} \langle O_{\Gamma_5} \rangle}{C_0}$$  (4.16)

where $|g_{\Gamma_5}| = 9.3$ K, $C_0 \simeq 34$, $\langle O_{\Gamma_5} \rangle \simeq 5$ at 0 K and $k_B = 1.38 \times 10^{-23}$ (J/K). The evaluated value ($\simeq 2.50 \times 10^{-4}$) was smaller than the experimental resolution.
4.3 Thermal expansion

Figure 32 shows temperature dependence of thermal expansion $\Delta l/l$ both for along the $a$ and $b$ axes. At high temperatures, both of $\Delta l/l$ along the $a$ and $b$ axes decrease monotonically with decreasing temperature. At low temperatures below $T_Q$, $\Delta l/l$ along the $a$ axis, that is $\Delta a/a$, rapidly increases with decreasing temperature, whereas $\Delta l/l$ along the $b$ axis, that is $\Delta b/b$, continues to decrease. As far as the crystal keeps a hexagonal symmetry, $\Delta a/a$ and $\Delta b/b$ should coincide with each other even though it thermally expands or contracts. But results of $\Delta a/a$ and $\Delta b/b$ differ with each other below $T_Q$. As clearly seen in Fig. 32, $\Delta a/a$ starts to deviate from $\Delta b/b$ at $\sim 20$ K. This behavior appears to correspond closely to that of the transverse modulus $C_{66}$ which starts to soften gradually below $\sim 20$ K. The precursor is possibly ascribed to the fluctuation of the quadrupolar ordering. Figure 33 shows the difference $\Delta a/a - \Delta b/b$, which is proportional to the expected spontaneous strain $\varepsilon_{xx} - \varepsilon_{yy}$. The $\varepsilon_{xx} - \varepsilon_{yy}$ strain is one of the $\varepsilon_{\Gamma_3}$ strains. Thus, we succeeded in direct confirmation of the macroscopic distortion due to the ferroquadrupolar ordering in UCu$_2$Sn. The ground state doublet $\Gamma_3$ has a degeneracy of quadrupoles $O_{xy}$ and $O_2^2$. One of these order parameters should emerge below $T_Q$ and therefore the corresponding strain of $\varepsilon_{xy}$ or $\varepsilon_{xx} - \varepsilon_{yy}$ is expected to appear spontaneously. In the present experiment, only the $\varepsilon_{xx} - \varepsilon_{yy}$ component which linearly couples to $O_2^2$ was detected. This result strongly suggests that the order parameter is $O_2^2$. The magnitude of the strain evaluated at 5 K is $\sim 4.5 \times 10^{-5}$. This is the reason why we could not detect any corresponding strain by the powder X-ray diffraction with a resolution of $10^{-3}$. However, the present value is one order of magnitude smaller than the value of $2.5 \times 10^{-4}$ which was estimated from the parameter values fitted to the elastic modulus observed. When a hexagonal system undergoes a structural transition, a 60 degrees ferroelastic-type domain is expected to appear in the ordered state. In the present case of UCu$_2$Sn, we believe to have observed the average of the spontaneous strain over those domains. The calculated value of $2.5 \times 10^{-4}$ should be regarded as the maximum value of the macroscopic strain expected for a
single-domain sample.

Shown in Fig. 34 is the temperature dependence of thermal expansion $\Delta l/l$ along the $c$ axis, that is $\Delta c/c$. At high temperatures, $\Delta c/c$ decreases monotonically with decreasing temperature. It increases gradually below $\sim 20$ K and rapidly below $T_Q$. The magnitude of the strain evaluated at 5 K is $\sim 2.0 \times 10^{-5}$. This behavior is difficult to explain by only quadrupolar ordering of $\Gamma_5$ since a change caused by $\Gamma_5$ strain is large within $xy$-plane. $\Delta c/c$ calculated by CEF was un reproducible for an increase of $\Delta c/c$ below $T_Q$. We have no convincing explanation for this increase in $\Delta c/c$, but a possible origin might be related to development of the secondary order parameter $O_Q^2$ which couples to $2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}$. The strain-quadrupole coupling constant between $2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}$ and $O_Q^0$ is very large shown in Table 2.

The thermal expansion coefficient $\alpha_i$ is related to $\delta l/l$ by the following equation:

$$\alpha_i = \frac{1}{\delta T} \frac{\delta l_i}{l_i},$$

where $\delta$ and the subscript $i$ denote an infinitesimal difference and each axis, respectively. Figure 35 shows the thermal expansion coefficients $\alpha$ as a function of temperature along the $a$, $b$ and $c$ axes. Here, we assumed that the background variation of the thermal expansion coefficient is given by $\alpha_{bg} = AT + BT^3$ [20]. The values used for the fitting parameters $A$ and $B$ are listed in Table 3. From these data, we can estimate the pressure effects on the transition temperature $T_Q$, using the Ehrenfest relation:

$$\frac{dT_Q}{dP} = \frac{\Delta \beta T_Q V_m}{\Delta C_p},$$

where the volume expansion coefficient $\Delta \beta$ is assumed as $\Delta \beta = \Delta \alpha_a + \Delta \alpha_b + \Delta \alpha_c$. $V_m$ is the molar volume and $\Delta C_p$ is the change in the isobaric specific heat at $T_Q$. We used the difference between $\alpha_{bg}$ and $\alpha_i$ for $\Delta \alpha_i$ at $T_Q$. The uniaxial pressure effects on the transition temperature $T_Q$ are estimated from this result. The values of $dT_Q/dP$ along the $a$, $b$ and $c$ axes are listed in Table 4. We can estimate the uniaxial pressure dependence of transition temperature in UCu$_2$Sn for the first time. The hydrostatic pressure effect on $T_Q$ is also estimated to be $dT_Q/dP = -6.0 \times 10^{-1}$ K/GPa. This value is quite consistent with the value $dT_Q/dP = -9.6 \times 10^{-1}$ K/GPa reported for polycrystalline UCu$_2$Sn in the hydrostatic pressure by Kurisu et al. [21].
The quantum critical point, that ferroquadrupolar ordering disappears, will be seen about 26 GPa. The diamond anvil cell which generates high pressure is required to attain the quantum critical point in UCu₂Sn.

4.4 Pressure cell for ultrasonic measurements

To search a influence of pressure to the quadrupolar ordering, we are developing the pressure cell which is possible to measure the elastic modulus with the ultrasound. A diagram of the pressure cell for ultrasonic measurement is shown in Fig. 36. The Co-Ni alloy (MP35N) which is high intensity and non-magnetic was used for the pressure cell [22]. The diameter of a sample space is 5 mm. The sample space which is filled by a pressure medium is pressurized by hand-operated press machine and retained pressure by closing a clamping bolt. We used a fluorinert as the pressure medium. The pressure in low temperature is checked at the superconductivity transition temperature of Pb. The pressure, which is put at room temperature, decreases with decreasing temperature, since a percentage of heat contraction of the pressure cell differs from that of the fluorinert. The pressure in the pressure cell at low temperature, \( P_{L.T.} \), is estimated by following equation [23]:

\[
T_c(P) = T_c(0) - 0.365P_{L.T.}
\]

Figure 37 shows a diagram of the electrical feedthrough and sample space. A co-axial cable, which transmits a signal without the influence of electromagnetic wave from the surrounding, is needed for ultrasonic measurement. However, the fluorinert escapes from the co-axial cable at the time of pressurization in case of the co-axial cable is put into the sample space. At the beginning, co-axial cables were changed into Cu wires at a outside of electrical feedthrough. In this case, measurement was difficult due to the noise from a coupling of high frequency and so on. Therefore, co-axial cables were put into the position hardened with the stycast near the sample space. Though the stycast became weak to inner pressure, the noise of a signal decreased sharply. Core wires and shield wires of co-axial cables are changed into Cu wires within stycast. Signal and ground side of transducer made from LiNbO₃ are contacted to Cu wires with In solder. Since LiNbO₃ is a ferroelectric, signal
and ground side of transducer are needed to earth at the time of pressurization.
Figure 38 shows a pulse-echo of quartz pressurized by 1 GPa at room temperature.
The pulse-echo which is a little noise is measurable.
Chapter 5

Conclusion

We measured the elastic modulus $C_{66}$ in the magnetic field parallel to [100], [001] and [110] by the phase-comparison type pulse-echo method and made out the $H - T$ phase diagram of UCu$_2$Sn. So, we optimized the CEF parameters so as to reproduce the data of entropy, magnetic susceptibility, elastic moduli and $C_{66}$ in the magnetic field parallel to [100], [001] and [110]. The proposed level scheme is the ground state doublet $\Gamma_5$, the first excited state $\Gamma_4$ at 109 K and $\cdots$. The $H - T$ phase diagram is well reproduced. To confirm the ferroquadrupolar ordering in UCu$_2$Sn which is indicated from the fitting of elastic modulus, we manufactured the capacitance cell and measured the thermal expansion of single-crystalline UCu$_2$Sn along the a, b and c axes. The change in the thermal expansion below $T_Q$ clearly indicates the spontaneous emergence of the macroscopic strain $\varepsilon_{xx} - \varepsilon_{yy}$, which couples to the quadrupole $O_2^q$. As a result, it is completely proved that the transition in UCu$_2$Sn at $T_Q$ originates from the ferroquadrupolar ordering. The enhancement of $\Delta c/c$ below $T_Q$ might be regarded as due to the development of the secondary order parameter $O_2^q$. We also discussed the uniaxial pressure effect on $T_Q$, and succeeded in evaluating $dT_Q/dP_1$ for the first time.
Acknowledgement

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References


Table 1: CEF parameters of UCu$_2$Sn obtained from the fitting of entropy, magnetic susceptibility, elastic moduli and $C_{66}$ in the magnetic field.

<table>
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<tr>
<th></th>
<th>$B_2^0$ (K)</th>
<th>$B_4^0$ (K)</th>
<th>$B_6^0$ (K)</th>
<th>$B_8^0$ (K)</th>
</tr>
</thead>
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<td></td>
<td>0.1083</td>
<td>$-3.899 \times 10^{-2}$</td>
<td>$-3.973 \times 10^{-3}$</td>
<td>0.1532</td>
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</table>

Table 2: Obtained parameters in the fitting of elastic moduli. $|g_{T_1}|$ (K), $g_{T_i}^t$ (K), $a$ (GPa) and $b$ ($\times 10^{-3}$ GPa/K)

<table>
<thead>
<tr>
<th>Op.</th>
<th>$O_{xy}$</th>
<th>$O_{yx}$</th>
<th>$O_2^0$</th>
<th>$O_4^0$</th>
<th>$O_6^0$</th>
<th>$O_8^0$</th>
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<tr>
<td>$</td>
<td>g_{T_1}</td>
<td>$</td>
<td>9.32</td>
<td>130.4</td>
<td>24.36$^a$</td>
<td>28.83$^b$</td>
</tr>
<tr>
<td>$g_{T_i}^t$</td>
<td>0.496</td>
<td>-1.080</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>mode</td>
<td>$C_{66}$ ($\Gamma_5$)</td>
<td>$C_{44}$ ($\Gamma_6$)</td>
<td>$C_{33}$ ($\Gamma_{11}^B$, $\Gamma_{11}^a$)</td>
<td>$C_{11}$ ($\Gamma_{11}^B$, $\Gamma_{11}^a$, $\Gamma_5$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>33.85</td>
<td>40.04</td>
<td>62.25</td>
<td>80.70</td>
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</tr>
<tr>
<td></td>
<td>-5.000</td>
<td>-6.752</td>
<td>-11.99</td>
<td>-16.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
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Table 3: Fitting parameters $A$ and $B$ for the background $\alpha_{bg}$ of thermal expansion coefficients.

<table>
<thead>
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<th>axis</th>
<th>$A$ (K$^{-2}$)</th>
<th>$B$ (K$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, b</td>
<td>$3.21 \times 10^{-5}$</td>
<td>$3.73 \times 10^{-11}$</td>
</tr>
<tr>
<td>c</td>
<td>$6.46 \times 10^{-5}$</td>
<td>$4.75 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Table 4: Uniaxial pressure effects on the transition temperature $T_Q$. The values for $dT_Q/dP_i$ are listed in K/Pa.

<table>
<thead>
<tr>
<th>$dT_Q/dP_a$</th>
<th>$dT_Q/dP_b$</th>
<th>$dT_Q/dP_c$</th>
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<tbody>
<tr>
<td>$-4.02 \times 10^{-10}$</td>
<td>$+2.65 \times 10^{-10}$</td>
<td>$-4.60 \times 10^{-10}$</td>
</tr>
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</table>
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Figure 23: The $H$-$T$ phase diagram of UCu$_2$Sn. The solid circles, squares and triangles show the transition temperature $T_Q$ in $H \parallel [100]$, [001] and [110], respectively assuming that $T_Q$ is the minimum point of data.
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Figure 27: The magnetic susceptibility of UCu$_2$Sn along $a$ and $b$ axes are shown by open circles and solid triangles, respectively. The red and blue solid curves show the fitting result with CEF along $a$ and $b$ axes, respectively. The green solid curve shows the theoretical curve assumed for equally probability 60 degree domain structure.

Figure 28: The magnetic entropy of UCu$_2$Sn derived from 5$^f$ electrons. The solid curve shows the entropy calculated by CEF parameters.
Figure 29: The CEF level scheme corresponding to CEF parameters in Table 1.

\[ \Gamma_3 = 881 \, [K] \]
\[ \Gamma_5 = 585 \, [K] \]
\[ \Gamma_1 = 461 \, [K] \]
\[ \Gamma_6 = 332 \, [K] \]
\[ \Gamma_4 = 109 \, [K] \]
\[ \Gamma_5 = 0 \, [K] \]

Figure 30: The $H$-$T$ phase diagram of UCu$_2$Sn. Solid curves show theoretical curves calculated by fitting parameters.
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(2) Thermal expansion of UCu$_2$Sn in the basal plane
(1) Elastic anomaly of UCu₂Sn in the magnetic fields

(2) Quadrupolar ordering of 5f electrons in UCu₂Sn

(3) Jahn-Teller instability in a ternary uranium compound

(4) Elastic quantum oscillation of LuB₁₂
N. Okuda, T. Suzuki, I. Ishii, S. Hiura, F. Iga, T. Takabatake, T. Fujita,
H. Kadomatsu, H. Harima