



HOKKAIDO UNIVERSITY

Title	Ultrasonic Investigation of Phenomena Originating from the Electric Quadrupole in the f-Electron Caged Compounds
Author(s)	日比野, 瑠央
Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第16242号
Issue Date	2025-03-25
DOI	https://doi.org/10.14943/doctoral.k16242
Doc URL	https://hdl.handle.net/2115/95366
Type	doctoral thesis
File Information	Ruo_Hibino.pdf



HOKKAIDO UNIVERSITY

GRADUATE SCHOOL OF SCIENCE

DEPARTMENT OF CONDENSED-MATTER PHYSICS

Ultrasonic Investigation of Phenomena
Originating from the Electric Quadrupole in
the f -Electron Caged Compounds

(超音波測定を用いた f 電子系籠状化合物における
電気四極子由来の物性に関する研究)

Author:
Ruo Hibino

Supervisor:
Prof. Tatsuya Yanagisawa
Co-supervisors:
Prof. Hiroshi Amitsuka
Prof. Satoru Hayami
Dr. Yoshihiko Ihara
Dr. Sergei Zherlitsyn

March, 2025

Acknowledgement

First of all, I would like to express my gratitude to Prof. Tatsuya Yanagisawa for his invaluable guidance throughout this work, numerous fruitful discussions, and experimental advice based on his extensive experience. His sincere approach to physics gave me not only profound insights into the subject but also an understanding of what is essential for an experimental scientist. I learned many things that I will keep in mind in my future research endeavors. I also express my deep appreciation to my co-supervisors, Prof. Hiroshi Amitsuka, Prof. Satoru Hayami, Dr. Yoshihiko Ihara (Hokkaido University), and Dr. Sergei Zherlitsyn (Hochfeld-Magnetlabor Dresden, Helmholtz-Zentrum Dresden-Rossendorf, HLD-HZDR) for their helpful discussions and valuable suggestions during the examination of this thesis.

In this ultrasonic investigation, high-quality single-crystalline samples were essential. Single-crystalline samples of $(Y, Pr)Ir_2Zn_{20}$ were provided by Prof. Takahiro Onimaru, Dr. Keisuke T. Matsumoto, Dr. Yu Yamane (Hiroshima University). Single-crystalline samples of $(U, Th)Be_{13}$ were provided by Prof. Tatsuya Yanagisawa with support from Prof. M. Brian. Maple, Dr. Duygu Yazici (University of California, San Diego), and Dr. Yusei Shimizu (Tohoku University). I am sincerely grateful to all of them for their great effort in synthesizing high-quality single-crystalline samples. In particular, Prof. Onimaru and Yamane provided significant guidance on interpreting the elastic responses due to a quadrupolar Kondo effect.

Ultrasonic measurements at very low temperatures and under high magnetic fields were made possible through the cooperation of various experimental facilities. In particular, I spent a very long time in Dresden conducting ultrasonic measurements using 3He - 4He dilution refrigerators and a 3He refrigerator (Oxford Instruments Heliox). I also performed the ultrasonic measurements under pulsed magnetic fields for $(U, Th)Be_{13}$ thanks to their cooperation. These experiments, which were carried out over six months (from Aug. 1, 2022 to Jan. 31, 2023), were supported by the JSPS Overseas Challenge Program for Young Researchers. Dr. Sergei Zherlitsyn, Prof. Joachim Wosnitza (HLD-HZDR), Dr. Atsuhiko Miyata (ISSP, the University of Tokyo), and Dr. Koji Araki (National Defense Academy of Japan) kindly supported both my experiments and daily life in Germany.

The experiments using the 3He refrigerator were also performed at Niigata University, with support from Dr. Yuichi Nemoto, Dr. Mitsuhiro Akatsu (Niigata University), and students at the university. Furthermore, when we developed the Two-Axial-Rotation (TARO) probe for ultrasonic measurements at Hokkaido University,

Dr. Motoi Kimata (Tohoku University), who originally designed the probe, provided invaluable technical advice and assistance. I would like to sincerely thank them for their experimental support.

My six years in this laboratory have provided me with a great deal of knowledge and experience essential for becoming a researcher. Prof. Hiroshi Amitsuka, Prof. Tatsuya Yanagisawa, and Dr. Hiroyuki Hidaka (Hokkaido University) in my laboratory were always available for discussions on physics in the daily life. I have learnt a lot of things from how to present and interpret the experimental results from a physical perspective. The depth and breadth of their knowledge often amazed me and inspired me to continue learning. Daily discussions with other students in the laboratory also provided me with fresh perspectives and ideas that I would not have arrived at on my own.

I would also like to thank all staff members of Liquid Helium Center, the machine shop, and Advanced Physical Property Open Unit (APPOU) at Hokkaido University for their essential support. Finally, I extend my deepest gratitude to my family and friends for their unwavering support and encouragement throughout my research journey.

Abstract

【Background and Objectives】

The study of “Magnetism” has been a subject of intensive research for a long time. In recent years, fundamental findings in this field have been applied to various applications in daily life such as magnetic memory and sensors. Conventional study of magnetism primarily focused on the physics arising from interactions mediated by magnetic dipolar degrees of freedom. Fruitful physical phenomena arising from magnetic interactions such as exchange interaction, Kondo effect, and RKKY interaction, have been discovered by great scientists, greatly advancing our understanding of magnetism. Beyond magnetic dipoles, further studies considering higher-rank magnetic/electric multipoles are currently underway. For instance, the order parameter associated with higher-rank multipoles, previously referred as “hidden order parameter”, could be revealed by the progress of the measurement techniques, such as resonant x-ray scattering. However, experimental verification for the research on higher-rank multipoles still remains relatively limited, compared with the substantial progress in theoretical investigations. In the present study, we focus on the experimental investigation for physics originating from the “Electric Quadrupole”.

Furthermore, extended multipolar theory has been constructed recently and broadening the scope of interest to include odd-parity higher magnetic and electric multipolar physics in the non-centrosymmetric systems. As a result, we consider multipolar physics to be a promising curious research topic for further development.

To reveal intriguing phenomena associated with electric quadrupoles, we performed ultrasonic measurements of f -electron compounds. This method has a significant advantage in directly detecting electric quadrupolar degrees of freedom. Moreover, the caged compounds investigated in this study are expected to exhibit strong hybridization between localized f -electrons and conduction electrons, making them promising candidates for investigating the two-channel Kondo effect mediated by electric quadrupolar degrees of freedom.

【Contents】

In this study, we investigate $(Y, Pr)Ir_2Zn_{20}$ and $(U, Th)Be_{13}$ to explore physics originating from electric quadrupoles. Since Pr^{3+} and U^{4+} ions each have two f -electrons, these compounds generally might have non-Kramers degenerate crystalline electric field (CEF) ground state. In this state, the electric quadrupole can be active, whereas the magnetic dipolar degrees of freedom remain inactive. In particular, $(Y, Pr)Ir_2Zn_{20}$ has been confirmed to have a non-Kramers Γ_3 doublet as its CEF ground state, making it an ideal candidate for studying electric quadrupolar physics. In contrast, CEF ground state of $(U, Th)Be_{13}$ remains unclear due to the duality of the $5f$ electrons, namely their coexistence of localized and itinerant characteristics. Therefore, we investigated the electronic state, including the CEF ground state, to verify whether $(U, Th)Be_{13}$ is suitable for the study of quadrupolar physics, as suggested by the theoretical predictions.

In addition to the pure compounds $PrIr_2Zn_{20}$ and UBe_{13} , we also investigated non

magnetic Y- and Th-diluted compounds to elucidate the single-site many-body effect mediated by the electric quadrupole. This thesis consists of the following contents.

Quadrupolar Kondo Effect on (Y, Pr)Ir₂Zn₂₀ (Chapter 6)

We systematically performed ultrasonic measurements on (Y, Pr)Ir₂Zn₂₀ to investigate the elastic response associated with the Quadrupolar Kondo Effect (QKE). In the Pr-3.4% system, a logarithmic temperature dependence of Γ_3 -type quadrupolar susceptibility, originating from single-site QKE has already been reported. Building upon this findings, we investigated the elemental dilution effect on the elastic response due to the QKE. It is simply considered that single-site quadrupolar Kondo model is not valid in Pr-rich systems where localized quadrupolar interaction cannot be neglected. Furthermore, we discuss the possibility of forming a novel quantum ground state in (Y, Pr)Ir₂Zn₂₀ where localized quadrupoles, conduction electrons, and phonons are intricately entangled.

Phase Pocket “A” near the AFQ phase boundary of PrIr₂Zn₂₀ (Chapter 7)

We investigated the intriguing small phase pocket “A” near the antiferro-quadrupolar (AFQ) ordering phase boundary of PrIr₂Zn₂₀ using ultrasonic measurements. We mainly focused on the behavior of the Γ_3 -symmetrical elastic constant at the phase boundary of phase pocket “A”. In addition to the experimental investigation, we performed a mean-field analysis to elucidate the phenomena occurring in the AFQ phase of PrIr₂Zn₂₀.

Electronic State of UBe₁₃ and (U, Th)Be₁₃ (Chapter 8)

UBe₁₃ is well known as a first discovered U-based heavy-fermion superconductor. Furthermore, its significance extends beyond the superconducting phase to the normal phase where enigmatic non-Fermi-liquid-like behavior is observed. We performed the ultrasonic measurements of single crystalline samples of UBe₁₃ and (U, Th)Be₁₃ (Th-2.7%) to investigate the electronic state in the normal phase. In particular, we focused on the electronic state under high magnetic fields and carried out the ultrasonic measurements under pulsed magnetic fields. Additionally, we also investigated the superconducting phase transition of UBe₁₃ and (U, Th)Be₁₃ (Th-2.7%).

Chapter 1 presents the background of this study, along with an overview of the development and current status of research on the hybridization between localized moments and conduction electrons. In the latter part of chapter 1, the main topics of the present study, quadrupolar Kondo effect, is explained. Chapter 2 reviews the previous study of the target compounds, Pr 1-2-20 compounds, while chapter 3 focuses that for (U, Th)Be₁₃ compounds. Chapter 4 outlines the objectives of this study, and Chapter 5 describes the experimental methods of these studies. Chapter 6, 7, and 8 present the experimental results and discussions for each material. Chapter 9 concludes the study and offers perspectives for future research.

【Conclusions】

The new insights gained from the research presented in this dissertation can be summarized as follows:

(Y, Pr)Ir₂Zn₂₀

- We discovered a change in the ground state of (Y, Pr)Ir₂Zn₂₀ due to the quadrupolar Kondo effect as a function of Pr concentration. Specifically, we discovered Γ_3 -symmetrical elastic constant proportional to $\sqrt{T}$ in the Pr-8 and 37% systems, which differs from the behavior in the Pr-3.4% system. This temperature dependence is consistent with the theoretical predictions of the quadrupolar Kondo (virtual) lattice model where finite localized quadrupolar interaction is introduced. We believe that this is the first observation of a crossover from single-site quadrupolar Kondo model to quadrupolar Kondo lattice model, as evidenced by the quadrupolar susceptibility.
- In the Pr-37% system, we discovered ultrasonic dispersion in the Γ_3 -symmetrical mode at around 1 K, with an energy scale closely matching that of the quadrupolar Kondo effect in the system. We propose that the energy scale of the ultrasonic dispersion is modified by Pr concentration, and that coincidentally aligns with the QKE energy scale in the Pr-37% system. Since this ultrasonic dispersion is sensitive to magnetic fields, we suggest a possibility of the vibronic ground state, where Γ_3 -symmetrical phonon is coupled to localized quadrupole in the Pr-37% system.
- We observed a Γ_3 -symmetrical elastic anomaly at the phase boundary of the newly proposed phase pocket “A” in PrIr₂Zn₂₀. Additionally, we found other elastic anomalies in the antiferro-quadrupolar (AFQ) ordering phase. Based on an analysis using a simple mean-field model, we conclude that these anomalies will arise from the switching of the order parameters. This switching might be related to the field-induced phase pocket “A”.

(U, Th)Be₁₃

- The elastic softening of the Γ_3 -symmetrical mode, which would suggest the presence of the Γ_3 -symmetrical quadrupolar degrees of freedom, is not clearly observed in UBe₁₃ and (U, Th)Be₁₃ (Th-2.7%) under zero magnetic field. This is inconsistent with the scenario of the quadrupolar Kondo effect originally proposed by Dr. D. L. Cox.
- We observed a large elastic softening of the longitudinal C_{11} mode ($\Gamma_1 \oplus \Gamma_3$ -symmetrical mode) in UBe₁₃ and the Th-2.7% system, which is robust to the

applied magnetic field. The temperature at which the softening ceases coincides with the temperature of “2 K anomaly” observed in electrical resistivity and thermal expansion measurements, suggesting that the softening is related to this anomaly. Since this type of the softening is not observed in the Γ_3 -symmetrical mode, we suggest that the softening originates from the Γ_1 -symmetrical volume change due to (magnetic) c - f hybridization.

- We found that Γ_3 - and Γ_5 -symmetrical elastic constants exhibit the elastic softening enhanced by an applied magnetic field in UBe_{13} and the Th-2.7% system. These results suggest that the Γ_3 - and Γ_5 -symmetrical quadrupolar degrees of freedom are enhanced by the applied magnetic fields. In particular, the Γ_5 -symmetrical quadrupolar degrees of freedom remain up to ~ 38 T in the Th-2.7% system. These behaviors cannot be reproduced by theoretical calculations based on the simple localized $5f$ electron description. We propose that $5f$ electrons in the system may be relatively itinerant even under high magnetic fields, potentially due to the high energy scale of the c - f hybridization.

Contents

1	Introduction	11
1.1	Strongly Correlated Electron System	11
1.1.1	f Electron Systems; Lanthanoid and Actinoid	11
1.1.2	Development in Physics of Multipolar Moments	13
1.1.3	(Magnetic) Kondo Effect	14
1.1.4	Two-Channel Kondo Effect; Quadrupolar Kondo Effect	16
2	Introduction to Pr 1-2-20 systems	20
2.1	Crystal Structure	20
2.2	Systematic Study for Pr 1-2-20 Systems	21
2.3	Physical Properties of $\text{PrIr}_2\text{Zn}_{20}$	23
2.3.1	Phase Transitions	24
2.3.2	Newly Proposed Phase Pocket “A” near the AFQ Phase Boundary	28
2.3.3	Non-Fermi-Liquid Behavior of $\text{PrIr}_2\text{Zn}_{20}$	29
2.3.4	Verification of the Single-Site Quadrupolar Kondo Model in Y-Diluted Systems (Y, Pr) $\text{Ir}_2\text{Zn}_{20}$	30
3	Introduction to UBe_{13}	33
3.1	Crystal Structure	33
3.2	First Discovered U-Based Heavy-Fermion Superconductor	34
3.3	Physical Properties of the Normal Phase of UBe_{13}	36
3.3.1	2 K Anomaly	36
3.3.2	Non-Fermi-Liquid Behavior under Magnetic Fields	38
3.4	Exotic Phenomena under High Magnetic Fields	39
3.5	Multiple Phase Diagram in Th-Diluted Systems	40
4	Purpose of Study	41
5	Experimental Methods	43
5.1	Sample Preparation	43
5.2	Elastic Constant	45
5.3	Crystalline-Electric-Field Effect	48
5.3.1	Contribution of Electric Hexadecapole	51
5.4	Measurement System	52

5.4.1	Phase Comparative Method (Feedback System)	52
5.4.2	Phase Orthogonal Method	53
5.5	Elastic Response Originating from Relaxation Phenomena	54
5.6	Apparatus	58
5.6.1	PPMS	58
5.6.2	^3He Refrigerator	58
5.6.3	^3He - ^4He Dilution Refrigerator	59
5.6.4	Two-Axial-Rotation (TARO) Probe for Ultrasonic Measurements	60
5.6.5	Pulsed Magnetic Field	62
6	Verification of Quadrupolar Kondo Effect on $(\text{Y}, \text{Pr})\text{Ir}_2\text{Zn}_{20}$	63
6.1	Experimental Procedure	63
6.2	Experimental Results of the Pr-8% System	64
6.2.1	Temperature Dependence of Elastic Constants	64
6.2.2	CEF Analysis	65
6.2.3	QKE Contribution	68
6.3	Experimental Results of the Pr-37% System	70
6.3.1	Ultrasonic Dispersion at High Temperature	70
6.3.2	CEF Analysis	75
6.3.3	QKE Contribution	77
6.4	Pr-Concentration Dependence of Parameters	80
6.5	Pr-Concentration Dependence of Quantum Ground State	82
6.6	Acoustic dHvA Oscillation	84
7	Verification of Phase Pocket “A” in AFQ Ordering of $\text{PrIr}_2\text{Zn}_{20}$	89
7.1	Experimental Procedure	89
7.2	Experimental Results	90
7.2.1	Temperature Dependence under Zero Magnetic Field	90
7.2.2	Temperature Dependence under $B \parallel [001]$	92
7.2.3	Temperature Dependence under $B \parallel [110]$	94
7.2.4	Magnetic-Field Dependence	95
7.3	Origin of the Phase Pocket “A”	97
7.3.1	B - T Phase Diagram obtained from Ultrasonic Measurements	97
7.3.2	Discussion with a Mean-Field Model	101
8	Investigation of Electronic State on UBe_{13} and $(\text{U}, \text{Th})\text{Be}_{13}$	105
8.1	Experimental Procedure	105
8.2	Longitudinal C_{11} Mode	107
8.2.1	Relationship between Elastic Softening and “2 K Anomaly”	107
8.2.2	Phase Transitions of Th-Diluted Systems	111
8.3	Transverse Modes (C_{44} Mode and $(C_{11} - C_{12})/2$ Mode)	113
8.3.1	Elastic Response in the Γ_5 -symmetrical C_{44} Mode	113
8.3.2	Elastic Response in the Γ_3 -Symmetrical $(C_{11} - C_{12})/2$ Mode	115
8.3.3	Electronic State under High Magnetic Fields	118

9	Concluding Remarks	123
10	Appendix 1: Power-Law Fitting Analysis in (Y,Pr)Ir₂Zn₂₀	126
10.1	Power-Law Fit Analysis of the Pr-8% System in Several Temperature Ranges	126
11	Appendix 2: CEF Analysis with the Contribution of Atomic Disorder in (Y,Pr)Ir₂Zn₂₀	128
11.1	CEF Analysis with Tetragonal Distortion	128

Chapter 1

Introduction

1.1 Strongly Correlated Electron System

In f -electron strongly correlated electron systems, c - f hybridization (hybridization effect between conduction electrons and f electrons) is regarded as one of the most crucial factors influencing their physical properties. Numerous compounds exhibiting a large effective mass of electrons (10^2 to 10^3 times to free electrons) due to the c - f hybridization have been discovered, which are well known as “Heavy Fermion” compounds and have been extensively studied.

1.1.1 f Electron Systems; Lanthanoid and Actinoid

Lanthanoid compounds, which might have $4f$ electrons, have attracted significant attention as a good target of the strongly correlated electron systems. This interest originates from the probability distribution of the wave function of $4f$ electrons. Figure 1.1(a) shows the probability distribution of electrons in Ce ($4f^1$) compounds obtained by the theoretical calculation [1]. This indicates that the $4f$ electron is well localized compared with other electrons forming closed shell (Xe-shell). This situation is considered to be suitable for the investigation of the interaction between localized moment and conduction electrons. For a similar reason, actinoid compounds, which might have $5f$ electrons, have also been studied. On the other hand, Fig. 1.1(b) shows that the probability distribution of the wave function of $5f$ electrons differs somewhat from that of $4f$ electrons; specifically, it extends further outside the closed shell compared to the $4f$ electrons. This characteristic makes the f -electronic state of actinoid compounds more complex, leading to what is known as “itinerant-localized duality”.

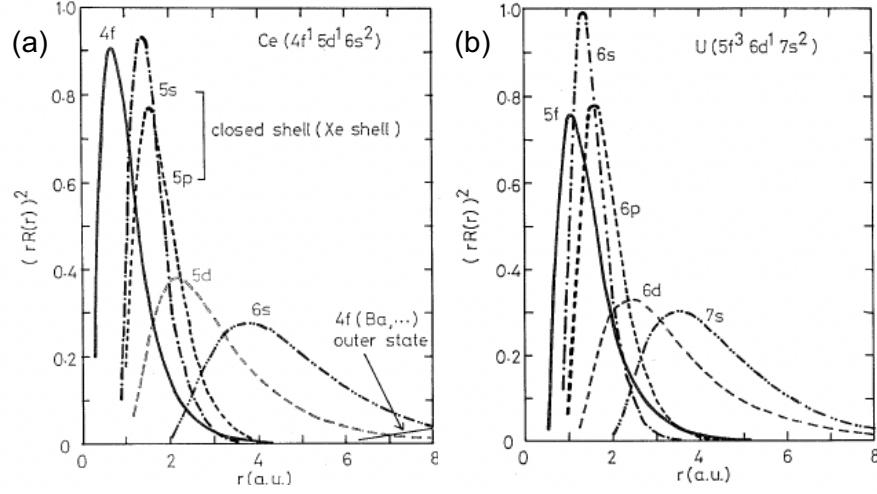


Figure 1.1: Effective radial distribution function of (a) Ce and (b) U [1].

As described in the previous paragraph, the f electron is relatively localized and surrounded by other electrons. Since the f electron is well screened by surrounding electrons, crystalline-electric-field (CEF) effect on the f electron is generally weaker than that for d electrons. As a result, total angular momentum $J = |L - S|, |L - S + 1|, \dots, |L + S|$ becomes a good quantum number, in other words, J multiplet is formed via LS coupling. (Here, we assume that a Coulomb interaction U is larger than the spin-orbit interaction λ . If λ is larger, the $j-j$ description is applicable.) Total orbital angular momentum L and total spin angular momentum S of the ground state are determined based on Hund's rule. The description of the J ground multiplet depends on the sign of the spin-orbit interaction, *i.e.*, $|L - S|$ when the number of f electrons is less than half-filling, $|L + S|$ in case that the number of f electrons is more than half-filling. Due to the weak CEF effect, the ground J multiplet is split according to the site symmetry of the magnetic ion.

1.1.2 Development in Physics of Multipolar Moments

In addition to the well-localized nature of the f -electron wave function, f electrons have a large orbital angular momentum $l = 3$. Thus, in case the system possesses high symmetry, orbital degrees of freedom could remain even after the CEF split of the J multiplet. The electric/magnetic charge distribution due to the spin and/or orbital degrees of freedom can be systematically described using the concept of “multipole” [2]. This description could be classically understood as a multipole expansion. The spatial distributions of the electric charge (ρ_e) and the magnetic charge (ρ_m) can be described as the following expression projected onto the spherical harmonics Y_{pq} .

$$\rho_e(\hat{\mathbf{r}}) = \sum_{lm} (2l+1) \frac{Q_{lm}}{e \langle \mathbf{r}^l \rangle} Z_{lm}(\hat{\mathbf{r}}) \quad (1.1)$$

$$\rho_m(\hat{\mathbf{r}}) = \sum_{lm} (2l+1) \frac{M_{lm}}{\mu_B \langle \mathbf{r}^l \rangle} Z_{lm}(\hat{\mathbf{r}}) \quad (1.2)$$

Here, $\hat{\mathbf{r}} = \mathbf{r}/r$ is the unit radial vector, and

$$Z_{pq}(\hat{\mathbf{r}}) = \sqrt{\frac{4\pi}{2p+1}} Y_{pq}(\hat{\mathbf{r}}) \quad (1.3)$$

is the spherical harmonics with Racah normalization.

Q_{lm} and M_{lm} in Eq. (1.1) and (1.2) represent electric multipole and magnetic multipole, respectively. They are described as below,

$$\begin{aligned} Q_{pq} &= \int d\mathbf{r} r^p Z_{pq}^*(\hat{\mathbf{r}}) \rho_e(\mathbf{r}) \\ &= -e \sum_{j=1}^n r_j^p Z_{pq}^*(\hat{\mathbf{r}}_j) \end{aligned} \quad (1.4)$$

$$\begin{aligned} M_{lm} &= \int d\mathbf{r} r^p Z_{pq}^*(\hat{\mathbf{r}}) \rho_m(\mathbf{r}) \\ &= -\mu_B \sum_{j=1}^n \nabla [r_j^p Z_{pq}^*(\hat{\mathbf{r}}_j)] \cdot \left(\frac{2\mathbf{l}_j}{l+1} + \mathbf{s}_j \right). \end{aligned} \quad (1.5)$$

Recently, the electric toroidal multipole G_{lm} (which corresponds to the time-reversal inversion of Q_{lm}) and the magnetic toroidal multipole T_{lm} (which corresponds to the time-reversal inversion of M_{lm}) have been introduced, enabling the description of the arbitrary degrees of freedom of the electron using multipoles [3]. Beyond conventionally investigated physics originating from the magnetic dipole, physics originating from higher-rank multipoles has been intensively studied in terms of experimental verification using the f -electron compounds. For example, the electric quadrupolar ordering in DyB_2C_2 [4] and the magnetic octupolar ordering in $\text{Ce}_{1-x}\text{La}_x\text{B}_6$ [5] are well known. In the present study, we focus primarily on the phenomena originating from the electric quadrupole, one of the higher-order multipoles.

1.1.3 (Magnetic) Kondo Effect

In a narrow sense, (magnetic) Kondo effect is defined as the phenomenon that the electrical resistivity of the non-magnetic good metal (*e. g.*, Au, Cu) containing a small amount of magnetic impurity exhibits a local minimum as a function of temperature. An example is described in Ref. 1.2 [6]. The origin of this phenomenon remained unclear for a long time, however, Dr. J. Kondo theoretically resolved this issue in 1964 [7]. In Kondo theory, the following Hamiltonian (*s-d* Hamiltonian) is assumed.

$$H_{\text{sd}} = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \frac{J_{\text{eff}}}{2N} \sum_{kk'\sigma\sigma'} \mathbf{S} \cdot \mathbf{s}_{\sigma\sigma'} c_{k\nu\sigma}^\dagger c_{k'\nu\sigma'} \quad (1.6)$$

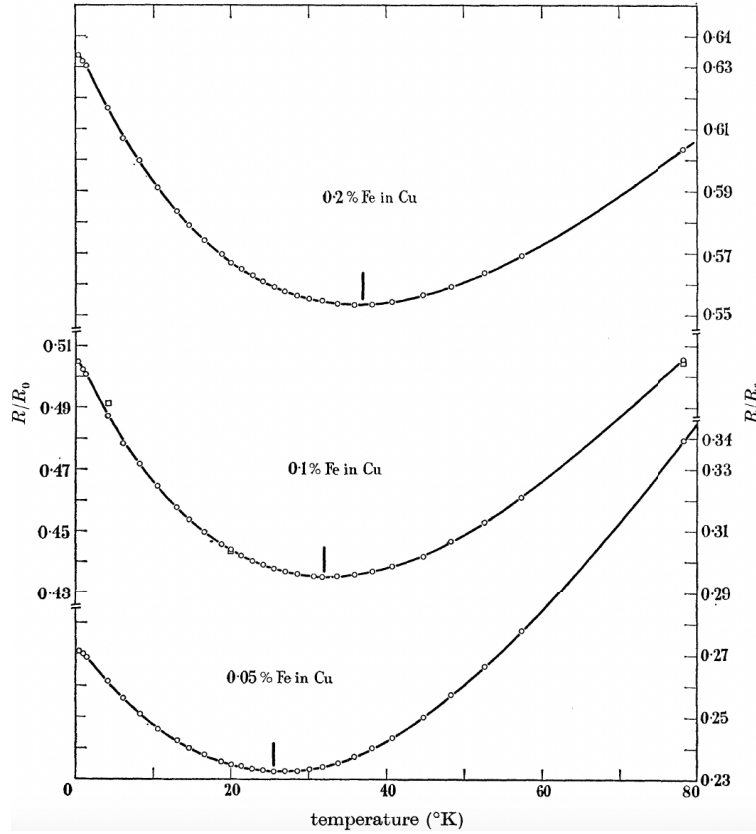


Figure 1.2: Electrical resistivity of Cu including a small amount of Fe [6].

This Hamiltonian is constructed based on the impurity Anderson model. The second term of the Hamiltonian represents the exchange interaction between localized spin and conduction-electron's spin. Here, J_{eff} means a coupling constant of the exchange interaction, which is a positive and causes an antiferromagnetic interaction between the localized spins and the conduction electron spin. The hybridization is included as a perturbation under the assumption that it is sufficiently weaker than Coulomb

energy. Dr. J. Kondo succeeded in deriving a temperature dependence of the electrical resistivity proportional to $-\sqrt{T}$ at low temperatures by considering the second Born approximation. The characteristic temperature $k_{\text{B}}T_{\text{K}} = W \exp(-1/J_{\text{eff}}N(\varepsilon_{\text{F}}))$, which indicates the strength of the hybridization, is referred to as Kondo temperature. Here, W represents the bandwidth of conduction electrons, and $N(\varepsilon_{\text{F}})$ represents the density of states at the Fermi level.

Afterward, further understanding was developed. Dr. K. Yosida revealed that the ground state of the Kondo system is a non-magnetic singlet (local Fermi liquid) where localized spin momentum is completely screened by the antiferromagnetic interaction with the conduction electrons, which is known as Kondo-Yosida singlet [8]. In addition to the impurity model in the early stages of research, the study of Kondo “lattice” systems was promoted in the context of the discovery of CeB_6 [9]. In the research topic, f -electron compounds, in which localized f electrons are periodically arranged, became a major focus. Figure 1.3 shows the temperature dependence of the electrical resistivity of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ [10]. In the low Ce-concentration systems ($x \leq 0.50$), the electrical resistivity shows the behavior proportionally to $-\sqrt{T}$ and saturated to the unitarity limit, which is interpreted in a impurity Kondo model. On the other hand, in the high Ce-concentration system ($0.73 \leq x$), the resistivity decreases proportional to $+T^2$ as the temperature goes down, which suggests the formation of Fermi liquid. The “A coefficient” ($\rho \propto AT^2$) takes relatively large values and this state is known as a “heavy fermion” state explained in the previous section. This system serves as a prime example of a crossover from an impurity (single-site) Kondo model to a Kondo lattice model. In this way, the study of the f -electron systems diluted by nonmagnetic ions, particularly Ce-based compounds, has played a significant role in developing the understanding of Kondo effect.

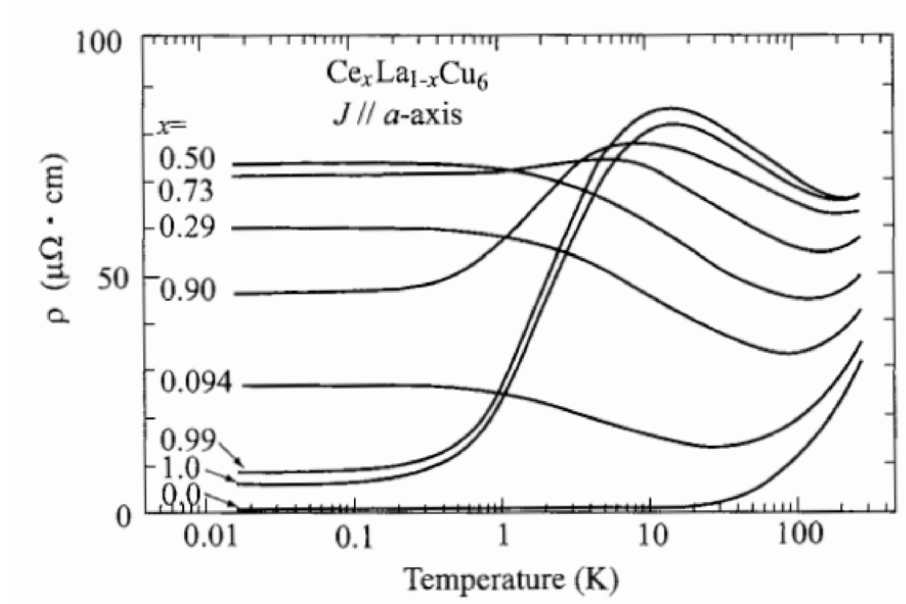


Figure 1.3: Electrical resistivity of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ as a function of the temperature [10].

1.1.4 Two-Channel Kondo Effect; Quadrupolar Kondo Effect

Beyond the conventional single-channel Kondo effect (magnetic Kondo effect), the possibility of the multi-channel Kondo effect was theoretically proposed [11]. In this model, the effective Hamiltonian is expanded as follows. Here, a channel refers to the number of degrees of freedom in the hybridizing conduction electrons.

$$H_{\text{MCKE}} = \sum_{\nu=1}^n \left[\sum_{k\sigma} \epsilon_k c_{k\nu\sigma}^\dagger c_{k\nu\sigma} + \frac{J_{\text{eff}}}{2N} \sum_{kk'\sigma\sigma'} \mathbf{S} \cdot \mathbf{s}_{\sigma\sigma'} c_{k\nu\sigma}^\dagger c_{k'\nu\sigma'} \right] \quad (1.7)$$

In this description, n corresponds to the number of the channels. When the number of the channel exceeds the localized spin ($n > 2S$), the localized spin is overscreened by conduction electrons. Theoretical studies propose that the overscreening can induce the non-Fermi-liquid (NFL) behavior and residual entropy even at absolute zero. Then, approximate calculations are derived for various physical quantities as functions of temperature and magnetic field [12], highlighting the need for experimental verification. The derived expressions for the physical quantities are presented in Eqs. (1.8) and (1.9). Figure 1.4 shows the temperature dependence of the susceptibility χ of the localized moment, calculated using the multi-channel Kondo model. T_K is the characteristic temperature at which the coupling between the localized moment and conduction electrons develops in multi-channel Kondo model. This characteristic temperature corresponds to the Kondo temperature in the conventional Kondo effect.

$$C/T, \chi \propto \begin{cases} \ln(T/T_K) & n = 2 \\ (T/T_K)^{-(n-2)/(n+2)} & n > 2 \end{cases} \quad (1.8)$$

$$\rho = \rho_0 + \alpha (T/T_K)^{2/(n+2)} \quad (1.9)$$

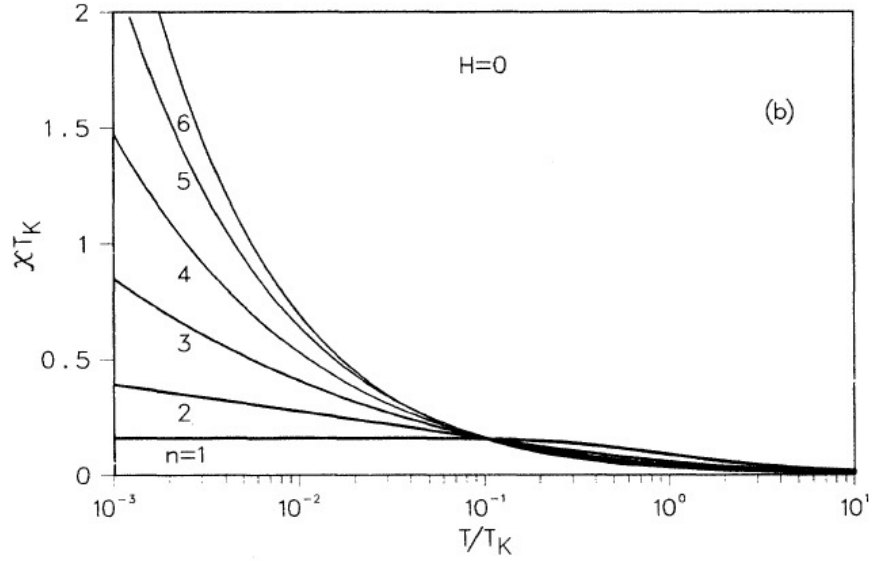


Figure 1.4: Temperature dependence of the susceptibility of localized momentum calculated based on the n -channel Kondo effect [12]. Horizontal axis is normalized by Kondo temperature T_K .

Theoretical research on the multi-channel Kondo effect had progressed, whereas, no actual system for experimental verification had been found. In 1987, Dr. D. L. Cox proposed that the NFL behavior observed in UBe_{13} (details are given in Chapter 3) originates from the two-channel quadrupolar Kondo effect [13]. He assumed the $5f^2$ electronic configuration (U^{4+}) where the non-Kramers Γ_3 doublet could be a CEF ground state. In this doublet, there are Γ_3 -type electric quadrupolar degrees of freedom. The schematic view of the scattering process is shown in Fig. 1.5. Through hybridization between the localized Γ_3 -symmetrical quadrupolar moment and the Γ_8 -symmetrical partial wave of conduction electrons, $|\Gamma_3+\rangle = \frac{\sqrt{42}}{12}(|+4\rangle + |-4\rangle) - \frac{\sqrt{15}}{6}|0\rangle$ state is transferred to the $|\Gamma_3-\rangle = \frac{1}{\sqrt{2}}(|+2\rangle + |-2\rangle)$ via the Γ_7 state ($5f^1$ configuration). The quadrupolar Kondo effect corresponds to the case where $n = 2$, $S = 1/2$ in Eq. (1.7). Here, since $|\Gamma_3+\rangle$ and $|\Gamma_3-\rangle$ could be regarded as a pseudo-spin (“up” and “down”), S is equal to $1/2$. As described above, this situation causes the overscreening, and NFL behaviors ($C/T, \chi \propto \ln(T/T_K)$, $\rho \propto \sqrt{(T/T_K)}$) in various physical properties could be derived from Eq. (1.8) and (1.9).

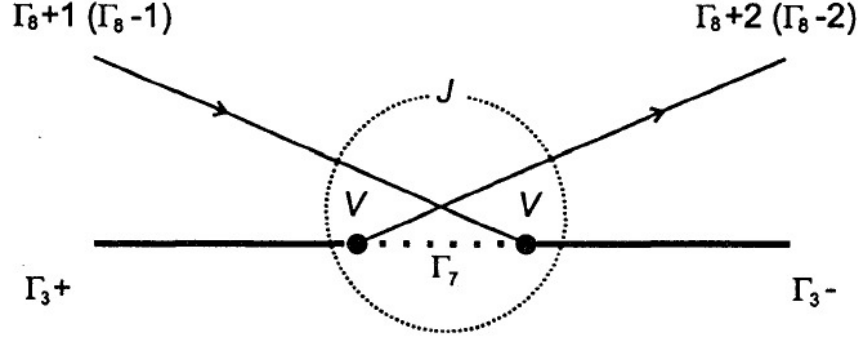


Figure 1.5: Schematic view of the scattering process of the two-channel electric quadrupole [14].

After theoretical suggestion of QKE, a lot of experiments have been performed for the verification. As suggested by Dr. D. L. Cox, cubic uranium compounds with a possible non-Kramers Γ_3 CEF doublet have been considered as a first candidate. In particular, uranium compounds diluted by non-magnetic ions (Th or Y) were regarded as a good target to reveal the single-site effect of the mysterious QKE. For example, (U, Y)Pd₃, (U, Th)Ru₂Si₂, and (U, Th)Be₁₃ exhibit NFL behaviors in some physical quantities [15, 16, 17], however, a uniform interpretation consistent with all physical quantities has yet to be provided. This can be partly attributed to the experimental challenges arising from the “itinerant-localized duality” inherent to uranium compounds as mentioned at the beginning of this chapter. In addition to actinoid compounds, the investigation using cubic Pr-based compounds has been carried out because the $4f$ -electronic configuration of Pr³⁺ ions is $4f^2$ where non-Kramers Γ_3 doublet could be CEF ground state as well as U⁴⁺ compounds. Recently, Pr 1-2-20 systems, one of our target compounds, have attracted much attention to investigate the physics originating from QKE. Details of the recent studies are explained in Chapter 2.

Recently, the theory of the QKE has progressed, and it has expanded to the quadrupolar Kondo “lattice” model assuming that magnetic ions with quadrupolar degrees of freedom are periodically aligned. Dr. A. Tsuruta and Dr. K. Miyake developed the theory using the two-channel Anderson lattice model, and they used the $1/N$ -expansion method, based on the expansion from the limit of the large spin-orbital degeneracy, to consider a strong electronic correlation [18, 19]. They derived the temperature dependence of physical quantities as following equations

$$\Delta\rho(T) = \frac{a_1}{1 + a_2 \left(T_0^{(\rho)} / T \right)}, \quad (1.10)$$

$$C(T) = b_1 \left(1 - b_2 \sqrt{\frac{T}{T_0^{(C)}}} \right), \quad (1.11)$$

where a_i and b_i ($i = 1$ and 2) are parameters. Furthermore, they suggested the possibility that the above discussion could also be applied to the systems partially diluted by non-magnetic ions by assuming that “virtually” magnetic ions form the periodic alignment after averaging over random distribution as shown in Fig. 1.6. The possibility that the electrical resistivity of $(Y, Pr)Ir_2Zn_{20}$ obeys this model is proposed, however, further experimental verification is required [19, 20].

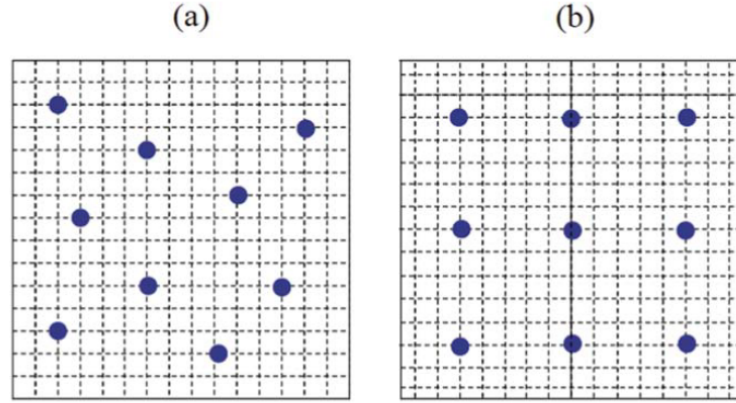


Figure 1.6: (a) Square lattice version of original system. (b) “Virtual” system obtained after average over random distribution of magnetic sites. Blue circle represents the magnetic ions [19].

Chapter 2

Introduction to Pr 1-2-20 systems

2.1 Crystal Structure

RT_2X_{20} . (R ; Lanthanoid, T ; Transition metals, X ; Al, Zn, and Cd) has attracted much attention triggered by the discovery of Yb-based heavy fermion families [21]. In particular, $\text{YbCo}_2\text{Zn}_{20}$ shows a huge electronic specific heat coefficient $\gamma \sim 8000 \text{ mJ/K}^2\text{mol}$. The series crystallizes in the cubic $\text{CeCr}_2\text{Al}_{20}$ -type structure with the space group $Fd\bar{3}m$ as shown in Fig. 2.1. Since the guest lanthanoid is surrounded by 16 ligand ions (Frank-Kasper cage), a strong c - f hybridization could be expected. As well as Yb compounds, other lanthanide systems are also attracting attention [22].

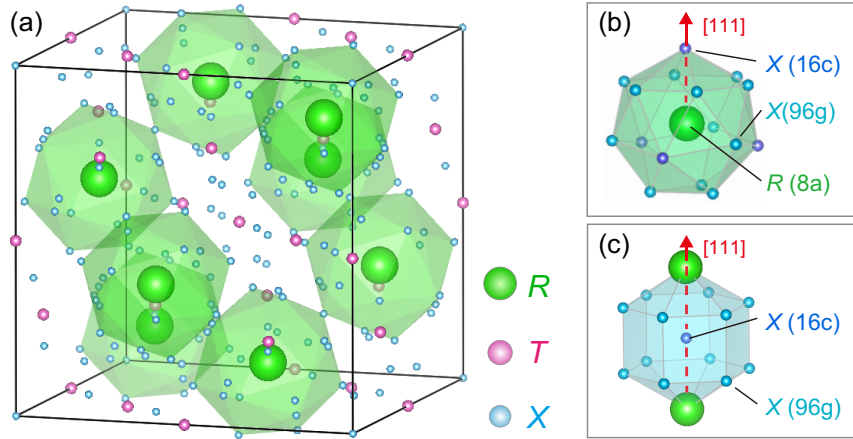


Figure 2.1: Crystal structure of RT_2X_{20} . (R ; Lanthanoid, T ; Transition metals, X ; Al, Zn, and Cd) (a) A unit cell (the number of formula units per unit cell is 8), (b) R atom encapsulated in the cage of X atoms (the sites 16c and 96g), and (c) X atom at the site 16c encapsulated in the cage of R_2X_{12} , where the direction connecting R atom (on site 8a) and X atom (on site 16c) is $[111]$. These illustrations are drawn using VESTA [23].

Among them, we focus on the Pr compounds to investigate the c - f hybridization mediated by an electric quadrupole in the present study. Due to Kramers's theorem,

$4f^2$ configuration (even number) of the Pr^{3+} ion does not necessarily need to have a Kramers degeneracy. This means that the situation, where an electric quadrupole is active but a magnetic dipole is not, could be achieved. In other words, these compounds are suitable to investigate electric quadrupolar physics. Previous studies on the Pr compounds of the series are summarized in the next section.

2.2 Systematic Study for Pr 1-2-20 Systems

As described in the previous section, Pr-based 1-2-20 compounds are expected to be a good target to investigate electric quadrupolar physics. In particular, the following four compounds, $\text{PrIr}_2\text{Zn}_{20}$, $\text{PrRh}_2\text{Zn}_{20}$, $\text{PrV}_2\text{Al}_{20}$, and $\text{PrTi}_2\text{Al}_{20}$, have attracted much attention because they show a coexistence of the quadrupolar ordering and superconductivity [24, 25, 26, 27]. Physical properties of these compounds are summarized in the review paper written by Dr. T. Onimaru and Dr. H. Kusunose [28]. Crystalline-electric-field (CEF) ground state is commonly non-Kramers Γ_3 (Γ_{23}) doublet as shown in Fig. 2.2(a) [28]. Here, Pr-site symmetry of $\text{PrRh}_2\text{Zn}_{20}$ has T symmetry because of a structural phase transition at high temperature. This phase transition is observed as a wide hysteresis of the electrical resistivity between 170 and 470 K [25].

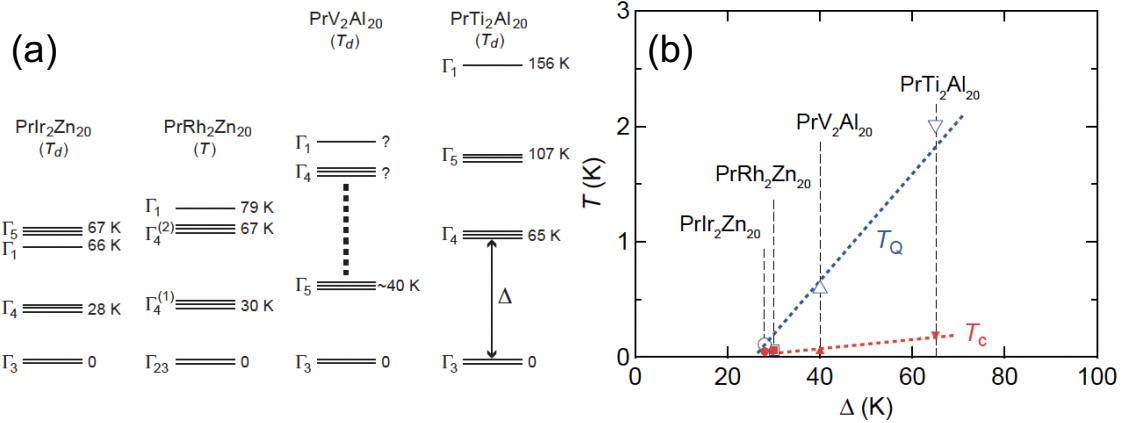


Figure 2.2: (a) CEF level schemes of $\text{PrIr}_2\text{Zn}_{20}$, $\text{PrRh}_2\text{Zn}_{20}$, $\text{PrV}_2\text{Al}_{20}$, and $\text{PrTi}_2\text{Al}_{20}$. (b) Transition temperatures for each compound. The horizontal axis corresponds to the first CEF excited energy [28].

The transition temperatures for the quadrupole order T_Q and superconducting phase T_c of these compounds are summarized in Fig. 2.2(b) [28]. It is noted that only $\text{PrTi}_2\text{Al}_{20}$ shows a ferro-quadrupolar ordering, and others show antiferro-quadrupolar ordering. The sign of the coupling constant between localized electric quadrupole is clarified by the ultrasonic measurements [29, 30, 31]. Figure 2.2(b) indicates that transition temperatures are roughly scaled by the first CEF excitation energy Δ . In other words, energy scale increases in the order of $\text{PrIr}_2\text{Zn}_{20}$ ($\text{PrRh}_2\text{Zn}_{20}$) $<$ $\text{PrV}_2\text{Al}_{20}$ $<$ $\text{PrTi}_2\text{Al}_{20}$. The energy scale of the c - f hybridization is also considered to be large in Al

systems. In fact, the electronic specific heat coefficient γ is large as ~ 100 mJ/molK² for PrTi₂Al₂₀ [26], and ~ 900 mJ/molK² for PrV₂Al₂₀ [27], respectively. Due to a strong c - f hybridization in these compounds, electrical resistivity of each compound shows a broad maximum at around 40 K (PrTi₂Al₂₀) and 60 K (PrV₂Al₂₀) as shown in Fig. 2.3 [32]. These energy scales roughly correspond to Δ , and the $-\ln T$ behavior is considered to come from the (magnetic) Kondo effect using the first excited magnetic state. In the lower temperature region, electrical resistivity of PrTi₂Al₂₀ shows a T^2 -behavior typically observed in heavy-fermion materials, whereas, PrV₂Al₂₀ shows a non-Fermi-liquid (NFL) behavior proportional to $+\sqrt{T}$. The authors suggest that the NFL behavior originates from a quadrupolar Kondo effect predicted by Dr. D. L. Cox [13].

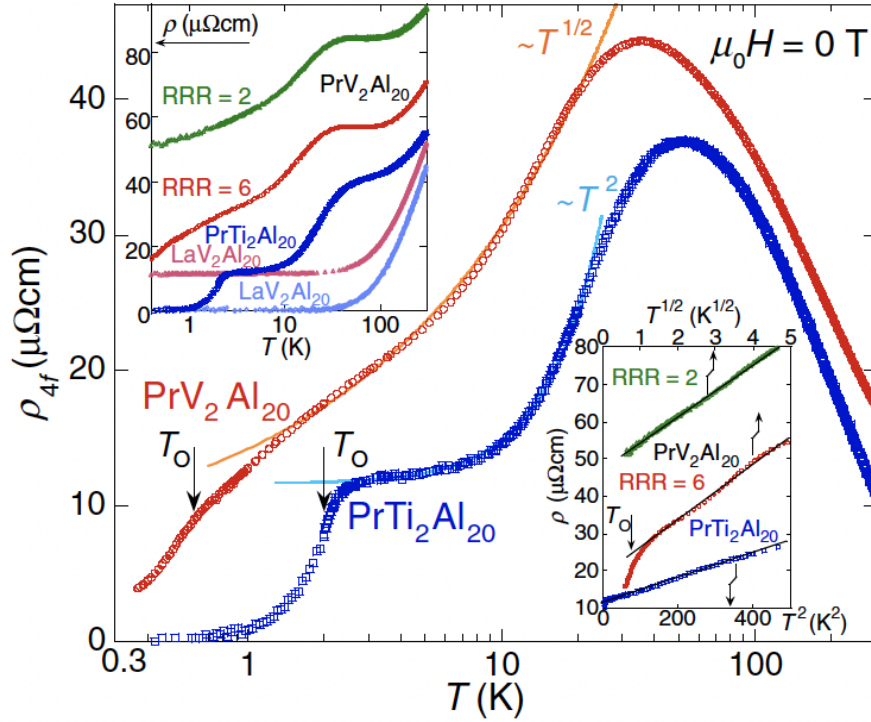


Figure 2.3: Temperature dependence of 4*f*-electron contribution to the electrical resistivity ρ_{4f} in PrTi₂Al₂₀ (blue) and PrV₂Al₂₀ (red). Insets show those of reference compounds and other samples with various sample quality [32].

2.3 Physical Properties of $\text{PrIr}_2\text{Zn}_{20}$

Here, the physical properties of the target compound, $\text{PrIr}_2\text{Zn}_{20}$, are introduced. This compound has a non-Kramers Γ_3 doublet CEF ground state as shown in Fig. 2.4, which is confirmed by the inelastic neutron scattering measurements [33].

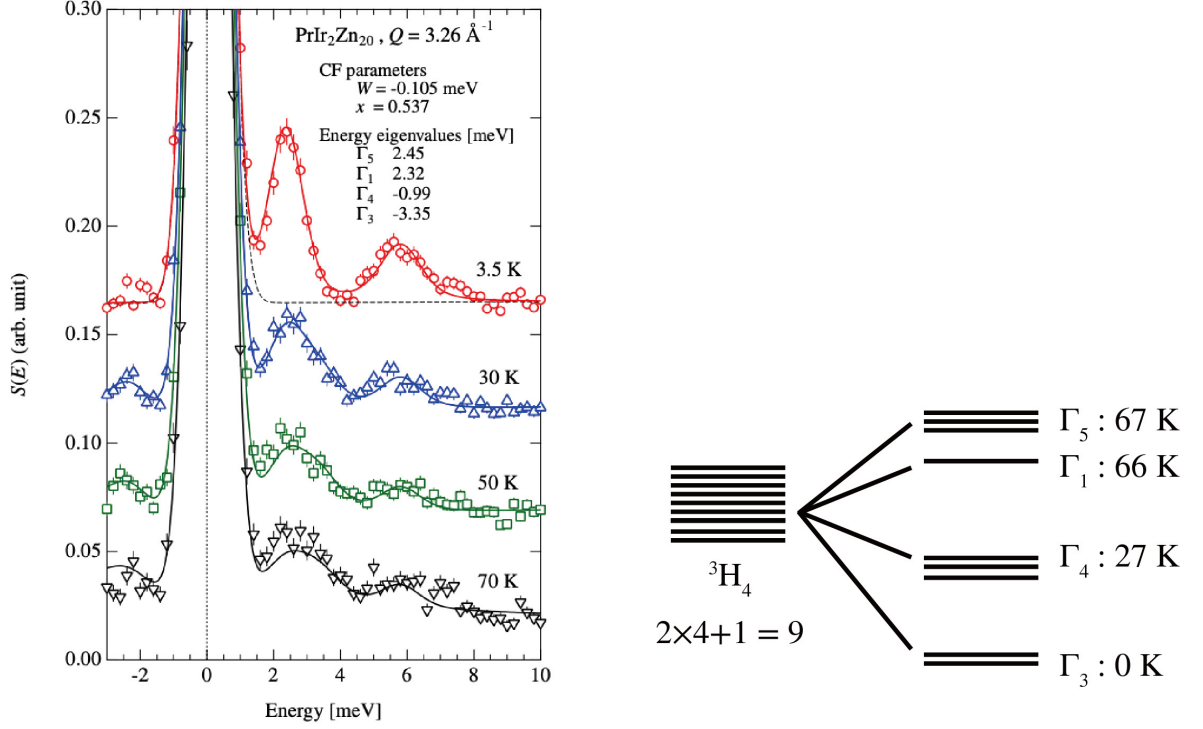


Figure 2.4: CEF excitation observed by inelastic neutron scattering measurements (left) and confirmed CEF energy scheme (right) of $\text{PrIr}_2\text{Zn}_{20}$ [33].

In sections (2.3.1) and (2.3.2), the previous studies about phase transitions of $\text{PrIr}_2\text{Zn}_{20}$ are introduced. Our investigation of the topic is mainly described in chapter 7. In section (2.3.3), the previous studies about non-Fermi-liquid behavior in $\text{PrIr}_2\text{Zn}_{20}$ and Y-diluted systems are introduced. Our investigation of the topic is mainly described in chapter 6.

2.3.1 Phase Transitions

In 2010, Dr. Onimaru *et al.* investigated the physical properties of RT_2X_{20} including $\text{PrIr}_2\text{Zn}_{20}$ [34]. They reported the presence of a superconducting phase in $\text{LaRu}_2\text{Zn}_{20}$, $\text{LaIr}_2\text{Zn}_{20}$, and $\text{PrIr}_2\text{Zn}_{20}$, which was the first observation of superconductivity in the family of RT_2X_{20} (T = transition metal; X = Al and Zn). Among them, T_c of $\text{PrIr}_2\text{Zn}_{20}$ is ~ 0.05 K. This superconductivity is considered as a non-BCS-type superconductivity and it has been studied intensively.

In addition to the superconducting-phase transition, another phase transition was reported at $T_Q \sim 0.11$ K [24]. The main panel of Fig. 2.5(a) shows the specific heat of $\text{PrIr}_2\text{Zn}_{20}$ [24]. This phase transition is detected clearly in specific-heat measurements, whereas magnetization does not show any anomalies at T_Q . These facts indicate that the order parameter of the phase transition is non-magnetic one. Furthermore, B - T phase diagram shown in Fig. 2.5(b) is similar to that of PrPb_3 where antiferro-quadrupolar ordering is confirmed [35]. In conjunction with these facts, the authors suggested that order parameter of this transition is an electric quadrupole in the paper.

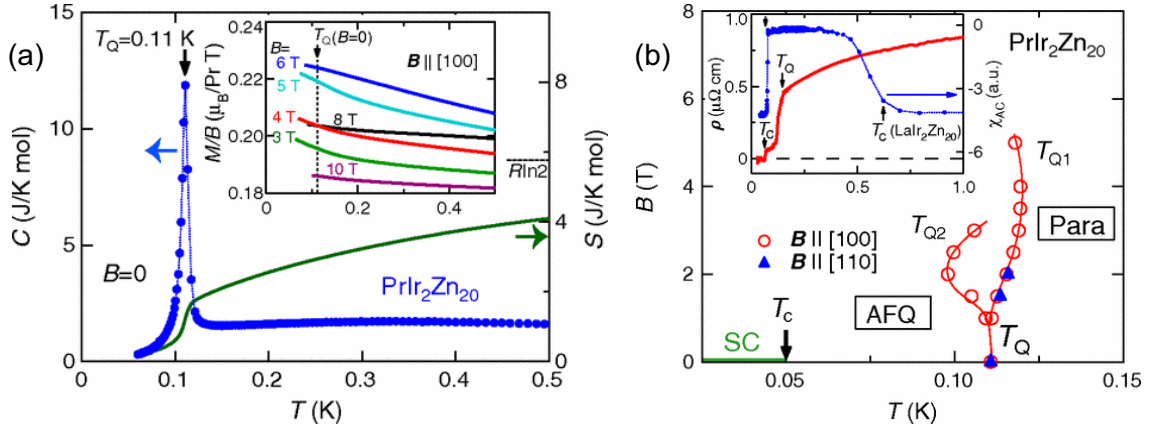


Figure 2.5: (a) Temperature dependence of the specific heat (left-hand scale) and the entropy (right-hand scale) for $\text{PrIr}_2\text{Zn}_{20}$. Inset shows the temperature dependence of M/B ($B \parallel [001]$). (b) B - T phase diagram proposed in reference [24]. Inset shows the temperature dependence of the ac magnetic susceptibility and electrical resistivity [24].

The phase transition at T_Q has been investigated by various measurement methods. Ultrasonic measurements by Dr. Ishii *et al.* found an anti-ferro interaction between localized Γ_3 -type electric quadrupoles and suggested that an antiferro quadrupolar (AFQ) ordering occurs at T_Q [30]. Figure 2.6 shows the temperature dependence of the elastic constants C_{11} , $(C_{11} - C_{12})/2$, and C_{44} . Γ_3 -symmetrical elastic constant $(C_{11} - C_{12})/2$ shows a low-temperature softening and a clear anomaly at T_Q . (Interpretation of other symmetrical modes is discussed later in chapter 7.) The evidence of the AFQ ordering is observed also in the neutron diffraction measurements after that [36].

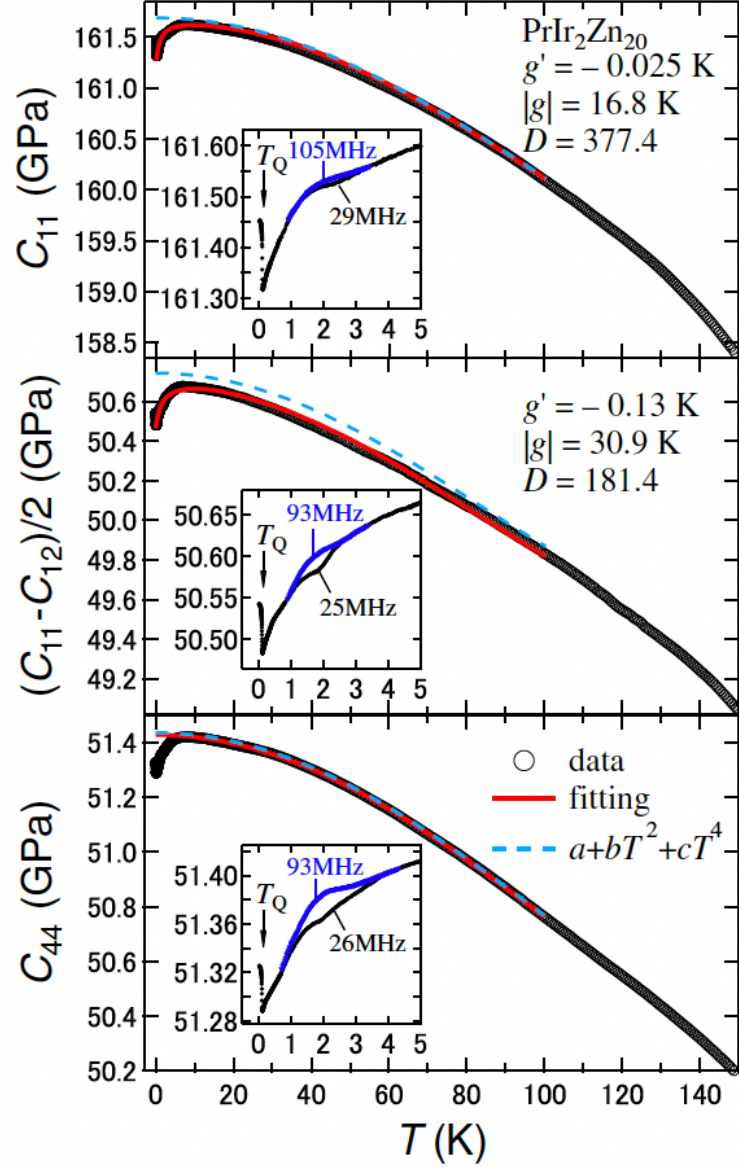


Figure 2.6: Temperature dependence of the elastic constant C_{11} , $(C_{11} - C_{12})/2$, and C_{44} [30].

Important fact reported in the early study is that the anomaly of the specific heat at T_Q shows a double peak structure in the field range $1.5 \text{ T} \leq B \leq 3 \text{ T}$ for $B \parallel [001]$. The split is not observed in similar measurements in $B \parallel [110]$. Figure 2.7 shows the temperature dependence of the specific heat in (a) $B \parallel [100]$ and (b) $B \parallel [110]$ [24].

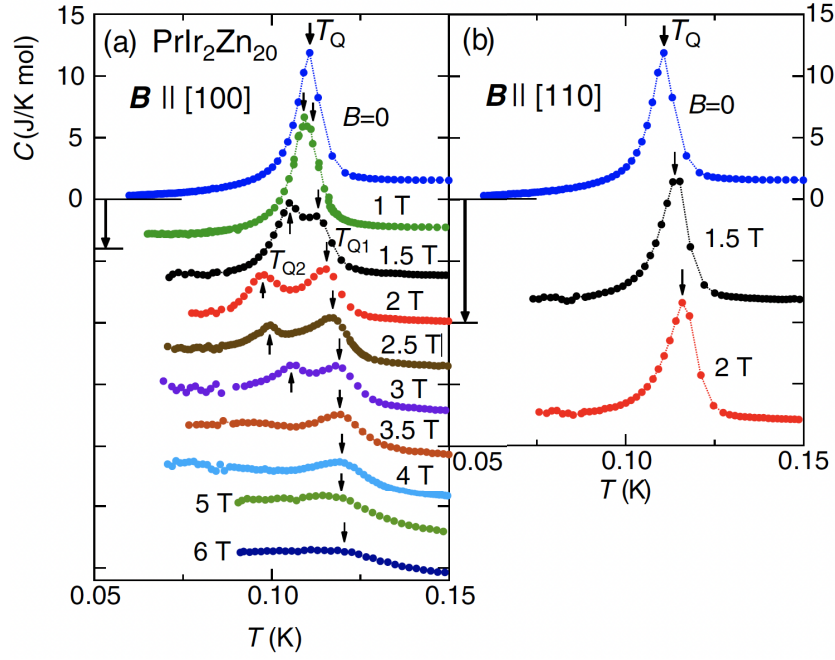


Figure 2.7: Temperature dependence of the specific heat of $\text{PrIr}_2\text{Zn}_{20}$ in (a) $B \parallel [100]$ and (b) $B \parallel [110]$ [24].

In addition to the specific-heat measurements, other measurements also reported several anomalies in the AFQ ordering phase. For example, the phase diagrams based on the results of ultrasonic measurements and magnetoresistance measurements are shown in Fig. 2.8 [30, 37]. Clear anomalies in the AFQ phase are observed for both measurements, however, the origin of the anomalies has not been revealed yet.

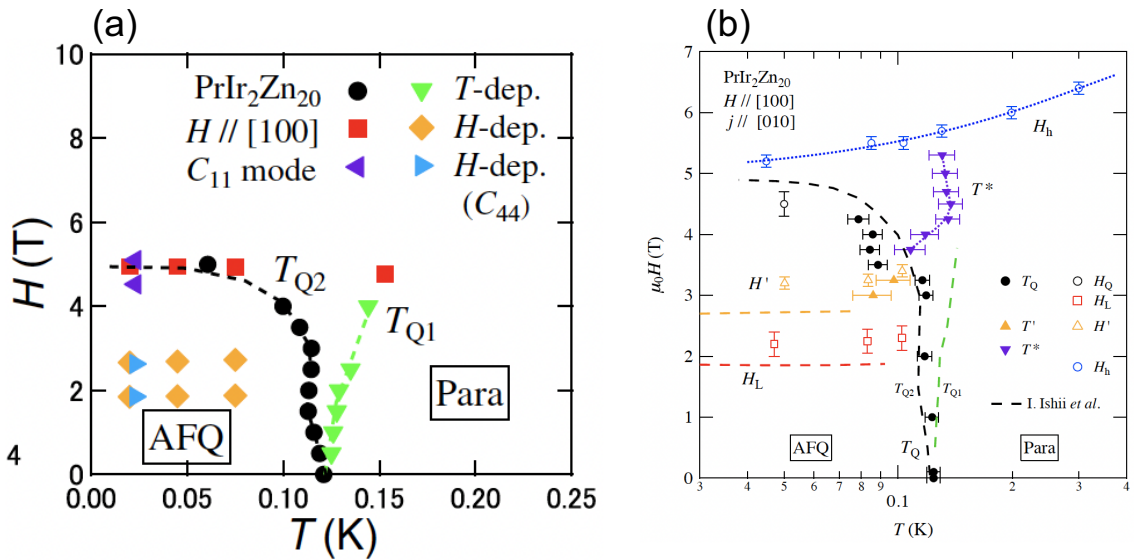


Figure 2.8: B - T phase diagram of $\text{PrIr}_2\text{Zn}_{20}$ based on the (a) ultrasound measurements [30] and (b) magnetoresistance measurements [37].

On the other hand, the same research group reported the phase diagram without the split under the magnetic field along [100] in 2016 [38]. The B - T phase diagram ($B \parallel [100]$) is shown in Fig. 2.9. They suggested the possibility that the split of T_Q in the previous study originated from the sample quality, however, details of the origin could not be concluded.

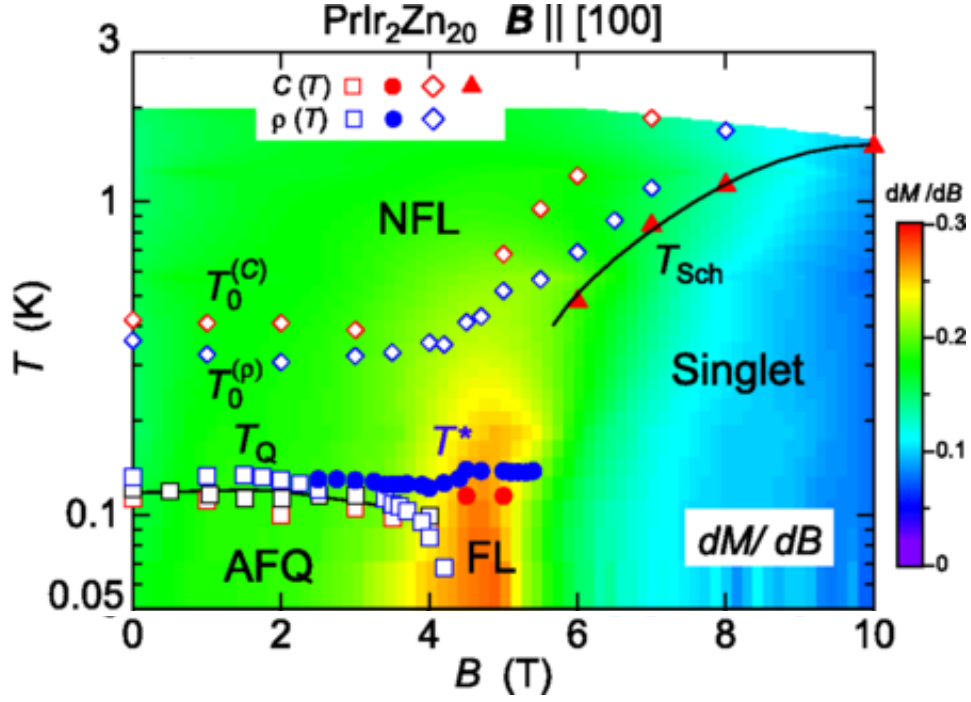


Figure 2.9: B - T phase diagram ($B \parallel [100]$) of $\text{PrIr}_2\text{Zn}_{20}$ based on the measurements of the specific heat and electrical resistivity [38].

2.3.2 Newly Proposed Phase Pocket “A” near the AFQ Phase Boundary

Very recently, important experimental results about the AFQ phase of $\text{PrIr}_2\text{Zn}_{20}$ have been reported [39]. They performed precise field-angle-resolved measurements of the specific heat and proposed that the double transition is intrinsic and strongly depends on the field strength and its orientation. Figure 2.10 shows contour plots of C_{4f}/T in the B - T plane for magnetic-field orientations along the (a) [001], (b) [112], (c) [111], and (d) [110] axes. They named the field-induced phase pocket as phase “A”. This small phase pocket “A” is most enhanced under fields along [001], and completely disappears in $B \parallel [110]$.

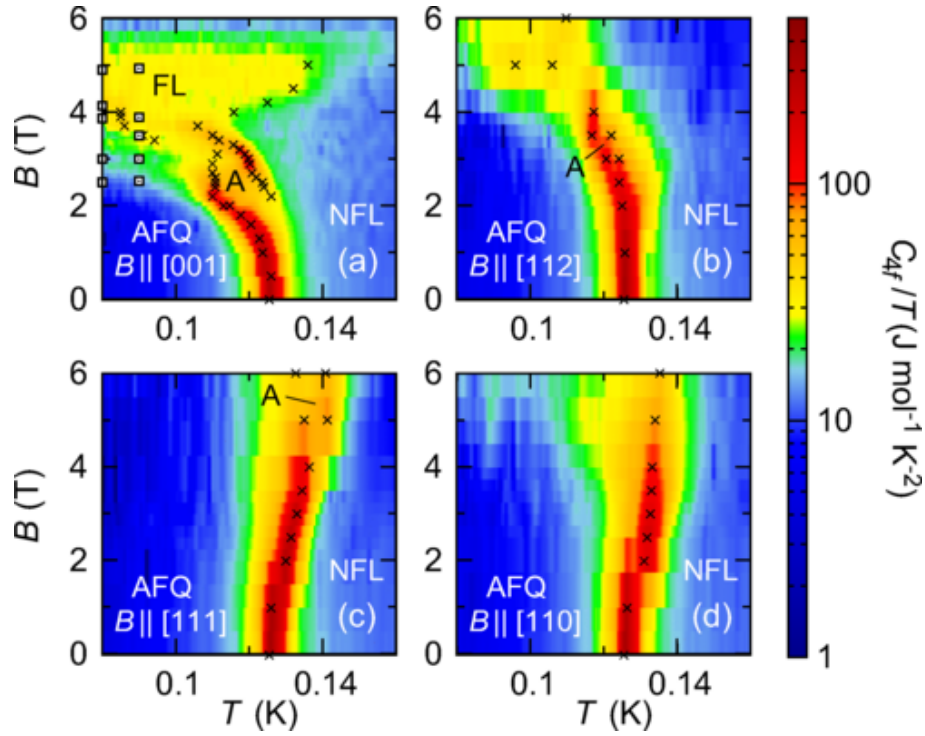


Figure 2.10: B - T phase diagram ($B \parallel [100]$) of $\text{PrIr}_2\text{Zn}_{20}$ based on the measurements of the specific heat and electrical resistivity [38].

Based on the experimental results, they suggested two possibilities of the origin of the phase pocket “A”; (1) switching of the order parameters, and (2) exotic quadrupolar ordering such as triple- q quadrupolar ordering [39]. The latter possibility is inspired by the fact that the field-induced phase pocket “A” is reminiscent of the skyrmion-lattice phase (the so-called A phase) in MnSi . In the A phase of MnSi , triple- q state was confirmed by neutron scattering experiments [40]. The origin of the phase pocket “A” in $\text{PrIr}_2\text{Zn}_{20}$ is still unveiled, whereas the intriguing ordering state involving a Γ_3 -symmetrical electric quadrupole is to be expected. Further experimental verification to probe an electric quadrupole is necessary to reveal what happens in the phase “A”.

2.3.3 Non-Fermi-Liquid Behavior of $\text{PrIr}_2\text{Zn}_{20}$

Here, we focus on the paramagnetic phase above T_Q where Γ_3 -symmetrical electric quadrupolar degrees of freedom in the CEF ground doublet remains. Figure 2.11 shows the temperature dependence of the specific heat and the electrical resistivity [38]. Each panel is normalized by the characteristic temperatures $T_0^{(C)}$ and $T_0^{(\rho)}$. Both physical quantities show non-Fermi-liquid (NFL) behavior scaled by the characteristic temperatures. $T_0^{(C)}$ is defined as the temperature where S_{4f} reaches $\frac{3}{4}R\ln 2$, and $T_0^{(\rho)}$ is defined as the temperature where $\rho(T)$ starts deviating from the $\sqrt{T}$ dependence on heating.

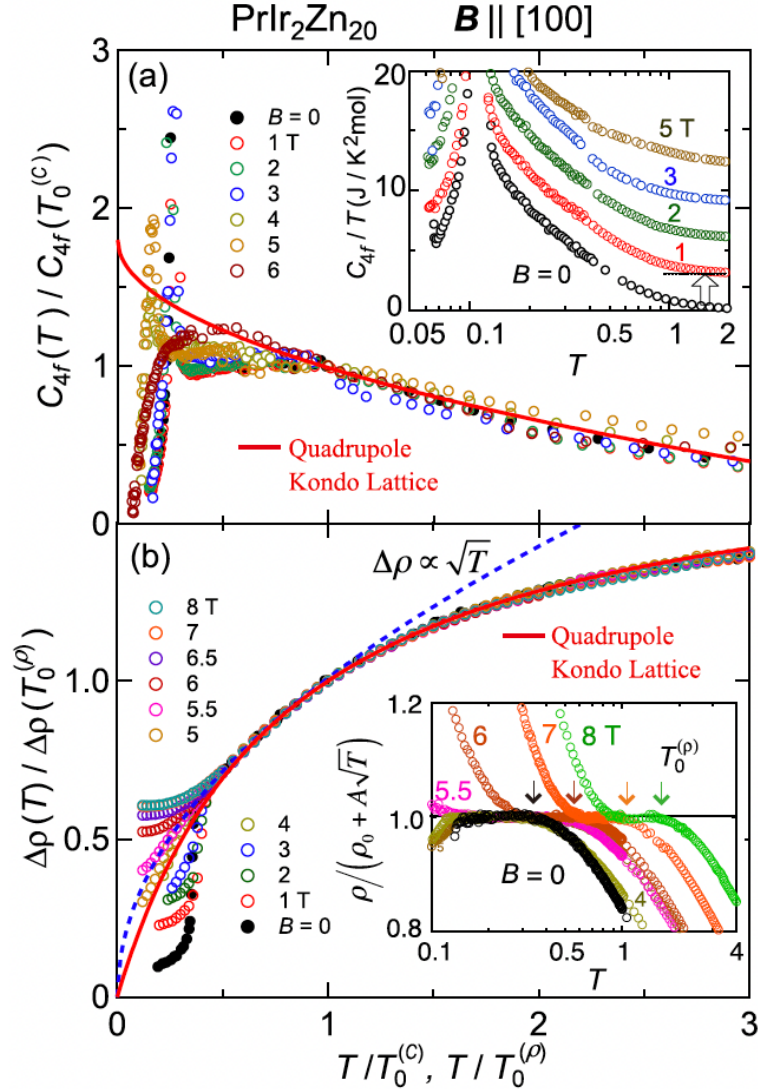


Figure 2.11: Temperature dependence of the specific heat and the electrical resistivity of $\text{PrIr}_2\text{Zn}_{20}$ [38].

Red solid curves in Fig. 2.11 show the fitting curves with the quadrupolar Kondo

“virtual” lattice model [18]. The theoretical analyses on the temperature variations of ρ and C have led to the following relations:

$$\Delta\rho(T) = \frac{a_1}{1 + a_2 \left(T_0^{(\rho)}/T \right)}, \quad (2.1)$$

$$C(T) = b_1 \left(1 - b_2 \sqrt{\frac{T}{T_0^{(C)}}} \right), \quad (2.2)$$

where a_i and b_i ($i = 1$ and 2) are parameters. The curves are in better agreement with their experimental data for a wider temperature range than those calculated by the single-site quadrupole Kondo model as shown with the blue dashed line in Fig. 2.11. Since Pr ions are periodically aligned in $\text{PrIr}_2\text{Zn}_{20}$, it is reasonable that the theory with the two-channel Anderson lattice model is more appropriate than that based on the single-site quadrupolar Kondo model.

2.3.4 Verification of the Single-Site Quadrupolar Kondo Model in Y-Diluted Systems (Y, Pr) $\text{Ir}_2\text{Zn}_{20}$

To investigate the details of NFL behavior due to a QKE, non-magnetic Y-diluted systems (Y, Pr) $\text{Ir}_2\text{Zn}_{20}$ has also been studied. By substituting Pr ions with non-magnetic ions, the situation where localized quadrupolar interaction weakens is considered to be achieved. Figure 2.12 shows the temperature dependence of the electrical resistivity and the magnetic specific heat divided by T of $\text{Y}_{1-x}\text{Pr}_x\text{Ir}_2\text{Zn}_{20}$ ($x = 0.024, 0.044, 0.085, 0.44$), which are normalized by the characteristic temperature T_0 [20]. The definition of T_0 is the temperature where S_{4f} reaches $\frac{3}{4}R\ln 2$. Electrical resistivity ($0.024 \leq x \leq 0.44$) shows the temperature dependence proportional to $\sqrt{T}$. The magnetic specific heat divided by T ($x = 0.024, 0.044$) shows the temperature dependence proportional to $-\ln T$. These temperature variations are consistent with the single-site quadrupolar Kondo model theoretically predicted by Dr. D. L. Cox [13]. On the other hand, the systems with $x = 0.085, 0.44$ shows that the behavior of C_m/T deviates from the theoretical model. The authors suggested the possibility that it originates from the atomic disorder due to elemental substitution and the behaviors are interpreted by random two level model [41, 42].

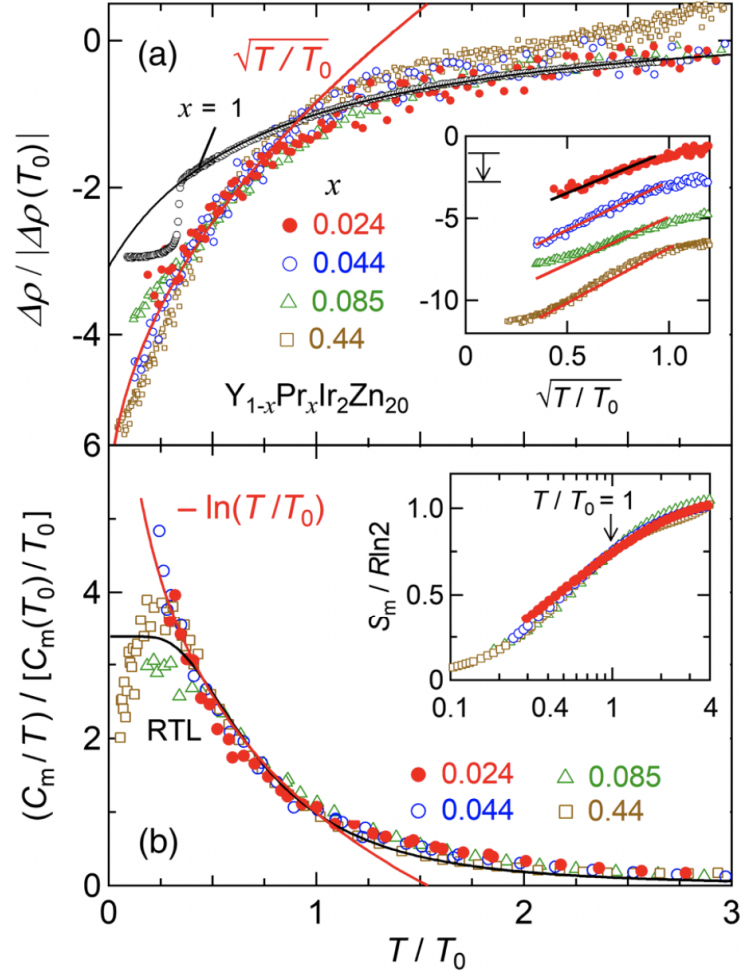


Figure 2.12: Temperature dependence of the electrical resistivity and the magnetic specific heat divided by T of $Y_{1-x}Pr_xIr_2Zn_{20}$ ($x = 0.024, 0.044, 0.085, 0.44$) [20].

Further investigation for the non-magnetic Y-diluted systems $(Y, Pr)Ir_2Zn_{20}$ has already been performed by means of ultrasound. Figure 2.13 shows the temperature dependence of the Γ_3 -symmetrical elastic constant $(C_{11} - C_{12})/2$ of $Y_{0.966}Pr_{0.034}Ir_2Zn_{20}$ (Pr-3.4% system) [43]. The data below $T_0 \sim 0.3$ K under low fields $B \leq 1.5$ T show the temperature variation proportional to $+\ln T$, which is consistent with the single-site quadrupolar Kondo model [13]. Since the elastic constant corresponds to the negative sign of the Γ_3 electric quadrupolar susceptibility, the observation is the first time to directly detect the single-site quadrupolar Kondo effect as a quadrupolar susceptibility. This is an important result because the direct experimental evidence for QKE had not been confirmed since the theory was proposed around 35 years ago.

In addition to the ultrasonic investigation, experimental results of thermal-expansion measurements for $Y_{0.964}Pr_{0.036}Ir_2Zn_{20}$ (Pr-3.6% system) also support the scenario of the single-site quadrupolar Kondo model [44]. They suggested that a quadrupolar Grüneisen ratio Γ_u obtained by the specific heat and the thermal expansion coefficient are consistent with the theoretical prediction based on the model.

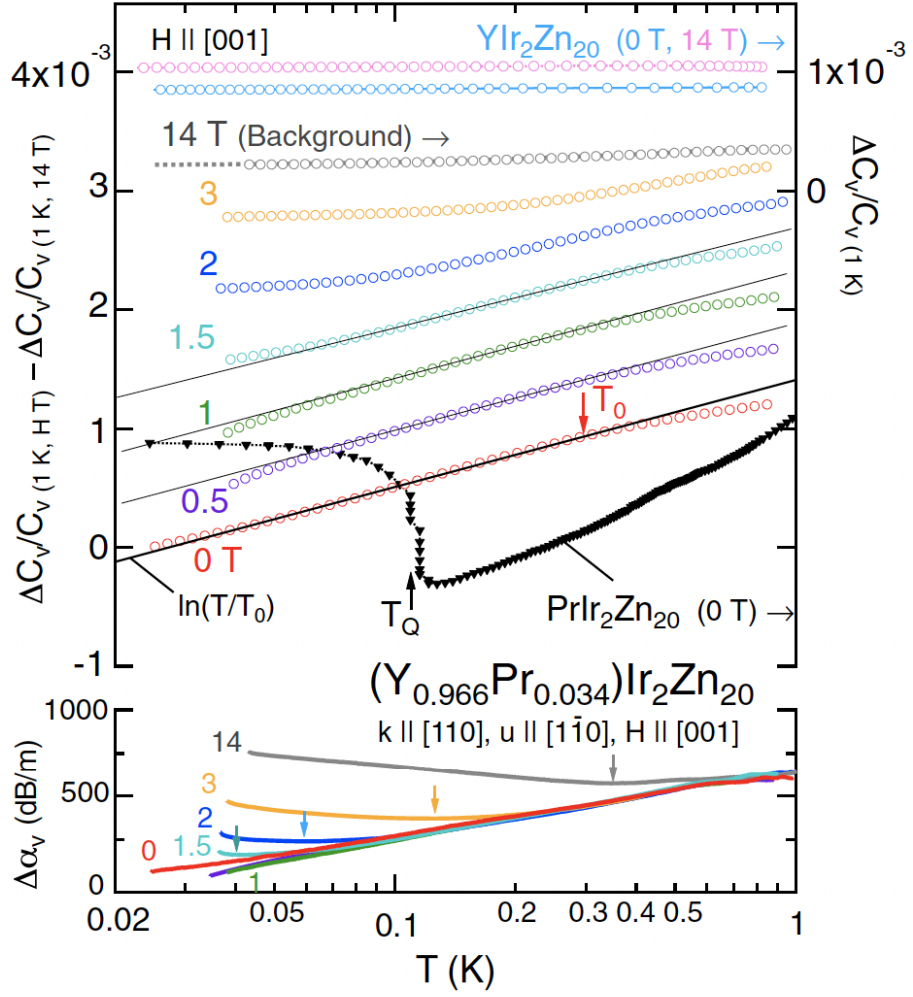


Figure 2.13: Temperature dependence of the Γ_3 elastic constant $(C_{11} - C_{12})/2$ and the ultrasonic attenuation coefficient $\Delta\alpha_v$ in the Pr-3.4% system. [43].

Chapter 3

Introduction to UBe_{13}

3.1 Crystal Structure

The target compound of the present study, UBe_{13} , crystallizes in a NaZn_{13} -type cubic structure with the space group $Fm\bar{3}c$ (No. 226, O_h^6) [45, 46]. Figure 3.1 shows a crystal structure of UBe_{13} . U atoms are surrounded by 24 Be atoms (site $96i$). A low-energy phonon excitation originating from the caged structure is observed in the inelastic neutron scattering measurements [47]. The isotropic atomic displacement parameter of U atoms obtained by recent XRD measurements also obeys the Einstein model, and Einstein temperature θ_E is estimated ~ 160 K [48].

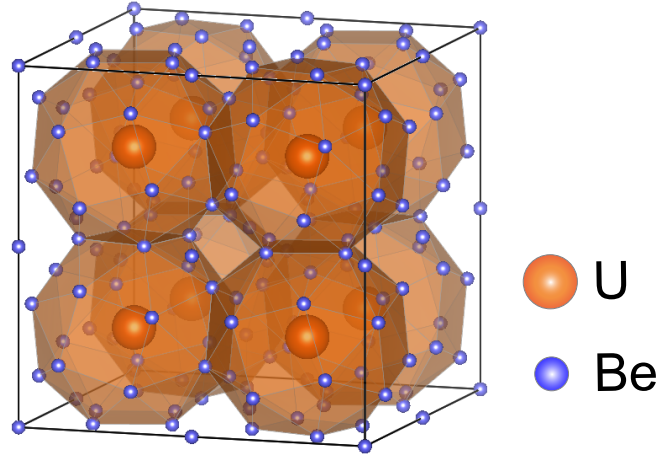


Figure 3.1: Crystal structure of UBe_{13} [46]. The illustrations are drawn using VESTA [23].

3.2 First Discovered U-Based Heavy-Fermion Superconductor

This compound, UBe_{13} , has attracted much attention as a first discovered U-based heavy-fermion superconductor ($T_c \sim 0.8 - 0.9$ K, $\gamma \sim 1.1$ J/mol $\cdot$ K²) [49]. Figure 3.3 shows the temperature dependence of AC magnetic susceptibility and the specific heat.

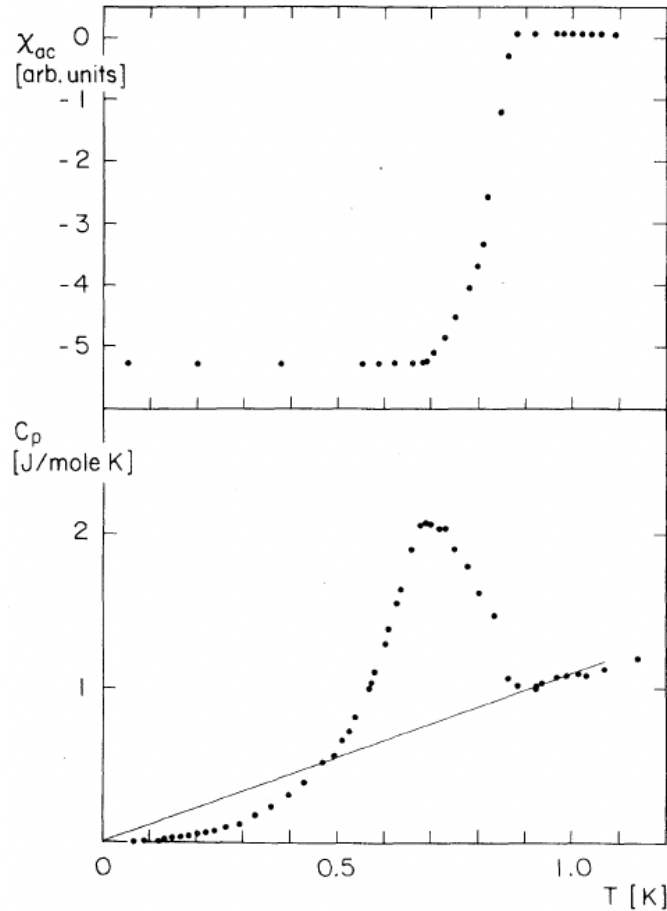


Figure 3.2: Temperature dependence of the AC magnetic susceptibility and the specific heat of UBe_{13} .

From the early stage of the research, it was suggested that this compound shows a non-BCS type superconductivity based on the temperature dependence of the specific heat [50]. Furthermore, UBe_{13} shows a large upper critical field H_{c2} exceeding the Pauli limit, which suggests a possibility of p -wave superconductor (spin-triplet superconductor) [51]. The experimental results of the NMR Knight shift of ^9Be decreases below T_c , which is interpreted as a spin-triplet superconductor [52]. On the other hand, the μSR Knight shift does not show a decrease [53]. As seen above, the parity of the Cooper pairing of this superconductor is still controversial.

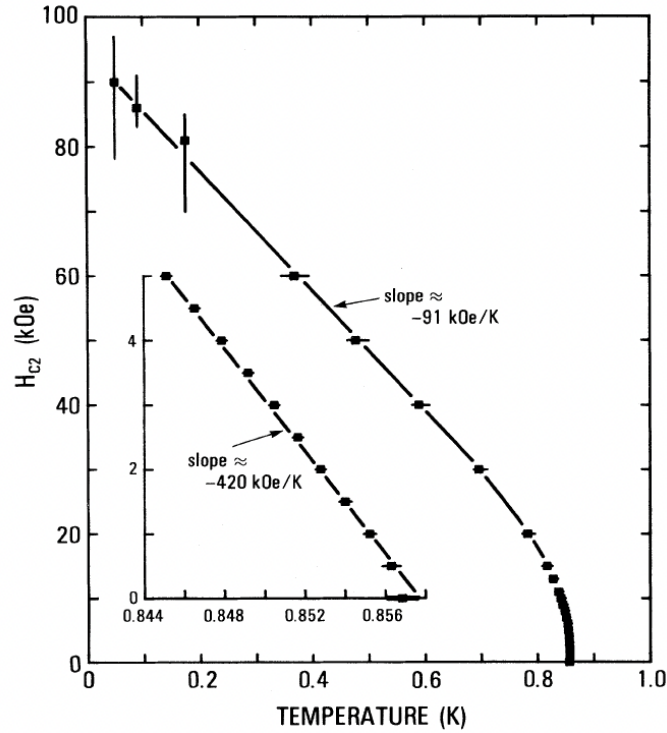


Figure 3.3: Upper critical magnetic field H_{c2} vs temperature of UBe_{13} [51].

To reveal the superconducting gap structure, a number of studies had been performed on the compound, however, the nodal structure is also still open question. For example, experimental results of the specific heat in the early stage [49] and the magnetic penetration depth [54] suggest the point node; in contrast, the results of NMR spin-relaxation rate [55] and ultrasonic attenuation [56] rather suggest the line node. Recent specific-heat measurements in a rotating field suggest the possibility that the gap is fully open over the Fermi surfaces [57]. The mechanism of the superconductivity in UBe_{13} is still veiled, and the interest in the mysterious superconductivity is insatiable.

3.3 Physical Properties of the Normal Phase of UBe_{13}

Open issue of UBe_{13} is not only about the superconducting phase but also about the normal phase. Here, physical properties of the normal phase, where non-trivial non-Fermi-liquid behavior is observed, are explained.

3.3.1 2 K Anomaly

In the first report of UBe_{13} by H. R. Ott *et al.*, a broad maximum of the electrical resistivity at around 2 K in the normal phase was observed as shown in Fig. 3.4 [49], the origin of which is still veiled. Kondo temperature of this compound is considered to be around 8 - 30 K [58, 59], whereas, this anomaly suggests the possibility of another characteristic temperature with a smaller energy scale.

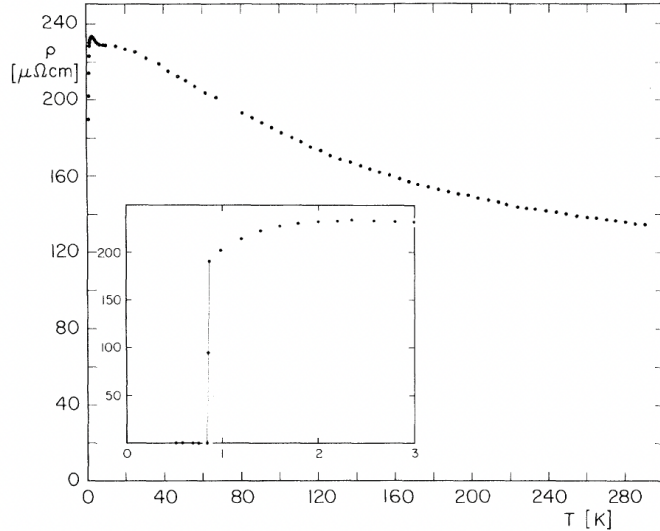


Figure 3.4: Temperature dependence of the electrical resistivity of UBe_{13} [49].

After the first observation of “2 K anomaly” by the measurements of the electrical resistivity, several measurements also reported some anomalies considered to be related to the anomaly. For example, thermal expansion shows a local maximum at around 2 K (T_{max}) as shown in Fig. 3.5 [60]. They also investigated the non-magnetic Th-diluted effect for the anomaly, and revealed that T_{max} is linearly shifted to a lower temperature as the Th concentration increases. Furthermore, it is reported that the longitudinal sound velocity of the C_{11} mode shows an elastic softening below 2 K by means of ultrasound [61]. Temperature dependence of the sound velocity is shown in Fig. 3.6. In chapter 8, we would compare our experimental results with their reports.

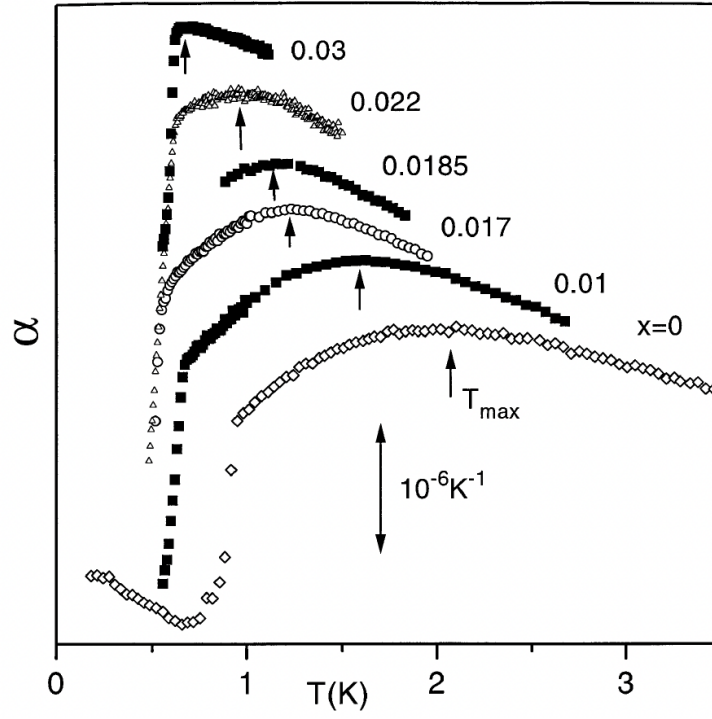


Figure 3.5: The thermal expansion of $U_{1-x}Th_xBe_{13}$. [60].

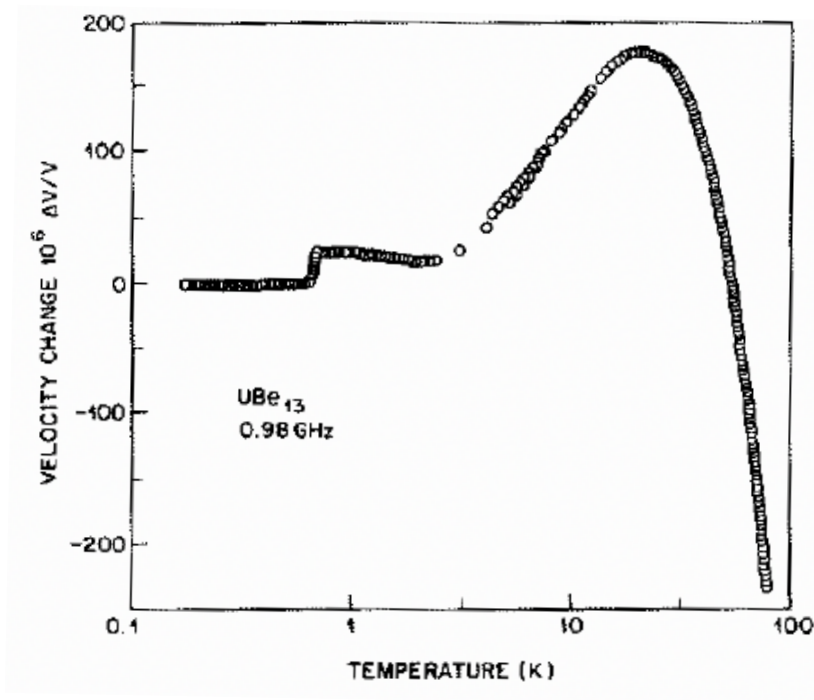


Figure 3.6: Temperature dependence of the longitudinal sound velocity of UBe_{13} [61].

3.3.2 Non-Fermi-Liquid Behavior under Magnetic Fields

Here, exotic non-Fermi-liquid (NFL) behavior under magnetic fields is explained. It is found that the temperature dependence of the electrical resistivity shows NFL behavior (proportional to $T^{3/2}$) under weak magnetic fields ($4 \text{ T} \leq B \leq 10 \text{ T}$), while this behavior changes to Fermi-liquid-like behavior (proportional to T^2) under higher magnetic fields above 14 T[62]. The change of the temperature dependence of the electrical resistivity by fields is summarized in Fig. 3.7. Closed symbols correspond to “ B^* anomaly” in the superconducting phase, which is observed in the thermal-expansion (circle markers, defined as T_L) and the specific-heat (triangle markers) measurements. The authors focused on the fact that T_L vanishes around 4.5 T, above which the universal NFL behavior in $\rho(T)$ is observed. They suggested the possibility of a field-induced quantum critical point (QCP) due to a short-range antiferromagnetic interaction.

As other candidates of the origin of the NFL behavior, quadrupolar Kondo effect assuming the non-Kramers Γ_3 CEF doublet (detail is described in the chapter 1) [13] and competition between Kondo Yosida singlet and crystalline-electric-field ground singlet[63, 64] are proposed.

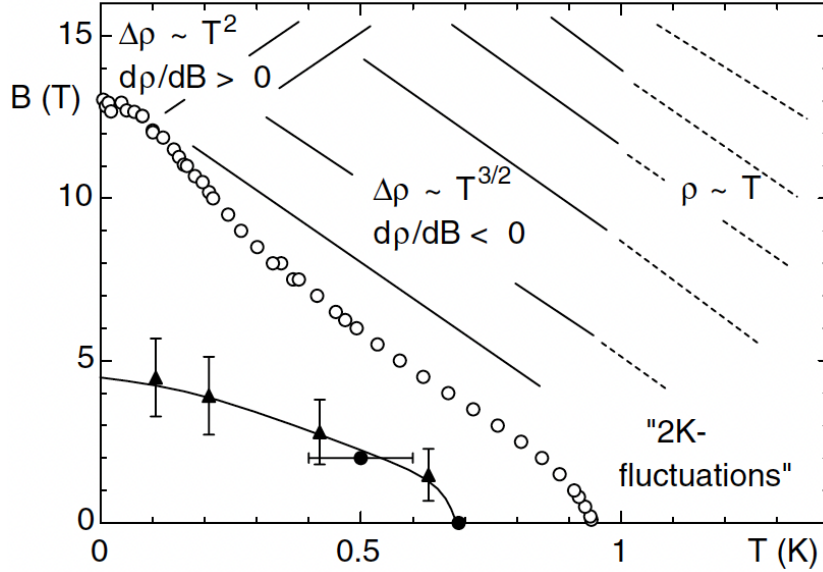


Figure 3.7: B - T phase diagram of UBe_{13} [62]. Closed symbols correspond to “ B^* anomaly” (detail is described in the main text.). Open symbols indicates the superconducting phase boundary as derived from the measurements of the electrical resistivity.

3.4 Exotic Phenomena under High Magnetic Fields

Recently, thermoelectric-power (TEP) measurements under high magnetic fields have been performed [65]. Temperature dependence of thermoelectric power S shows anomalies (T_{A1}^{TEP} and T_{A2}^{TEP}) under high magnetic fields (above ~ 9 T), which are summarized in the H - T phase diagram shown in Fig. 3.8. These anomalies could not be explained by the scenario of the field-induced anti-ferro QCP, and the authors suggested the possibility of the reconstruction of the Fermi surface under high magnetic fields. Electronic states of the compound under high magnetic fields are still not clear. As for the experiments under higher magnetic field with the pulsed magnet, only magnetization measurement has yet to be reported, which shows no clear anomaly up to 60 T [66]. We consider that further investigation of the electronic state under high magnetic fields is necessary.

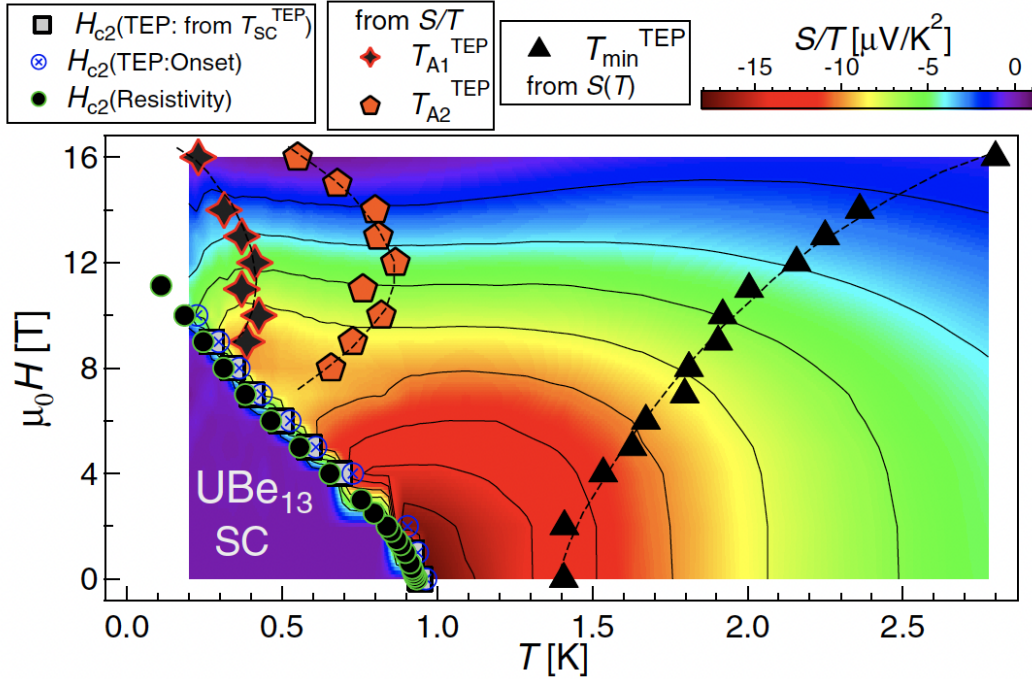


Figure 3.8: H - T phase diagram of UBe_{13} obtained from resistivity and TEP measurements [65]. $T_{\min}^{\text{TEP}}$ indicates the local minimum of S , which may characterize the energy scale of the Kondo effect and correspond to “2 K anomaly”.

3.5 Multiple Phase Diagram in Th-Diluted Systems

Non-magnetic Th-diluted systems $(\text{U}, \text{Th})\text{Be}_{13}$ have also attracted much attention, which is motivated as a verification of the single-site effect of the quadrupolar Kondo effect [17]. Furthermore, it is discovered that Th-diluted systems $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ (Th concentration x is between $0.019 \leq x \leq 0.045$.) show that the peak of the specific heat at T_c splits into two peaks [67, 68]. T - x phase diagram is shown in Fig. 3.9. The origin of the multiple superconducting phase diagram is still an open question. Recently, multiple superconducting phase diagrams in the candidates of the spin-triplet superconductor have drawn a great deal of attention, and the change of the gap symmetry is studied intensively.

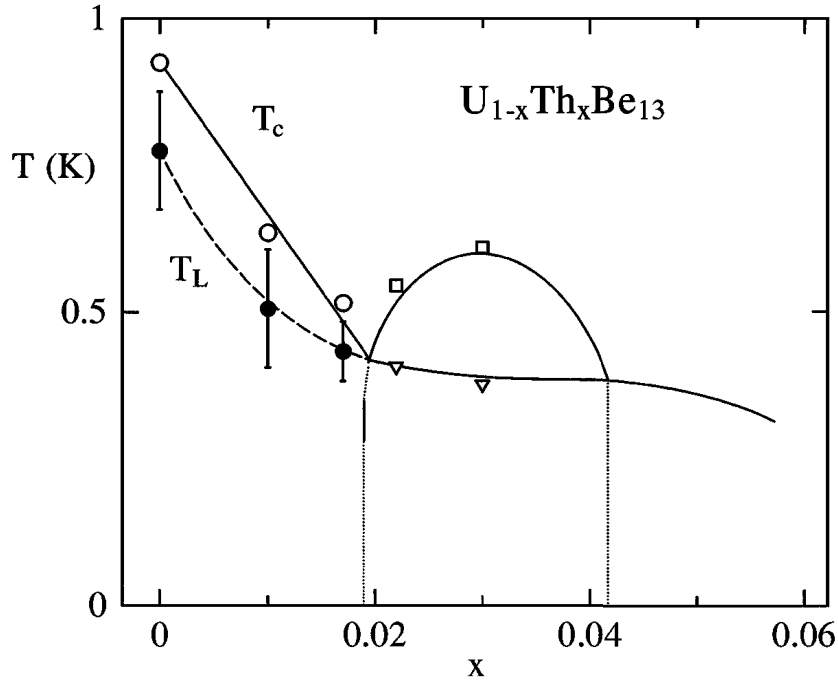


Figure 3.9: Schematic T - x phase diagram of $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ [68]. Open symbols indicate second-order phase transitions, while closed symbols show anomalies at T_L observed in the thermal expansion measurements.

Chapter 4

Purpose of Study

Main purpose of the present study is to reveal novel physical properties originating from the electric quadrupole. For the purpose, we mainly performed ultrasonic measurements of “*f*-electron caged compounds”, which can directly detect quadrupolar degrees of freedom as a susceptibility. One of advantages for this measurement method is that it can detect mode-selective quadrupolar susceptibility, which contains fruitful information about the symmetry. The reason why we focused on *f*-electron caged compounds is noted as;

- *f*-electron is well localized, and expected to form a degeneracy originating from orbital degrees of freedom based on LS description.
- CEF split is not so large because guest ion is surrounded by a high symmetrical cage, which easily causes multipolar degrees of freedom.
- The number of ligand ions is much, which enhances *c-f* hybridization and causes a strong many-body effect.
- The space in the cage is large and a guest ion weakly couples to the cage. Thus, intriguing physics originating from the coupling between the localized *f*-electronic state and phonon can be expected.

In particular, we focus on the following two systems in the present study. We would summarize what we aim to reveal in each system.

(Y, Pr)Ir₂Zn₂₀

To reveal the detail of quadrupolar Kondo effect (QKE), we systematically performed ultrasonic measurements of (Y, Pr)Ir₂Zn₂₀ where interaction between localized quadrupolar moments could be tuned by the Pr concentration. In particular, we accurately measured Γ_3 -symmetrical elastic constant $(C_{11} - C_{12})/2$ at very low temperatures where elastic behaviors are deviated from the localized crystalline-electric-field (CEF) model due to a *c-f* hybridization. Furthermore, we found that an energy scale

of phonon originating from the cage structure is very close to that of QKE in the intermediate system, $\text{Y}_{0.63}\text{Pr}_{0.37}\text{Ir}_2\text{Zn}_{20}$ (Pr-37% system). We discuss the possibility to form a novel quantum ground state where localized electric quadrupole, conduction electron, and phonon are entangled.

Additionally, new phase pocket “A” near the antiferro-quadrupolar (AFQ) ordering phase boundary of $\text{PrIr}_2\text{Zn}_{20}$ has been proposed recently. In this ordered phase, the possibilities of the exotic quadrupolar ordering with multi- q and the switching of order parameters (Γ_3 -type quadrupoles) are proposed. We aim to reveal the origin of this curious phase from the perspective of elastic responses.

(U, Th)Be₁₃

We aim to reveal the origin of non-trivial non-Fermi-liquid (NFL) behavior observed in UBe_{13} using ultrasonic measurements. Our first motivation was to verify QKE proposed by Dr. D. L. Cox in the early stage. Additionally, we investigated the electronic state under high magnetic fields, where the possibility of reconstruction of Fermi surface has been proposed recently.

Non-BCS type superconductivity of the system has also attracted much attention. Especially, multiple superconducting phase diagram observed in $(\text{U}, \text{Th})\text{Be}_{13}$ is in focus. We performed ultrasonic measurements of $(\text{U}, \text{Th})\text{Be}_{13}$ (Th-2.7% system) as well UBe_{13} to compare the elastic behavior in superconducting phases. Our final goal is to reveal the superconducting gap symmetry and order parameter of these mysterious superconductors.

Chapter 5

Experimental Methods

5.1 Sample Preparation

$(Y, Pr)Ir_2Zn_{20}$

Samples of $Y_{1-x}Pr_xIr_2Zn_{20}$ for ultrasonic measurements are provided by Dr. T. Onimaru, K. T. Matsumoto, and Y. Yamane at Hiroshima university. These single crystalline samples are grown by the Zn-self-flux method with pre-arc-melting alloys of Y, Pr, and Ir as described in previous papers [69, 20]. Pictures of the samples are shown in Fig. 5.1. The Pr composition of the Y-diluted samples was confirmed by using of an electron probe micro analysis (EPMA) and CEF analysis of low-temperature magnetization measurements. The sample dimensions of the rectangular parallelepiped shape are $[110] - [1\bar{1}0] - [001]$ for all sample. Sample orientation is clarified by the author using Laue method in Hokkaido university. For example, Fig. 5.2 shows the Laue photo of the $[110]$ surface of the Pr-8% system.

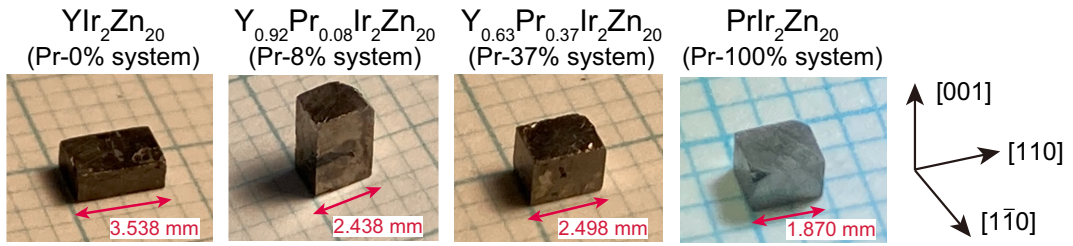


Figure 5.1: Sample pictures of $Y_{1-x}Pr_xIr_2Zn_{20}$ ($x = 0, 0.08, 0.37$, and 1.0).

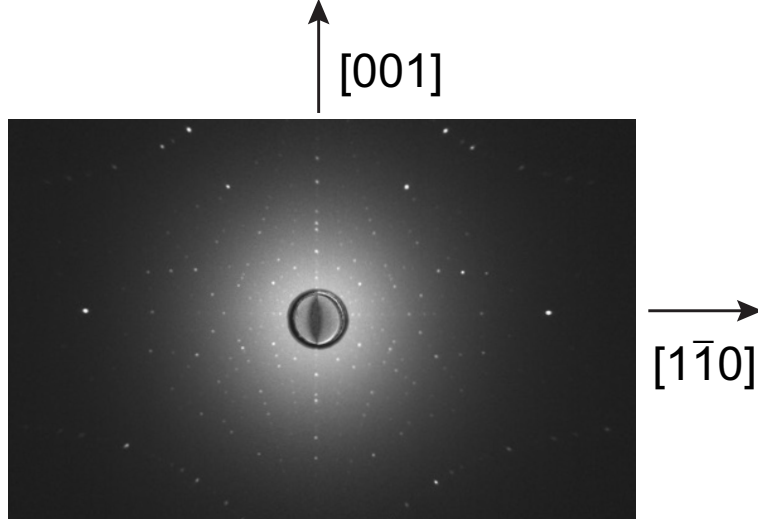


Figure 5.2: Laue photo of the $[110]$ surface of the Pr-8% system.

$(\text{U}, \text{Th})\text{Be}_{13}$

Samples of $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ ($x = 0, 0.027$) for ultrasonic measurements are prepared by Dr. T. Yanagisawa in Hokkaido university. Both UBe_{13} and $\text{U}_{0.973}\text{Th}_{0.027}\text{Be}_{13}$ (Th-2.7% system) are grown by the Al-flux method in M. B. Maple group at UC San Diego. Th concentration of the latter one is estimated based on the preparation ratio and T_c measured by the electrical resistivity. (Details are described in section 8.1.) Pictures of the samples are shown in Fig. 5.3. The sample dimension of the rectangular parallelepiped shape is $[100] - [010] - [001]$ for UBe_{13} , and $[110] - [1\bar{1}0] - [001]$ for the Th-2.7% system. Sample orientation is clarified by the author using Laue method in Charles university (Czech Republic). For example, Fig. 5.4 shows the Laue photo of the $[001]$ surface of UBe_{13} .

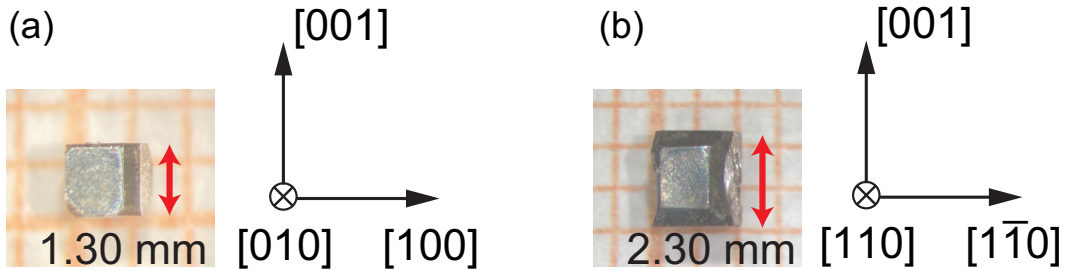


Figure 5.3: Sample pictures of (a) UBe_{13} and (b) Th-2.7% system.

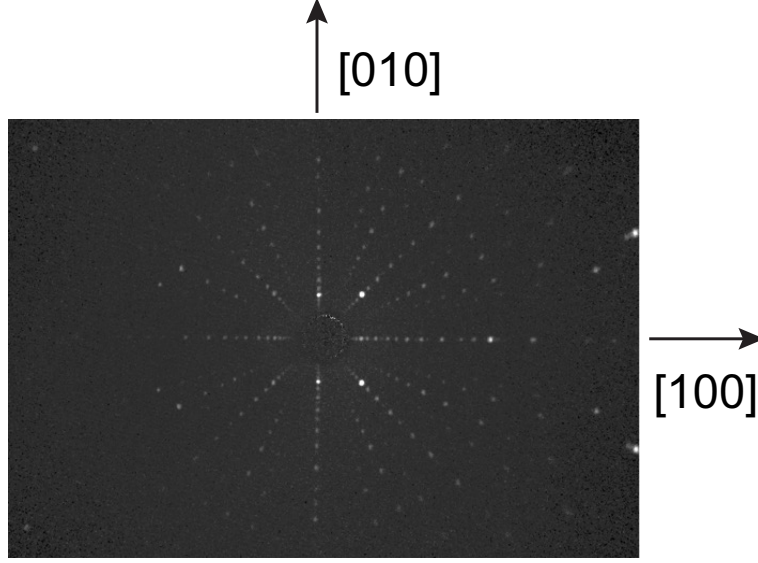


Figure 5.4: Laue photo of the $[001]$ surface of UBe_{13} .

5.2 Elastic Constant

The measurement frequency of the ultrasound is about $10 \sim 200$ MHz, thus, wavelength of the acoustic wave is $10^{-6} \sim 10^{-7}$ m. In contrast, typical atomic distance is $\sim 10^{-10}$ m. Since the atomic distance is much shorter than the wavelength, continuum approximation could be valid. So, we describe the elastic constant as below, which is same as the discussion of general elastic body [70].

Strain tensor ε_{ij} ($i, j = x, y, z$), which is second rank tensor, is described using displacement component u_i ($i = x, y, z$) as below.

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) = \varepsilon_{ji} \quad (5.1)$$

Here, ε_{ij} is a symmetric tensor ($\varepsilon_{ij} = \varepsilon_{ji}$). Assuming that induced strain is sufficient small, stress σ_{ij} is described as a linear combination of the strain derived from a Hooke's law.

$$\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl} \quad (5.2)$$

Fourth rank tensor C_{ijkl} in the equation (5.2) is an elastic stiffness constant, which has a dimension of energy per unit volume. In the thesis, we call this value as an “elastic constant”.

Unless considering the rotation ($\omega_{ij} = \frac{1}{2} \left(\frac{\partial u_j}{\partial x_i} - \frac{\partial u_i}{\partial x_j} \right)$), strain is symmetrical as well as stress ($\sigma_{ij} = \sigma_{ji}$). By using Voigt's notation, the index is described as that

$xx \rightarrow 1$, $yy \rightarrow 2$, $zz \rightarrow 3$, $yz \rightarrow 4$, $zx \rightarrow 5$, $xy \rightarrow 6$, and eq. (5.2) can be described in the matrix description as below.

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{zx} \\ \varepsilon_{xy} \end{pmatrix} \quad (5.3)$$

The matrix element of the elastic constant could be reduced depending on the crystalline symmetry. For example, independent matrix elements in the cubic symmetry are only three components C_{11} , C_{12} , and C_{44} . Equation (5.3) could be described as below.

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{zx} \\ \varepsilon_{xy} \end{pmatrix} \quad (5.4)$$

Here, symmetrical strains are introduced to consider the coupling between multipole and strain induced by ultrasound. Symmetrical strains in the cubic symmetry are as shown in Fig. 5.5

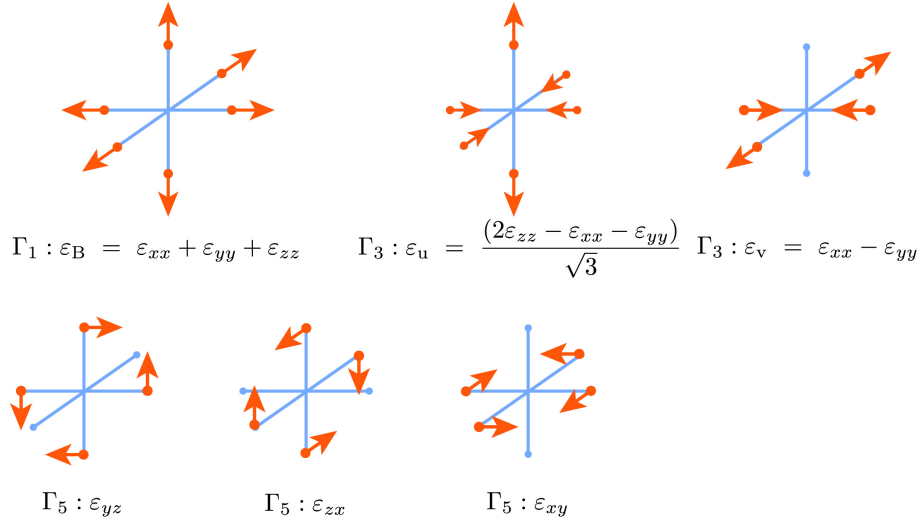


Figure 5.5: Symmetrized strains in the cubic symmetry.

Elastic energy induced by the strain is described as shown in Eq. (5.5). Each term is symmetrically categorized. This indicates which symmetrical strain corresponds to which mode of the elastic constants.

$$\begin{aligned}
U_{elastic} &= \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} \varepsilon_i \varepsilon_j \\
&= \frac{(C_{11} + 2C_{12})}{3} \varepsilon_B^2 + \frac{1}{2} \frac{(C_{11} - C_{12})}{2} (\varepsilon_u^2 + \varepsilon_v^2) \\
&\quad + \frac{1}{2} C_{44} (\varepsilon_{yz}^2 + \varepsilon_{zx}^2 + \varepsilon_{xy}^2)
\end{aligned} \tag{5.5}$$

Next, we consider the relationship between ultrasound and elastic mode based on equation of motion. In the cubic symmetry, equation of motion for each axis is described as below.

$$\rho \frac{\partial^2 u_i}{\partial t^2} = C_{11} \frac{\partial^2 u_i}{\partial x_i^2} + C_{44} \left(\frac{\partial^2 u_i}{\partial x_j^2} + \frac{\partial^2 u_i}{\partial x_k^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 u_j}{\partial x_i \partial x_j} + \frac{\partial^2 u_k}{\partial x_k \partial x_i} \right) \tag{5.6}$$

Here, we assume the transverse ultrasound with $k \parallel [110]$ and $u \parallel [\bar{1}\bar{1}0]$. k is a propagation vector, and u is a displacement vector.

$$u_x = -u_y = u_0 \exp \left[i \left(\frac{kx}{\sqrt{2}} + \frac{ky}{\sqrt{2}} - \omega t \right) \right] \tag{5.7}$$

By substituting above plane wave equation into Eq. (5.6), we could obtain the relationship between the elastic constant and the sound velocity as below.

$$\frac{1}{2} (C_{11} - C_{12}) = \rho \left(\frac{\omega}{k} \right)^2 \equiv \rho v_{\Gamma_3}^2 \tag{5.8}$$

The sound velocity of the transverse mode ($k \parallel [110]$, $u \parallel [\bar{1}\bar{1}0]$) is defined as $v_{\Gamma_3} \equiv \frac{\omega}{k}$. Equation (5.8) indicates that Γ_3 -symmetrical elastic constant $\frac{(C_{11}-C_{12})}{2}$ can be obtained by measuring the sound velocity of this transverse ultrasound.

In the same way, we consider the case of the transverse ultrasound with $k \parallel [110]$ and $u \parallel [001]$.

$$u_z = u_0 \exp \left[i \left(\frac{k}{\sqrt{2}} x + \frac{k}{\sqrt{2}} y - \omega t \right) \right] \tag{5.9}$$

$$C_{44} = \rho \left(\frac{\omega}{k} \right)^2 \equiv \rho v_{\Gamma_5}^2 \tag{5.10}$$

The sound velocity of the transverse mode ($k \parallel [110]$, $u \parallel [001]$) is defined as $v_{\Gamma_5} \equiv \frac{\omega}{k}$. Thus, Γ_5 -symmetrical elastic constant C_{44} can be obtained by measuring the sound velocity of this transverse ultrasound. In other words, we can obtain different symmetrical elastic constant by measuring the sound velocity of different geometrical

ultrasounds. Such mode selectivity is a good advantage of the ultrasonic measurements. And, symmetrical strain could be coupled to the same symmetrical electric quadrupole. Considering this interaction as a perturbation Hamiltonian, quadrupolar susceptibility could be detected from the elastic constant. (Details are discussed in the next section.)

5.3 Crystalline-Electric-Field Effect

4*f* electron in the crystal is affected by the electrostatic potential came from ligand ions, and the degeneracy of J multiplet is split. This effect is called as a crystalline-electric-field (CEF) effect. Hamiltonian of the CEF effect, $\mathcal{H}_{\text{CEF}}$, depends on the site symmetry of the magnetic ion. For example, CEF Hamiltonian in the cubic symmetry O_h is described using total angular momentum J as below.

$$\mathcal{H}_{\text{CEF}} = B_4^0 (O_4^0 + 5O_4^4) + B_6^0 (O_6^0 - 21O_6^4). \quad (5.11)$$

This description using J could be obtained by Wigner-Eckart theorem. B_l^m is a CEF parameter, and O_l^m is Stevens Operator.

$$\begin{aligned} O_4^0 &= 35J_z^2 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2 \\ O_4^4 &= \frac{1}{2}(J_+^4 + J_-^4) \\ O_6^0 &= 231J_z^6 - [315J(J+1) - 735]J_z^4 + [105J^2(J+1)^2 - 525J(J+1) + 294]J_z^2 \\ &\quad - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1) \\ O_6^4 &= \frac{1}{4}[\{11J_z^2 - J(J+1) - 38\}(J_+^4 + J_-^4) + (J_+^4 + J_-^4)\{11J_z^2 - J(J+1) - 38\}] \end{aligned}$$

We assume that the Hamiltonian is

$$\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{QS}} + \mathcal{H}_{\text{QQ}}. \quad (5.12)$$

Here, the first term describes the CEF hamiltonian and the second term corresponds to Zeeman interaction. The third term describes the interaction between the elastic strain and an effective multipole, and the fourth term describes the intersite quadrupole-quadrupole interaction.

First, We consider only the coupling Hamiltonian of the elastic strain to an electric quadrupole, $\mathcal{H}_{\text{QS}}(\Gamma) = -g_\Gamma O_\Gamma \varepsilon_\Gamma$ (third term of Eq. (5.12)) as a perturbation Hamiltonian. (We ignore the fourth term as a first step.) $E_i(\varepsilon_\Gamma)$ is a perturbed CEF level as a function of strain ε_Γ up to second-order perturbation, which can be written as

$$\begin{aligned}
E_i(\varepsilon_\Gamma) &= E_i^0 + \langle i | \mathcal{H}_{\text{QS}} | i \rangle + \sum_{j \neq i} \frac{|\langle j | \mathcal{H}_{\text{QS}} | i \rangle|^2}{E_j^{(0)} - E_i^{(0)}} \\
&= E_i^0 - g_\Gamma \langle i | O_\Gamma | i \rangle \varepsilon_\Gamma + g_\Gamma^2 \sum_{j \neq i} \frac{|\langle j | O_\Gamma | i \rangle|^2}{E_j^{(0)} - E_i^{(0)}} \varepsilon_\Gamma^2.
\end{aligned} \tag{5.13}$$

The Helmholtz free energy of the local $4f$ -electron states in the CEF can be written as,

$$\begin{aligned}
F &= U - Nk_B T \ln \sum_i \exp \{ -E_i(\varepsilon_\Gamma) / k_B T \} \\
&= \frac{1}{2} \sum_\Gamma C_\Gamma \varepsilon_\Gamma^2 - Nk_B T \ln \sum_i \exp \{ -E_i(\varepsilon_\Gamma) / k_B T \},
\end{aligned} \tag{5.14}$$

where N is the number of ions in a unit volume, i is the number index for J multiplets and their degenerate states. $U = \frac{1}{2} \sum_\Gamma C_\Gamma \varepsilon_\Gamma^2$ is the internal energy for the strained system. Since the elastic constant with Γ -type symmetry, C_Γ , is defined as the second derivative of the free energy with respect to strain ε_Γ , C_Γ is derived as follows from Eq. (5.14):

$$\begin{aligned}
C_\Gamma(T, B) &= \left(\frac{\partial^2 F}{\partial \varepsilon_\Gamma^2} \right)_{\varepsilon_\Gamma \rightarrow 0} \\
&= C_\Gamma^0 + N \left[\left\langle \frac{\partial^2 E_i}{\partial \varepsilon_\Gamma^2} \right\rangle - \frac{1}{k_B T} \left\{ \left\langle \left(\frac{\partial E_i}{\partial \varepsilon_\Gamma} \right)^2 \right\rangle - \left\langle \frac{\partial E_i}{\partial \varepsilon_\Gamma} \right\rangle^2 \right\} \right].
\end{aligned} \tag{5.15}$$

Here, C_Γ^0 is the background of the elastic constant. The single-ion quadrupolar susceptibility χ_Γ is defined as

$$g_\Gamma^2 \chi_\Gamma = - \left\langle \frac{\partial^2 E_i}{\partial \varepsilon_\Gamma^2} \right\rangle + \frac{1}{k_B T} \left[\left\langle \left(\frac{\partial E_i}{\partial \varepsilon_\Gamma} \right)^2 \right\rangle - \left\langle \frac{\partial E_i}{\partial \varepsilon_\Gamma} \right\rangle^2 \right]. \tag{5.16}$$

Thus, C_Γ is described as follows from Eqs. (5.15) and (5.16):

$$C_\Gamma(T, B) = C_\Gamma^0 - N g_\Gamma^2 \chi_\Gamma(T, B). \tag{5.17}$$

In addition to the quadrupole-strain interaction $\mathcal{H}_{\text{QS}}$, the intersite quadrupole-quadrupole interaction can also be added by using a molecular-field approximation of the quadrupolar moment O_Γ as

$$\mathcal{H}_{\text{QQ}}(\Gamma) = \sum_\Gamma g'_\Gamma \langle O_\Gamma \rangle O_\Gamma. \tag{5.18}$$

This corresponds to considering the effective strain $\varepsilon_{\Gamma}^{\text{eff}}$ as

$$\begin{aligned}\mathcal{H}_{QS} + \mathcal{H}_{QQ} &= \sum_{\Gamma} g_{\Gamma} \left(\varepsilon_{\Gamma} + \frac{g'_{\Gamma}}{g_{\Gamma}} \langle O_{\Gamma} \rangle \right) O_{\Gamma} \\ &= - \sum_{\Gamma} g_{\Gamma} \varepsilon_{\Gamma}^{\text{eff}} O_{\Gamma}.\end{aligned}\quad (5.19)$$

The elastic constant C_{Γ} is rewritten as

$$C_{\Gamma}(T, B) = C_{\Gamma}^0 - N g_{\Gamma}^2 \frac{\chi_{\Gamma}(T, B)}{1 - g'_{\Gamma} \chi_{\Gamma}(T, B)}.\quad (5.20)$$

From Eqs. (5.13) and (5.16), the multipolar susceptibility χ_{Γ} is described as

$$\begin{aligned}\chi_{\Gamma}(T, B) &= \frac{1}{k_B T} \left\{ \sum_i \rho_i |\langle i | O_{\Gamma} | i \rangle|^2 - \left(\sum_i \rho_i \langle i | O_{\Gamma} | i \rangle \right)^2 \right\} \\ &+ \sum_{j \neq i} \frac{\rho_j - \rho_i}{E_i - E_j} |\langle j | O_{\Gamma} | i \rangle|^2.\end{aligned}\quad (5.21)$$

It can be seen that the diagonal terms of the matrix elements of the electric quadrupole O_{Γ} correspond to the Curie terms, and the non-diagonal terms to the Van-Vleck terms from Eq. (5.21). Here, $\rho_i = \frac{\exp(-\beta E_i)}{Z}$ means the probability based on statistical mechanics. For example, the Γ_3 -type electric quadrupole O_v , which is a main target of the study, has matrix elements in the cubic symmetry as below.

$$O_v = \begin{matrix} & \begin{matrix} |\Gamma_3^{(\alpha)}\rangle & |\Gamma_3^{(\beta)}\rangle & |\Gamma_4^{(\alpha)}\rangle & |\Gamma_4^{(\beta)}\rangle & |\Gamma_4^{(\gamma)}\rangle & |\Gamma_1\rangle & |\Gamma_5^{(\alpha)}\rangle & |\Gamma_5^{(\beta)}\rangle & |\Gamma_5^{(\gamma)}\rangle \end{matrix} \\ \begin{matrix} \langle \Gamma_3^{(\alpha)} | \\ \langle \Gamma_3^{(\beta)} | \\ \langle \Gamma_4^{(\alpha)} | \\ \langle \Gamma_4^{(\beta)} | \\ \langle \Gamma_4^{(\gamma)} | \\ \langle \Gamma_1 | \\ \langle \Gamma_5^{(\alpha)} | \\ \langle \Gamma_5^{(\beta)} | \\ \langle \Gamma_5^{(\gamma)} | \end{matrix} & \begin{pmatrix} \frac{8}{\sqrt{3}} & 0 & 0 & 0 & 0 & 4\sqrt{\frac{35}{6}} & 0 & 0 & 0 \\ 0 & -\frac{8}{\sqrt{3}} & 0 & 0 & 0 & -4\sqrt{\frac{35}{6}} & 0 & 0 & 0 \\ 0 & 0 & 14 & 0 & 0 & 0 & 0 & 0 & \sqrt{7} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\sqrt{7} & 0 \\ 0 & 0 & 0 & 0 & -14 & 0 & -\sqrt{7} & 0 & 0 \\ 4\sqrt{\frac{35}{6}} & -4\sqrt{\frac{35}{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{7} & 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 2\sqrt{7} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{7} & 0 & 0 & 0 & 0 & 0 & -4 \end{pmatrix} \end{matrix}$$

5.3.1 Contribution of Electric Hexadecapole

In some Pr compounds which have Γ_3 - Γ_4 CEF ground state, Γ_3 -symmetrical hexadecapolar contribution to the elastic constant cannot be ignored as well as electric quadrupolar contribution [71]. This higher multipolar effect could be introduced by considering expanded Hilbert space, $(\Gamma_3 \oplus \Gamma_4) \otimes (\Gamma_3 \oplus \Gamma_4) = 2\Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_3 \oplus 3\Gamma_4 \oplus 3\Gamma_5$. The matrix elements of Γ_3 -symmetrical hexadecapole $H_v = 1/4[\{7J_z^2 - J(J+1) - 5\}(J_+^2 + J_-^2) + (J_+^2 - J_-^2)\{7J_z^2 - J(J+1) - 5\}]$ in the cubic system are as below.

$$H_v = \begin{matrix} & |\Gamma_3^{(\alpha)}\rangle & |\Gamma_3^{(\beta)}\rangle & |\Gamma_4^{(\alpha)}\rangle & |\Gamma_4^{(\beta)}\rangle & |\Gamma_4^{(\gamma)}\rangle & |\Gamma_1\rangle & |\Gamma_5^{(\alpha)}\rangle & |\Gamma_5^{(\beta)}\rangle & |\Gamma_5^{(\gamma)}\rangle \\ \begin{matrix} \langle\Gamma_3^{(\alpha)}| \\ \langle\Gamma_3^{(\beta)}| \\ \langle\Gamma_4^{(\alpha)}| \\ \langle\Gamma_4^{(\beta)}| \\ \langle\Gamma_4^{(\gamma)}| \\ \langle\Gamma_1| \\ \langle\Gamma_5^{(\alpha)}| \\ \langle\Gamma_5^{(\beta)}| \\ \langle\Gamma_5^{(\gamma)}| \end{matrix} & \begin{pmatrix} -160\sqrt{3} & 0 & 0 & 0 & 0 & 12\sqrt{\frac{35}{6}} & 0 & 0 & 0 \\ 0 & 160\sqrt{3} & 0 & 0 & 0 & -12\sqrt{\frac{35}{6}} & 0 & 0 & 0 \\ 0 & 0 & -105 & 0 & 0 & 0 & 0 & 0 & 45\sqrt{7} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 90\sqrt{7} & 0 \\ 0 & 0 & 0 & 0 & 105 & 0 & -45\sqrt{7} & 0 & 0 \\ 12\sqrt{\frac{35}{6}} & -12\sqrt{\frac{35}{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -45\sqrt{7} & 0 & 75 & 0 & 0 \\ 0 & 0 & 0 & 90\sqrt{7} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 45\sqrt{7} & 0 & 0 & 0 & 0 & 0 & -75 \end{pmatrix} \end{matrix}$$

To include the electric hexadecapolar contribution, an effective multipole $\tilde{O}_v = O_v + \lambda H_v$ is necessary to be introduced. Here, λ means the contribution ratio of the hexadecapole to the quadrupole. In fact, analysis by using Γ_3 -symmetrical effective multipole reproduces the experimental results well in PrMg_3 , PrPb_3 , and PrAg_2In [71]. Example of PrPb_3 is shown in Fig. 5.6. Also in the present study, we analyzed the data of $(\text{Y, Pr})\text{Ir}_2\text{Zn}_{20}$ with the contribution of electric hexadecapole H_v .

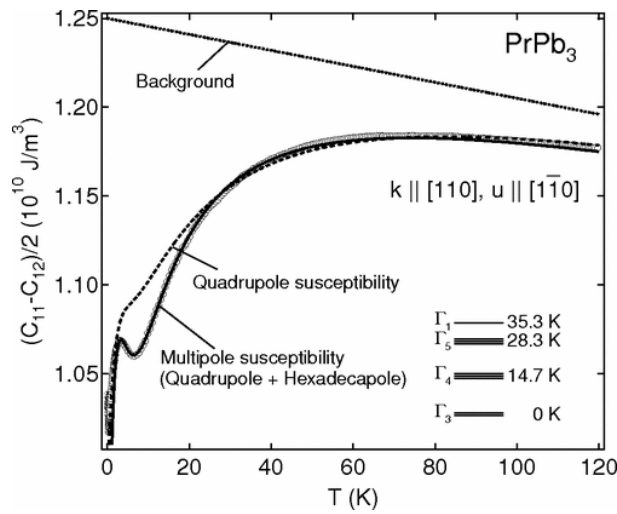


Figure 5.6: Temperature dependence of the Γ_3 -symmetrical elastic constant of PrPb_3 [71]. Solid curve shows a calculation with the electric hexadecapolar contribution, and dotted curve shows a calculation without that.

5.4 Measurement System

5.4.1 Phase Comparative Method (Feedback System)

As shown in the previous section, elastic constant could be obtained by measuring a sound velocity of the corresponding mode. In the present study, we measured the sound velocity precisely by using a phase comparative method. Schematic view is described in Fig. 5.7. In the method, pulsed ultrasound is injected to the sample. By using the reference signal (V_{Ref}) and the sample signal (V_{Sample}), we could obtain the phase difference due to the propagation in the sample. By using a feedback to keep this phase difference zero, relative change of the sound velocity could be obtained from the relative change of the frequency. A detailed explanation using formulae is given below.

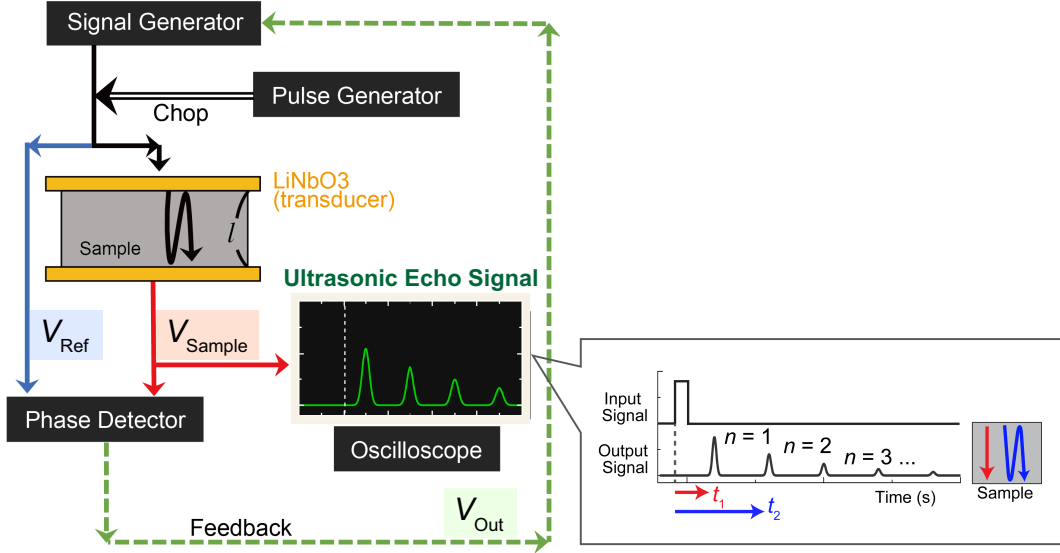


Figure 5.7: Schematic view of phase comparative method. Right illustration shows a schematic view of the ultrasonic echo.

First, we define signal of the reference signal generated by a signal generator (V_{Ref}) as,

$$V_{\text{Ref}} = A \cos(2\pi ft).$$

This signal is RF signal with $f \sim 100$ MHz. On the other hand, phase of V_{Sample} is modulated by propagation in the sample as below.

$$V_{\text{Sample}} = B \exp[-\alpha(2n-1)l] \cos(2\pi ft + \phi_n) \quad (5.22)$$

Here, n means the number of echo (schematic view is described in the right side of Fig. 5.7). For V_{Sample} , an effect of exponential-type ultrasonic attenuation is considered, which depends on ultrasonic attenuation coefficient α and path length $(2n-1)l$. Most

important part, ϕ_n is described as

$$\phi_n = 2\pi f t_n = 2\pi f \frac{(2n-1)l}{v}.$$

V_{Out} is a multiplication of V_{Ref} and V_{Sample} .

$$\begin{aligned} V_{\text{Out}} &= V_{\text{Ref}} V_{\text{Sample}} \\ &= \frac{1}{2} AB \exp[-\alpha (2n-1)l] \{ \cos(4\pi f t + \phi_n) + \cos(\phi_n) \} \end{aligned} \quad (5.23)$$

Since the first term has much higher frequency than the second term, we could obtain only DC component, $V \propto \cos\phi_n$ by using low pass filter. In other words, remained component after low pass filter only depends on the phase difference. The feedback to keep V_{OUT} constant corresponds to keep the phase difference constant, thus, following equation is valid.

$$\frac{(f + \Delta f)(l + \Delta l)}{v + \Delta v} = \frac{fl}{v} \quad (5.24)$$

Assuming that change of the lattice constant is sufficient small and we only consider the first-order terms in microquantities,

$$\frac{\Delta v}{v} = \frac{\Delta f}{f} \quad (5.25)$$

Thus, relative change of the frequency is equal to relative change of the sound velocity. Because $C = \rho v^2$, relative change of the elastic constant is two times to that of the sound velocity. Frequency could be measured with very high accuracy, thus, we could obtain high accurate relative change of the elastic constant by using this method. Absolute value of the sound velocity (elastic constant) is derived from $v = 2(m-n)l / (t_m - t_n)$ as shown in the right side of Fig. 5.7

5.4.2 Phase Orthogonal Method

In the present measurements with static magnetic fields, all elastic constant is obtained by phase comparison method as shown in the previous section. Furthermore, we used phase orthogonal method mainly to obtain the ultrasonic attenuation coefficient α . In this method, multiplication of each phased reference signal and sample signal let us detect cos component $\cos\phi_n = I_n$ and sin component $\sin\phi_n = Q_n$.

First, how to obtain the ultrasonic attenuation coefficient α is explained below. Amplitude of the ultrasonic echo is described by these two components as below.

$$V_n = V_0 \exp[-\alpha (2n-1)l] = \sqrt{I_n^2 + Q_n^2} \quad (5.26)$$

$$\alpha = \frac{1}{(2n-1)l} \ln \left(\frac{V_0}{V_n} \right) \quad (5.27)$$

Based on the definition, $\Delta\alpha$ could be described as below.

$$\begin{aligned}
\Delta\alpha(x) &= \alpha(x) - \alpha(x_0) \\
&= \frac{1}{(2n-1)l} \ln \left(\frac{V_0}{V_n(x)} \right) - \frac{1}{(2n-1)l} \ln \left(\frac{V_0}{V_n(x_0)} \right) \\
&= \frac{1}{(2n-1)l} \ln \left(\frac{V_n(x_0)}{V_n(x)} \right) \\
&= \frac{1}{(2n-1)l} \ln \left(\frac{\sqrt{I_n(x_0)^2 + Q_n(x_0)^2}}{\sqrt{I_n(x)^2 + Q_n(x)^2}} \right)
\end{aligned} \tag{5.28}$$

In addition to the ultrasonic attenuation coefficient α , it is also possible to measure the elastic constant in this method because we could obtain $\phi_n = \arctan(Q_n/I_n)$. However, the data measured by the phase comparative method is more accuracy. This method is suitable for short time measurements such as the ultrasonic measurements under pulsed magnetic fields (details are described in section 5.7.5.) since the feedback to keep the phase difference is not necessary in the method. In the measurements with pulsed fields, sample signal is directly saved in the digital oscilloscope. By the analysis of the storage data later, I_n and Q_n could be obtained.

5.5 Elastic Response Originating from Relaxation Phenomena

In this section, phenomenological theory of ultrasonic dispersion originating from relaxation phenomena is explained. Ultrasonic dispersion, frequency dependence of elastic constant and ultrasonic attenuation coefficient, originates from the dynamical phenomena with a finite relaxation time. When the time scale of the relaxation phenomena with an attempt time τ matches to the ultrasonic frequency ω (~ 100 MHz), the dynamical response could be detected by ultrasonic measurements. In other words, ultrasonic dispersion is resonated in case of

$$\omega\tau \sim 1. \tag{5.29}$$

Here, we consider the most simple case of relaxation process. We assume that the parameter η is deviated from the equivalent value η_0 by dynamical effect. By taking finite time, η is considered to be back to the equivalent value.

$$\frac{d\eta}{dt} = -\frac{\eta - \eta_0}{\tau} \tag{5.30}$$

Assuming $\eta = \eta'$ when $t = 0$, the solution of the differential equation is described as below.

$$\eta - \eta_0 = (\eta' - \eta_0) \exp \left(-\frac{t}{\tau} \right) \tag{5.31}$$

Such exponential-type relaxation is well known in Debye-type relaxation on dielectric materials. In case of ultrasonic measurements with measurement frequency ω , induces strain also vibrates with ω . Thus, relaxation function η also vibrates with ω and should be described in exponential-type time dependence as below.

$$\eta \propto \exp(-i\omega t) \quad (5.32)$$

Substituting this one to Eq. (5.30), we could obtain following equation.

$$\frac{d\eta}{dt} = i\omega\eta = -\frac{\eta - \eta_0}{\tau} \quad (5.33)$$

$$\eta = \frac{\eta_0}{1 - i\omega\tau} \quad (5.34)$$

Since a complex elastic modulus χ^* is first-derivative of σ with respect to ε , it could be described by using a relaxation function η as below.

$$\begin{aligned} \chi^* &= \left(\frac{\partial\sigma}{\partial\varepsilon}\right)_\eta + \left(\frac{\partial\sigma}{\partial\eta}\right)_\varepsilon \frac{\partial\eta}{\partial\varepsilon} \\ &= \frac{1}{1 - i\omega\tau} \left[\left(\frac{\partial\sigma}{\partial\varepsilon}\right)_\eta + \left(\frac{\partial\sigma}{\partial\eta}\right)_\varepsilon \frac{\partial\eta_0}{\partial\varepsilon} - i\omega\tau \left(\frac{\partial\sigma}{\partial\varepsilon}\right)_\eta \right] \end{aligned} \quad (5.35)$$

Here, we consider the low-frequency limit and high-frequency limit for the complex elastic modulus. Low-frequency limit could be described as below.

$$\chi_0 = \chi(\omega \rightarrow 0) = \left(\frac{\partial\sigma}{\partial\varepsilon}\right)_\eta + \left(\frac{\partial\sigma}{\partial\eta}\right)_\varepsilon \frac{\partial\eta_0}{\partial\varepsilon} \quad (5.36)$$

In contrast, high-frequency limit is like this.

$$\chi_\infty = \chi(\omega \rightarrow \infty) = \left(\frac{\partial\sigma}{\partial\varepsilon}\right) \quad (5.37)$$

By using above relationships, we could reconstruct the description of χ^* as below,

$$\begin{aligned} \chi^* &= \chi_\infty + \frac{\chi_0 - \chi_\infty}{1 - i\omega\tau} \\ &= \left(\chi_\infty + \frac{\chi_0 - \chi_\infty}{1 + \omega^2\tau^2} \right) + i \left[\frac{\omega\tau(\chi_0 - \chi_\infty)}{1 + \omega^2\tau^2} \right]. \end{aligned} \quad (5.38)$$

The real part of χ^* corresponds to a dynamical elastic constant $C(\omega)$,

$$C(\omega) = \text{Re}(\chi^*). \quad (5.39)$$

Here, the ultrasonic attenuation coefficient α could be defined using the complex wave number k^* as below,

$$k^* = k_r + i\alpha, \quad (5.40)$$

where k_r is the real part of the complex wave number.

Then, the relationship between k^* and χ is considered. By using the complex sound velocity v^* , k^* could be described as below,

$$k^* = \frac{\omega}{v^*} = \frac{\omega\sqrt{\rho}}{\sqrt{\chi}} \quad (5.41)$$

For small dissipation ($\text{Im}(\chi) \ll \text{Re}(\chi)$), we can expand $\sqrt{\chi}^{-1}$ as

$$\sqrt{\chi}^{-1} \approx \sqrt{\text{Re}(\chi)}^{-1} \left(1 - i \frac{\text{Im}(\chi)}{2\text{Re}(\chi)} \right). \quad (5.42)$$

Thus, complex wave number k^* and the imaginary part of k^* (ultrasonic attenuation coefficient $\alpha(\omega)$) could be described as below,

$$k^* = \frac{\omega\sqrt{\rho}}{\sqrt{\chi}} \approx \frac{\omega\sqrt{\rho}}{\sqrt{\text{Re}(\chi)}} \left[1 - i \frac{\text{Im}(\chi)}{2\text{Re}(\chi)} \right], \quad (5.43)$$

$$\begin{aligned} \alpha(\omega) &= \text{Im}(k^*) = \frac{-\omega\sqrt{\rho}\text{Im}(\chi)}{2\text{Re}(\chi)\sqrt{\text{Re}(\chi)}} \\ &= \frac{-\omega\text{Im}(\chi)}{2\rho v^3}. \end{aligned} \quad (5.44)$$

Using Eqs. (5.38), (5.39), and (5.44), frequency-dependence dynamical elastic constant $C(\omega)$ and ultrasonic coefficient $\alpha(\omega)$ are derived as below,

$$C(\omega) = C_\infty + \frac{C_0 - C_\infty}{1 + \omega^2\tau^2}, \quad (5.45)$$

$$\alpha(\omega) = -\frac{C_0 - C_\infty}{2\rho v_\infty^3} \frac{\omega^2\tau}{1 + \omega^2\tau^2}, \quad (5.46)$$

where C_∞ and C_0 correspond to the high-frequency limit $\chi(\omega \rightarrow \infty)$ and low-frequency limit $\chi(\omega \rightarrow 0)$.

Finally, examples exhibiting the ultrasonic dispersion are shown. In f -electron caged compounds, filled skutterudite, 3-20-6 Clathrate compounds and so on, ultrasonic dispersion has already been reported [72, 73]. Figure 5.8 shows a temperature dependence of the elastic constant C_L in $\text{PrOs}_4\text{Sb}_{12}$ [72]. The data shows frequency-dependent shoulder structure at around 30 K, which corresponds to the resonant condition $\omega\tau \sim 1$. In the previous study, an analysis assuming the Arrhenius-type temperature dependence of relaxation time, $\tau = \tau_0 \exp\left(\frac{E}{k_B T}\right)$, could reproduce the experimental results well.

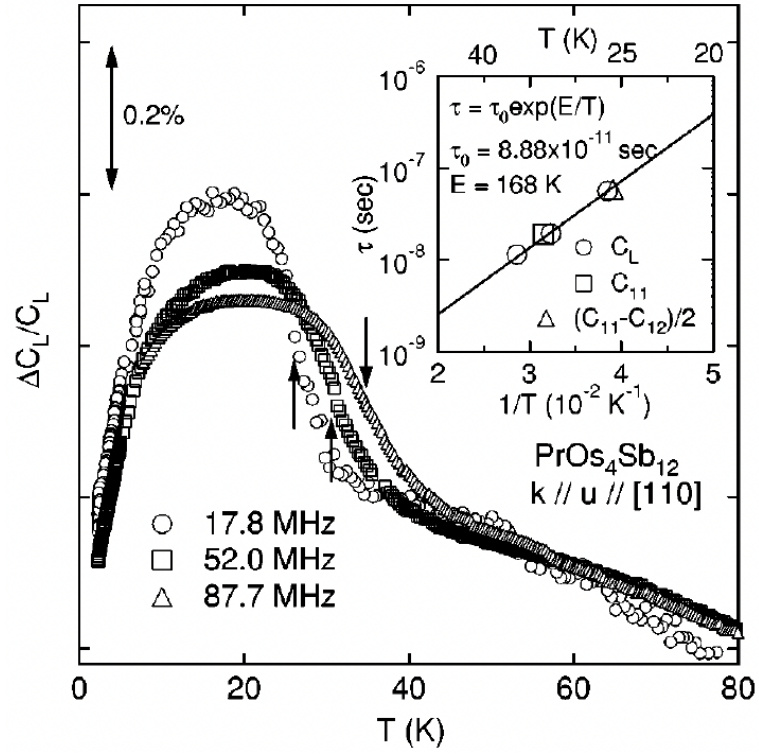


Figure 5.8: Temperature dependence of the elastic constant C_L in $\text{PrOs}_4\text{Sb}_{12}$. Inset shows temperature dependence of relaxation time.

5.6 Apparatus

5.6.1 PPMS

In the present measurements for $T > 2$ K, the temperature was controlled by using a physical property measurements system (Quantum Design PPMS). Range of the magnetic field is $0 \leq B \leq 14$ T.

5.6.2 ^3He Refrigerator

For the measurements in the temperature range of $300 \text{ mK} \leq T \leq 2$ K, we used ^3He refrigerator in Niigata University and Helmholtz-Zentrum Dresden-Rossendorf (HZDR). Simple schematic view is described in Fig. 5.9. ^3He is condensed by thermal touch with 1K pot cooled by ^4He pumping. Then, stored ^3He liquid is cooled down to 300 mK by pumping. As shown in the Fig. 5.9, the sample space of ^3He refrigerator at Niigata University is directly touching ^3He liquid. On the other hand, ^3He space is closed and the sample space is cooled by the cold finger from the ^3He pot in the ^3He refrigerator (Oxford Instrument Heliox) at HZDR.

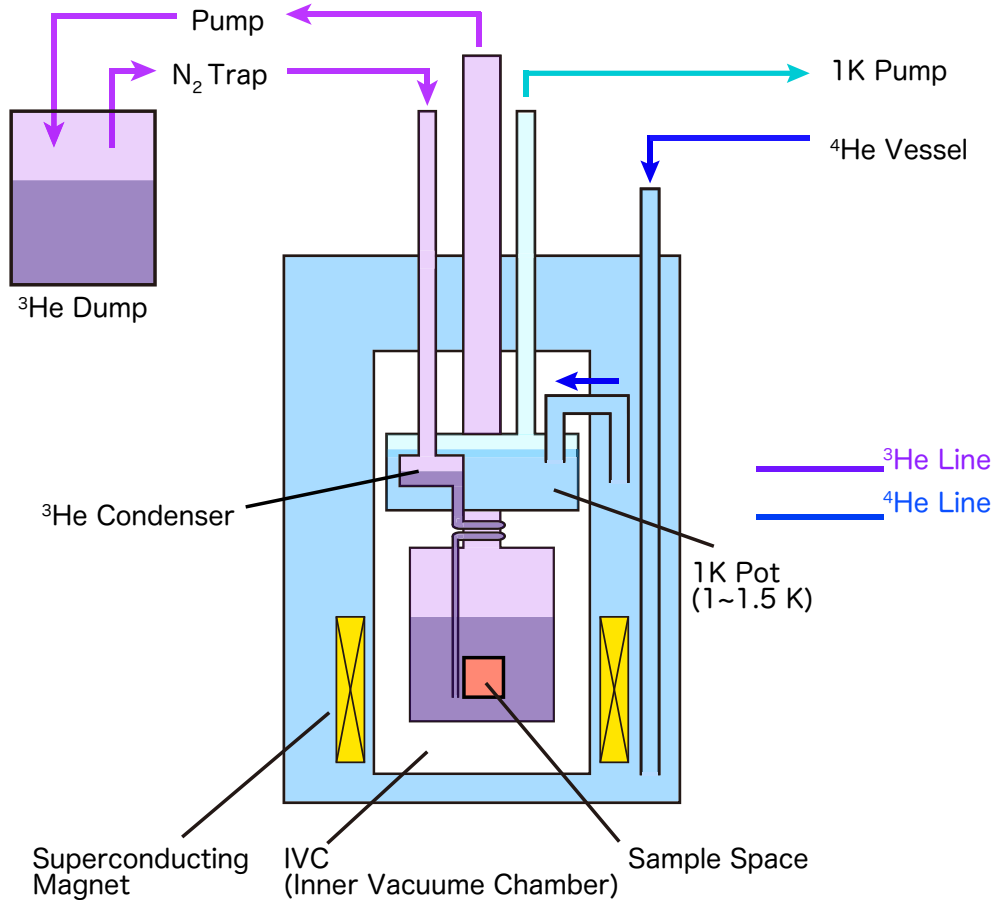


Figure 5.9: Schematic view of ^3He refrigerator.

5.6.3 ^3He - ^4He Dilution Refrigerator

In the present study, ultrasonic measurements at very low temperature is most important. We used ^3He - ^4He dilution refrigerator in Helmholtz-Zentrum Dresden-Rossendorf (HZDR) to achieve the experiment in the temperature range of $30 \text{ mK} \leq T \leq 400 \text{ mK}$. Simple schematic view is described in the Fig. 5.10. Cooling power of the ^3He - ^4He dilution refrigerator is generated by using large entropy of the mixture of ^3He and ^4He . The mixture of ^3He and ^4He has a two different phases below 0.87 K . Here, ^3He -rich phase is called as a concentrated phase (C-phase) and ^3He -poor phase is called as a dilute phase (D-phase). By controlling the temperature of still to $\sim 0.7 \text{ K}$, ^3He in D-phase is selectively evaporated. Then, ^3He in C-phase merges into D-phase, which causes thermal absorption due to entropy difference. The mixture part principally goes down to $\sim 10 \text{ mK}$. In the present measurements, sample is put in the mixing chamber directly, and sample temperature is controlled by a heater in the mixing chamber.

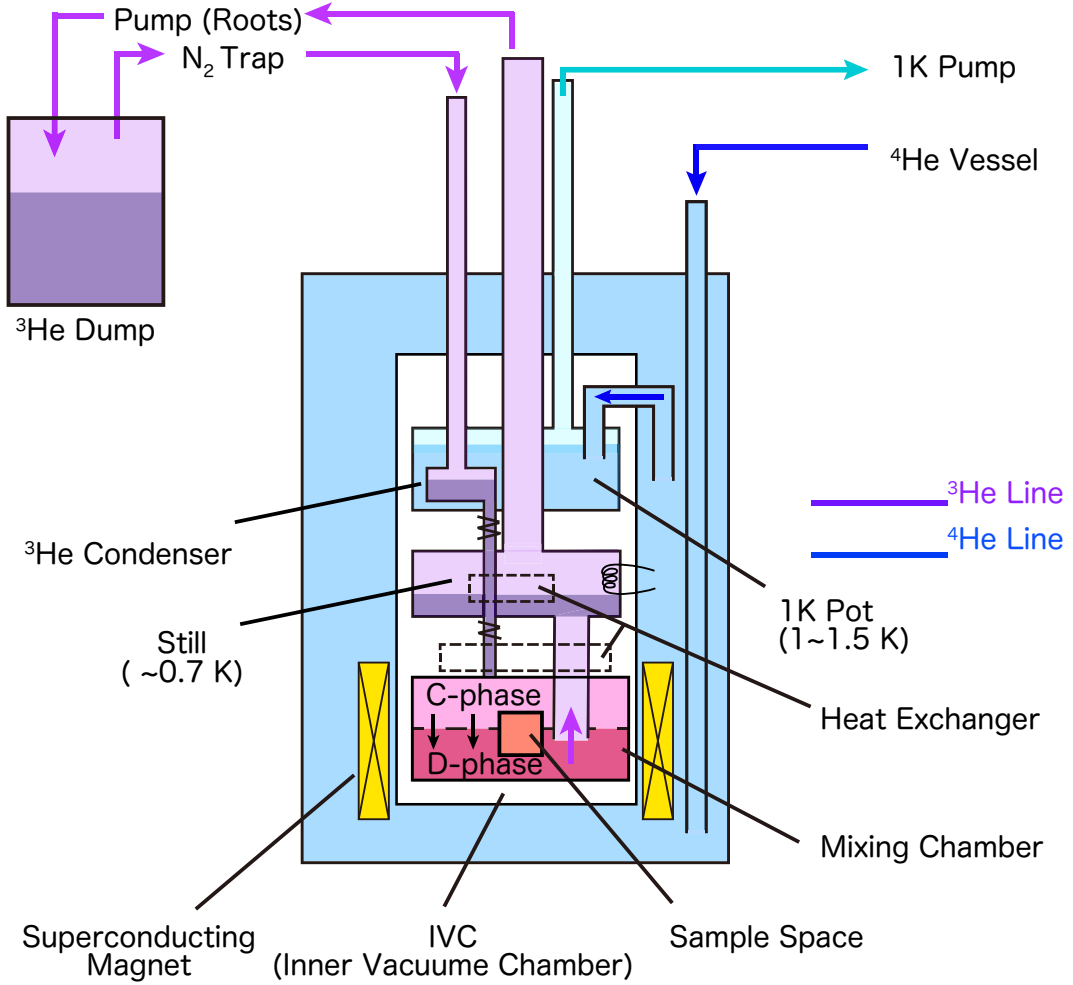


Figure 5.10: Schematic view of ^3He - ^4He dilution refrigerator

5.6.4 Two-Axial-Rotation (TARO) Probe for Ultrasonic Measurements

We used a superconducting magnet for ultrasonic measurements under static magnetic fields, which is not a vector magnet. Thus, we need to rotate the sample to change the direction of the applied magnetic field in situ. For example, field-angle-resolved measurements are useful for a study of Fermi surface by an acoustic dHvA oscillation as shown in section 6.6. For that, we developed Two-Axial-Rotation (TARO) Probe for ultrasonic measurements with a technical support of Dr. M. Kimata in Tohoku university. Rotating of the sample stage with two coaxial cables are achieved by using very thin coaxial cables (AWG42, ϕ : 0.32 mm).

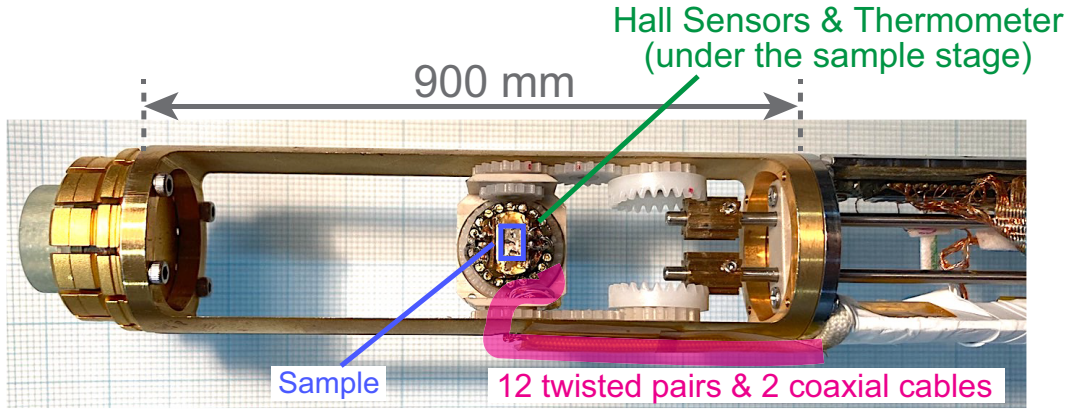


Figure 5.11: Pictures of TARO probe for ultrasonic measurements.

Since this probe has two rotation axis, fine tuning of the field angle is also possible. The TARO probe is designed for the measurements with PPMS ($1.9 \text{ K} \leq T$) now, however, we are planning to extend the temperature region by using different refrigerators in future. The probe would be useful for the study on the field-induced phase pocket “A” in $\text{PrIr}_2\text{Zn}_{20}$ which has a clear field-angle dependence.

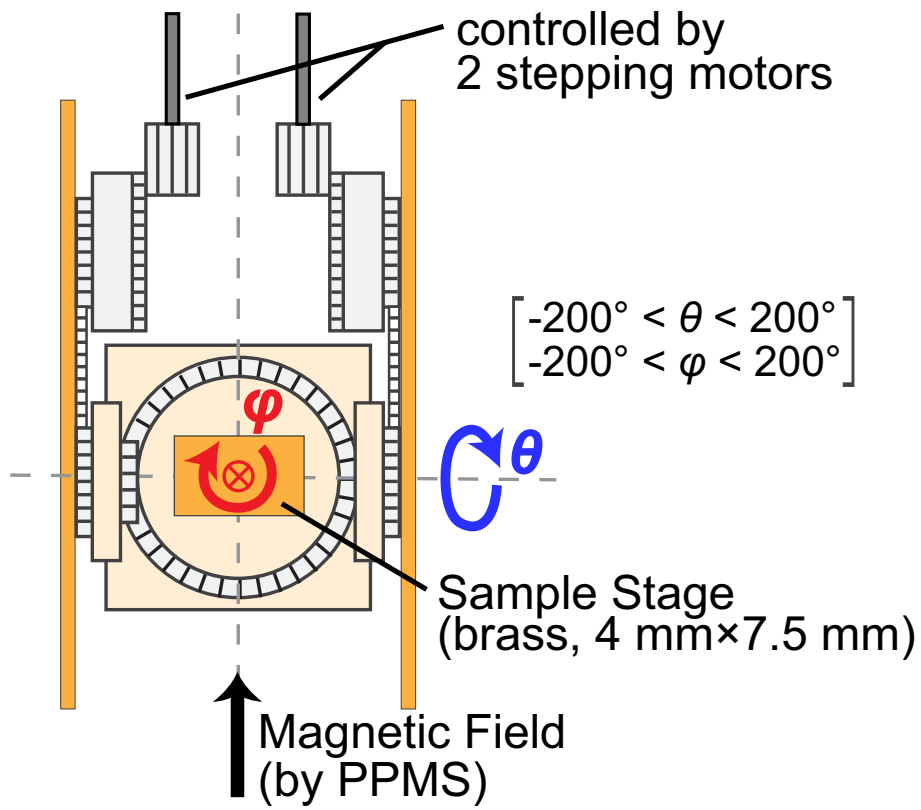


Figure 5.12: Schematic view of TARO probe for ultrasonic measurements.

5.6.5 Pulsed Magnetic Field

In the present study, we performed ultrasonic measurements of $(\text{U,Th})\text{Be}_{13}$ under pulsed magnetic fields. These experiments are carried out in High Field Magnetic Laboratory Dresden (HLD-HZDR). Figure 5.13 shows time dependence of applied magnetic field in the actual experiments of our study. Time duration is about 100 ms, and maximum field is 68 T in case that charge voltage is 21 kV. Pictures of the magnet and the cryostat are shown in Fig. 5.14. By pumping out ^4He filled in the cryostat, ^3He in the double-sealed probe stick could be condensed. In this way, the ultrasonic measurements under pulsed magnetic field could be performed at very low temperature down to ~ 0.5 K.

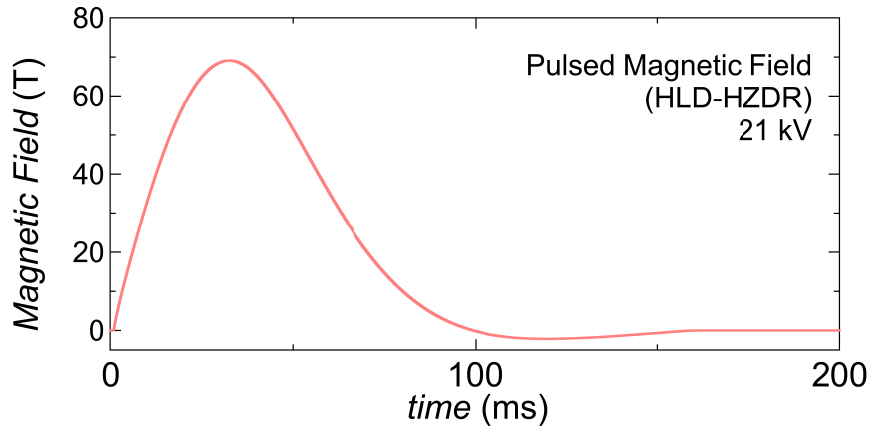


Figure 5.13: Time dependence of pulsed magnetic field in HLD-HZDR.



Figure 5.14: The pictures of the facility for the ultrasonic measurements with pulsed magnetic fields in HLD-HZDR. (a) Magnet for the pulsed field, (b) cryostat, and (c) overview of the actual measurement.

Chapter 6

Verification of Quadrupolar Kondo Effect on (Y, Pr)Ir₂Zn₂₀

6.1 Experimental Procedure

We performed the ultrasonic measurements of (Y, Pr)Ir₂Zn₂₀ to reveal the Pr-concentration dependence of the elastic response originating from a quadrupolar Kondo effect. We mainly focused on the experiment of the Pr-8% and 37% systems, which were intermediate concentrations of the Pr-3.4% and 100% systems in the previous study [43, 30]. Most important measurements for the verification of the quadrupolar Kondo effect is to measure the elastic constant $\frac{(C_{11}-C_{12})}{2}$, which corresponds to the Γ_3 symmetrical mode. In the present study, we also measured another symmetrical mode, Γ_5 mode (elastic constant C_{44}) to check the mode dependency. Since the characteristic temperature for quadrupolar Kondo effect should be lower than ~ 1 K as suggested from the previous study of the Pr-3.4% system, our measurements were focused in the very low temperature down to 20 mK with the ³He-⁴He dilution refrigerator (section 5.7.3). In addition to such measurements at very low temperature, we also performed the measurements at high temperatures and high magnetic fields to estimate the contribution of phonon and CEF effect.

6.2 Experimental Results of the Pr-8% System

This section describes the experimental results of the Pr-8% system, which is higher than the Pr-3.4% where the logarithmic elastic response originating from a single-site quadrupolar Kondo model were observed [43]. First, the contribution of phonon and CEF effect are estimated to discuss the elastic response due to a quadrupolar Kondo effect. After the discussion about such background, the difference of the elastic response originating from QKE with the Pr-3.4% system is discussed in subsection 6.2.3.

6.2.1 Temperature Dependence of Elastic Constants

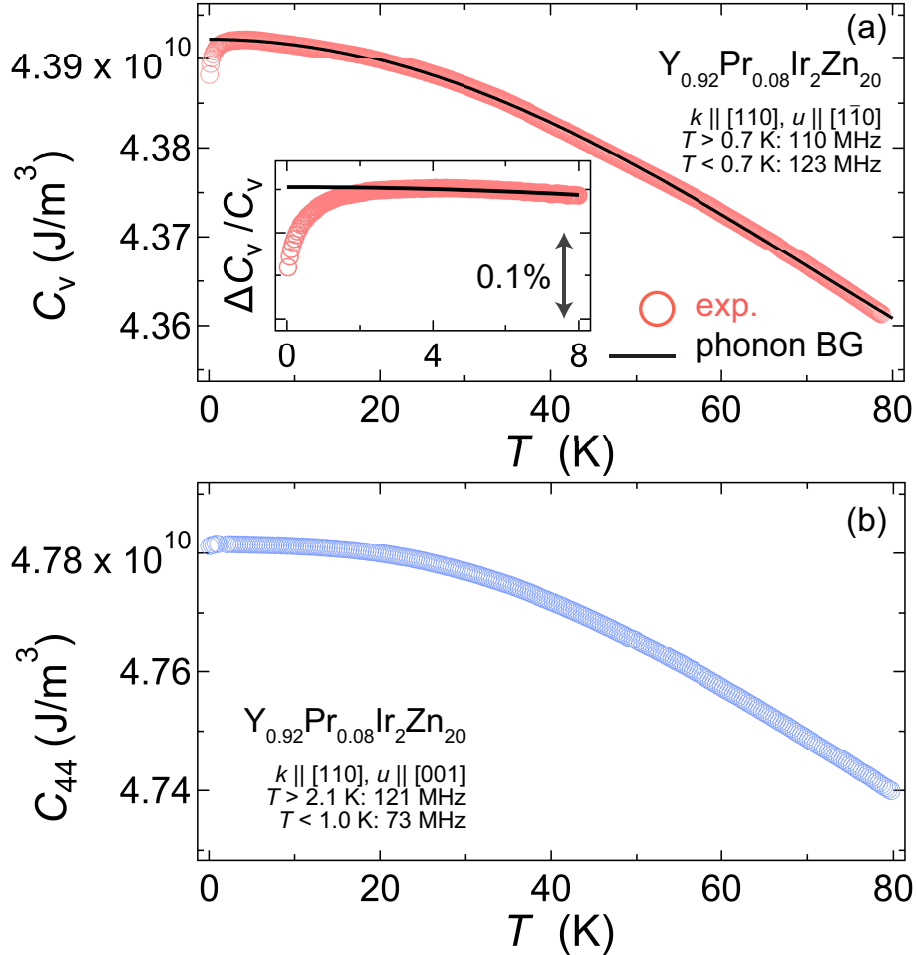


Figure 6.1: Elastic constants (a) $C_v = (C_{11} - C_{12})/2$ and (b) C_{44} of the Pr-8% system as a function of temperature. The black solid curve in panel (a) indicates the phonon background C_{phonon} . C_{44} between 1.0 and 2.1 K has not been measured yet. Inset of panel (a) shows an enlarged view of the relative change of C_v .

Figure 6.1(a) and (b) show the temperature dependence of the elastic constants $C_v = (C_{11} - C_{12})/2$ and C_{44} of $\text{Y}_{0.92}\text{Pr}_{0.08}\text{Ir}_2\text{Zn}_{20}$. Here, the absolute values of the elastic constants are calculated by using the formula $C_{ij} = \rho v_{ij}^2$. In the Pr-8% system, $\rho = 8.284 \text{ g/cm}^3$ is the density estimated from the lattice constant $a = 14.2006 \text{ \AA}$ for the Pr-concentration system [69]. In both C_v and C_{44} modes, the elastic constant shows a hardening as the temperature decreases, which is interpreted as the contribution of phonons. Then, only the C_v mode shows a softening below $\sim 3 \text{ K}$. To analyze this softening in detail, it is necessary to estimate the phonon contribution for the C_v mode. The black-solid curve in Fig. 6.1(a) is the result of analyzing the data in the high-temperature range between 60 and 80 K using the phenomenologically obtained expression, $C_{\text{phonon}} = C_0 + AT^2 + BT^4$. As shown in Fig. 6.1(a), this description above $\sim 3 \text{ K}$ reproduces the experimental result very well.

6.2.2 CEF Analysis

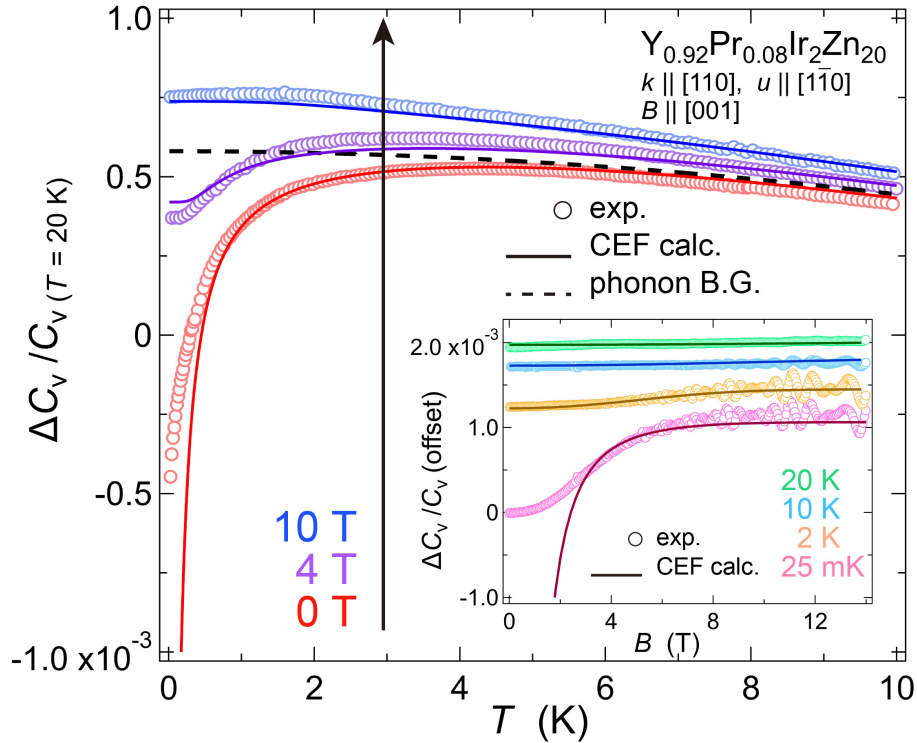


Figure 6.2: Relative change of the elastic constants C_v of the Pr-8% system as a function of temperature at several magnetic fields $B \parallel [001]$. Solid curves are calculated from the multipolar susceptibility with electric hexadecapolar contribution ($\lambda = 0.006$) and the phonon background. The black dashed line indicates the phonon background. The inset shows the relative change of C_v as a function of magnetic field at several fixed temperatures. Solid curves in the inset are calculated from the multipolar susceptibility at each temperature.

Figure 6.2 shows the temperature dependence of the elastic constant C_v below 10 K under several applied magnetic fields ($B \parallel [001]$). The softening described above is suppressed by magnetic fields, and the temperature dependences of C_v can be analyzed by localized $4f$ -electron models considering the following Hamiltonian [74, 75],

$$\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{QS}} + \mathcal{H}_{\text{QQ}}. \quad (6.1)$$

We use the CEF parameters for $\text{PrIr}_2\text{Zn}_{20}$: $B_4^0 = -0.0109$ K and $B_6^0 = -0.4477$ mK in the present CEF Hamiltonian $\mathcal{H}_{\text{CEF}}$, which is obtained from the inelastic neutron scattering measurement for $\text{PrIr}_2\text{Zn}_{20}$ [33]. The CEF level scheme based on these parameters is as follows; Γ_3 (0 K)- Γ_4 (27 K)- Γ_1 (66 K)- Γ_5 (67 K). They as well can be used for the analysis for the ultrasonic data of the Y-diluted Pr-3.4% system [43]. The third term in the equation (6.1) describes the interaction between the elastic strain and a electric quadrupole, and the fourth term describes the intersite quadrupole-quadrupole interaction. (We would consider the interaction with an effective multipole $\tilde{O}_v$ described in section 5.3.1 instead of the electric quadrupole O_v later on.) In principle, it is necessary to consider the hyperfine interaction between nuclear spins and localized quadrupoles, since the nuclear spin of the ^{141}Pr nucleus (natural abundance is 100%) is non-zero ($I = 5/2$). In the previous study of the Pr-3.4% system, the analysis taking into account the effect of hyperfine interactions could explain the appearance of a local minimum of the elastic constant C_v in the magnetic-field swept measurements at low magnetic fields [43]. The present results do not show such a local minimum as shown in the inset of Fig. 6.2. In fact, our calculations without hyperfine interaction already reproduce the experimental results well, therefore, we conclude that the contribution of the hyperfine interaction is sufficiently small to be negligible at least in the present system.

In the analysis, we assume an effective multipole $\tilde{O}_v = O_v + \lambda H_v$ with Γ_3 symmetry. As details are described below, the elastic behaviors of C_v in $\text{Y}_{1-x}\text{Pr}_x\text{Ir}_2\text{Zn}_{20}$ due to CEF effect could be explained by the analysis taking account to not only the contribution of the electric quadrupole $O_v = J_x^2 - J_y^2$ but also that of the electric hexadecapole $H_v = 1/4[\{7J_z^2 - J(J+1) - 5\}(J_+^2 + J_-^2) + (J_+^2 - J_-^2)\{7J_z^2 - J(J+1) - 5\}]$. Since the effect of the electric hexadecapole H_v is relatively large in high Pr-concentration systems, the comparison between CEF calculations with/without the contribution of the electric hexadecapole for the Pr-37% system in section 6.3.2 (Fig. 6.8). Examples where electric hexadecapolar contribution cannot be ignored in other Pr compounds are explained in section 5.3.1.

Here, λ means the contribution ratio of the hexadecapole to the quadrupole. The solid lines in Fig. 6.2 show the results using $\lambda = 0.006$ which is same as used for other Pr concentrations. The elastic constant $C_{\Gamma_3}^{4f}(T, B)$ can be expressed by the following formula [70]:

$$C_{\Gamma_3}^{4f}(T, B) = C_{\Gamma_3}^0(T) - \frac{N g_{\Gamma_3}^2 \chi_{\Gamma_3}(T, B)}{1 - g'_{\Gamma_3} \chi_{\Gamma_3}(T, B)}, \quad (6.2)$$

$$\begin{aligned} \chi_{\Gamma_3}(T, B) = & \frac{1}{k_B T} \left\{ \sum_i \rho_i \left| \langle i | \tilde{O}_{\Gamma_3} | i \rangle \right|^2 - \left(\sum_i \rho_i \langle i | \tilde{O}_{\Gamma_3} | i \rangle \right)^2 \right\} \\ & + \sum_{j \neq i} \frac{\rho_j - \rho_i}{E_i - E_j} \left| \langle j | \tilde{O}_{\Gamma_3} | i \rangle \right|^2. \end{aligned} \quad (6.3)$$

In the equation (6.2), $N = 2.24 \times 10^{26} \text{ m}^{-3}$ is the number of Pr ions per unit volume in the Pr-8% sample estimated from the lattice constant at room temperature, and $C_{\Gamma_3}^0$ is the background which originates from the phonon described above. g_{Γ_3} and g'_{Γ_3} are the coupling constants of the multipole-strain interaction and the multipole-multipole interaction, respectively. Then, χ_{Γ_3} is the susceptibility of the effective multipole $\tilde{O}_v$, and ρ_i a probability based on statistical mechanics.

The coupling constants, $g_{\Gamma_3} = 25 \text{ K}$ and $g'_{\Gamma_3} = -0.02 \text{ K}$ are obtained from the best fit to the data at various magnetic fields above 0.6 K, since the QKE affects the data at lower temperatures. Amplitudes of coupling constants would be discussed in section 6.4, together with results for other Pr-concentration systems. The present parameter set for the calculations also reproduces the magnetic field dependences except for the region at 25 mK below $\sim 3 \text{ T}$, as shown in the inset of Fig. 6.2. It is considered that a localized model cannot be applied and that many-body effects are dominant at 25 mK below 3 T. Then, it should be noted that acoustic dHvA oscillations are observed above 7 T at low temperatures. (Details will be described in section 6.6.) This phenomenon proves the high quality of the present single crystal and high accuracy of the measurements.

6.2.3 QKE Contribution

Finally, we discuss the many-body effects, which are dominant below $T^* \sim 0.6$ K. Figure 6.3 shows the enlarged view of the temperature dependence of C_v in the low temperature region. In the temperature region, the Curie-like softening is suppressed and the temperature dependence is better consistent with a temperature dependence proportional to $\sqrt{T}$ based on the quadrupolar Kondo virtual lattice model, rather than a logarithmic temperature dependence based on the single-site quadrupolar Kondo effect observed in the Pr-3.4% system [43]. (Details of the power-law fitting analysis is described in Appendix 1.) This fact suggests that the local quadrupolar interaction becomes non-negligible with increasing Pr concentration in $Y_{1-x}Pr_xIr_2Zn_{20}$.

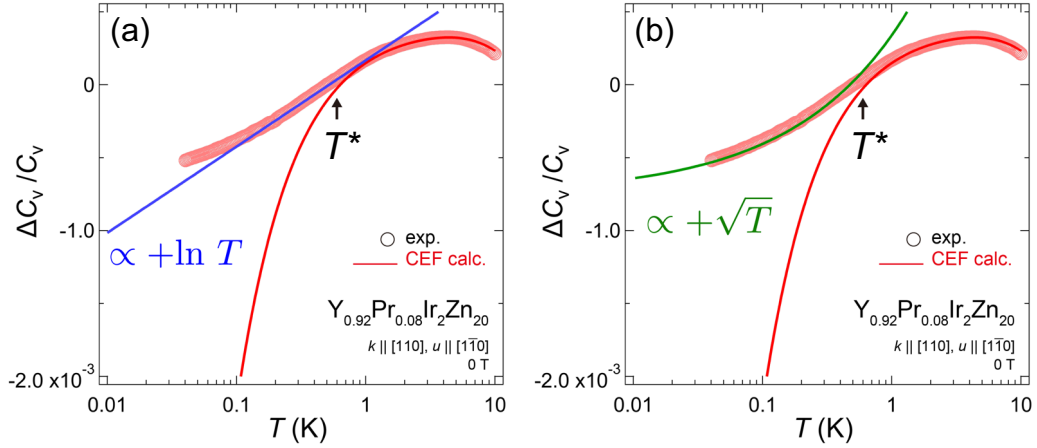


Figure 6.3: Relative change of the elastic constants C_v of the Pr-8% system as a function of temperature under zero magnetic field. Red solid curve is calculated from the multipolar susceptibility with electric hexadecapolar contribution ($\lambda = 0.006$). Blue solid curve in panel (a) describes fitting curve proportional to $+\ln T$ based on single-site quadrupolar Kondo model, and green solid curve in panel (b) describes fitting curve proportional to $+\sqrt{T}$ based on quadrupolar Kondo lattice model.

Assuming that Pr ions and Y ions uniformly exists (“Virtual lattice” model which we applies to the Pr-8% system assumes that Pr ions are aligned periodically.), the effective lengths between Pr ions are 18.976 Å for the Pr-3.4% system and 14.271 Å for the Pr-8% system, respectively. (On the other hand, the effective length is 6.18035 Å in case of the mother compound, $PrIr_2Zn_{20}$.) Our results suggest that intersite licalized-quadrupole interaction becomes non-negligible in case where the effective length is shorter than the Pr-8% system, and the quantum ground state shows a crossover from a single-site model to a lattice model at intermediate Pr concentrations between the 3.4% and 8%.

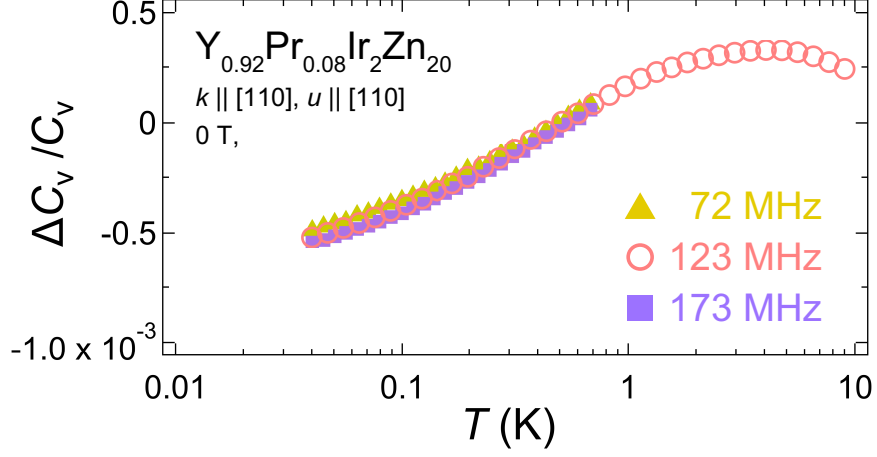


Figure 6.4: Relative change of the elastic constants C_v of the Pr-8% system obtained by several ultrasonic frequencies.

Furthermore, we verified the frequency dependence of the elastic behavior in the Pr-8% system as shown in Fig. 6.4. Obvious differences between data with different frequencies are not observed as well as the Pr-3.4% system [43], which means that the discussion about the function of $C_v(T)$ does not depend on the frequency.

Our experimental result could be explained by the quadrupolar Kondo theory, however, we also need to consider another possibility showing such suppression of the elastic softening (quadrupolar degrees of freedom). One possibility is a split of the non-Kramers Γ_3 doublet due to a localized atomic distortion generated by elemental substitution. Our calculation assuming the tetra distortion with a normalized distribution causes the suppression of the Curie-like softening, which is rather close to the logarithmic behavior. Details for the calculation are described in the Appendix 2. The calculation suggests that more experimental verification is necessary to exclude the possibility except for the quadrupolar Kondo effect. Additional experiments under uniaxial pressure which intentionally causes the split of the Γ_3 doublet are considered to be efficient for the verification.

6.3 Experimental Results of the Pr-37% System

As well as the Pr-8% system, we performed ultrasonic measurements for the Pr-37% system. As a result, we found a temperature dependence proportional to $\sqrt{T}$ was observed in $(C_{11} - C_{12})/2$ on cooling below 0.15 K, which is similar to the behavior in the Pr-8% system. On the other hand, we also observed two ultrasonic dispersions (UD1 and UD2), which are not observed in other Y-diluted systems (Pr-3.4% and 8% systems). Since the lower energy scale of UD2 is close to the energy scale of QKE in this system, we suggest the possibility that the low-energy phonon modulate the QKE. We also discuss the possibility to form “vibronic” state by the coupling between the low-energy phonons and the electric quadrupoles of the non-Kramers doublet in the Pr-37% system.

6.3.1 Ultrasonic Dispersion at High Temperature

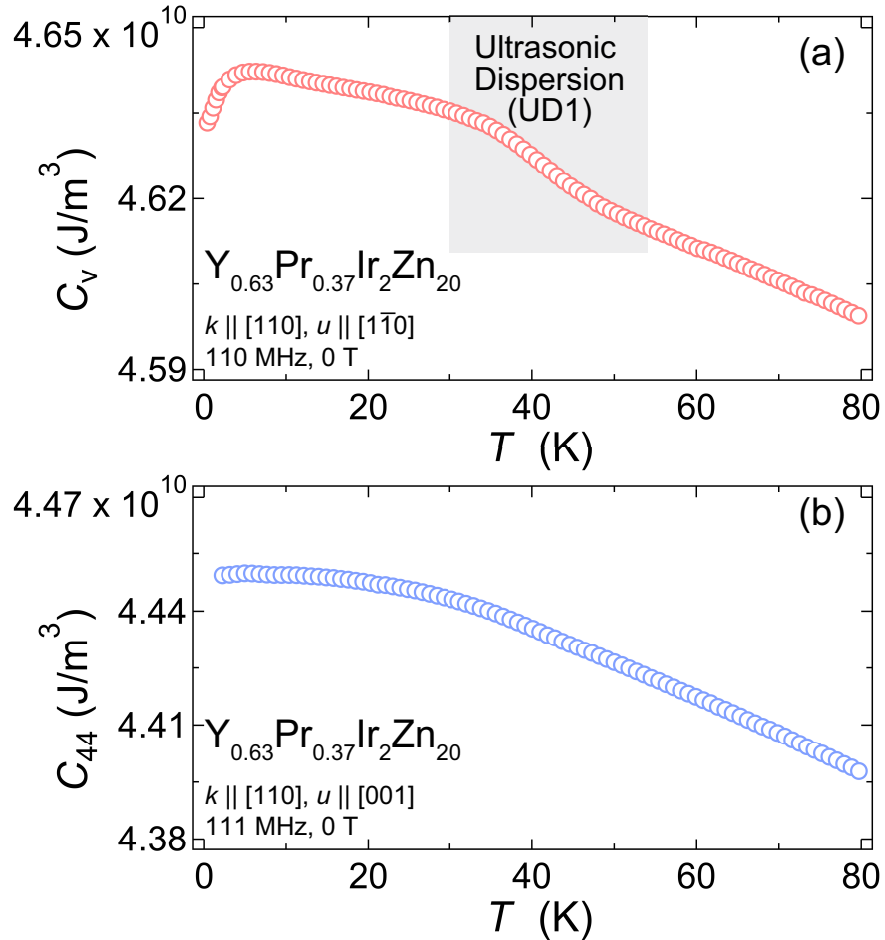


Figure 6.5: Elastic constants (a) $C_v = (C_{11} - C_{12})/2$ and (b) C_{44} of the Pr-37% system as a function of temperature.

Figures 6.5(a) and (b) show the temperature dependence of the elastic constants $C_v = (C_{11} - C_{12})/2$ and C_{44} , respectively, of the Pr-37% system. Here, the absolute values of the elastic constants are calculated by using the formula $C_{ij} = \rho v_{ij}^2$. In the Pr-37% system, $\rho = 8.314 \text{ g/cm}^3$ is the density estimated from the lattice constant $a = 14.2234 \text{ \AA}$ for the Pr-concentration system [69]. C_v shows a remarkable upturn at around 40 K and Curie-like softening below 5 K. On the other hand, C_{44} displayed in Fig. 6.5(b) increases monotonically on cooling at least down to 2.3 K with no obvious frequency dependence.

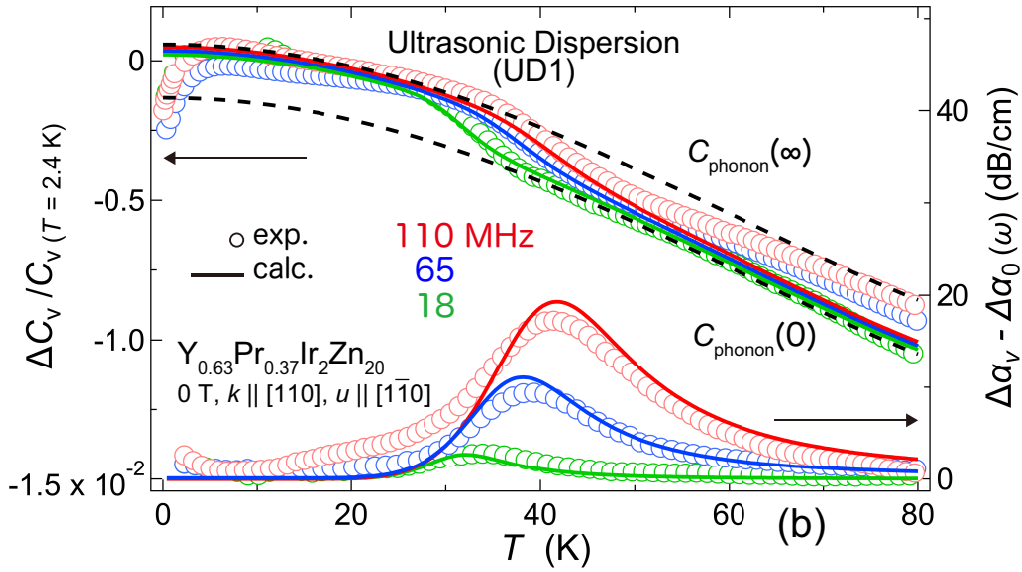


Figure 6.6: Relative change of the elastic constants (a) $C_v = (C_{11} - C_{12})/2$ of the Pr-37% system as a function of temperature in the upper panel. The ultrasonic attenuation coefficients for the $C_v = (C_{11} - C_{12})/2$ mode are shown in the lower panel. Three different measurement frequencies are shown in different colors. Black-dashed lines in the upper panel indicate the phonon background of the high- and low-frequency limit, $C_{\text{phonon}}(\infty, T)$ and $C_{\text{phonon}}(0, T)$, respectively. Solid lines are the calculation results analyzed based on a Debye-type dispersion to reproduce UD1 (see text).

The upper part of the Fig. 6.6 shows a frequency dependence of the elastic constant C_v . Clear frequency dependence is observed in the range from 18 to 110 MHz, and the upturn shifts to higher temperature region as the ultrasonic frequency increases. As shown in the lower part of Fig. 6.6, the background-subtracted ultrasonic attenuation coefficient exhibits a local maximum at which the elastic constant C_v shows the upturn. Here, a frequency-dependent background $\Delta\alpha_0(\omega, T)$ exhibiting monotonic increase with temperature is subtracted. These mode-selective frequency dependences are reminiscent of the ultrasonic dispersion (UD) found in cage compounds such as $R_3\text{Pd}_{20}\text{Ge}_6$ (R = rare earth) [73] and the filled-skutterudites RT_4X_{12} (T = Os, Ru, and Fe; X = P, Sb, and As) [72, 76, 77]. Some examples of the UD in the Pr-based compounds including the present system are summarized in Table I. The origin of

these UD is considered as a “rattling” motion due to the cage-like crystal structure [72]. Here, the rattling means a thermally activated oscillation of the guest atom in an oversized atomic cage [78, 79]. Pr atoms at the site 8a and Zn atoms at the site 16c in $Y_{1-x}Pr_xIr_2Zn_{20}$ are surrounded by highly symmetric cages as shown in Fig. 2.1. For the analysis of the UD in $C(\omega, T)$ and $\alpha(\omega, T)$, we adopt a Debye-type dispersion [73] as

$$C(\omega, T) = C(\infty, T) - \frac{C(\infty, T) - C(0, T)}{1 + \omega^2\tau^2}, \quad (6.4)$$

$$\alpha(\omega, T) = \frac{C(\infty, T) - C(0, T)}{2\rho v_\infty^3} \frac{\omega^2\tau}{1 + \omega^2\tau^2}. \quad (6.5)$$

Here, ω is the angular frequency of the ultrasonic wave and τ is the relaxation time of the system. $C(\infty, T)$ and $C(0, T)$ denote the high- and low-frequency limits for the frequency-dependent elastic constant $C_v(\omega, T)$, respectively. Since the contribution of the phonons is obviously large compared to that of the CEF excitation at around 40 K, we estimated that $C_{\text{phonon}}(0, T) = 4.600 \times 10^{10} - 9.28T^2 + 4.176T^4$ J/m³ from the experimental data and $C_{\text{phonon}}(\infty, T)$ is vertically shifted by 0.025×10^{10} J/m³ as shown with the broken lines in Fig. 6.6(a). The colored solid lines in Fig. 6.6 are the results of a calculation assuming an Arrhenius-type relaxation represented by $\tau(T) = \tau_0 \exp(E/k_B T)$, which roughly reproduces the experimental results. We obtained a characteristic relaxation time $\tau_0 = 2.4 \times 10^{-11}$ s and an activation energy $E = 250$ K from the Arrhenius plot as shown in Fig. 6.7(b). We defined this UD as UD1.

Table 6.1: Ultrasonic dispersions observed in the Pr-based cubic systems. Resonant temperature means the temperature which satisfies the resonant equation ($\omega\tau(T) = 1$) at around $\omega = 100$ MHz. The parameters for the UD of $PrIr_2Zn_{20}$ (Pr-100% system) are estimated by us from the data described in the original paper [30].

compounds	resonant temperature (K)	activation energy E (K)	characteristic relaxation time τ_0 (s)	Refs.
$PrIr_2Zn_{20}$ (Pr-100%)	2	~ 10	$\sim 2.0 \times 10^{-10}$	[30]
$Y_{0.63}Pr_{0.37}Ir_2Zn_{20}$ (Pr-37%)	40 (UD1)	250	2.4×10^{-9}	-
	0.5 (UD2)	0.55	3.1×10^{-9}	-
$Y_{0.966}Pr_{0.034}Ir_2Zn_{20}$ (Pr-3.4%)	-	-	-	[43]
$PrRh_2Zn_{20}$	50 (UDH)	440	2.0×10^{-13}	[29]
	2 (UDL)	2.50	8.0×10^{-10}	[29]
$PrOs_4Sb_{12}$	35	168	8.8×10^{-11}	[72]
$PrMg_3$	0.2	0.50	8.5×10^{-10}	[80]

In addition, we investigated the magnetic-field dependence of UD1. Figure 6.7(a) exhibits results for C_v obtained at selected frequencies (19, 65, and 109 MHz) and magnetic field of $B = 8$ T ($B \parallel [001]$). As shown in Fig. 6.7(b), the characteristic relaxation time and the activation energy are independent of the magnetic field, which is ascribed to the lattice vibrations.

As shown in the previous report by Ishii *et al.* [30], a UD at around 2 K was observed in the Pr-100% system. The activation energy of this UD was estimated to be about 10 K. Assuming that the origin of this UD is same as for UD1 of the Pr-37% system, the energy scale of the UD decreases as the Pr concentration increases.

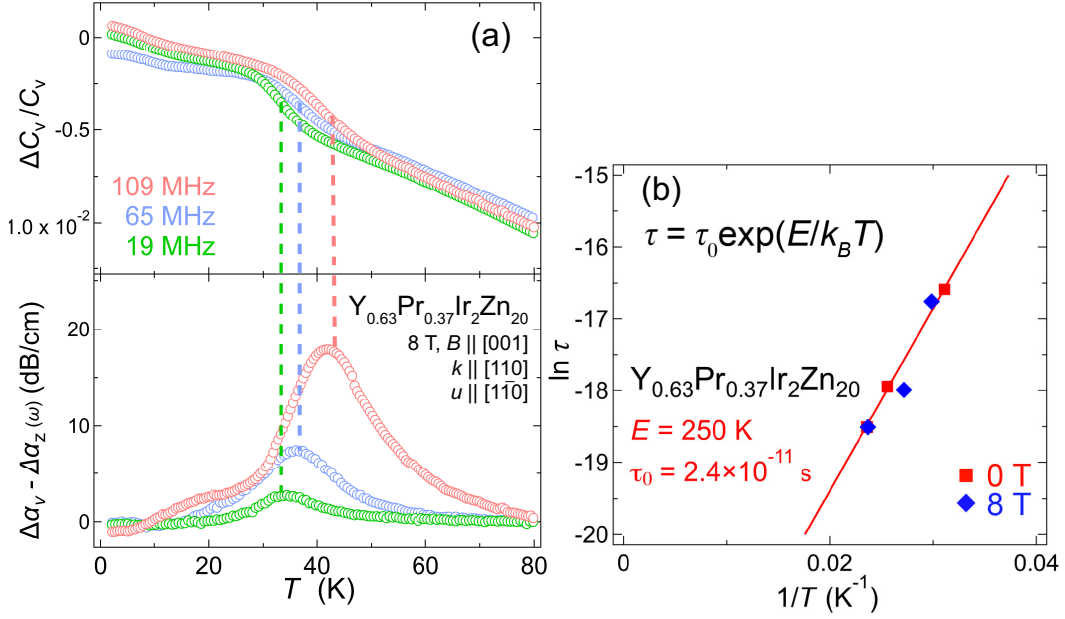


Figure 6.7: (a) Relative change of the elastic constant $C_v (= (C_{11} - C_{12})/2)$ and the ultrasonic attenuation coefficient of the Pr-37% system at 8 T ($B \parallel [001]$) as a function of temperature. The results at three different measurement frequencies are shown in different colors. Each arrow shows the resonant point ($\omega\tau = 1$). (b) Arrhenius plot of the logarithm of the relaxation time $\ln\tau$ vs the reciprocal temperature $1/T$ for UD1 at $B = 0$ (red) and 8 T (blue). The solid line shows the fitted straight line to the data in $B = 0$.

Previous powder x-ray diffraction measurements pointed out that the lattice constant of $\text{Y}_{1-x}\text{Pr}_x\text{Ir}_2\text{Zn}_{20}$ increases as the Pr concentration increases [69]. Thus, this Pr-concentration dependence can be interpreted as a size increase of the atomic cage together with an energy decrease of the vibration as the Pr concentration increases. Since no UD was observed for the Pr-3.4% [43] and 8% system below 150 K, it may be possible that such a UD exists at higher temperatures for the Pr-3.4% and 8% system. However, the UD in the Pr-100% system reported by Ishii *et al.* shows some differences from that of the Pr-37% system, such as that UD is observed for both C_v and C_{44} modes.

On the other hand, a mode-selective UD was observed previously for $\text{PrRh}_2\text{Zn}_{20}$, having the same crystal structure as $\text{PrIr}_2\text{Zn}_{20}$ [29]. This UD is named as “UDH” in the original paper [29]. ($\text{PrRh}_2\text{Zn}_{20}$ has the other UD named as “UDL”, which has a similar energy scale to UD2 described in section 6.3.3 later.) The activation energy of UDH is $E = 440$ K, which is close to the present values of UD1 ($E = 250$ K). Recently, low-energy optical-phonon excitations at ~ 7 meV were observed by inelastic x-ray scattering (IXS) in $\text{PrT}_2\text{Zn}_{20}$ ($T = \text{Rh, Ir}$). It was concluded that such low-energy phonon modes originate from the oscillation of Zn atoms (site 16c) encapsulated in the $\text{Pr}_2\text{Zn}_{12}$ cage [81, 82]. First-principal calculations for $\text{LaRu}_2\text{Zn}_{20}$ (same structure

as $\text{PrIr}_2\text{Zn}_{20}$) suggests that the vibrations of the Γ_3 (E_g) and Γ_5 (T_{2g}) modes in the (111) plane have very low energies. As their frequencies are so low and sensitive to the parameters of the calculation, thus, the symmetry of vibrations has not been revealed yet [83]. The present ultrasonic results suggest that this vibration corresponds to the Γ_3 mode. Further experiments are needed to clarify the origin of the ultrasonic dispersion.

6.3.2 CEF Analysis

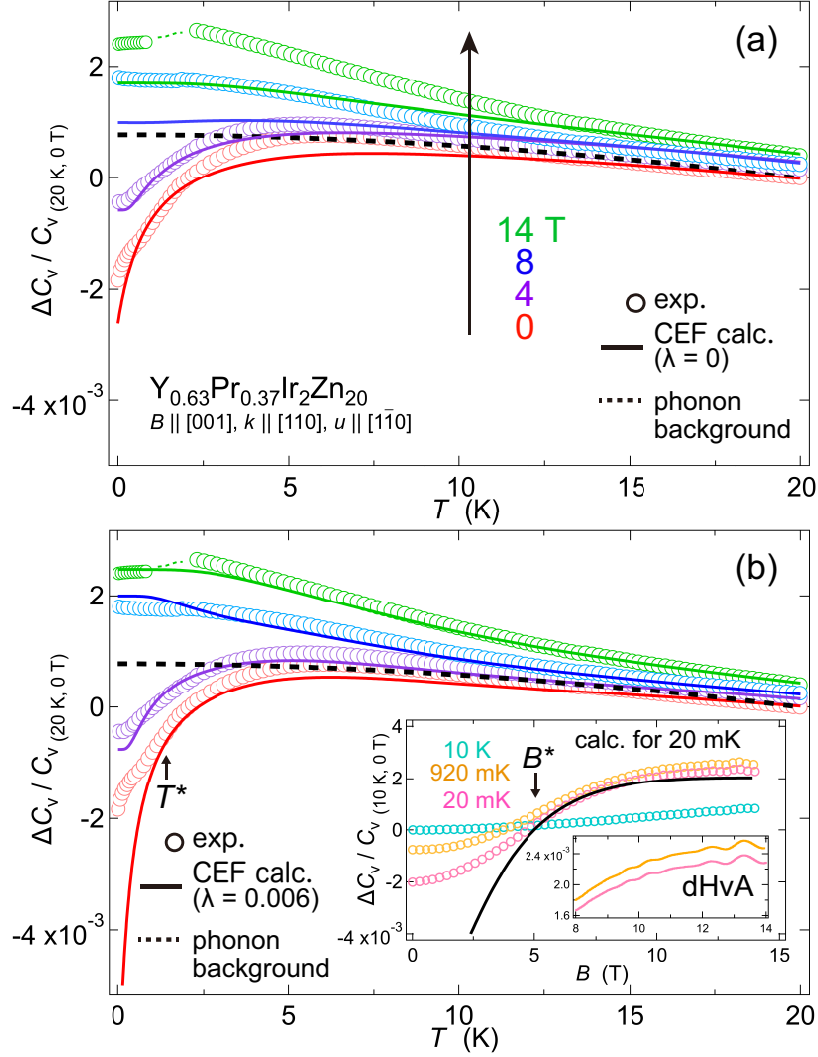


Figure 6.8: Relative change of the elastic constant C_v of the Pr-37% system as a function of temperature at various magnetic fields $B \parallel [001]$. Data above and below 0.5 K were measured with frequency of 110 and 201 MHz, respectively. Solid lines in (a) and (b) show the calculation results, respectively, without and with the contribution of the electric hexadecapole H_v ($\lambda = 0.006$). The black broken line indicates the background elastic constant (high-frequency limit). The inset in (b) shows the relative change of C_v as a function of magnetic field at $T = 0.020, 0.920$, and 10 K. The black solid curve in the inset is the CEF calculation for 20 mK. B^* is the characteristic magnetic field (see text). In addition, magneto-acoustic quantum oscillations were observed above 9 T at 20 and 920 mK (as shown in the enlarged view).

The main panels of Fig. 6.8 show the temperature dependences of C_v at various magnetic fields $B \parallel [001]$ below 20 K. These temperature dependences of C_v can be

analyzed by localized CEF models with the following Hamiltonian [74, 75], $\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{QS}} + \mathcal{H}_{\text{QQ}}$. We use the CEF parameters for $\text{PrIr}_2\text{Zn}_{20}$: $B_4^0 = -0.0109$ K and $B_6^0 = -0.4477$ mK in the present CEF Hamiltonian $\mathcal{H}_{\text{CEF}}$ for the Pr-37% sample, which is same as the analysis of the Pr-8% system.

Under the assumption with an effective multipole $\tilde{O}_v = O_v + \lambda H_v$ with Γ_3 symmetry, we compare the results with and without the contribution of H_v in Figs. 6.8(a) and (b). The calculation with $\lambda = 0.006$ (Fig. 6.8(b)) reproduces the experimental data much better than the calculation without including the electric hexadecapolar contribution (Fig. 6.8(a)), in particular, in the range of $B > 8$ T. Thereby, it is necessary to consider not only the contribution of the electric quadrupole O_v but also that of the electric hexadecapole H_v to reproduce the data.

As well as the Pr-8% system, the elastic constant $C_{\Gamma_3}^{4f}(T, B)$ can be expressed by the equation 6.3, and $N = 8x/a(x)^3 = 1.03 \times 10^{27} \text{ m}^{-3}$ is the number of Pr ions per unit volume in the Pr-37% sample, estimated from the lattice constant $a(x)$ at room temperature.

The coupling constants, $g_{\Gamma_3} = 40$ K and $g'_{\Gamma_3} = -0.05$ K are obtained from the fit to the data at various magnetic fields above 1 K, since a QKE and a change in the ground state due to a low-energy phonon excitations affect the data at lower temperatures (as described in detail below). The present parameter set for the calculation reproduces the magnetic-field dependence above 5 T, as shown in the inset of Fig. 6.8(b). Here, we define the characteristic magnetic field B^* below which the localized $4f$ -electron model is no longer valid. B^* can be estimated as 5 T at the lowest temperature of 20 mK. In addition, it should be noted that acoustic dHvA oscillations were observed above 9 T at 20 and 920 mK. The magnitude of the oscillation is smaller than the Pr-8% system, whereas, this phenomenon proves the high quality of the present single crystal.

6.3.3 QKE Contribution

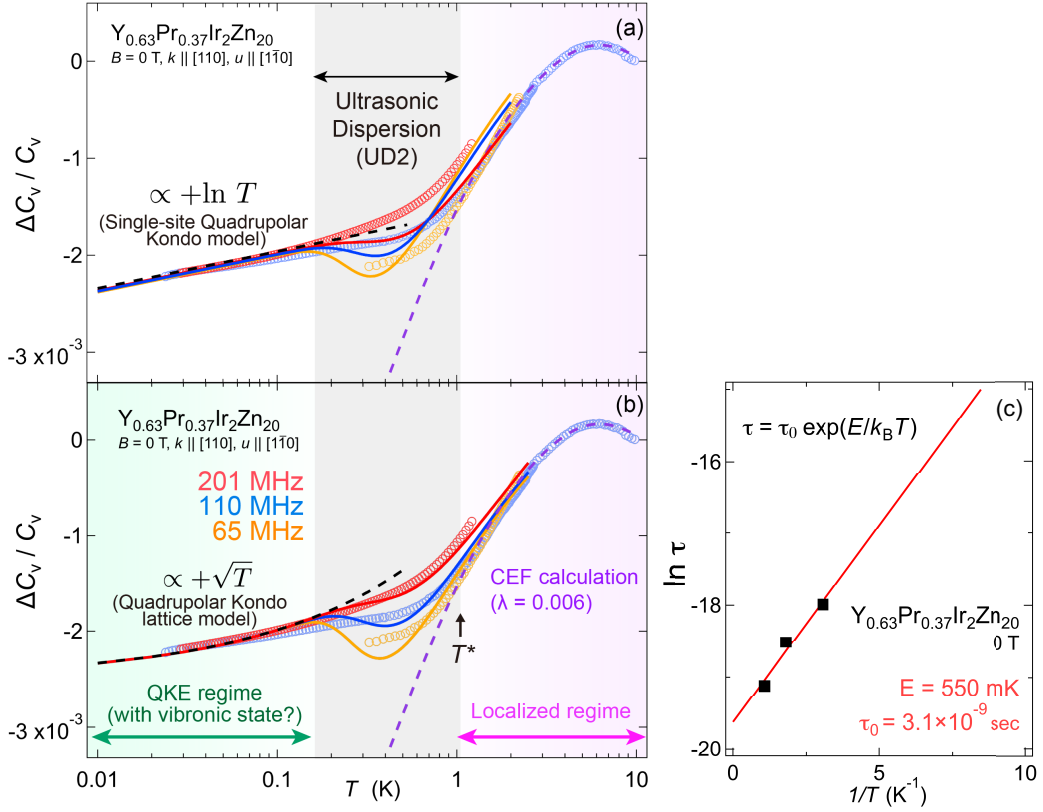


Figure 6.9: Relative change of the elastic constants C_v of the Pr-37% system as a function of temperature below 10 K. The purple broken lines show the CEF calculation using $\lambda = 0.006$. The black broken lines show the elastic constants estimated for the high-frequency limit, $C_v(\infty)$ (the line in (a) is proportional to $\ln T$, though that in (b) follows $\sqrt{T}$). Solid lines in panel (a) and (b) are the calculations assuming a Debye-type dispersion to reproduce UD2. Panel (c) shows Arrhenius plot for UD2, and the solid line shows the fitted straight line to the data.

Figure 6.9 shows the temperature dependence of the elastic constant C_v at the frequencies of 65, 110, and 201 MHz below 10 K. The data with 201 and 64 MHz were obtained by using a ^3He - ^4He dilution refrigerator and PPMS, respectively. The data with 110 MHz was obtained by connecting data from different refrigerators and different measurement environments. The purple dashed line at higher temperatures is obtained using the CEF calculation as described above. C_v at 110 MHz deviates from the calculation below $T^* \sim 1$ K. Here, we defined T^* as the characteristic temperature below which the localized CEF model seems to be no longer applicable. In the present Pr-37% system, C_v shows frequency dependences at around 0.5 K, while C_{44} does not show a frequency dependence also at this low-temperature region. It is different from that C_v in the Pr-3.4% and 8% systems shows no frequency dependence down to 0.04 K [43].

Here, for UD2, we apply the same Arrhenius-type analysis as for UD1 at high temperatures. The solid lines in Figs. 6.9(a) and 6.9(b) show the results based again on a Debye-type dispersion (Eq. 6.4). Here, we assume that the high-frequency limit $C(\infty, T)$ has (a) a logarithmic temperature dependence based on the single-site quadrupolar Kondo model and (b) a square-root temperature dependence based on the quadrupolar Kondo (virtual) lattice model[19]. For both calculations, we assume that the low-frequency limit $C(0, T)$ is calculated using the localized CEF model. The latter analysis reproduces the experimental data better, in particular, for the data at high frequency. This suggests that the quadrupolar Kondo (virtual) lattice model should be applied in the Pr-37% system, where the interaction between localized quadrupoles is not negligible as well as the Pr-8% system.

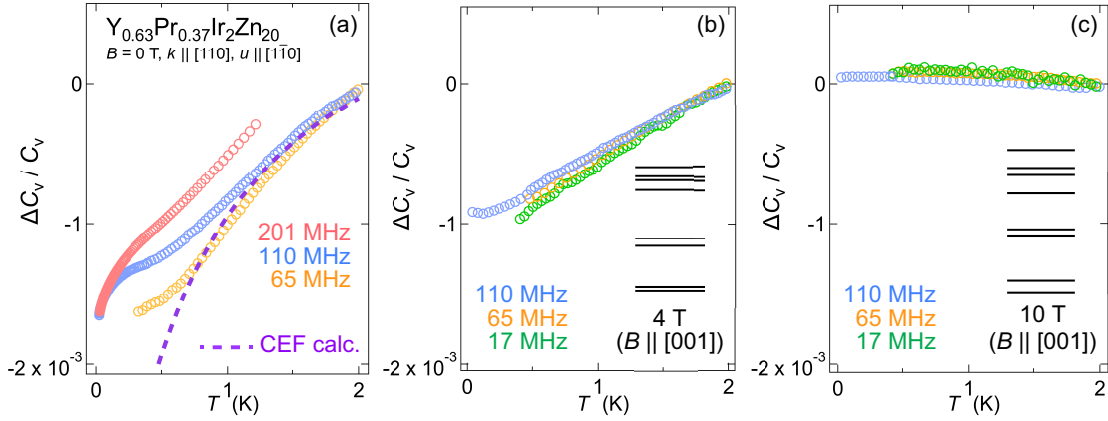


Figure 6.10: Frequency dependence of the elastic constants C_v of the Pr-37% under (a) 0 T (b) 4 T (c) 10 T ($B \parallel [001]$). The purple broken lines in panel (a) show the CEF calculation using $\lambda = 0.006$. Energy schemes in panel (b) and (c) describe the CEF energy schemes under magnetic fields.

We obtain the relatively slow characteristic relaxation time $\tau_0 = 3.1 \times 10^{-9}$ s and the low activation energy $E \approx 550$ mK from the Arrhenius plot as shown in Fig. 6.9(c). This energy scale is much smaller than that of UD1, indicating that UD1 and UD2 have different origins. The energy scale of UD2 is as well much smaller than that of UD observed in the Pr-100% system ($E \sim 10$ K). On the other hand, a similar low-energy UD was observed in the non-Kramers compound PrMg_3 ($\tau_0 = 0.85 \times 10^{-9}$ s, $E = 500$ mK) [80]. PrMg_3 shows no long-range quadrupolar order at least down to 20 mK [84]. Previously, Araki *et al.* pointed out possible formation of a vibronic state, which is a quantum state caused by the coupling between the non-Kramers doublet and the phonons of the surrounding lattice near absolute zero [80]. It has been theoretically predicted that a Kondo-like singlet can be formed by the coupling of the Γ_3 doublet to dynamical Jahn-Teller phonons [85, 86]. We also investigated the magnetic-field dependence of UD2 as shown in the Fig. 6.10. We discovered that the frequency dependency due to UD2 is suppressed by the magnetic fields, which is in contrast to the magnetic-field robust UD1 originating from an atomic vibration. We consider that this is one of the evidences that the origin of UD2 is related

to the electric quadrupolar degrees of freedom, since CEF calculation indicates that the Γ_3 electric quadrupolar degrees of freedom is suppressed by the Zeeman splitting under fields. The suppression of the ultrasonic dispersion is reported also in PrMg_3 [87].

Based on these experimental and theoretical proposals and the similarities to the present case, it is possible that a vibronic state is formed in the NFL region of the Pr-37% system. From the perspective of the crystal structure, a Pr atom is surrounded by the high-symmetry cage of sixteen Zn atoms as shown in Fig. 2.1(a), which suggests the existence of an isolated low-energy phonon at the Pr site (interpreted as Einstein phonon). Due to this structural situation, it is relatively easy to form a "vibronic state" coupling between the low-energy phonons and the localized electric quadrupoles to release the entropy of the CEF ground-state doublet Γ_3 .

In the Pr-37% system, it is possible to form a vibronic state, whereas a square-root temperature dependence of C_v expected for the quadrupolar Kondo lattice model was observed below 0.15 K. The temperature dependence is close to that of the Pr-8% system showing no frequency dependence. In the present study, we analyze the temperature dependence of C_v at very low temperatures assuming that UD2 originating from electron-phonon coupling and the temperature dependence proportional to $\sqrt{T}$, caused by the quadrupolar Kondo (virtual) lattice effect are independent. Such analysis qualitatively explains the present experimental results. However, whether these quantum states are independent or entangled is still an open question. To address the issue, it is necessary to construct a new theory including a localized quadrupolar moment and conduction electrons as well as phonons to describe the quantum ground state of $\text{Y}_{1-x}\text{Pr}_x\text{Ir}_2\text{Zn}_{20}$.

6.4 Pr-Concentration Dependence of Parameters

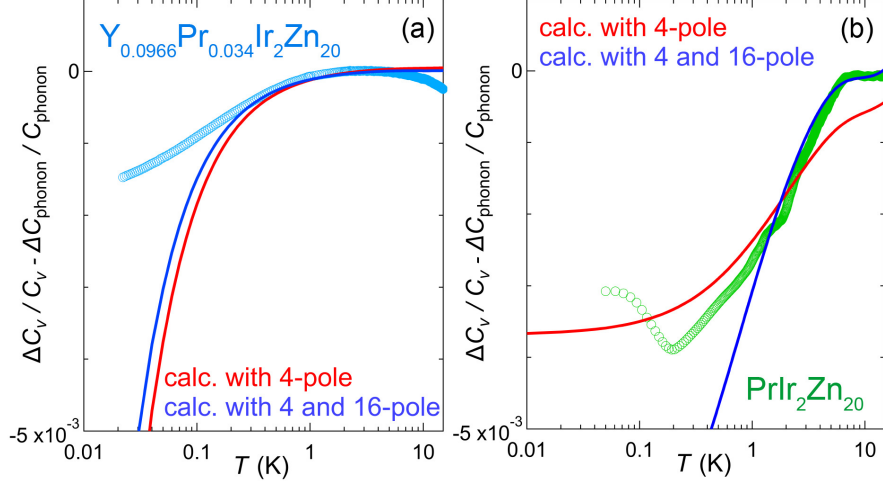


Figure 6.11: Relative change of the elastic constants C_v with phonon background subtracted of (a) the Pr-3.4% system [43] and (b) the Pr-100% system [30] as a function of temperature. The red and blue lines show the calculations without and with the contribution of the electric hexadecapole H_v ($\lambda = 0.006$).

In addition to the Pr-8% and 37% system which we measured in the present study, we reanalyzed previously reported data for the Pr-3.4% system [43] and the Pr-100% system [30] under zero magnetic field by considering hexadecapolar contributions using the same parameter $\lambda = 0.006$ (Fig. 6.11). In case of the Pr-3.4% system, g' is equal to zero, indicating that the contribution of the electric hexadecapole is almost negligible. On the other hand, the electric hexadecapolar contribution cannot be ignored in the Pr-100% system. The analysis as well $\lambda = 0.006$ reproduces the data well for all Pr concentrations. Figure 6.12(a) shows g_{Γ_3} obtained with $\lambda = 0.006$ (calc. 1) and $\lambda = 0$ (calc. 2) for each Pr concentration. Figure 6.12(b) shows g'_{Γ_3} correspondingly. The hexadecapolar contribution suppresses the Curie-like softening. Thus, the values of g_{Γ_3} are larger than those considering only the contribution of the electric quadrupole. The value of g_{Γ_3} in the present Pr-37% system is ~ 1.5 times larger than for $\lambda = 0$. In any case, the absolute values of both g_{Γ_3} and g'_{Γ_3} increase linearly with Pr concentration.

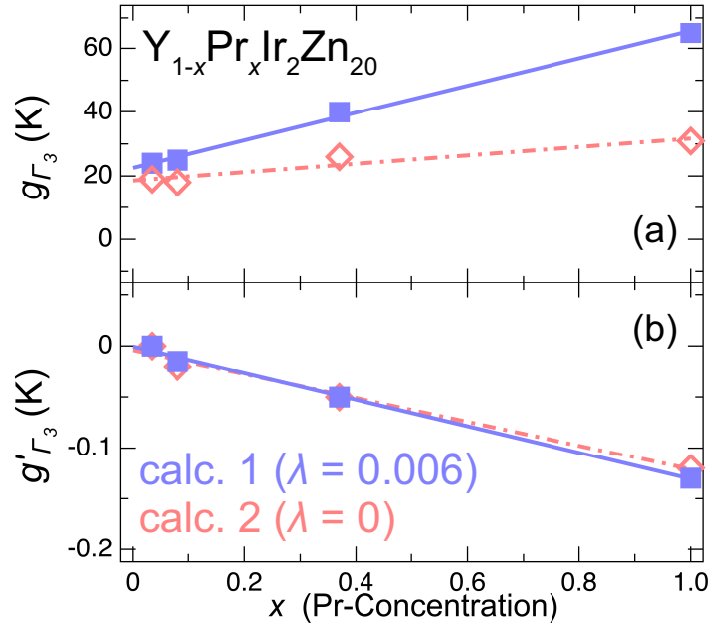


Figure 6.12: (Color online) The coupling constants of (a) the multipole-strain interaction g_{Γ_3} and (b) the multipole-multipole interaction g'_{Γ_3} as a function of Pr concentration x for $\text{Y}_{1-x}\text{Pr}_x\text{Ir}_2\text{Zn}_{20}$ [43, 30]. Blue closed markers (calc. 1) and red open diamonds (calc. 2) are parameters obtained by fits with ($\lambda = 0.006$) and without ($\lambda = 0$) electric hexadecapolar contribution, respectively.

6.5 Pr-Concentration Dependence of Quantum Ground State

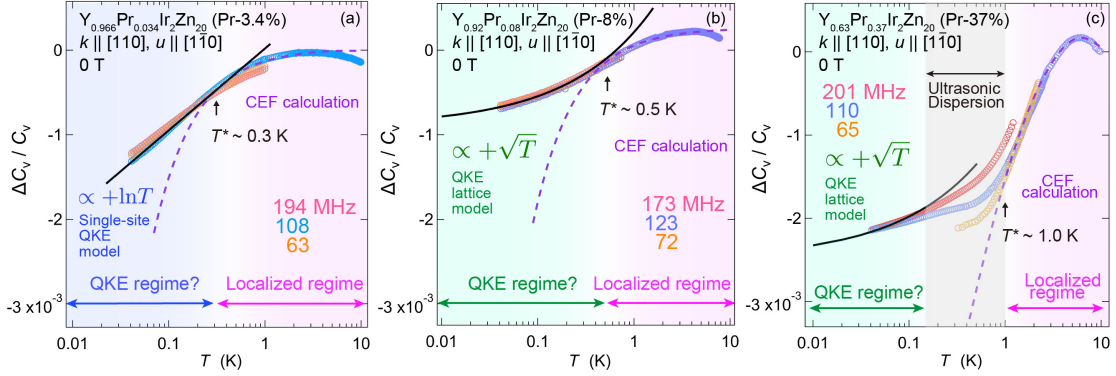


Figure 6.13: Temperature dependences of the elastic constants C_v in the (a) Pr-3.4% system [43], (b) Pr-8% system, and (c) Pr-37% system. Different colored markers show the experimental results at different frequencies. Purple dashed curves show the CEF calculation results with $\lambda = 0.006$. Black solid curves show fits based on the “single-site” quadrupolar Kondo model (a) and the quadrupolar Kondo “lattice” model (b, c). T^* is the characteristic temperature deviated from the localized model. (Our method for determining the characteristic temperature contains an uncertainty of about ± 0.1 K).

Finally, we discuss the multiple effects of the elemental dilution. The elastic response of $Y_{1-x}Pr_xIr_2Zn_{20}$ at very low temperature changes drastically depending on the Pr-concentration x , which is shown in Figs. 6.13(a) - 6.13(c). Quantum states at very low temperatures in the series are summarized in the phase diagram in Fig. 6.14. Here, T_0 is the characteristic temperature of NFL behavior, which is obtained by specific-heat measurements [20]. T^* , the QKE characteristic temperature observed by our ultrasonic measurements, shows good agreement with T_0 .

The Y-dilution changes the following three factors, i) the number density of the localized Pr moments, ii) the lattice constant, and iii) the atomic disorder. These three contributions can affect the magnitude of the Ruderman-Kittel-Kasuya-Yosida (RKKY)-type interaction among the localized quadrupoles. As the Pr concentration decreases, the lattice constant decreases [69]. However, as the AFQ order observed in the Pr-100% system collapses in Y-containing systems, the effective RKKY-type interaction between the Pr^{3+} ions becomes weakened with the Y dilution. Indeed, the absolute value of the interaction between multipoles g'_{Γ_3} (Fig. 6.12(b)) decreases linearly with decreasing Pr concentration. Then, the characteristic temperature of the QKE, T^* (or T_0) increases as the Pr concentration increases up to 37%. We assume that the change of T^* is ascribed to the atomic disorder which lowers the site symmetry of Pr^{3+} and locally splits the ground-state doublet Γ_3 . Since the atomic disorder is generally largest for $x = 0.5$ (Y : Pr = 1 : 1), this assumption is consistent with

the Pr-concentration dependence of the characteristic temperatures. It is necessary to investigate the Pr-concentration dependence of the energy scale of the low-energy UD and compare it with that of the QKE characteristic temperature, which would serve for understanding the relationship between the QKE and the vibronic ground state.

The present systems $\text{Y}_{1-x}\text{Pr}_x\text{Ir}_2\text{Zn}_{20}$ could have various ground states depending on the Pr concentration, in other words, this series is very good target to investigate the novel interaction between localized electric quadrupole, conduction electrons, and dynamical Jahn-Teller phonon.

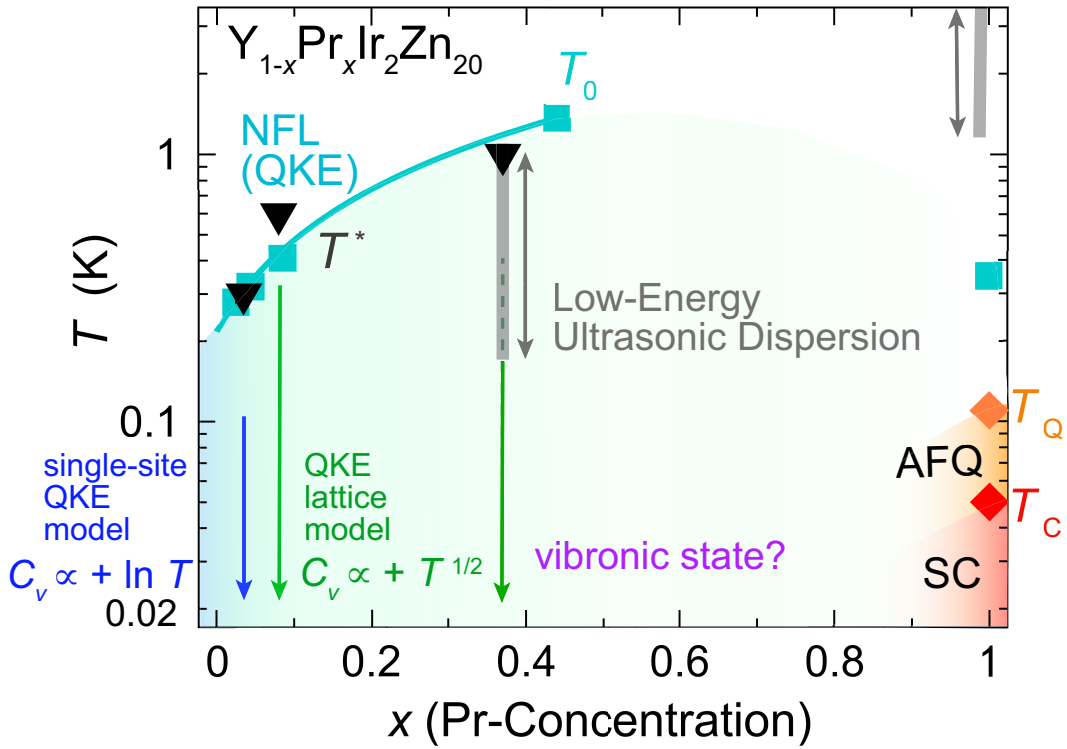


Figure 6.14: T - x phase diagram of $\text{Y}_{1-x}\text{Pr}_x\text{Ir}_2\text{Zn}_{20}$. T_0 is the characteristic temperature of the QKE determined from specific-heat experiments [20]. T^* is the temperature where the behavior of C_v deviates from the CEF model extracted from ultrasonic measurements [43, 30].

6.6 Acoustic dHvA Oscillation

As described above, we observed the acoustic de Haas-van Alphen (dHvA) oscillation in magnetic-field swept measurements of the Γ_3 -symmetrical elastic constant C_v in each Pr-concentration system. It is known that the behavior could be observed only in case that sample quality is adequate, since sample quality affects Dingle temperature. As shown in Fig. 6.15(a), the amplitude of the oscillation depends on the Pr concentration. Low Pr-concentration systems (Pr-0 and 3.4% systems) show relatively clear acoustic dHvA oscillation, whereas, the oscillation of the Pr-37% system is quite small. (Enlarged view for the Pr-37% system is shown in the inset of Fig.6.8(b).)

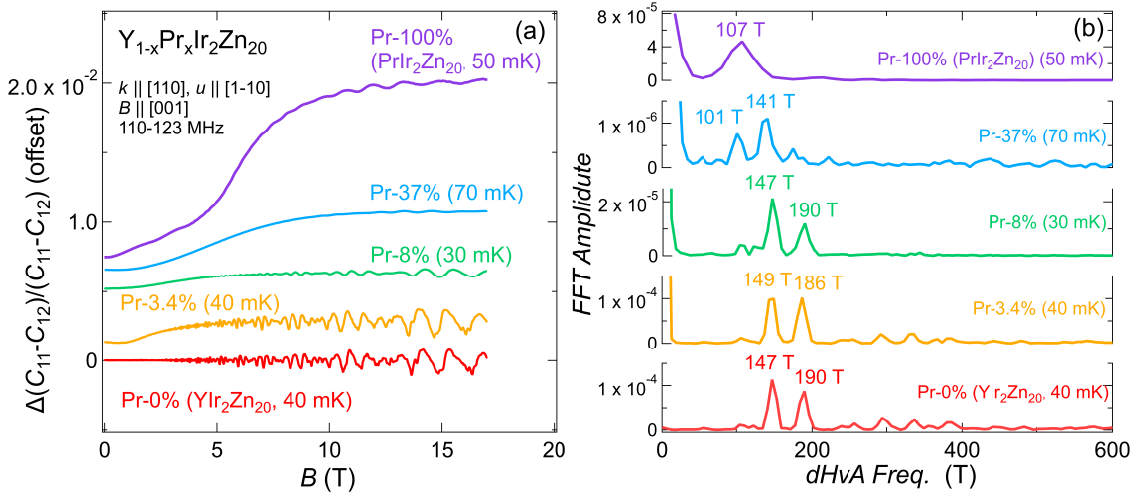


Figure 6.15: Acoustic de Haas-van Alphen oscillations observed in $Y_{1-x}Pr_xIr_2Zn_{20}$ ($x = 0, 0.034$ [43], 0.08, 0.37, and 1.0). Panel (a) shows the raw data of magnetic-field swept measurements of C_v , and panel (b) shows the results of the FFT analysis for the oscillation parts of the raw data.

By using the oscillating part of the raw data, we performed fast Fourier transform (FFT) analysis. FFT spectra shown in Fig. 6.15(b) for each Pr-concentration system are obtained from the following magnetic-field range; 4.5-17 T for the Pr-0% system, 4.6-17 T for the Pr-3.4% system, 4.5-17 T for the Pr-8% system, 9-14 T for the Pr-37% system, and 7.5-17 T for the Pr-100% system. We found that dHvA frequency as well as dHvA amplitude depends on the Pr concentration, which means it is possible that Fermi surface is modified by the Pr concentration. $4f$ electrons of Pr^{3+} in the present system has been considered to be well localized, however, our results suggests the possibility that it affects the conduction electrons.

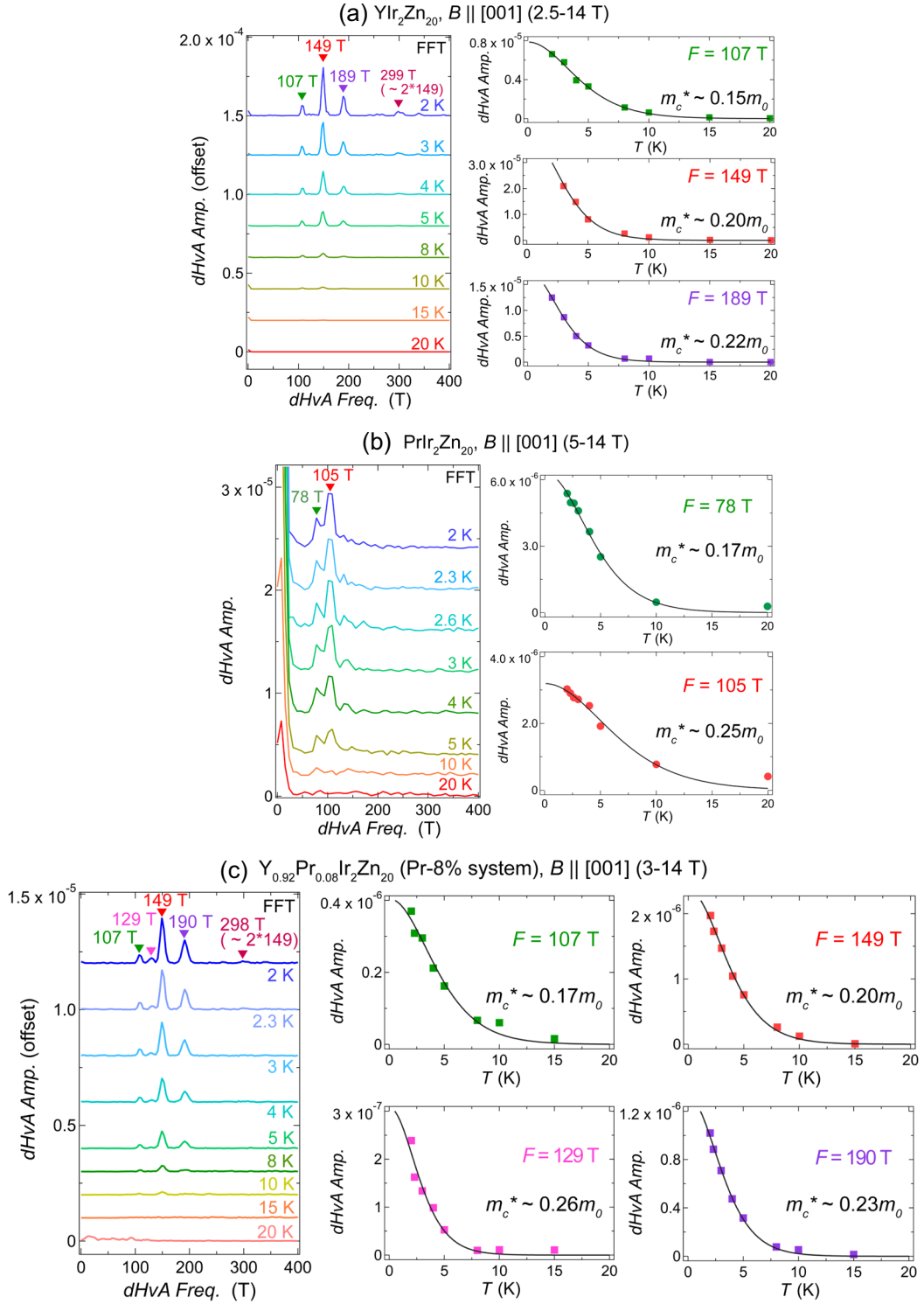


Figure 6.16: FFT spectra above 2 K and temperature dependences of dHvA amplitude in some obvious spectra for (a) $\text{YIr}_2\text{Zn}_{20}$ (Pr-0% system), (b) $\text{PrIr}_2\text{Zn}_{20}$ (Pr-100% system), (c) Pr-8% system. Black solid curves are calculated based on Lifshitz-Kosevich formula. (Details are written in the main text.)

To investigate the detail of each dHvA branch, we clarified the temperature dependence of the oscillation for the Pr-0, 8, and 100% systems. For the verification, we used PPMS and performed the measurements above 2 K. Figure 6.16 shows the temperature dependence of FFT spectrum and dHvA amplitude. We analyzed the data of dHvA amplitude by using the following equation of temperature factor R_T in Lifshitz-Kosevich formula.

$$R_T = \frac{2\pi k_B T / \mu_B^* H_0}{\sinh(2\pi^2 k_B T / \mu_B^* H_0)} \quad (6.6)$$

Here, μ_B^* and H_0 are defined by the following equations.

$$\mu_B^* = \frac{e\hbar}{m^*c}$$

$$\frac{1}{H_0} = \frac{1}{1/2(H_{min} + H_{max})}$$

Table 6.2: Comparison of the magnetic-field-angle dependence of the dHvA frequency between previous study and present study. (a) Experiment results of $\text{PrIr}_2\text{Zn}_{20}$ by the conventional field modulation method [88], (b) Theoretical calculation without the contribution of $4f$ electrons (lattice parameter is of $\text{PrIr}_2\text{Zn}_{20}$) [88], (c) Our results obtained by ultrasonic measurements of the Pr-8% system.

(a) Previous Study (Field Modulation Method)				(b) Present Study (Ultrasonic Method)					
$\text{PrIr}_2\text{Zn}_{20}$ (exp.)		$\text{PrIr}_2\text{Zn}_{20}$ (La-base theory)		$\text{PrIr}_2\text{Zn}_{20}$		$\text{Y}_{0.92}\text{Pr}_{0.08}\text{Ir}_2\text{Zn}_{20}$		$\text{YIr}_2\text{Zn}_{20}$	
F (T)	$m_c^* (m_0)$	F_b (T)	$m_b (m_0)$	F (T)	$m_c^* (m_0)$	F (T)	$m_c^* (m_0)$	F (T)	$m_c^* (m_0)$
g		g	122						
f	84	f	135		0.17	107	0.17	107	0.15
				105	0.25				
						129	0.26		
e	125	e	153			149	0.20	149	0.20
	207					190	0.23	189	0.22
d	257	d	276						

Black solid curves in Fig. 6.16 are calculation results. For the Pr-100% system, fitting is performed based only on the data below 10 K, since the dHvA amplitude at 20 K is quite small. As described in eq. 6.6, we could estimate the cyclotron effective mass m^* for each branch. Obtained dHvA frequencies and cyclotron effective masses are compared with the previous experimental results which is obtained by the conventional field modulation method and the calculation results in Table 6.18 [88]. Present results roughly reproduce the previous report in some branches (branch e and f), whereas, we also observed some differences. To reveal more details, we also investigated the magnetic-field anisotropy of the acoustic dHvA oscillation with new developed Two Axial ROtating (TARO) probe for ultrasonic measurements (section 5.7.4). Figure 6.17 shows the results of the field-angle dependence of the acoustic dHvA oscillation and FFT spectra at 2 K in the Pr-8% system. We also tried similar measurements

in the Pr-100% system to reveal the Pr-concentration dependence, however, dHvA amplitude in the Pr-100% system is smaller than the low Pr-concentration systems and it is challenging to analyze the data except for $B \parallel [001]$ at 2 K.

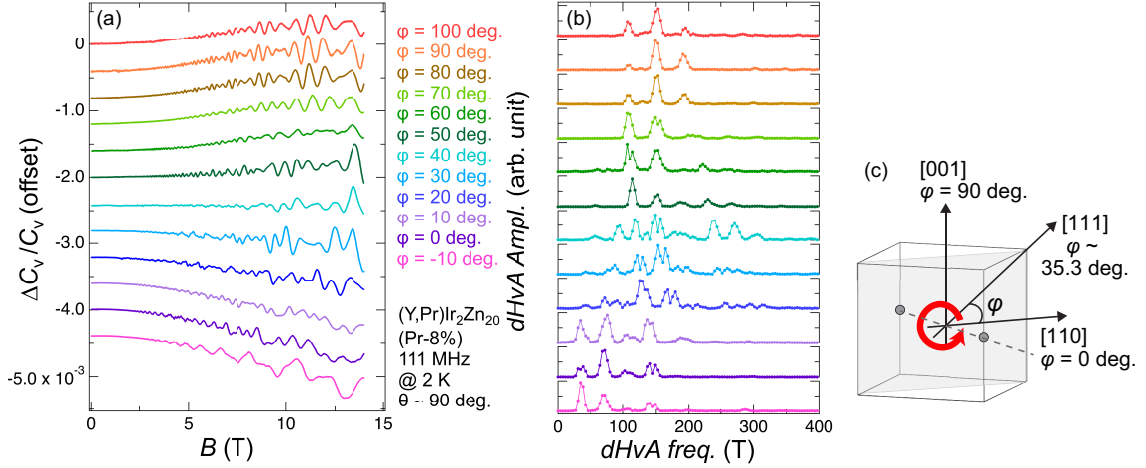


Figure 6.17: Field-angle dependence of the acoustic dHvA oscillation in the Pr-8% system. Panel (a) shows the raw data of magnetic-field swept measurements of C_v , and panel (b) shows the results of the FFT analysis for the oscillation parts of the raw data. Field angle, ϕ , is defined as shown in panel (c). Rotation axis is along with $[1\bar{1}0]$.

As shown in the Fig. 6.17, we succeeded in obtaining a clear field-angle dependence of the acoustic dHvA oscillation by using TARO probe. dHvA frequencies under each direction of the magnetic field are summarized in Fig. 6.18(c). We observed relatively spherical branches with low dHvA frequencies, which is considered to correspond to branches e and f reported in the previous study [88]. As described above, the cyclotron effective masses of them are close to the previous report of $\text{PrIr}_2\text{Zn}_{20}$. On the other hand, We could also observe some differences with the previous reports. Acoustic dHvA oscillation is detected mediated by an electron-phonon coupling unlike the conventional dHvA oscillation, which means that it is possible that these differences originate from the difference of the measurement method. Another possibility is the contribution of $4f$ electrons of the Pr ion. Our results suggest that Fermi surface possibly depends on the Pr concentration. It is necessary to carry out additional measurements for the high Pr-concentration systems and theoretical calculation with the contribution of $4f$ electrons.

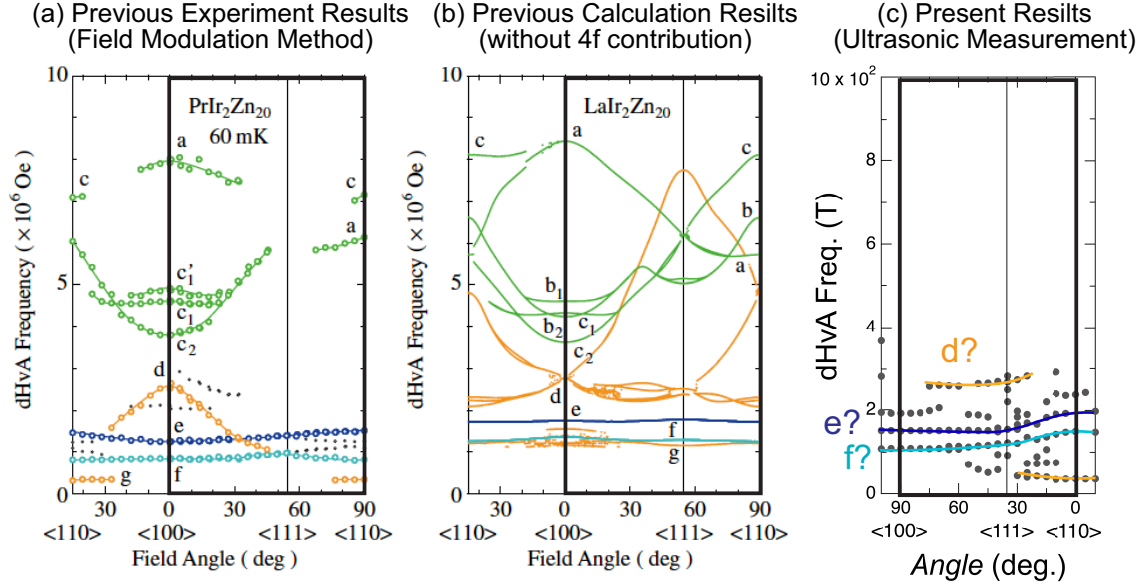


Figure 6.18: Comparison of the magnetic-field-angle dependence of the dHvA frequency between previous study and present study. (a) Experiment results of $\text{PrIr}_2\text{Zn}_{20}$ by the conventional field modulation method [88], (b) Theoretical calculation without the contribution of $4f$ electrons (lattice parameter is of $\text{PrIr}_2\text{Zn}_{20}$) [88], (c) Our results obtained by ultrasonic measurements of the Pr-8% system.

Chapter 7

Verification of Phase Pocket “A” in AFQ Ordering of $\text{PrIr}_2\text{Zn}_{20}$

7.1 Experimental Procedure

We investigated the intriguing small phase pocket “A” near the antiferro-quadrupolar (AFQ) ordering phase boundary by ultrasonic measurements of $\text{PrIr}_2\text{Zn}_{20}$. This small phase pocket “A” has been proposed very recently in the precise specific-heat measurements [39]. As the details are written in the section 2.3.2, the origin of this new phase pocket is still open question. Ultrasonic measurements of $\text{PrIr}_2\text{Zn}_{20}$ had already been performed by Ishii *et al.* [30], whereas, the different symmetrical modes Γ_3 mode and Γ_5 mode are not separated in the experimental results. The reason is possibly mode-mixing originating from “twin” in the synthesized crystal at 2011 [89]. In the present study, we used later single-crystalline sample and remeasured the Γ_3 and Γ_5 -symmetrical elastic constants to obtain information of mode-separated quadrupolar degrees of freedom. It is essential for revealing the origin of the phase “A” to investigate the pure Γ_3 -symmetrical elastic constant under magnetic fields in precise directions, since previous study revealed that phase “A” has a large field-angle dependence; the phase is most enhanced under $B \parallel [001]$ but that is disappeared under $B \parallel [110]$ [39]. We performed the ultrasonic measurements of $\text{PrIr}_2\text{Zn}_{20}$ under the magnetic field along $B \parallel [001]$ and $[110]$ in the present study.

7.2 Experimental Results

7.2.1 Temperature Dependence under Zero Magnetic Field

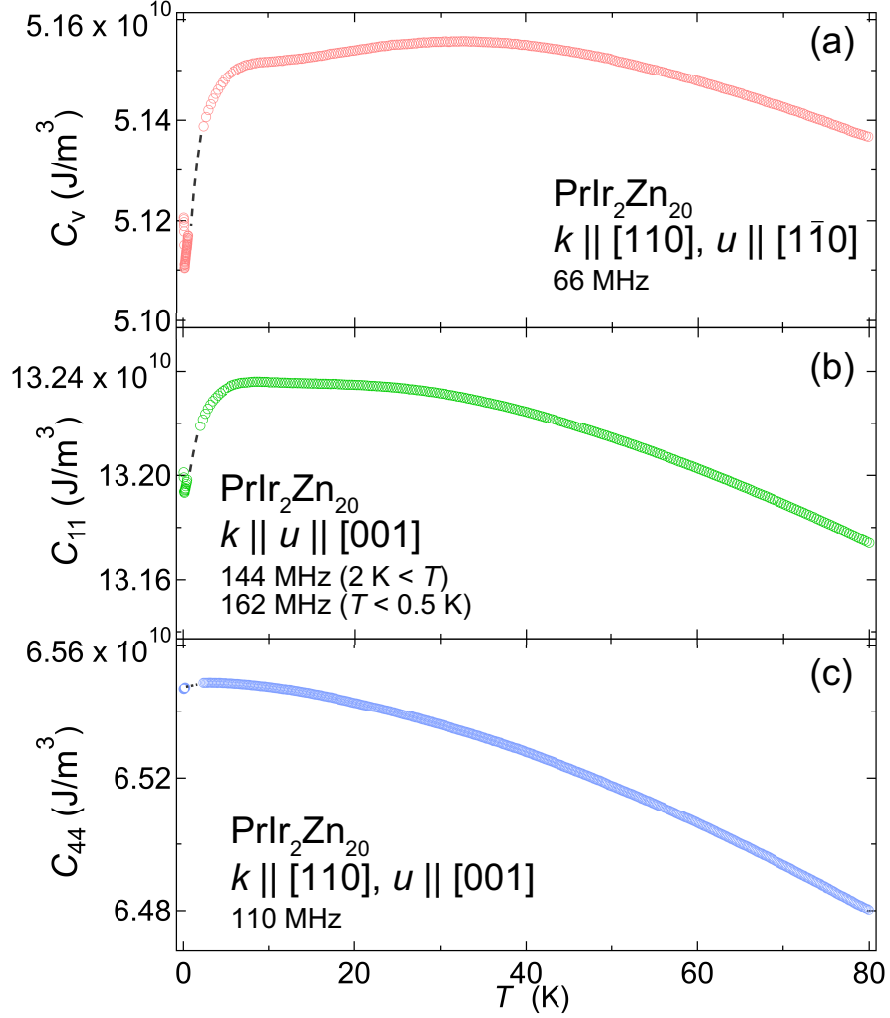


Figure 7.1: Elastic constants (a) C_v , (b) C_{11} and (c) C_{44} on $\text{PrIr}_2\text{Zn}_{20}$ as a function of temperature. The data in the temperature range from 0.5 K to 1.5 K is not measured due to the lack of ^3He refrigerator.

Figure 7.1 shows temperature dependences of the elastic constants (a) C_v , (b) C_{11} and (c) C_{44} of $\text{PrIr}_2\text{Zn}_{20}$ in the wide temperature region. The absolute values of the elastic constants are calculated by using the formula $C_{ij} = \rho v_{ij}^2$. In the present system, $\rho = 8.377 \text{ g/cm}^3$ is the density estimated from the lattice constant $a = 14.2729 \text{ \AA}$ [34]. In contrast to monotonically hardening of the C_{44} mode, the C_v mode and the C_{11} mode show an elastic softening below $\sim 30 \text{ K}$ and 8 K , respectively. Here, C_{11} corresponds to the $\Gamma_1 \oplus \Gamma_3$ -symmetrical mode, and the elastic softening in the mode is considered to arise from including Γ_3 -symmetrical component. The experimental results of the present single-crystalline sample shows a clear mode dependence, similar

to other Y-diluted systems, which is different from the previous report in 2011 [30]. Thus, we consider that the present sample is suitable for the verification of the small phase pocket “A”. Elastic constants C_v and C_{11} show cusp anomalies at $T_Q \sim 0.1$ K as shown in Fig. 7.2, which is consistent with the order parameter of the AFQ phase being the Γ_3 -symmetrical electric quadrupole, as indicated by several previous reports [24, 36].

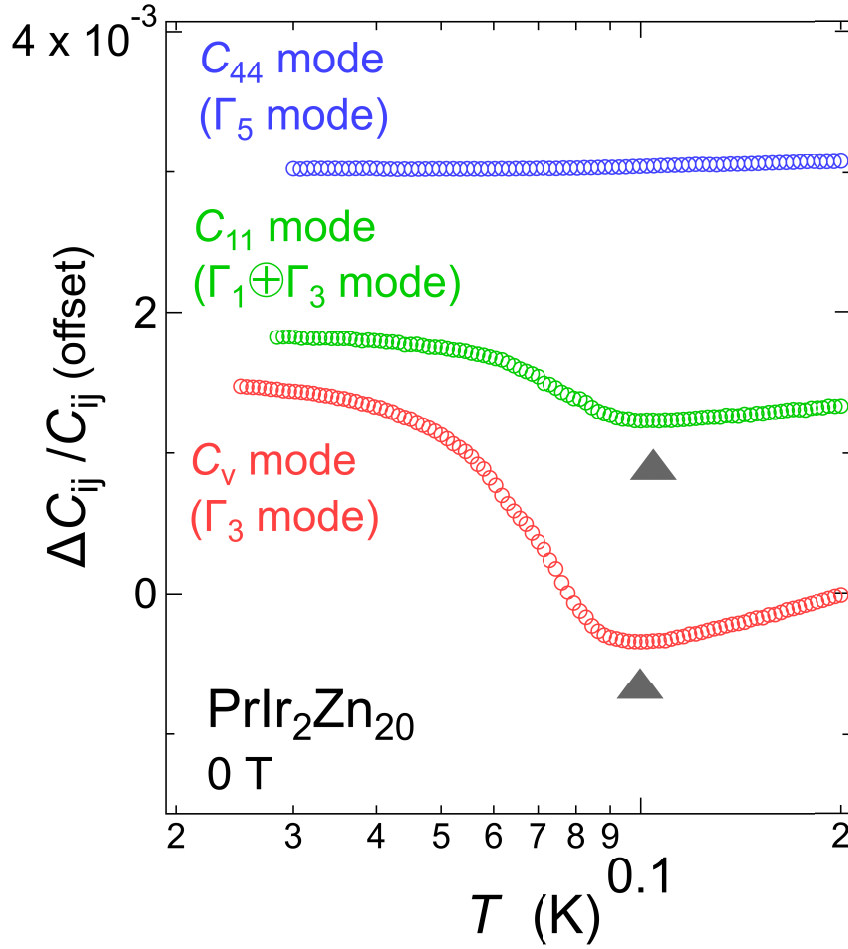


Figure 7.2: Relative change of the elastic constants C_{44} (blue), C_{11} (green), and C_v (red) on $\text{PrIr}_2\text{Zn}_{20}$ as a function of temperature below 0.2 K. Arrows describe the temperature points showing a local minimum of the elastic constant, which corresponds to T_Q .

7.2.2 Temperature Dependence under $B \parallel [001]$

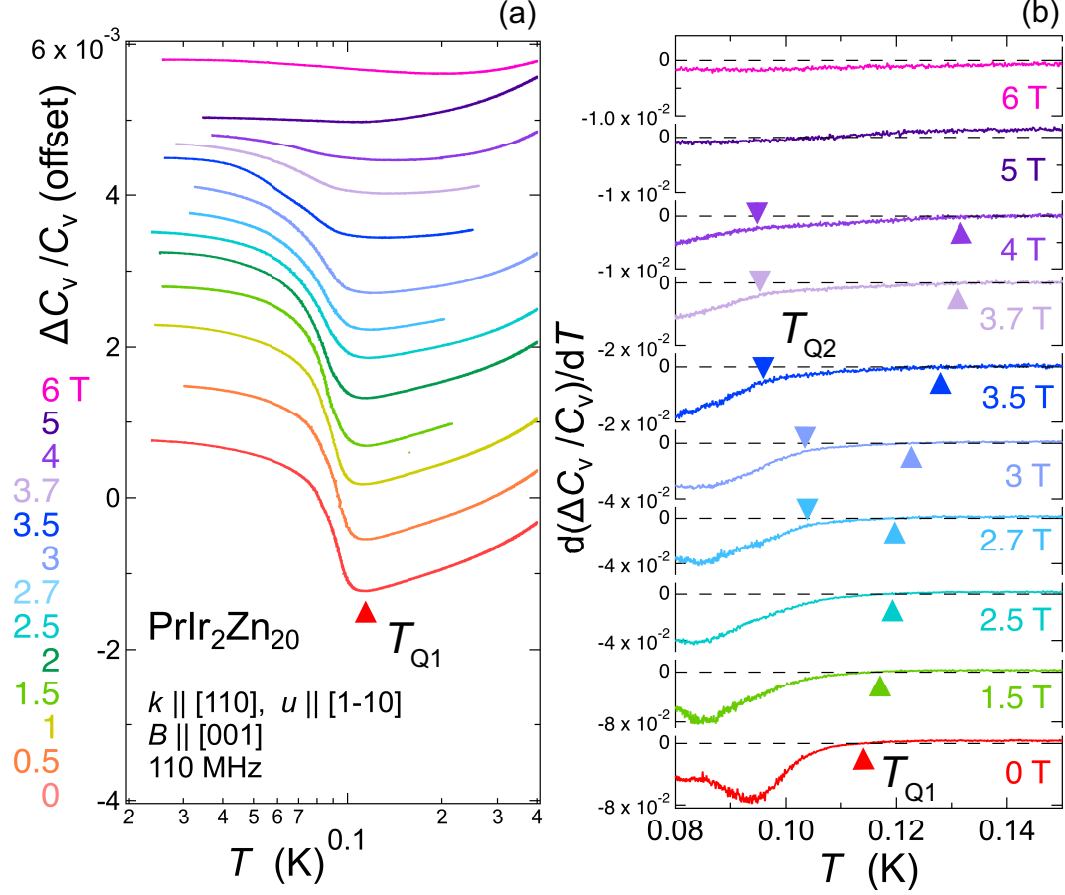


Figure 7.3: (a) Relative change of the elastic constants C_v as a function of the temperature under several magnetic fields ($B \parallel [001]$). Each data is vertically shifted for ease of viewing. (b) Derivative data of the elastic constants C_v with respect to temperature. Broken lines in panel (b) represent $d(\Delta C_v / C_v) / dT = 0$. Intersection points between this broken line and the derivative data corresponds to T_{Q1} (local minimum).

We investigated the magnetic-field dependence of the elastic anomaly at T_Q . The temperature dependences of the Γ_3 -symmetrical elastic constant C_v under several magnetic fields $B \parallel [001]$ are shown in Fig. 7.3(a). A local minimum of the elastic constant C_v is defined as T_{Q1} . Disappearance of the Curie-like softening below T_{Q1} indicates that the Γ_3 -type quadrupolar degrees of freedom is vanished at T_{Q1} , which is consistent with the scenario of the Γ_3 -type AFQ ordering. As shown in Fig. 7.3(a), the cusp anomaly becomes more broad as the magnetic field is applied, and gradually disappears at around 5 T. Furthermore, we performed to differentiate the data, and the derivative data is shown in Fig. 7.3(b). In addition to T_{Q1} , we also found weak kink anomalies in the magnetic-field region from 2.7 T to 4 T, which are defined as T_{Q2} . As described in detail below, we consider that T_{Q2} corresponds to the phase boundary from the small phase pocket “A” to the AFQ ordering phase.

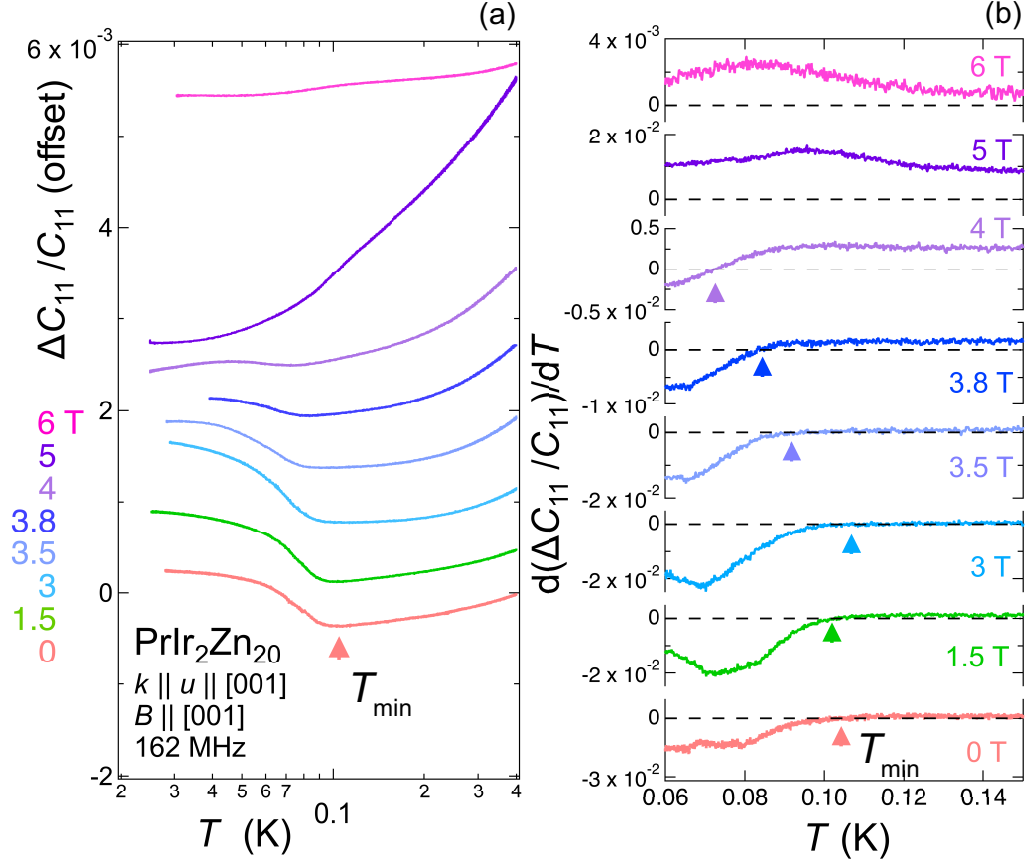


Figure 7.4: (a) Relative change of the elastic constants C_{11} as a function of the temperature under several magnetic fields ($H \parallel [001]$). Each data is vertically shifted for ease of viewing. (b) Derivative data of the elastic constants C_{11} with respect to temperature. Broken lines in panel (b) represent $d(\Delta C_{11}/C_{11})/dT = 0$. Intersection points between this broken line and the derivative data corresponds to $T_{\min}$ (local minimum).

In addition to the pure Γ_3 -symmetrical mode (C_v mode), we measured the temperature dependence of the elastic constant C_{11} under the magnetic fields along $[001]$ as shown in Fig. 7.4. First, the data around 5 T is quite different from the data of the pure Γ_3 mode, C_v . The large softening in the C_{11} mode is considered to originate from the Γ_1 -symmetrical mode, because the C_{11} mode is symmetrically mixed of the Γ_1 and the Γ_3 mode. We consider that the origin of the softening is related to Fermi-liquid state under magnetic fields around 5 T suggested by the previous report [38] (Details are described in section 7.3.1).

This mode also shows the local minimum below 4 T, which is defined as $T_{\min}$. It is noted that the magnetic-field-dependence of T_{Q1} (in the C_v mode) and $T_{\min}$ (in the C_{11} mode) is completely different, *i. e.*, T_{Q1} shifts to higher temperature as the field increases, whereas $T_{\min}$ shifts to lower temperature as the field increases. Furthermore, the derivative data in Fig. 7.4(b) shows no kink anomalies below $T_{\min}$, which is different from the behavior of the pure Γ_3 mode, C_v .

7.2.3 Temperature Dependence under $B \parallel [110]$

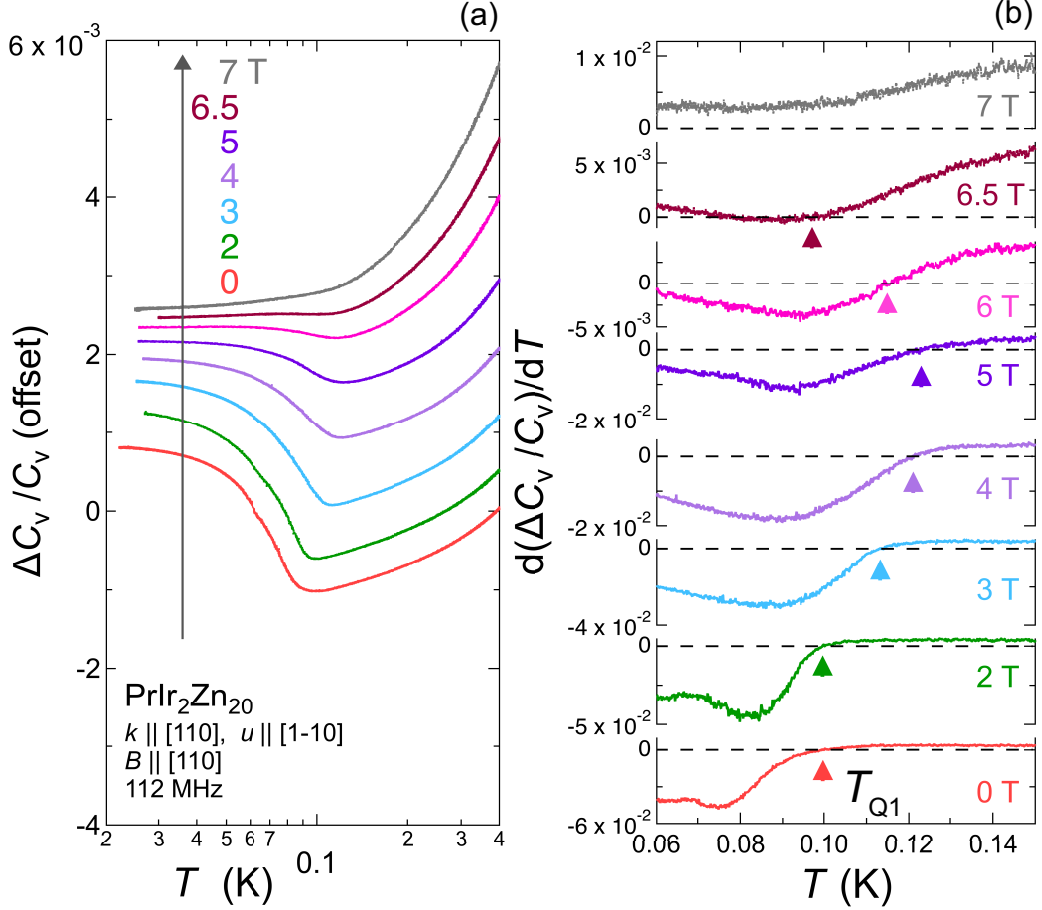


Figure 7.5: (a) Relative change of the elastic constants C_v as a function of the temperature under several magnetic fields ($B \parallel [110]$). Each data is vertically shifted for ease of viewing. (b) Derivative data of the elastic constants C_v with respect to temperature. Broken lines in panel (b) represent $d(\Delta C_v / C_v) / dT = 0$. Intersection points between this broken line and the derivative data corresponds to T_{Q1} (local minimum).

We also investigated the elastic anomalies under the magnetic field along the $[110]$ direction. Figure 7.5 shows the temperature dependence of the elastic constant C_v under magnetic fields along $[110]$. In contrast to the similar measurements under fields along $[001]$, as shown in Fig. 7.3, the local minima (denoted as T_{Q1}) in Fig. 7.5 are sharper even under magnetic fields and the kink anomalies below T_{Q1} (defined as T_{Q2} in section 7.2.2) were not observed in the measurements under the magnetic field ($B \parallel [110]$). We consider that this fact corresponds to the disappearance of phase pocket “A” under the magnetic field along the $[110]$ direction, as suggested in the previous report [39].

7.2.4 Magnetic-Field Dependence

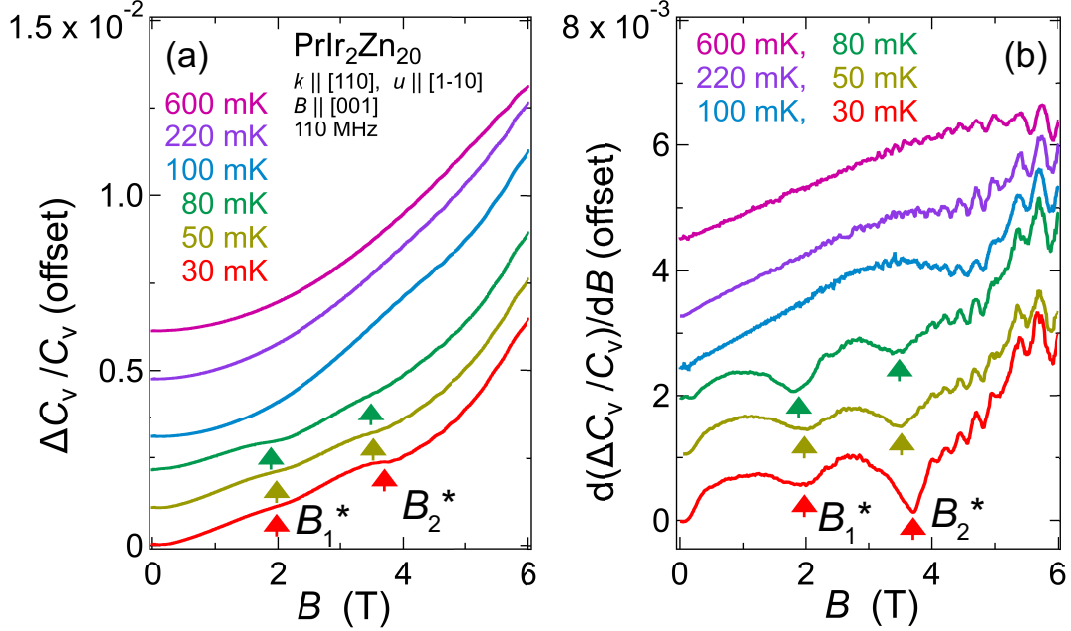


Figure 7.6: (a) Relative change of the elastic constants C_v as a function of magnetic field ($B \parallel [001]$). Each data is vertically shifted for ease of viewing. (b) Derivative data of the elastic constants C_v with respect to B .

We performed the magnetic-field swept measurements of the elastic constant C_v at several temperatures from 30 mK to 600 mK. Also in these measurements, magnetic field is applied along $[001]$. As shown in Fig. 7.6(a), we observed two inflection points, B_1^* and B_2^* , below 80 mK. It is noted that we did not observe these anomalies at 100 mK even where it is below T_{Q1} (0 T) $\sim$ 110 mK. We also performed to differentiate the data with respect to the field, and the derivative data is shown in Fig. 7.6(b). Two elastic anomalies could be clearly observed as local minima in the derivative data. We observed oscillations in the derivative data above $\sim$ 4 T in Fig. 7.6(b), which is considered to originate from the acoustic dHvA oscillation.

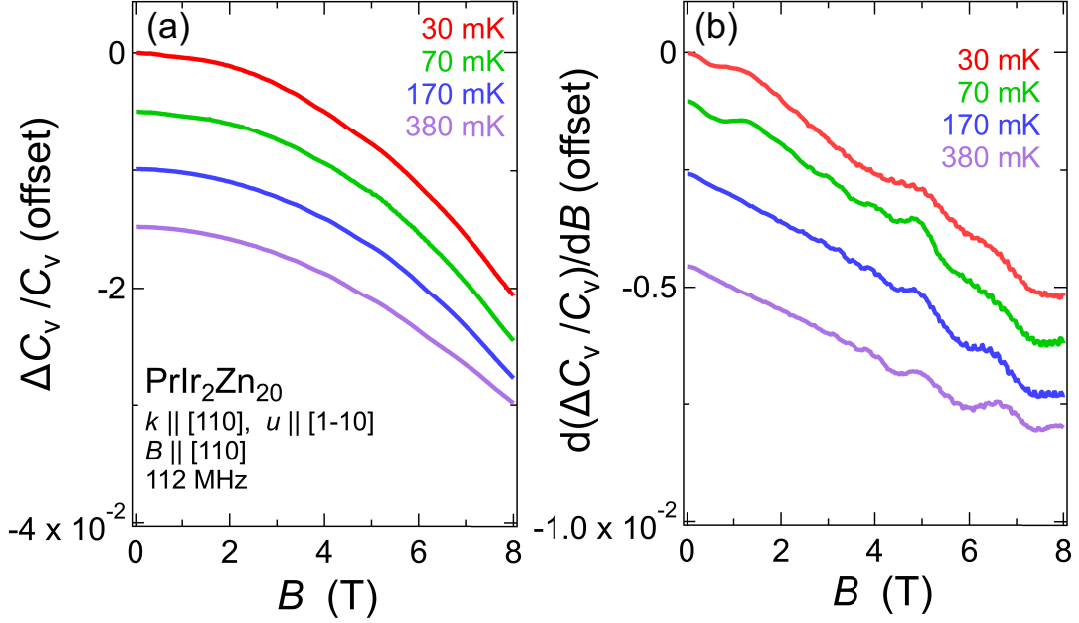


Figure 7.7: (a) Relative change of the elastic constants C_v as a function of magnetic field ($B \parallel [110]$). Each data is vertically shifted for ease of viewing. (b) Derivative data of the elastic constants C_v with respect to B .

Furthermore, we also performed the magnetic-field swept measurements of the elastic constant C_{11} in the field along $[001]$. Figure 7.8 shows the results at several temperatures from 30 mK to 450 mK. The local minimum is observed around 5 T, which is considered to correspond to the large softening in the temperature-swept measurements shown in Fig. 7.4(a). The magnetic field where the local minimum is observed is defined as $B_{\min}$. As the temperature increases, the elastic anomaly at $B_{\min}$ becomes more broad. The anomaly is observed even above the transition temperature of the AFQ ordering. The elastic anomaly associated with the phase boundary of AFQ is not clearly observed also in this mode. Two elastic anomalies observed in the C_v mode are not observed in the C_{11} mode. It is possible that this is because they are masked by a large Γ_1 -symmetrical anomaly in the vicinity of 5 T.

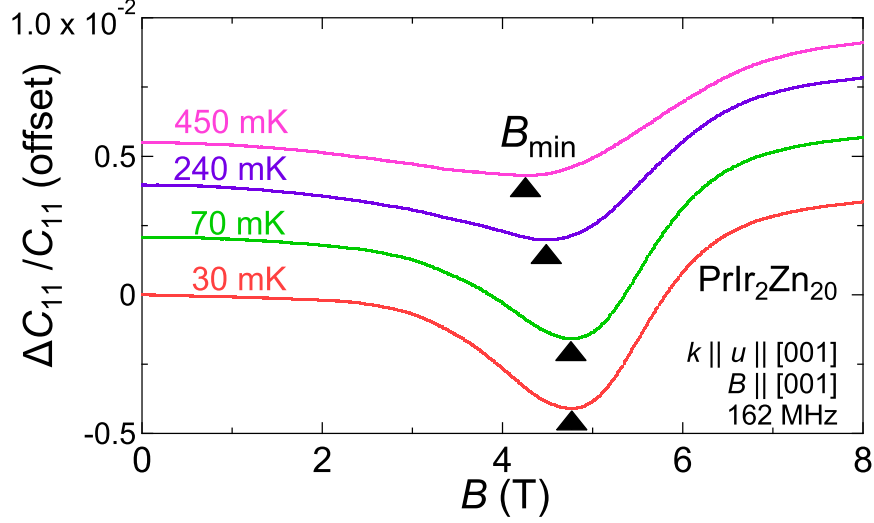


Figure 7.8: Relative change of the elastic constants C_{11} as a function of magnetic field ($B \parallel [001]$). Black arrows correspond to the $B_{\min}$, which is defined as a local minimum of the elastic constant C_{11} .

7.3 Origin of the Phase Pocket “A”

In the previous section, several elastic anomalies in the AFQ ordering phase of $\text{PrIr}_2\text{Zn}_{20}$ are reported. Here, we would summarize the elastic anomalies and discuss the relationship between our experimental results and recently proposed phase pocket “A” [39].

7.3.1 B - T Phase Diagram obtained from Ultrasonic Measurements

First, we focus on the large elastic softening observed in the C_{11} mode shown in Fig. 7.4. To make the discussion clear, we modified the data to the absolute value of the elastic constant C_{11} (J/m^3). Here, the absolute value is calculated by the sound velocity $v_{11} = 3.97 \times 10^3$ m/s at 240 mK under zero magnetic field. The lattice constant $a = 14.2729$ Å is referred in the previous report [34] and the density is calculated to $\rho = 8.377$ g/cm³. Figure 7.9(a) shows the absolute value C_{11} of $\text{PrIr}_2\text{Zn}_{20}$ as a function of the temperature under several magnetic fields. The data under the magnetic fields is estimated by the relative change of the C_{11} as a function of the magnetic field shown in Fig. 7.8.

Figure 7.9(b) shows a contour plot made from the absolute value of the elastic constant C_{11} . Red region corresponds to the region where the elastic softening is observed in the measurements of the temperature dependence and the magnetic-field dependence. As described in the previous section, this softening is considered to originate from the Γ_1 -symmetrical mode. In this magnetic-field region, Fermi-liquid (FL)

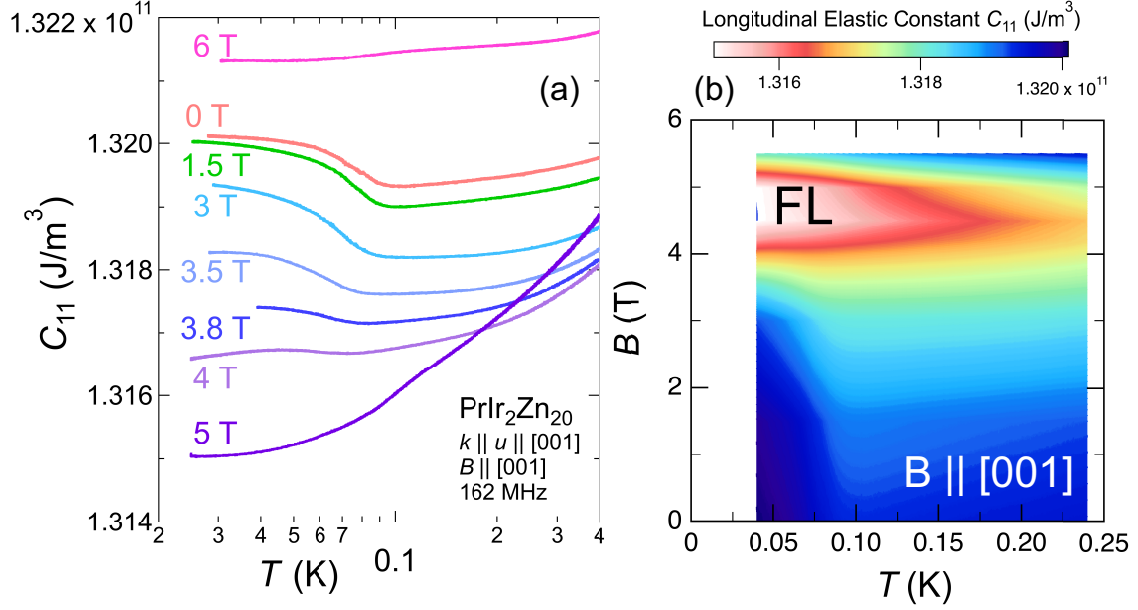


Figure 7.9: (a) Temperature dependence of the absolute value of the elastic constant C_{11} under several magnetic fields ($B \parallel [001]$). (b) Contour plot made from the absolute value of the elastic constant C_{11} .

behavior has been observed in various measurements [37, 38]. For example, Fig. 2.9 shows the contour plot made from the derivative of the magnetization with respect to the magnetic field [38]. We consider that the present elastic softening originates from the volume change due to c - f hybridization induced by the magnetic fields. Possibility to form the FL state by competing between magnetic and quadrupolar Kondo effect has been theoretically proposed [90, 91].

In Fig. 7.10, elastic anomalies observed in our ultrasonic measurements are summarized as a B - T phase diagram. The definitions of each elastic anomaly are described in the previous section. The FL state showing the large elastic softening in the C_{11} mode is located just above AFQ ordering phase and phase pocket “A”, which suggests the possibility that the origin of the phase pocket “A” is driven by the enhancement of the c - f hybridization. In our ultrasonic measurements, the phase boundary of the AFQ ordering phase is not clearly observed in the magnetic-field swept measurements. It is considered that the elastic anomaly associated with the phase boundary is merged into the large elastic anomaly arising from forming the FL state. As shown in Fig. 7.10, the slope of the phase boundary, corresponding to T_{Q1} in the Γ_3 mode, is positive. This point is still controversial; some reports in the early stage proposed the B - T phase diagram which is similar to the present one [24], on the other hand, latest study suggests the possibility that T_Q decreases as the field increases [39]. Here, we consider two reasons to explain the difference. One possibility is a sample dependence. In the present study, we performed the ultrasonic measurements by using one single-crystalline sample. It is necessary for the verification to carry out the additional measurements with

other samples. Another possibility is the effect of a small miss-alignment of the magnetic fields, since this sample has a clear magnetic-field-angle dependence [39]. To check this possibility, we need to perform the similar measurements under the field with a different direction. In future, we aim to extend measurement-temperature range of the TARO probe and perform the field-angle-resolved ultrasonic measurements at very low temperature with ^3He - ^4He dilution refrigerator.

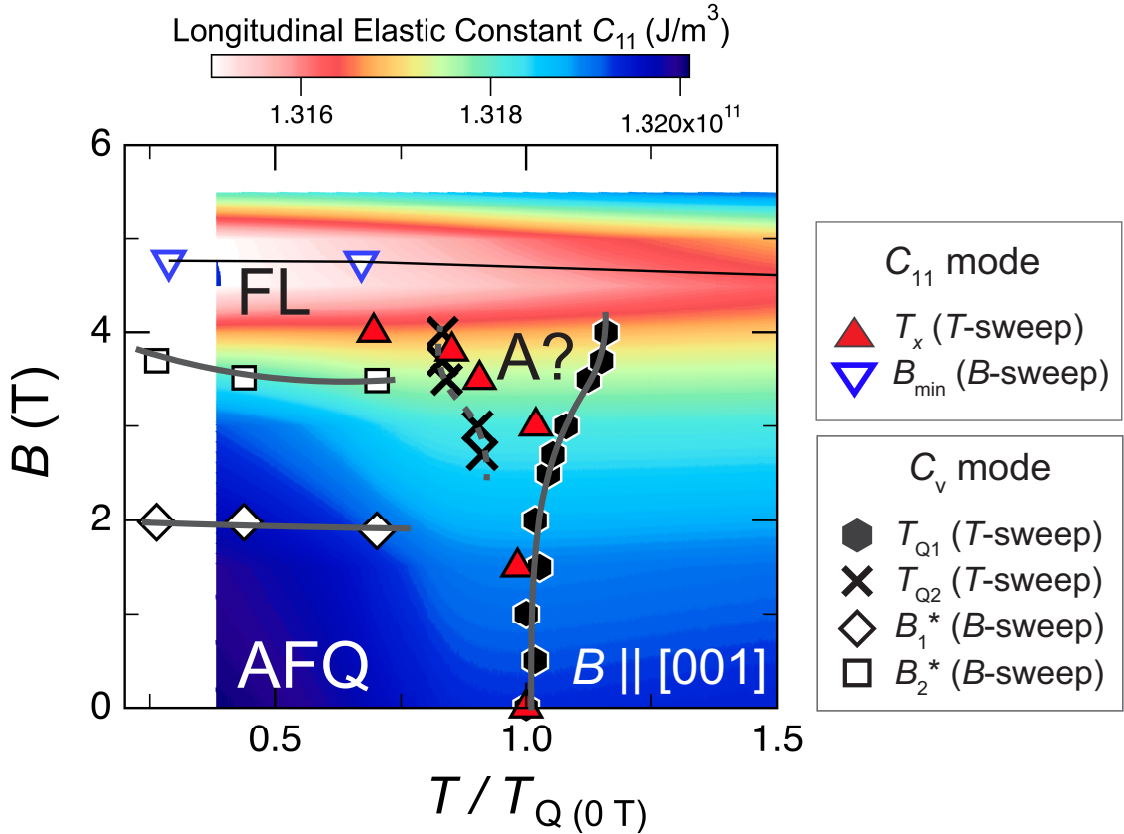


Figure 7.10: B - T phase diagram made from our ultrasonic measurements of the C_{11} mode and the C_v mode ($B \parallel [001]$). Anomalies corresponding to opened symbols are obtained from the temperature swept measurements, and that corresponding to closed symbols are obtained from the magnetic-field swept measurements. Horizontal axis is normalized by the transition temperature of the AFQ ordering under zero magnetic field.

We consider that the temperature region between T_{Q1} and T_{Q2} at $2.7 \leq B \leq 4$ T corresponds to the phase pocket “A”. The phase boundary from the paramagnetic phase to the phase “A” (T_{Q1}) is only observed in the pure Γ_3 mode. It is possible that the Γ_3 -symmetrical quadrupolar degrees of freedom is not completely quenched at T_{Q1} (phase boundary of the phase “A”), but it is completely quenched at T_{Q2} and $T_{\min}$ (phase boundary of the AFQ ordering). In any case, our experimental results indicate that the order parameter of the phase “A” is the Γ_3 -symmetrical quadrupole,

which is consistent with two possibilities of the origin of the phase “A”, (1) Switching of the Γ_3 -symmetrical order parameters, (2) Exotic quadrupolar ordering like a multi- q quadrupolar ordering, suggested by Dr. Kittaka *et al.* (Details are written in the section 2.3.2) [39]. We discuss the former hypothesis by using a simple mean-field analysis in the next subsection. For the latter hypothesis, it is non-obvious how the change of the ordering vector q affects the elastic constants, thus, further discussion with theorists is essential. In addition to the anomaly observed in the temperature swept measurements, we observed two different elastic anomalies B_1^* and B_2^* in the magnetic-field swept measurements of the Γ_3 -symmetrical mode. We discuss the origin of these anomalies by a mean-field analysis in the next subsection.

Figure 7.11 shows (a) temperature dependence and (b) magnetic-field dependence of the ultrasonic attenuation coefficients $\Delta\alpha$ of the Γ_3 mode. At first, we considered the possibility that the phase “A” originates from the fluctuations of the Γ_3 -symmetrical electric quadrupole. However, we consider that it is not a crossover but a phase transition now, since ultrasonic attenuation is not so enhanced in the phase “A”.

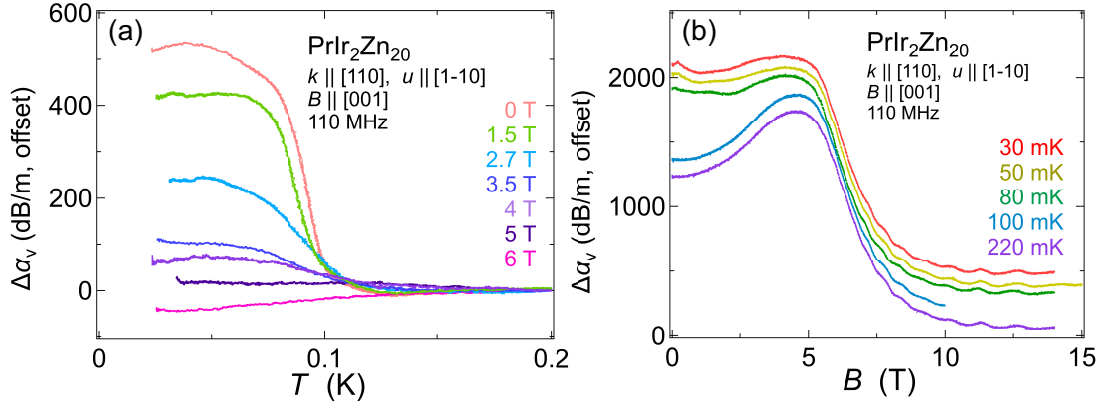


Figure 7.11: Ultrasonic attenuation coefficient $\Delta\alpha_v$ as a function of (a) temperature and (b) magnetic field.

7.3.2 Discussion with a Mean-Field Model

To reveal the origin of the Γ_3 -symmetrical elastic anomalies observed in the AFQ ordering phase, we performed an analysis with a simple mean-field model. In the analysis, we referred the previous study of PrPb_3 showing a Γ_3 -type AFQ ordering at 0.4 K by Dr. T. Tayama *et al.* [35]. They used a simple two-sublattice AFQ model (A site and B site), and assumed the following Hamiltonian with a contribution of higher multipole up to magnetic octupole.

$$\begin{aligned}\mathcal{H}_{\text{A(B)}} = & \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{Zeeman}} - \left(K_1 \langle \mathbf{J} \rangle_{\text{B(A)}} + K_2 \langle \mathbf{J} \rangle_{\text{A(B)}} \right) \mathbf{J} \\ & - K_{\Gamma_3} \left[\langle O_2^0 \rangle_{\text{B(A)}} O_2^0 + \langle O_2^2 \rangle_{\text{B(A)}} O_2^2 \right] \\ & - G_\beta \langle \mathbf{T}_\beta \rangle_{\text{B(A)}} \mathbf{T}_\beta\end{aligned}\quad (7.1)$$

Third term corresponds to a magnetic dipolar interaction, and K_1 and K_2 are the ordinary inter and the intra-sublattice magnetic exchange interaction coefficients, respectively. Fourth (fifth) term corresponds to the inter-sublattice electric quadrupolar (magnetic octupolar) interaction. $\mathbf{T}_\beta$ is a Γ_5 -symmetrical magnetic octupole. Here, the authors considered intra-sublattice interaction only for the magnetic dipole. By using this Hamiltonian, anisotropic phase diagram observed in the experiments of PrPb_3 are theoretically reproduced. In PrPb_3 , the possibility of the switching of the order parameter (OP) is suggested; OP under zero magnetic field is considered as $O_2^0 = (2J_z^2 - J_x^2 - J_y^2)/2$, whereas, OP under high magnetic fields along [110] is considered as $O_2^2 = \sqrt{3}(J_x^2 - J_y^2)/2$. To explain this switching of OP, it is considered to be essential to introduce an anisotropic quadrupolar interaction [92, 93].

We performed similar analysis to the present system $\text{PrIr}_2\text{Zn}_{20}$. At first, we assumed the following simple hamiltonian.

$$\mathcal{H}_{\text{A(B)}} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{Zeeman}} - K_{\Gamma_3} \left[\langle O_2^0 \rangle_{\text{B(A)}} O_2^0 + \langle O_2^2 \rangle_{\text{B(A)}} O_2^2 \right] \quad (7.2)$$

Here, we only consider the inter-sublattice electric quadrupolar interaction as a multipole-multipole interaction. We also tried the analysis with a magnetic dipolar interaction, however, it only affects the absolute value of a critical field and does not change the qualitative discussion. In the present system, Pr atom is located at site 8a, and the bond center of the first neighboring bond is (0, 0, 0) which is site 16c ($\bar{3}m$, D_{3d}). From the view point of the site symmetry of the bond center, quadrupolar interaction should be isotropic ($K_{O_2^0} = K_{O_2^2} = K_{\Gamma_3}$). Crystal structure only focused on the Pr atoms is described in Fig. 7.12.

Figure 7.13 shows phase diagrams [(a) $H \parallel [001]$ and (b) $H \parallel [110]$] obtained by the mean-field analysis based on the Hamiltonian (7.2). To reproduce T_Q roughly, we determined K_{Γ_3} as -5 mK. A negative sign corresponds to “antiferro”-quadrupolar interaction. We determined a stable state by the comparison of the free energy obtained after solving self-consistent equations, which is performed by our developed python program. Γ_3 -type electric quadrupoles O_2^0 and O_2^2 are completely equivalent under zero

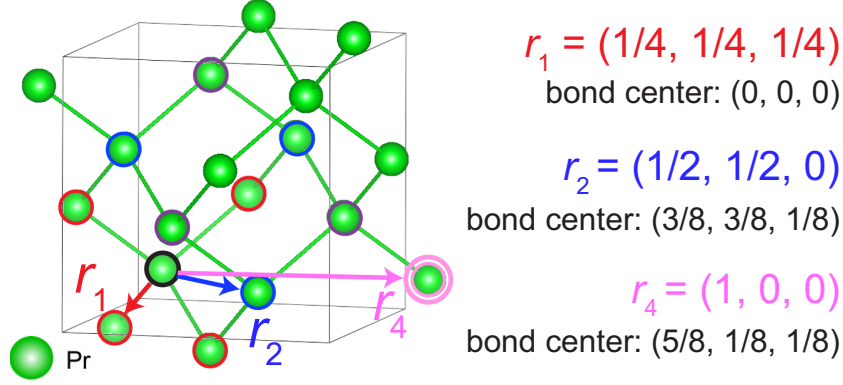


Figure 7.12: Crystal structure of $\text{PrIr}_2\text{Zn}_{20}$ only focused on Pr atoms. r_1 , r_2 , and r_4 correspond to the first, second, and fourth neighbor Pr atom, respectively.

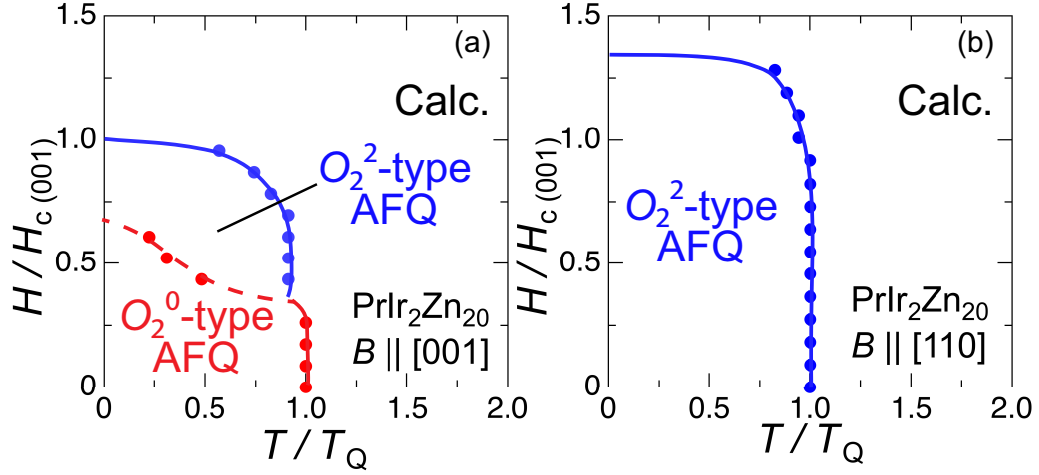


Figure 7.13: H - T phase diagram made by the mean-field analysis based on the equation 7.2 ((a) $H \parallel [001]$, (b) $H \parallel [110]$). Magnetic field and temperature are normalized.

magnetic field, whereas, they could be not equivalent under magnetic fields. Figure 7.13 shows that O_2^2 -type AFQ ordering state is more stable under magnetic fields along $[110]$. On the other hand, Fig. 7.13(a) shows that there is a switching of OP from O_2^0 to O_2^2 under the magnetic field along $[001]$. Experimentally observed phase pocket “A” is enhanced under the field in this direction. This analysis suggests the possibility that the origin of the phase “A” is related to the switching of OP.

Additionally, our field-swept measurements of Γ_3 -symmetrical elastic constant shows two elastic anomalies below 80 mK as shown in Fig. 7.6, thus, actual system is considered to be more complicated. Then, we performed the analysis assumed the following Hamiltonian.

$$\begin{aligned}
 \mathcal{H}_{A(B)} = & \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{Zeeman}} - K_{\Gamma_3} \left[\langle O_2^0 \rangle_{B(A)} O_2^0 + \langle O_2^2 \rangle_{B(A)} O_2^2 \right] \\
 & - K_{O_2^0}^2 \langle O_2^0 \rangle_{A(B)} O_2^0 - K_{O_2^2}^2 \langle O_2^2 \rangle_{A(B)} O_2^2
 \end{aligned} \quad (7.3)$$

Here, we added the intra-sublattice electric quadrupolar interaction as a fifth term. As shown in Fig. 7.12, the bond center of the second-neighbor coupling is $(3/8, 3/8, 1/8)$ which is site 48f ($2.mm, C_{2v}$). This site symmetry is lower than cubic symmetry and O_2^0 and O_2^2 may not be equivalent, thus, we used the independent coupling constants, $K_{O_2^0}^2$ and $K_{O_2^2}^2$ ($K_{O_2^0}^2 \neq K_{O_2^2}^2$) in the equation (7.3). (Strictly speaking, this assumption is considered appropriate only under magnetic fields since the Hamiltonian described in Eq. 7.3 violates the cubic symmetry of the present system.)

For the analysis, we used parameter set; $K_{\Gamma_3} = -5$ mK, $K_{O_2^0}^2 = 0.8$ mK, and $K_{O_2^2}^2 = 1.5$ mK. Here, we assumed a relatively large difference between $K_{O_2^0}^2$ and $K_{O_2^2}^2$ to make the effect of the anisotropic quadrupolar interaction clear. One of the reasons why we assumed $K_{O_2^0}^2 < K_{O_2^2}^2$ is not to occur the switching of OP under the field along $[110]$. Another reason is that neutron diffraction measurements suggest main OP in AFQ ordering phase is O_2^2 -type electric quadrupole [36]. Indeed, comparison of the free energy reveals that O_2^2 ordering state is more stable even under zero magnetic fields.

Figure 7.14 shows the phase diagrams ($H \parallel [001]$) obtained by the mean-field analysis based on the Hamiltonian (7.3). O_2^0 ordering phase emerges only under intermediate magnetic field along $[001]$. The phase diagram obtained from the theoretical analysis is compared with our experimental results in Fig. 7.15. We consider that two elastic anomalies observed in field-cooled measurements of the Γ_3 mode originate from such switching of Γ_3 -symmetrical OPs. We suggest the possibility that exotic ordering (for example, multi- q ordering) using the O_2^0 -type quadrupolar degrees of freedom occurs in the phase pocket ‘‘A’’ and it will be changed to a simple single- q O_2^0 -type ordering at very low temperature. Detail of the phase diagram is considered to be improved by introducing higher-rank multipolar interaction.

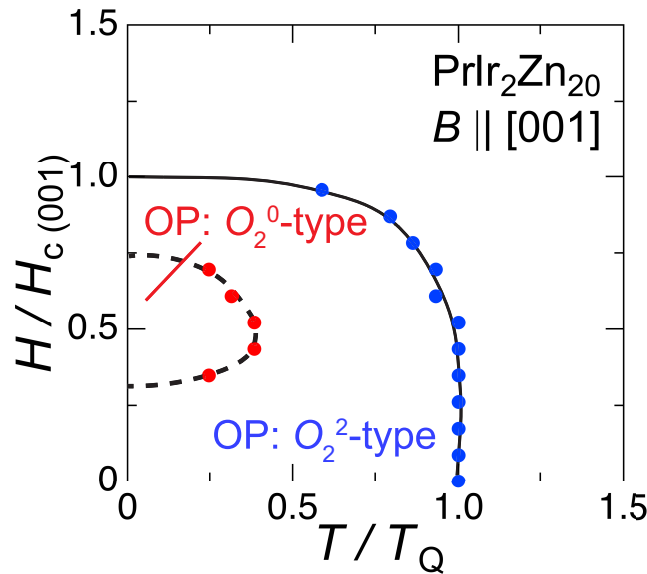


Figure 7.14: H - T phase diagram ($H \parallel [001]$) made by the mean-field analysis based on the equation (7.3).

In the above discussion, our analysis considered electric quadrupolar interactions between Pr atoms in the first and second-neighbor site with a simple two sublattice model. On the other hand, recent neutron diffraction measurements indicate that the ordering vector of the AFQ phase is $(1/2, 1/2, 1/2)$ [36]. For this order to occur, it is theoretically predicted that an interaction between Pr atoms at fourth neighbor sites should be dominant for the ordering [94]. Fourth neighbor site is located at the same site in the next unit cell as shown in Fig. 7.12. Considering the ordering vector, it is difficult to directly apply the present analysis to the actual system, however, it is possible that anisotropic quadrupolar interaction is important to explain complicated phase diagram in AFQ phase of $\text{PrIr}_2\text{Zn}_{20}$ as the present analysis suggests. It is necessary to consider the possibility of the anisotropic quadrupolar interaction originating from other origins.

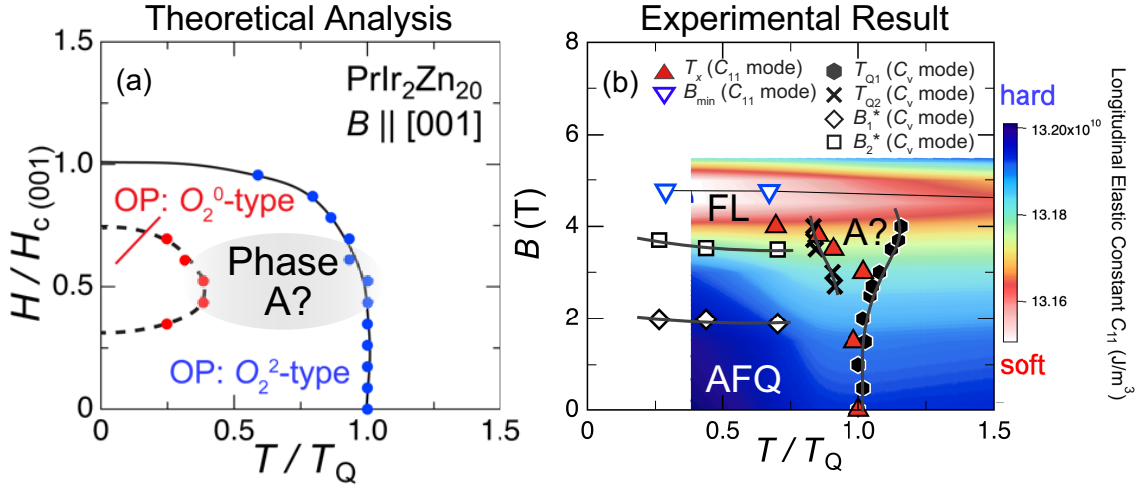


Figure 7.15: Comparison between H - T phase diagrams ($H \parallel [001]$) made by (a) the mean-field analysis based on the equation (7.2) and (b) experimental results.

Chapter 8

Investigation of Electronic State on UBe_{13} and $(\text{U}, \text{Th})\text{Be}_{13}$

8.1 Experimental Procedure

We performed ultrasonic measurements of single crystalline samples of UBe_{13} and $(\text{U}, \text{Th})\text{Be}_{13}$ (Th-2.7%). Th concentration of the diluted sample, 2.7%, is the prepared concentration at the time of sample growth, and we checked the critical temperature T_c by the electrical resistance measurements. Figure 8.1 shows the relative change of the electrical resistance of the Th-diluted sample which belongs to the same batch as the sample for the ultrasonic measurements. Compared with the previous report of the polycrystalline sample [68], $T_c \sim 0.54$ K corresponds to the case that the concentration of Th is around 2.2%, which is roughly consistent with the prepared concentration. It is noted that the Th-diluted sample shows double phase transitions, which are observed in our measurements of the longitudinal ultrasonic attenuation coefficient $\Delta\alpha_{11}$ as shown in Figs. 8.6 later. The successive phase transition was previously reported in $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ ($0.019 \leq x \leq 0.045$) by Kromer *et al.* [68]. Details about the elastic anomalies are described in section 8.2.2 later.

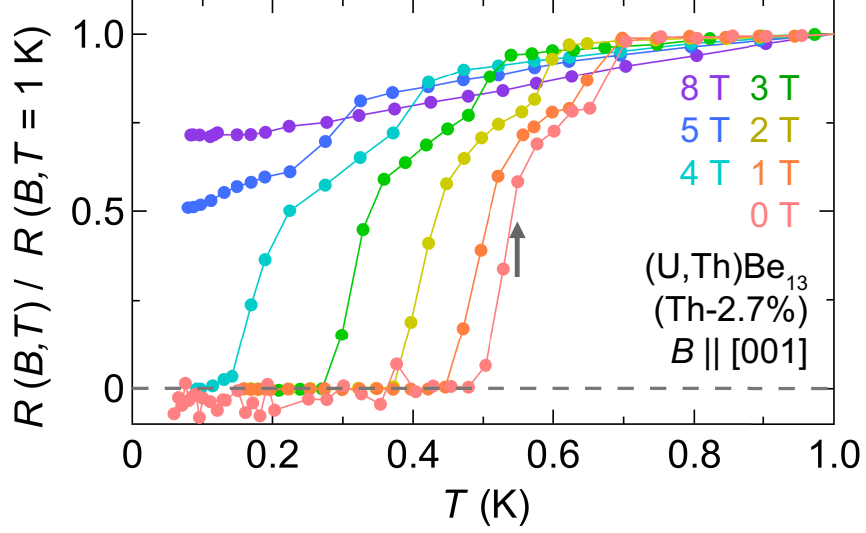


Figure 8.1: Relative change of the electrical resistance of $(\text{U}, \text{Th})\text{Be}_{13}$ (Th-2.7% system) under magnetic fields as a function of temperature.

For both samples, we measured the elastic constants, longitudinal C_{11} mode ($\Gamma_1 \oplus \Gamma_3$ mode) and transverse C_{44} mode (Γ_5 mode), in the temperature range from 40 mK to 120 K. Additionally, we measured the transverse $(C_{11} - C_{12})/2$ mode (Γ_3 mode) in the temperature range from 0.3 K to 5 K as well. We primarily focused on the elastic behaviors in the paramagnetic phase where non-Fermi-liquid-like behavior occurs. The longitudinal C_{11} mode shows an elastic softening below ~ 10 K, which is believed to be related to the “2 K anomaly”. Furthermore, we discovered that the transverse C_{44} and $(C_{11} - C_{12})/2$ modes exhibit the elastic softening enhanced by applied magnetic fields, which suggests the presence of the Γ_5 and Γ_3 -symmetrical quadrupolar degrees of freedom under high magnetic fields.

8.2 Longitudinal C_{11} Mode

8.2.1 Relationship between Elastic Softening and “2 K Anomaly”

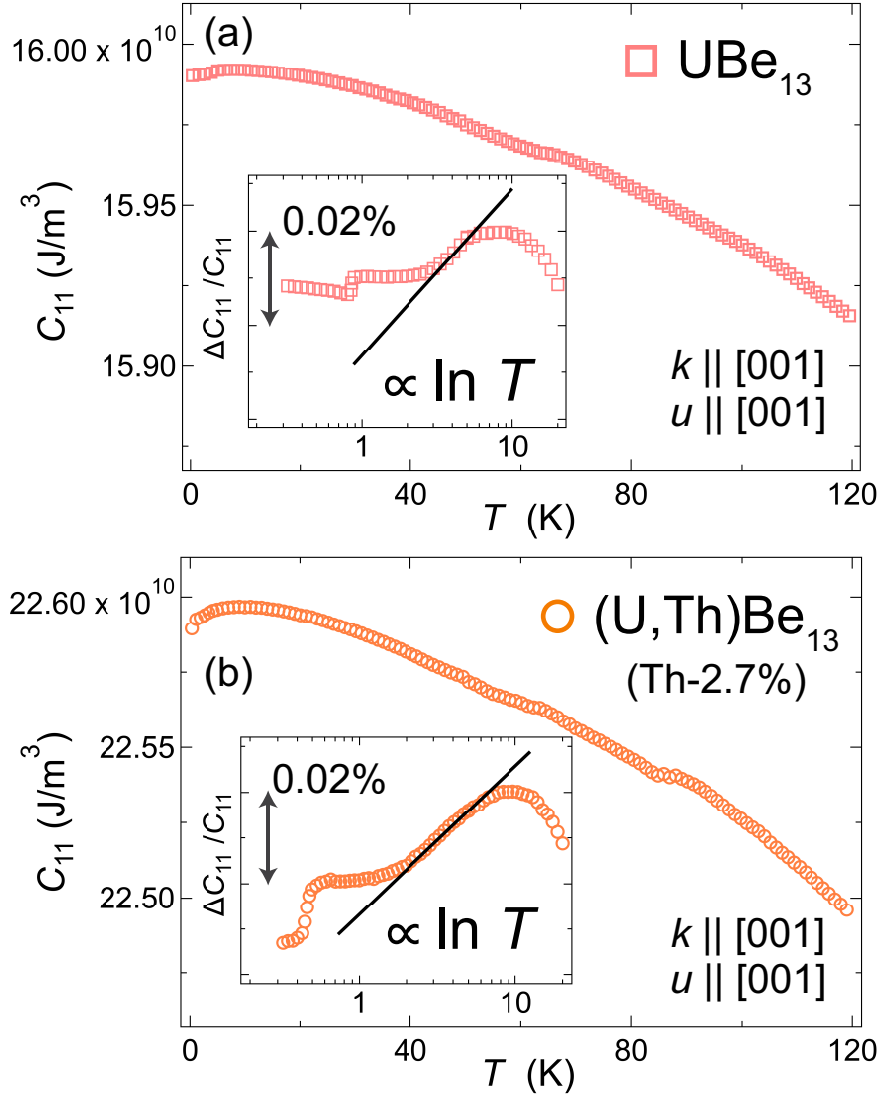


Figure 8.2: Elastic constant C_{11} of (a) UBe_{13} and (b) $(\text{U,Th})\text{Be}_{13}$ (Th-2.7% system) as a function of temperature. Inset of each panel shows a relative change of the elastic constant in the low temperature region. Horizontal axis of inset is logarithmic scale, and black solid lines are proportional to $+\ln T$.

Figure 8.2 shows the temperature dependence of the elastic constants C_{11} of (a) UBe_{13} and (b) $(\text{U,Th})\text{Be}_{13}$ (Th-2.7% system) under zero magnetic field in the wide temperature range. We used the densities $\rho = 4373.78 \text{ kg/m}^3$ for UBe_{13} , and $\rho = 4371.84 \text{ kg/m}^3$ for the Th-2.7% system to calculate the absolute value of the elastic constant. In the calculation of the density, we used the same lattice constant

10.256 Å [45] for both compounds. Here, measurement frequencies are different for each temperature range due to the measurement environments. UBe_{13} ; $f \sim 170$ MHz ($T \leq 5$ K) and $f \sim 120$ MHz ($5 \text{ K} \leq T$), $(\text{U}, \text{Th})\text{Be}_{13}$; $f \sim 80$ MHz ($T \leq 44$ K) and $f \sim 140$ MHz ($44 \text{ K} \leq T$). Figure 8.2(a) and (b) show the monotonically hardening as temperature decreases at high temperature. These behaviors are considered as a contribution of phonon. On the other hand, the C_{11} mode of both compounds shows an elastic softening below ~ 10 K as shown in the inset of Fig. 8.2. For both compounds, this softening is roughly proportional to $+\ln T$. This behavior is consistent with the previous ultrasonic study of UBe_{13} [61]. The previous report suggested that such logarithmic softening is related to “2 K anomaly” observed in the electrical resistivity [49], since this softening is stopped at around 2 K. We named this temperature point as $T_{\min}$.

In addition to the logarithmic softening, the C_{11} mode of the both compounds shows a clear jump at T_c (T_{c1}) as shown in Fig. 8.3. Figure 8.3 also shows the results under several magnetic fields $B \parallel [001]$. The critical temperatures decrease as magnetic field increases, which is consistent with the phase boundary reported by the previous research [51].

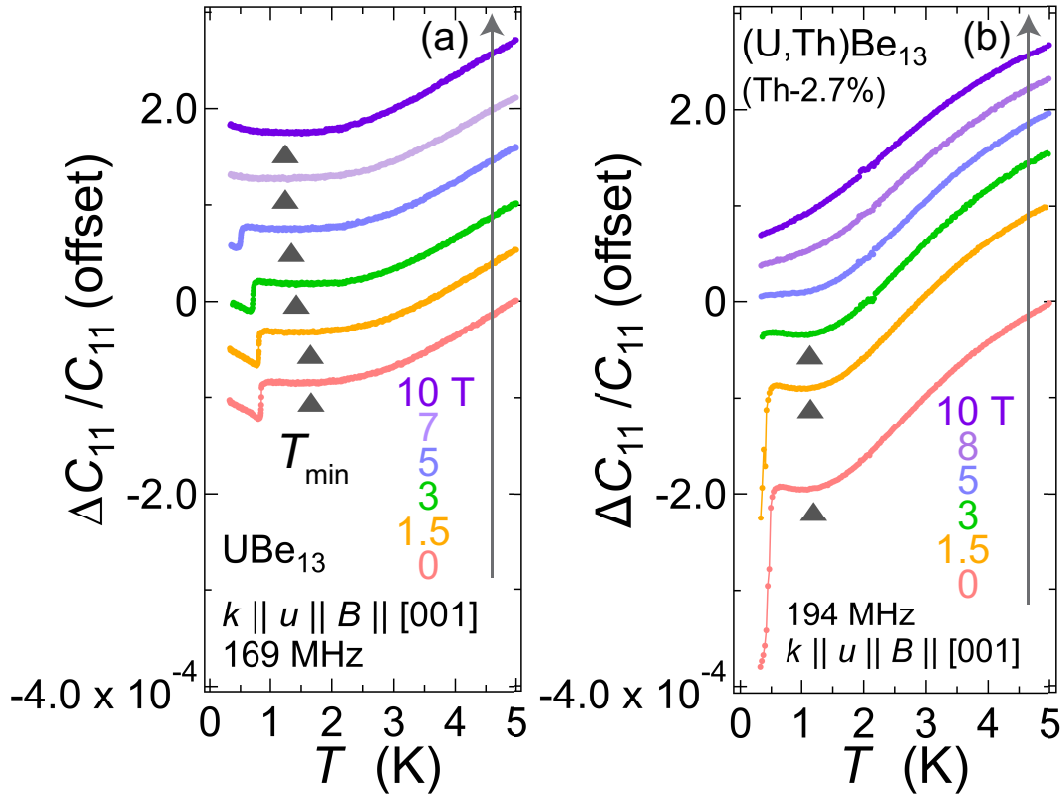


Figure 8.3: Relative change of the elastic constant C_{11} of (a) UBe_{13} and (b) $(\text{U}, \text{Th})\text{Be}_{13}$ (Th-2.7% system) under several magnetic fields as a function of temperature. Each arrow describes $T_{\min}$ where the C_{11} shows a local minimum.

We found that the Th-diluted system shows such softening which extends to the lower temperature down to around 1.2 K as shown in Fig. 8.3(b). The temperature point of “2 K anomaly” originally observed in UBe_{13} also decreases with the Th dilution [60, 59]. Our results also support the relevant between the elastic softening and “2 K anomaly”. Furthermore, we found that the elastic softening of UBe_{13} remains under magnetic fields up to 10 T, and $T_{\min}$ is slightly suppressed by the applied magnetic fields as shown in Fig. 8.3. In case of the Th-2.7% system, $T_{\min}$ is not observed above 5 T. This is consistent with the field-dependence of “2 K anomaly” observed by the electrical resistivity and the thermal expansion measurements [62, 95].

Similar logarithmic elastic softening was reported also in the Pr-based single-site quadrupolar Kondo system as shown in previous sections [43]. The theoretical quadrupolar Kondo model for UBe_{13} assumes that the CEF ground state is the non-Kramers Γ_3 doublet [13], in which, the elastic softening of the Γ_3 mode, originating from the Γ_3 -symmetrical quadrupolar degrees of freedom is expected. Because the C_{11} mode is described as $C_{11} = C_B + 4/3 [(C_{11} - C_{12})/2]$, which is the mixed mode of the Γ_1 and Γ_3 -symmetrical mode ($\Gamma_1 \oplus \Gamma_3$), we can distinguish which symmetrical mode is dominant in causing the elastic softening by comparing the data of the C_{11} and $(C_{11} - C_{12})/2$ modes. Figure 8.4 shows a rough comparison between the temperature dependencies of the relative change of the C_{11} mode and the Γ_3 -symmetrical $(C_{11} - C_{12})/2$ mode (Detail of the experimental results of the $(C_{11} - C_{12})/2$ mode are described in the next section). Since the large softening below ~ 10 K is observed only in the C_{11} mode, we conclude that the softening originates from the Γ_1 -symmetrical volume change. Our results, along with previous thermal-expansion measurements [95], indicate the possibility that an isotropic volume change originating from c - f hybridization occurs at the temperature point of the “2 K anomaly”.

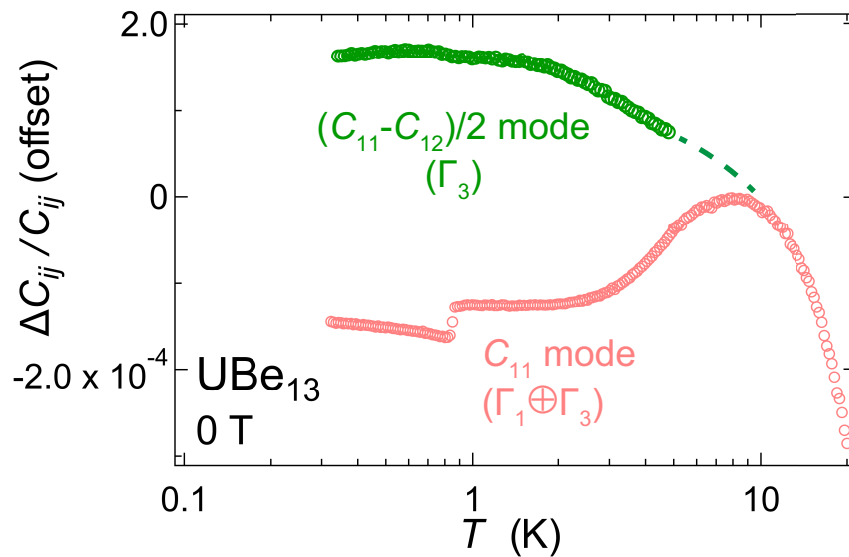


Figure 8.4: Relative change of the elastic constants C_{11} (red) and $(C_{11} - C_{12})/2$ (green) of UBe_{13} as a function of temperature.

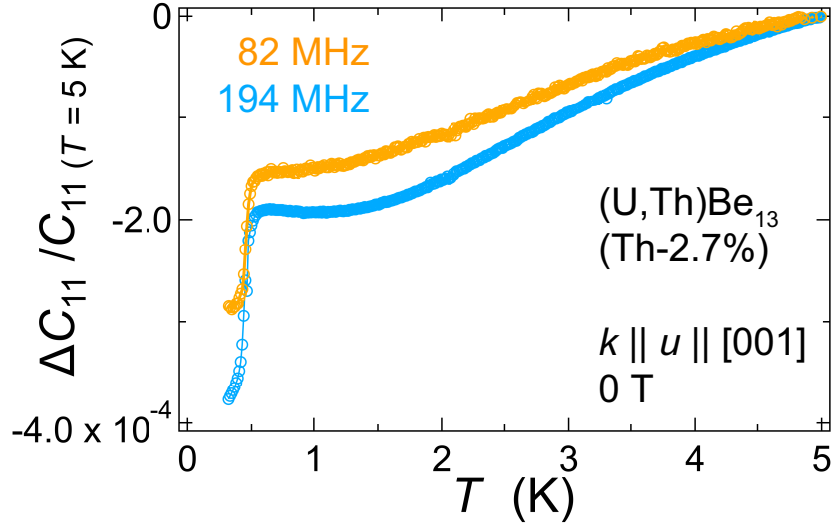


Figure 8.5: Frequency dependence of the elastic constant C_{11} of (U, Th) Be_{13} (Th-2.7% system).

At first glance, Fig. 8.3 indicate that the elastic softening of the Th-diluted system is larger than that of UBe_{13} . However, we observed a frequency dependence about an amount of change of the C_{11} mode. Figure 8.5 shows the frequency dependence of the elastic softening of C_{11} mode in (U, Th) Be_{13} (Th-2.7%) system, where the amount of softening clearly depends on the measurement frequency. Thus, it is challenging to conclude whether the Th-concentration dependence of the amount of softening is intrinsic or not.

8.2.2 Phase Transitions of Th-Diluted Systems

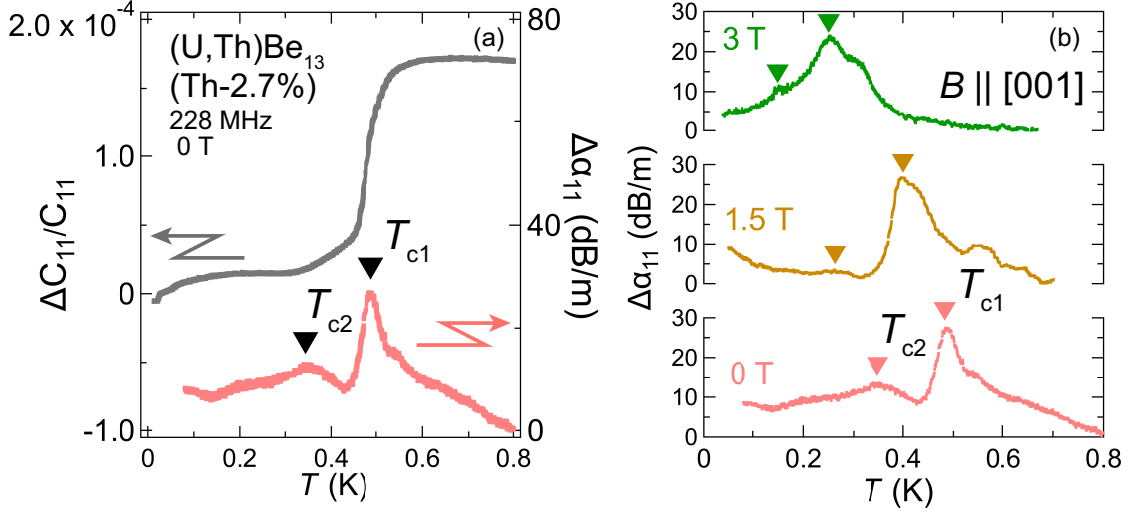


Figure 8.6: (a) Relative change of the elastic constant C_{11} and ultrasonic attenuation coefficient $\Delta\alpha_{11}$ (dB/m) of (U, Th) Be_{13} (Th-2.7% system) under zero magnetic field as a function of temperature. (b) Relative change of the ultrasonic attenuation coefficient $\Delta\alpha_{11}$ (dB/m) of the Th-2.7% system under magnetic fields ($B \parallel [001]$) as a function of temperature.

Figure 8.6(a) shows the temperature dependence of the elastic constant C_{11} and ultrasonic attenuation coefficient $\Delta\alpha_{11}$ (dB/m) of (U, Th) Be_{13} (Th-2.7% system) below 0.8 K under zero magnetic field. Ultrasonic attenuation coefficient shows double peaks at T_{c1} and T_{c2} . The measurement results under magnetic fields are shown in Fig. 8.6(b). Figure 8.7(a) shows the experimental results of the magnetic-field swept measurements. In addition to the critical magnetic field B_{c2} , we observed a kink anomaly at B^* in the superconducting phase, which is not observed in the similar measurements of UBe_{13} as shown in the inset of Fig. 8.7(a). B - T phase diagram including T_{c2} and B^* is summarized in Fig. 8.7(b). T_{c1} determined by the electrical resistivity measurements of the same batch as the ultrasonic measurements is also included (Figure 8.1). Since the blue dashed curve in Fig. 8.7(b) (B^* anomalies) does not follow the magnetic-field dependence of T_{c2} observed by the ultrasonic attenuation coefficients (black dashed curve), it is considered that they have different origins respectively. The temperature dependence of B^* is rather similar to that of “ B^* anomaly” reported by the thermal expansion measurements [68], thus, we consider that these anomalies have a same origin. On the other hands, the elastic constant C_{11} of the mother compound, UBe_{13} , does not show the kink anomaly at B^* as shown in the inset of Fig. 8.7(a), which is inconsistent with the previous reports that the thermal expansion shows “ B^* anomaly” also in UBe_{13} .

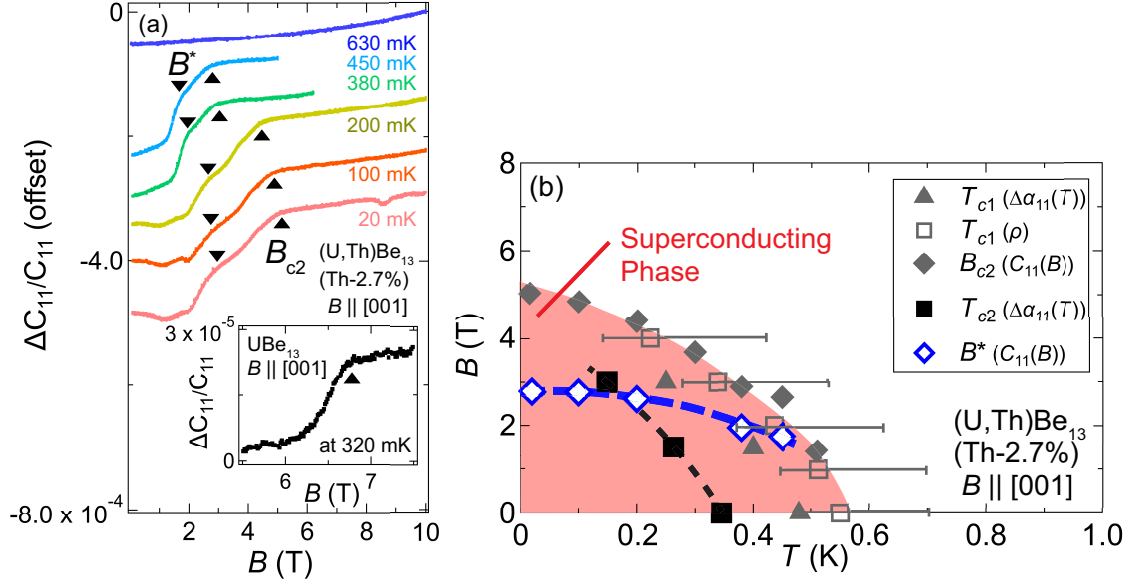


Figure 8.7: (a) Relative change of C_{11} of (U, Th)Be₁₃ (Th-2.7% system) as a function of magnetic field at several temperatures. As a contrast, inset of the panel (a) shows the magnetic-field dependence of C_{11} of UBe₁₃ at 320 mK, where a kink anomaly is observed only at B_{c2} . (b) B - T phase diagram of the Th-2.7% system based on the present data. Gray opened square marker represents superconducting critical temperature T_{c1} determined by the electrical resistivity as shown in Fig. 8.1. Error bar means the temperature range between the beginning of the decrease in electrical resistivity and zero resistivity.

Multiple superconducting phase diagram like Fig. 8.7(b) is observed also in UPt₃, which is well known as one of spin-triplet superconductors [96]. Recently, it has attracted much attention that an elastic anomaly of the shear mode (symmetry-breaking mode) can be a key to reveal the multi-component order parameter of unconventional superconductors [97, 98, 99]. Our experimental results of the transverse modes (C_{44} and $(C_{11} - C_{12})/2$) are described in the next section.

8.3 Transverse Modes (C_{44} Mode and $(C_{11} - C_{12})/2$ Mode)

8.3.1 Elastic Response in the Γ_5 -symmetrical C_{44} Mode

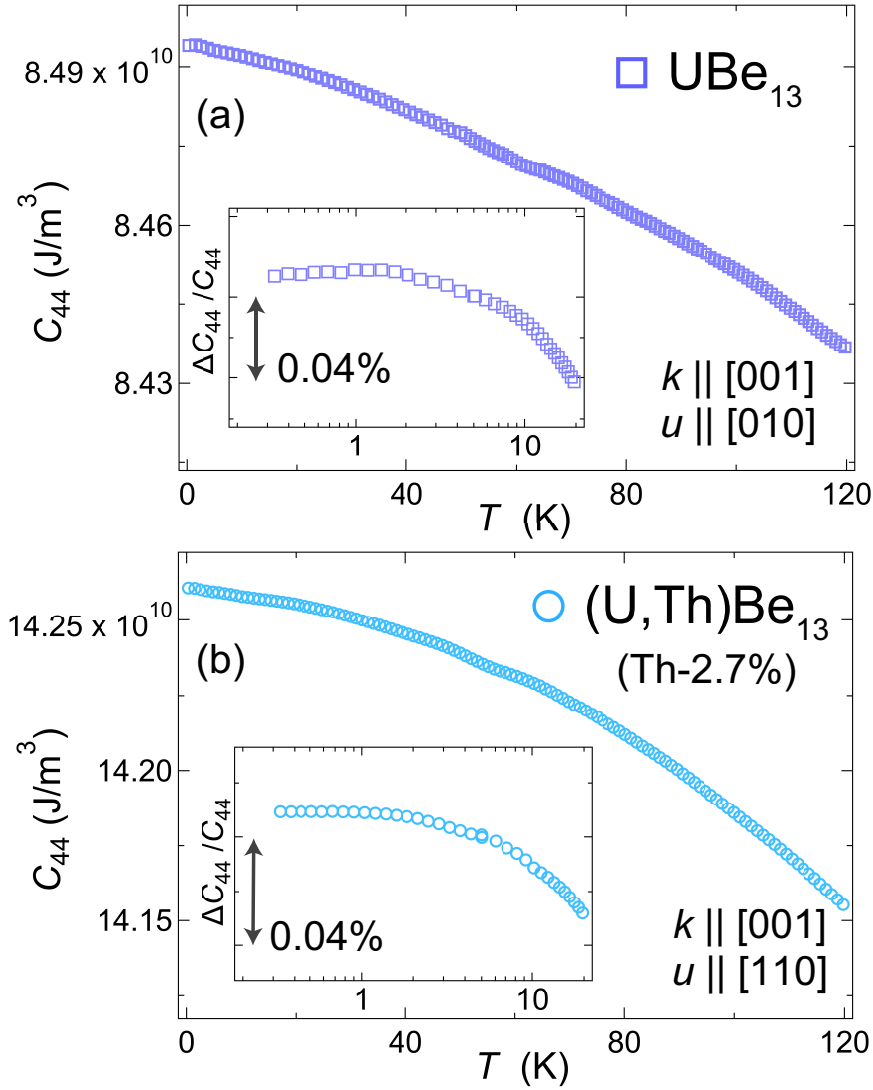


Figure 8.8: Elastic constant C_{44} of (a) UBe_{13} and (b) $(\text{U,Th})\text{Be}_{13}$ (Th-2.7% system) as a function of temperature. Inset of each panel shows relative change of the elastic constant in the low temperature region. Horizontal axis of inset is logarithmic scale.

Figure 8.8 shows the temperature dependence of the elastic constants C_{44} of (a) UBe_{13} and (b) $(\text{U,Th})\text{Be}_{13}$ (Th-2.7% system) under zero magnetic field in the wide temperature range. Direction of the displacement vector u is different between Fig. 8.8(a) and (b) due to the difference of the shape of the sample, however, both transverse waves

correspond to the Γ_5 -symmetrical elastic constant C_{44} . Here, measurement frequencies are different for each temperature range due to the measurement environments. UBe_{13} ; $f \sim 110$ MHz ($T \leq 5$ K), $f \sim 70$ MHz ($5 \leq T \leq 50$ K), and $f \sim 120$ MHz ($50 \text{ K} \leq T$). In the Th-2.7% system, the measurement frequency $f \sim 165$ MHz is common for all temperature region. Figure 8.8(a) and (b) show the monotonically hardening as the temperature decreases. These behaviors are considered as a contribution of phonon. Obvious elastic softening shown in the C_{11} mode is not observed in the C_{44} mode of both compounds. The difference means that we succeeded in separating two different symmetrical modes C_{11} mode and C_{44} mode.

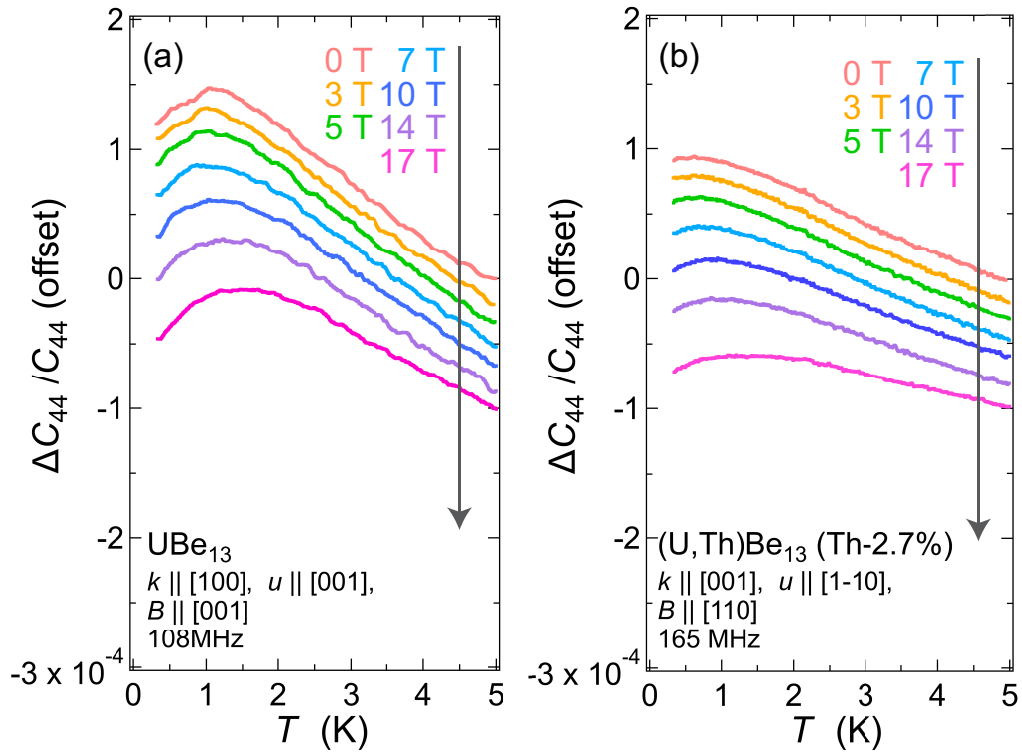


Figure 8.9: Relative change of elastic constant C_{44} of (a) UBe_{13} and (b) $(\text{U,Th})\text{Be}_{13}$ (Th-2.7% system) under magnetic fields ($B \parallel [100]$ for UBe_{13} and $[110]$ for the Th-2.7% system) as a function of temperature.

Figure 8.9 shows the temperature dependence of the elastic constants C_{44} of (a) UBe_{13} and (b) $(\text{U,Th})\text{Be}_{13}$ (Th-2.7% system) under several magnetic fields. Due to the difference of the shape of each sample, the applied magnetic field is along $[100]$ for UBe_{13} and $[110]$ for the Th-2.7% system. Unlike the results of the C_{11} mode as shown in Fig. 8.3(a), the C_{44} modes show no elastic anomaly at T_c for both compounds. In both-concentration systems, we observed weak elastic softening below ~ 1 K under magnetic fields. In terms of temperature range and an amount of softening, the elastic softening of the C_{44} mode is considered to have a different origin from that of the C_{11} mode. Additionally, the magnetic-field dependence is completely different from that

of the C_{11} mode. Elastic softening of the C_{44} mode is clearly enhanced by the applied magnetic fields.

Here, g_{Γ_i} is a coupling constant between electric quadrupole O_{Γ_i} and the same symmetrical strain ε_{Γ_i} . Considering the following Hamiltonian as a perturbation Hamiltonian, the elastic constant, which is defined as the second derivative of the free energy with respect to strain, shows low-temperature softening in the system with the quadrupolar degrees of freedom (Detail of the relationship between the elastic constant and the quadrupolar degrees of freedom is written in section 5.3.).

$$H_{\text{QS}} = -g_{\Gamma_i} O_{\Gamma_i} \varepsilon_{\Gamma_i}$$

In other words, the elastic softening in the present C_{44} measurements suggests that Γ_5 -symmetrical quadrupolar degrees of freedom are enhanced by the applied magnetic fields.

8.3.2 Elastic Response in the Γ_3 -Symmetrical $(C_{11} - C_{12})/2$ Mode

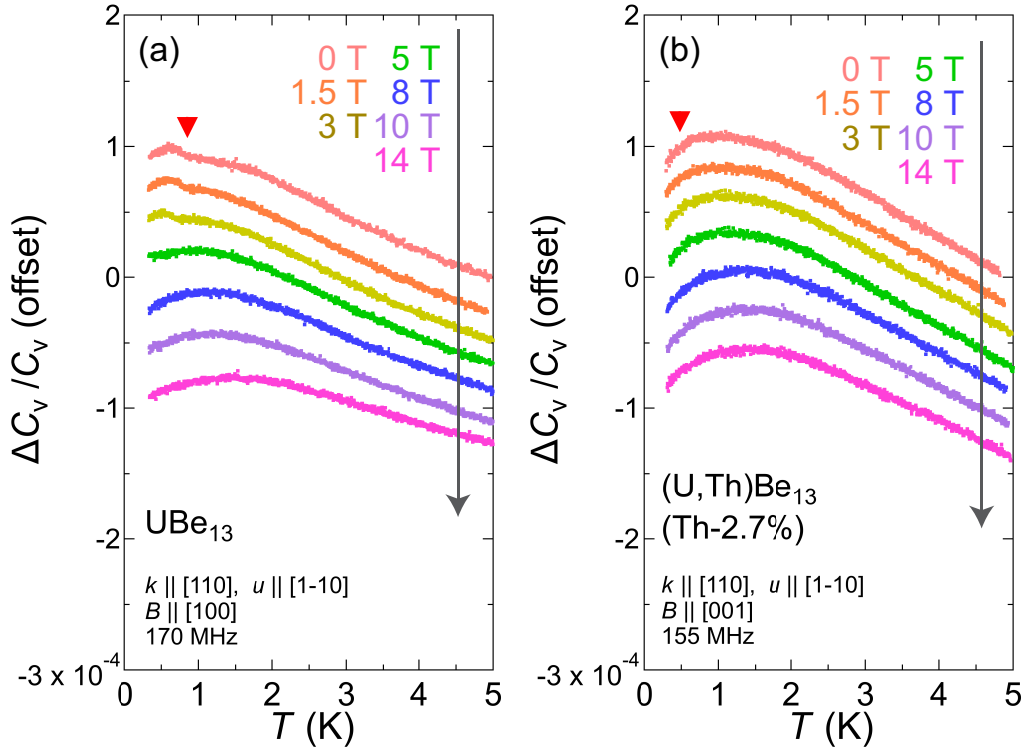


Figure 8.10: Relative change of elastic constant $(C_{11} - C_{12})/2 \equiv C_v$ of (a) UBe_{13} and (b) $(\text{U,Th})\text{Be}_{13}$ (Th-2.7% system) under magnetic fields ($B \parallel [100]$ for UBe_{13} and $[001]$ for the Th-2.7% system) as a function of temperature. Red arrow in each panel corresponds to T_c and T_{c1} determined by the present measurements of the C_{11} modes.

Figure 8.10 shows the temperature dependence of the elastic constants $(C_{11} - C_{12})/2 \equiv C_v$ for (a) UBe_{13} and (b) $(\text{U}, \text{Th})\text{Be}_{13}$ (Th-2.7% system) under several magnetic fields. Due to the difference in the shape of each sample, the applied magnetic field is along $[100]$ for UBe_{13} and $[001]$ for the Th-2.7% system. As described in Section 8.2.1, we found that the pure Γ_3 -symmetrical C_v modes for both compounds do not show large elastic softening like the C_{11} mode ($\Gamma_1 \oplus \Gamma_3$) below ~ 10 K shown in Fig. 8.2, which indicates that the Γ_3 -symmetrical quadrupolar degrees of freedom are not clearly observed under zero magnetic field. We found that the C_v modes in both compounds show the weak elastic softening below ~ 1 K under magnetic fields, resembling the elastic behavior of the Γ_5 -symmetrical C_{44} mode shown in the previous section. This indicates that the Γ_3 -symmetrical quadrupolar degrees of freedom are enhanced by the applied magnetic fields, along with the Γ_5 -symmetrical ones.

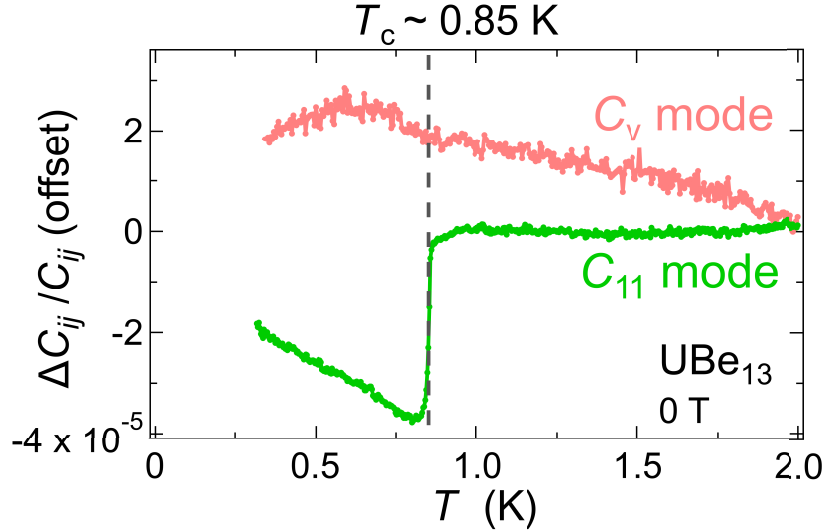


Figure 8.11: Temperature dependences of the relative change of the elastic constant C_{11} (red) and $(C_{11} - C_{12})/2$ (green) on UBe_{13} below 2.0 K.

Furthermore, we observed a hump anomaly at ~ 0.85 K in the C_v mode of UBe_{13} under zero magnetic field, as shown in Fig. 8.10(a). The red arrow in Fig. 8.10(a) indicates this anomaly. (Enlarged view is described in Fig. 8.11.) Compared to the results of the C_{11} mode in which a clear jump at $T_c \sim 0.85$ K is observed, this hump anomaly in the C_v mode is believed to correspond to T_c . The comparison between the C_{11} mode and the C_v mode is shown in Fig. 8.11. This anomaly is observed below 3 T in the present measurements down to 0.3 K, and it shifts to the lower temperatures as the magnetic field increases. The magnetic-field dependence of the anomaly is consistent with that of T_c (summarized as a phase diagram in Fig. 8.12), which suggests that this anomaly is accompanied with the superconducting transition in UBe_{13} . As noted in the previous section, an elastic anomaly at T_c of the shear mode can be key to revealing the single- or multi-component order parameter of unconventional superconductors, such as Sr_2RuO_4 [97, 98, 99]. It is possible that the Γ_3 -symmetrical elastic anomaly in UBe_{13}

provides some hints for revealing the mechanism of the mysterious superconducting phase in this compound. On the other hand, this anomaly is not observed around $T_{c1} \sim 0.48$ K in the Th-2.7% system shown in Fig. 8.13, which possibly reflects the difference in the mechanism of forming the superconducting phase depending on the Th concentration.

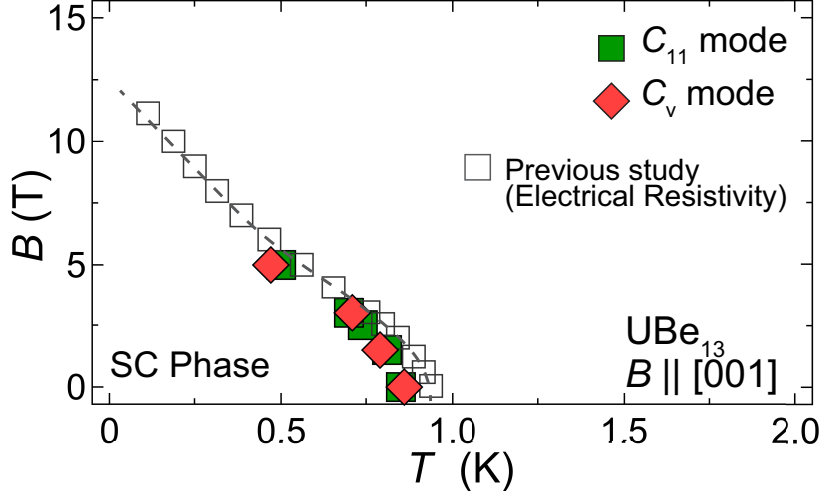


Figure 8.12: B - T phase diagram ($B \parallel [001]$) of UBe_{13} . Opened symbols represent the critical fields H_{C2} reported in the previous electrical-resistivity measurements [100]. Closed symbols represent the temperature points where elastic anomalies are observed in the C_{11} mode (green) and the C_v mode (red).

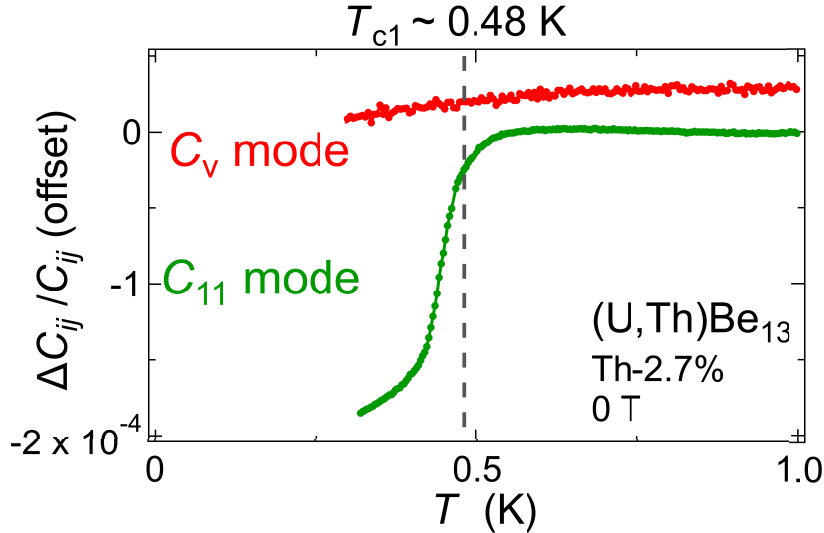


Figure 8.13: Temperature dependences of the relative change of the elastic constant C_{11} (red) and $(C_{11} - C_{12})/2$ (green) on the Th-2.7% system below 1.0 K. T_{c1} , which is represented by the dotted line, is determined by the peak of the ultrasonic attenuation α_{11} shown in Fig. 8.6.

8.3.3 Electronic State under High Magnetic Fields

As shown in the previous sections, our experimental results indicate that both UBe_{13} and the Th-2.7% system have Γ_5 - and Γ_3 -symmetrical quadrupolar degrees of freedom, which are enhanced by applied magnetic fields. As the first step in explain this, we attempted to discuss the origin from the perspective of a localized U^{4+} ($5f^2$) model. Initially, we considered the possibility of the non-Kramers Γ_3 doublet CEF ground state assumed in the quadrupolar Kondo theory proposed by Dr. D. L. Cox [13], however, we did not observed the clear elastic softening of the Γ_3 -symmetrical C_v mode under zero magnetic fields (as shown in Fig. 8.4), which suggests that the Γ_3 -symmetrical degrees of freedom do not remain in the ground state. Thus, we consider that the Γ_3 CEF ground state model assumed in the quadrupolar Kondo theory is not consistent with our results. As described in detail later, we attempted a different Γ_1 - Γ_5 model to explain the elastic behavior under higher magnetic fields.

In addition to the experiments under static magnetic fields up to 17 T, we measured the elastic constant C_{44} of (U, Th) Be_{13} (Th-2.7% system) under higher magnetic fields ($B \parallel [110]$) up to 68 T by using pulsed magnetic fields to investigate how quadrupolar degrees of freedom are modified under higher magnetic fields. The experiments are performed by the long pulsed magnetic field ($t \sim 100$ ms) in HZDR. As a result, we observed a broad local minimum of ~ 38 T at 0.34 K as shown in Fig. 8.14(c). The experimental result under low magnetic field is roughly consistent with the results by using static magnetic field.

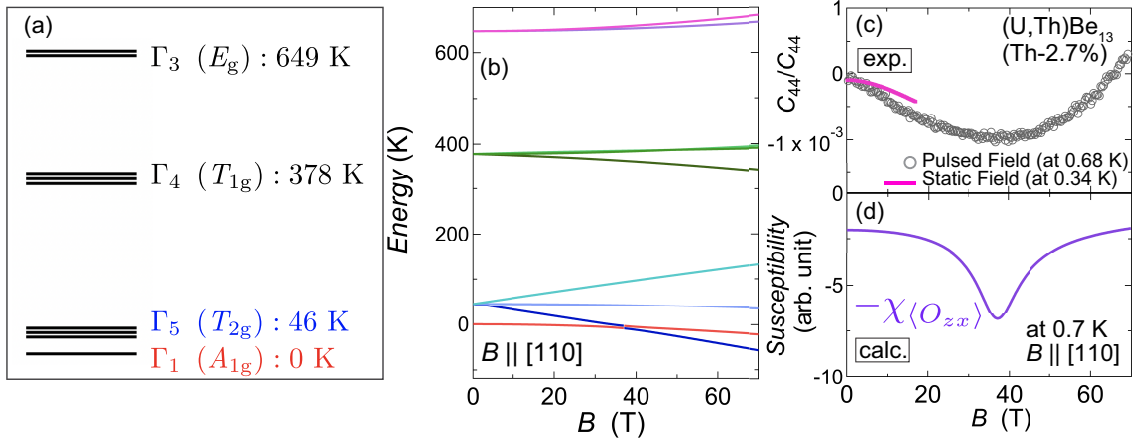


Figure 8.14: (a) Energy scheme of our proposed CEF model under zero magnetic field. (b) Zeeman split by applied magnetic field ($B \parallel [110]$). (c) Relative change of the elastic constant C_{44} of (U, Th) Be_{13} (Th-2.7% system) as a function of magnetic field at low temperatures. Open markers show data at $T = 0.68$ K by using pulsed magnetic fields, and pink solid curve shows data at $T = 0.34$ K by static magnetic fields. (d) Magnetic-field dependence of the susceptibility of electric quadrupolar O_{yz} (shown data is reversed sign), which is calculated based on our proposed CEF model.

First, we consider the elastic behavior of the Γ_5 -symmetrical C_{44} mode. To explain the broad minimum of C_{44} mode under high magnetic fields, we attempted a new crystalline-electric-field (CEF) model as shown in Fig. 8.14(a). CEF Hamiltonian in the cubic symmetry is described as [74, 75]

$$\mathcal{H}_{\text{CEF}} = B_4^0 (O_4^0 + 5O_4^4) + B_6^0 (O_6^0 - 21O_6^4).$$

The parameters of our CEF model are $B_4^0 = 0.085$ K, and $B_6^0 = 0.00425$ K. As described in Fig. 8.14(a), CEF ground state in our model is Γ_1 singlet,

$$|\Gamma_1\rangle = \frac{\sqrt{30}}{12} |J_z = -4\rangle + \frac{\sqrt{21}}{6} |J_z = 0\rangle + \frac{\sqrt{30}}{12} |J_z = +4\rangle.$$

One of the first excited Γ_5 triplet, which approaches the Γ_1 ground state with the application of the magnetic field $B \parallel [110]$, $|\Gamma_5^\alpha\rangle$ is described as

$$|\Gamma_5^\alpha\rangle = \frac{\sqrt{14}}{4} |J_z = -3\rangle - \frac{\sqrt{2}}{4} |J_z = +1\rangle.$$

Such Γ_1 singlet - Γ_5 triplet model is based on the previously proposed model by the electrical resistivity measurements of the U-dilute limit systems (U, Th) Be₁₃, where the maximum of electrical resistivity originating from Kondo effect is observed at around 80 K [101]. Based on the experimental results, the researchers suggested that CEF ground state is non magnetic Γ_1 singlet and the first excited state should be magnetic Γ_4 or Γ_5 triplet to induce the magnetic dipolar degrees of freedom at high temperature ($\Delta \sim 100$ K). One intriguing feature of our CEF model is that an energy level crossing happens at around 40 T which reflects the energy scale of the first excited Γ_5 triplet as shown in Fig. 8.14(b). In other words, CEF ground state changes to the Γ_5^α state under high magnetic fields above ~ 40 T. (In addition to the case of $B \parallel [110]$, we also calculated the energy split by the magnetic field $B \parallel [100]$, which shows similar energy level crossing at around 40 T.)

Here, we consider that the elastic softening of the C_{44} mode under magnetic fields originates from the Γ_5 -symmetrical electric quadrupolar degrees of freedom between Γ_1 state and Γ_5^α state. Matrix elements of Γ_5 -symmetrical O_{zx} in these two states are derived as

$$\langle O_{zx} \rangle = \begin{pmatrix} \langle \Gamma_1 | & \langle \Gamma_5^\alpha | \end{pmatrix} \begin{pmatrix} |\Gamma_1\rangle & |\Gamma_5^\alpha\rangle \\ 0 & -\frac{\sqrt{210}}{3} \\ -\frac{\sqrt{210}}{3} & 0 \end{pmatrix}.$$

The calculation results indicate that the Γ_5 -symmetrical quadrupolar degrees of freedom remains down to very low temperature at around 40 T because of quasi degeneracy caused by the level crossing. Figure 8.14(d) shows the calculation of the quadrupolar susceptibility $\chi_{\langle O_{zx} \rangle}$ (Elastic constant C_{44} is approximately proportional

to $-\chi_{\langle O_{zx} \rangle}$). This shows a local minimum at around 40 T, which is roughly consistent with our experimental results.

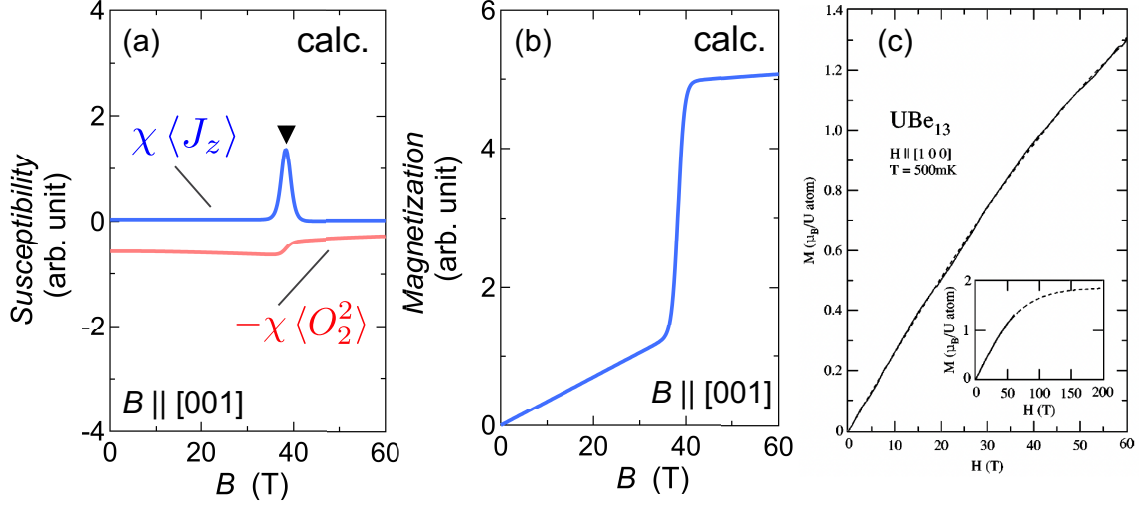


Figure 8.15: (a) Magnetic-field dependence of the susceptibility of the electric quadrupole O_2^2 (red, shown data is reversed sign) and the magnetic dipole J_z (blue) calculated based on our CEF model. (b) Magnetic-field dependence of the magnetization calculated from the magnetic dipolar susceptibility shown in the panel (a). (c) Experimental results of the magnetization of a single crystal of UBe₁₃ [66].

We also calculated the susceptibilities of the Γ_3 -symmetrical electric quadrupole O_2^2 and the Γ_5 -symmetrical magnetic dipole J_z . Figure 8.15(a) shows the magnetic-field dependence of the susceptibilities of the O_2^2 and J_z . Because the matrix elements of the Γ_3 -symmetrical O_2^2 in the Γ_1 state and Γ_5^α state are derived as

$$\langle O_2^2 \rangle = \begin{pmatrix} \langle \Gamma_1 | \\ \langle \Gamma_5^\alpha | \end{pmatrix} \begin{pmatrix} | \Gamma_1 \rangle & | \Gamma_5^\alpha \rangle \\ 0 & 0 \\ 0 & 0 \end{pmatrix},$$

the susceptibility of the O_2^2 does not show a clear enhancement by the applied magnetic fields, which is in contrast to the calculation for the O_{zx} shown in Fig. 8.14(d). Our experimental results indicate that the Γ_3 -symmetrical quadrupolar degrees of freedom are also enhanced by the applied magnetic fields. Our CEF model could not interpret the experimental results of the Γ_3 -symmetrical mode adequately.

On the other hand, since the matrix elements of the J_z in the Γ_1 state and Γ_5^α state are derived as

$$\langle J_z \rangle = \begin{pmatrix} \langle \Gamma_1 | \\ \langle \Gamma_5^\alpha | \end{pmatrix} \begin{pmatrix} | \Gamma_1 \rangle & | \Gamma_5^\alpha \rangle \\ 0 & 0 \\ 0 & -\frac{5}{2} \end{pmatrix},$$

the susceptibility of the J_z shows the local maximum at around 40 T as shown in Fig. 8.15(a), which is similar behavior of the calculation for the O_{zx} . By integrating this susceptibility with respect to the field, the magnetic-field dependence of the magnetization can be derived as shown in Fig. 8.15(b). The calculated magnetization shows a clear metamagnetism at around 40 T. However, the magnetization measurements of UBe_{13} have already been performed using pulsed magnetic fields up to 60 T [66], and the previous study of the magnetization did not report any anomalies under such high magnetic fields ($B \parallel [001]$) as shown in Fig. 8.15(c). Considering these discrepancies, we concluded that the present CEF model could not fully explain these experimental results. We also explored the possibility of other CEF models including the case with $5f^3$ configuration, however, the CEF model where both Γ_5 and Γ_3 -symmetrical quadrupolar degrees of freedom are enhanced by the magnetic fields could not be found.

Initially, we considered that the localized model appears to be relatively appropriate for the present case under magnetic fields, as decoupling of the (magnetic) Kondo effect is expected under high magnetic fields. However, it might be necessary to consider the possibility that $5f$ electrons are not fully localized. Previous electrical-resistivity measurements suggested the possibility that UBe_{13} exhibits two different energy scales of c - f hybridization: a low-energy scale associated with “2 K fluctuation” and a higher-energy scale interpreted as the characteristic “Kondo-lattice” scale T^* [62]. A broad maximum of resistivity was observed at T^* , ranging from 8 K [102] to 30 K [59], as shown in Fig. 8.16 in previous reports. We believe that the $5f$ electrons in UBe_{13} could retain their itinerant characteristics even under high magnetic fields owing to the large energy scale of the c - f hybridization. Further investigation, taking into account the duality of the $5f$ electrons, is needed to reveal the electronic state of UBe_{13} under high magnetic fields.

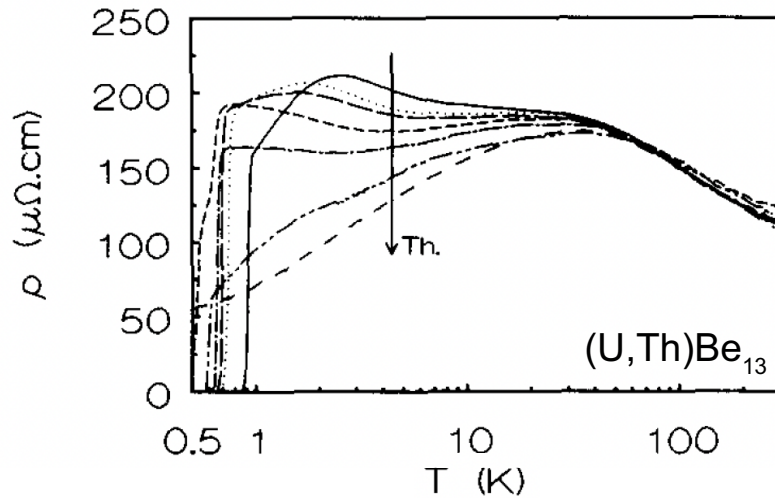


Figure 8.16: Temperature dependences of the electrical resistivities of $(\text{U,Th})\text{Be}_{13}$ (Th-concentrations are 0.00, 0.0066, 0.0101, 0.0194, 0.0245, 0.0355, and 0.060.) [59]. Solid curve corresponds to the result of UBe_{13} .

Finally, we propose an alternative possibility as the origin of the Γ_5 - and Γ_3 -symmetrical softening under magnetic fields. Since UBe_{13} has a caged structure as shown in Fig. 3.1, the elastic behavior could involve not only the (localized or itinerant) $5f$ electronic degrees of freedom but also the off-center degrees of freedom of the U ion. For example, $\text{La}_3\text{Pd}_{20}\text{Ge}_6$, one of the clathrate compounds, shows an elastic softening of the Γ_5 -symmetrical C_{44} mode below 3 K [103]. This compound also has a caged structure, and the ultrasonic dispersion around 20 K originating from the same symmetrical rattling motion was observed as shown in Fig. 8.17. The origin of the softening in $\text{La}_3\text{Pd}_{20}\text{Ge}_6$ is considered to be the Γ_5 -symmetrical off-center degrees of freedom associated with the quantum “tunneling” state, where the off-center charge distribution of the La atom exists. As mentioned in Chapter 3, a low-energy Einstein phonon has also been experimentally proposed for UBe_{13} [47, 48]. This experimental fact suggests the possibility that UBe_{13} has similar off-center degrees of freedom, which supports this scenario. However, further study on the coupling between phonon and $5f$ electronic state is necessary to explain the enhancement of the softening due to the applied magnetic field. This characteristic of the softening differs from that observed in $\text{La}_3\text{Pd}_{20}\text{Ge}_6$ which is insensitive to magnetic fields [103].

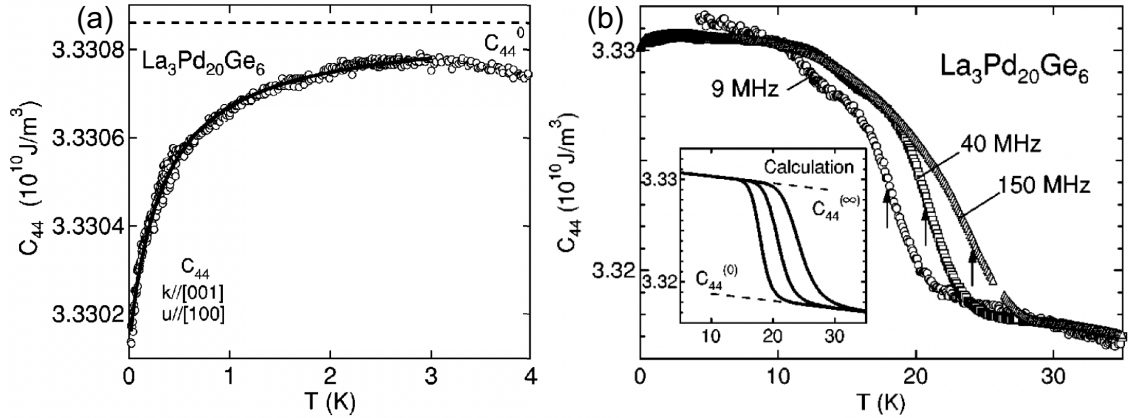


Figure 8.17: (a) Temperature dependence of the elastic constant C_{44} of $\text{La}_3\text{Pd}_{20}\text{Ge}_6$ below 4 K [103]. (b) Frequency dependence of the elastic constant C_{44} of $\text{La}_3\text{Pd}_{20}\text{Ge}_6$ [103]. The inset in (b) represents the calculation results based on the Debye-type dispersion.

Chapter 9

Concluding Remarks

In this work, we investigated the electric quadrupolar physics in the f -electron caged compounds $(Y, Pr)Ir_2Zn_{20}$ and $(U, Th)Be_{13}$ using ultrasonic measurements. The key conclusions drawn from the research are summarized as follows:

$(Y, Pr)Ir_2Zn_{20}$

- We discovered a change in the ground state of $(Y, Pr)Ir_2Zn_{20}$ due to a quadrupolar Kondo effect with Pr concentration. Specifically, we observed Γ_3 -symmetrical elastic constant proportional to $\sqrt{T}$ in the Pr-8 and 37% systems, which differs from the behavior in the Pr-3.4% system. This temperature dependence is consistent with theoretical predictions from the quadrupolar Kondo (virtual) lattice model, where finite localized quadrupolar interaction is introduced. We consider this to be the first observation of a crossover from single-site quadrupolar Kondo model to quadrupolar Kondo lattice model in terms of quadrupolar susceptibility.
- In the Pr-37% system, we observed an ultrasonic dispersion in the Γ_3 -symmetrical mode at around 1 K, with an energy scale is close to a quadrupolar Kondo effect in the system. We consider that the energy scale of the ultrasonic dispersion is modified by Pr concentration and that accidentally coincides with the QKE energy scale in the Pr-37% system. Since this ultrasonic dispersion is sensitive to the magnetic field, we suggest a possibility of the vibronic ground state, where Γ_3 -symmetrical phonon couples to the localized quadrupole in the Pr-37% system.
- We observed the Γ_3 -symmetrical elastic anomaly at the phase boundary of newly proposed phase pocket “A” in $PrIr_2Zn_{20}$. Additionally, we found other elastic anomalies in antiferro-quadrupolar (AFQ) ordering phase. Based on the analysis with a simple mean-field model, we suggest that these anomalies arise from the switching of the order parameters. It is possible that this switching is related to the field-induced phase pocket “A”.

(U, Th)Be₁₃

- We observed a large elastic softening of the longitudinal C_{11} mode ($\Gamma_1 \oplus \Gamma_3$ -symmetrical mode) in UBe₁₃ and (U, Th) Be₁₃ (Th-2.7%), which is robust to the applied magnetic field. The temperature at which the softening ceases corresponds to the temperature of “2 K anomaly” observed in electrical resistivity and thermal expansion measurements, suggesting that the softening is linked to this anomaly. Since this softening is not observed in the pure Γ_3 -symmetrical mode, we propose that this softening does not originate from the Γ_3 -symmetrical quadrupolar degrees of freedom but rather from the Γ_1 -symmetrical volume change due to (magnetic) c - f hybridization. Furthermore, the absence of the elastic softening in the Γ_3 -symmetrical mode indicates that the CEF ground state is not a non-Kramers Γ_3 doublet, which is inconsistent with the scenario of the quadrupolar Kondo effect originally proposed by Dr. D. L. Cox.
- We found that the Γ_5 - and Γ_3 -symmetrical elastic constants show the elastic softening enhanced by applied magnetic fields in UBe₁₃ and (U, Th) Be₁₃ (Th-2.7%). These behaviors suggest that the Γ_5 - and Γ_3 -type quadrupolar degrees of freedom are enhanced by applied magnetic fields, which cannot be explained by a localized $5f$ -electron description. Thus, we propose the possibility that c - f hybridization remains and $5f$ electronic state is relatively itinerant even under high magnetic fields.

【Future Perspective】

(Y, Pr)Ir₂Zn₂₀

- We observed a change of the elastic behavior in the non-magnetic Y-diluted systems (Y, Pr)Ir₂Zn₂₀ with Pr concentration, which could be interpreted as the change in the quantum ground state due to a quadrupolar Kondo effect (QKE). To exclude any extrinsic origins of the elastic behavior shown in Appendix. 1, we propose that the ultrasonic measurements under uniaxial pressure is valid. Furthermore, expansion to the ultrasonic measurements of other Pr-based caged compounds is also necessary to verify the universality of the elastic response due to a QKE. It is considered that accumulating fundamental experimental studies will deepen our understanding of QKE, which remains a mystery, and advance applied research, as seen in the case of the (magnetic) Kondo effect.
- We investigated thermodynamic response in the recently proposed small phase pocket “A” by means of ultrasonic measurements. To confirm the order parameter and/or ordering vector of the phase “A”, microscopic measurements such as a neutron diffraction scattering measurements, are necessary. In addition to the phase “A”, the possibility of the switching of the order parameter in the AFQ phase is also worth investigating thorough the microscopic measurements.

(U,Th)Be₁₃

- We observed that the Γ_5 - and Γ_3 -symmetrical electric quadrupolar degrees of freedom were enhanced under applied magnetic fields. We proposed the possibility that the degrees of freedom observed under high magnetic fields originate from strong c - f hybridization. To clarify how the itinerant electrons affect the physical properties, other measurement techniques to directly observe the electronic states of conduction electrons are required.

Chapter 10

Appendix 1: Power-Law Fitting Analysis in (Y, Pr)Ir₂Zn₂₀

10.1 Power-Law Fit Analysis of the Pr-8% System in Several Temperature Ranges

In the main text, we analyzed the elastic response arising from the QKE in the Pr-8% system by comparing the functions proportional to $+\ln T$ and $+\sqrt{T}$ as shown in Fig. 6.3. Notably, the down-convex curve of the Γ_3 -symmetrical mode C_v can be explained by $\sqrt{T}$ -proportional temperature dependence, as described in Chapter 6. In this chapter, we present the details of the power-law fitting analysis.

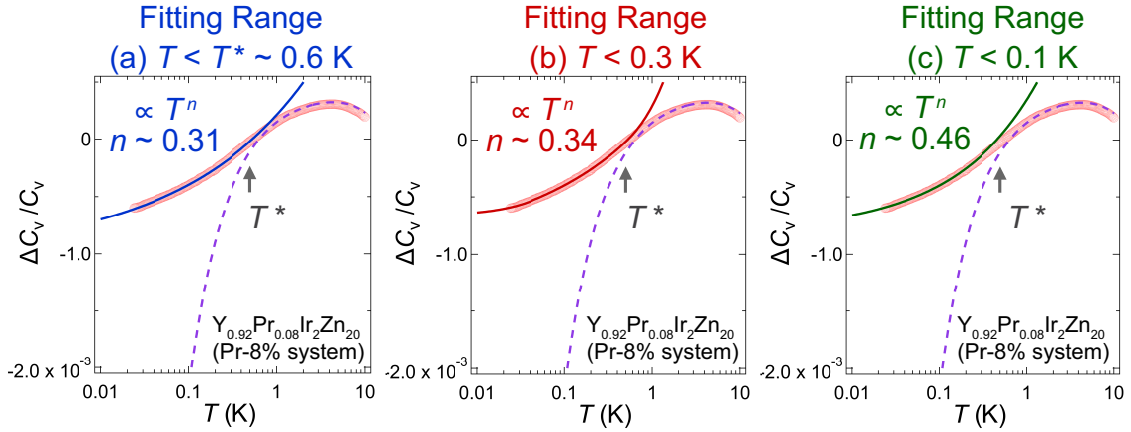


Figure 10.1: Power-law fitting results of the Pr-8% system in the temperature range below (a) $T < 0.6$ K, (b) $T < 0.3$ K, and (c) $T < 0.1$ K. Purple dashed curve represents the calculation result based on the localized CEF model. $T^* \sim 0.6$ K is the characteristic temperature where the experimental result deviates from the localized model.

First, we performed the analysis using a free parameter n ($C_v \propto T^n$) in the tem-

perature range just below the characteristic temperature $T^* \sim 0.6$ K, as shown in Fig. 10.1(a). The obtained value of n is ~ 0.31 , which is slightly smaller than 0.5 predicted by the quadrupolar Kondo lattice theory [18]. Although the fitting curve reproduces the experimental result well, the temperature range in the vicinity of T^* is considered the crossover region from the localized regime to the quadrupolar Kondo regime. Therefore, the analysis should be performed only at lower temperatures. Figures 10.1(b) and (c) show the fitting results in the temperature ranges below 0.3 K and 0.1 K, respectively. As the fitting range extends to lower temperatures, the value of n increases. Consequently, the obtained parameter, n , in the fitting range below 0.1 K is ~ 0.46 , which is close to the theoretical value of 0.5 [18]. Thus, we conclude that the ground state of the Pr-8% system can be well described by the quadrupolar Kondo lattice model.

Chapter 11

Appendix 2: CEF Analysis with the Contribution of Atomic Disorder in (Y, Pr)Ir₂Zn₂₀

11.1 CEF Analysis with Tetragonal Distortion

In the main text, we discuss the elastic response originating from QKE assuming that cubic symmetry is kept even in the Y-diluted systems. However, it is possible that an atomic disorder arising from the elemental substitution lowers the symmetry. The lowering of the symmetry could modify the CEF effect and the elastic response at very low temperature. In particular, Γ_3 doublet which couples to the strain can be split easily by the distortion.

Here, we discuss the possibility that the deviation of the Γ_3 -symmetrical elastic constant from the CEF calculation originates from atomic distortion rather than from QKE. The elastic behavior for each Pr-concentration system is summarized in the Fig. 6. 13. First, we recalculated the Γ_3 -symmetrical quadrupolar susceptibility considering tetragonal distortion. To consider the contribution of the tetragonal distortion, we used the following Hamiltonian,

$$\mathcal{H}_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 (O_4^0 + 5O_4^4) + B_6^0 (O_6^0 - 21O_6^4).$$

Calculation results for constant values of B_2^0 are summarized in Figs. 11.1. Figure 11.1(a) shows the relationship between B_2^0 and the energy splitting of the ground Γ_3 doublet (ΔE_{Γ_3}), which indicates that the splitting increases with increasing tetragonal distortion. As the Γ_3 doublet splits, the Curie-like divergence of the Γ_3 -symmetrical quadrupolar susceptibility χ_{Γ_3} is suppressed, as shown in Fig. 11.1(b). It is noted that the temperature at which calculated χ_{Γ_3} deviates from the cubic model [dashed line in Fig. 11.1(b)] also shifts to higher values as the absolute value of B_2^0 increases.

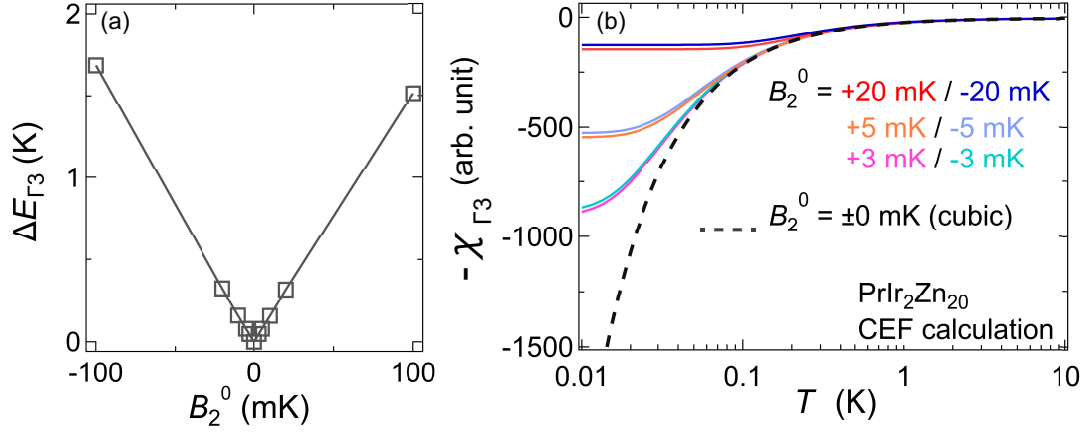


Figure 11.1: (a) Calculation results of the energy split of the ground Γ_3 doublet, ΔE_{Γ_3} , with constant values of B_2^0 . (b) Calculation results of the temperature dependence of the Γ_3 -symmetrical quadrupolar susceptibility with B_2^0 (solid curves) and without B_2^0 (dashed curve).

Then, we compared the suppression of the Curie-like softening obtained from the calculation with B_2^0 to the experimental results. Figure 11.4 shows the comparison between (a) the calculation result with $B_2^0 = 50$ mK and (b) the experimental result of the Pr-8% system. Since the characteristic temperature T^* is experimentally determined to be ~ 0.6 K in the Pr-8% system, B_2^0 is set to 50 mK in the calculation to reproduce this characteristic temperature. As shown in Fig. 11.1(a), when B_2^0 is 50 mK, the width of the energy split of the Γ_3 doublet, ΔE_{Γ_3} , corresponds to 0.8 K.

Figure 11.4 shows that the susceptibility below ~ 0.1 K is almost flat in the calculation with $B_2^0 = 50$ mK. However, the experimental results of the Pr-8% system show a gradual softening down to the lowest temperature (~ 40 mK), which is proportional to $\sqrt{T}$ as described in Chapter 3. Other Pr-concentration systems also do not show any flat behavior in the lowest temperature range. Thus, we conclude that the sample quality is high and the samples do not exhibit uniform tetragonal distortion (*i. e.*, a constant value of B_2^0) due to elemental substitution.

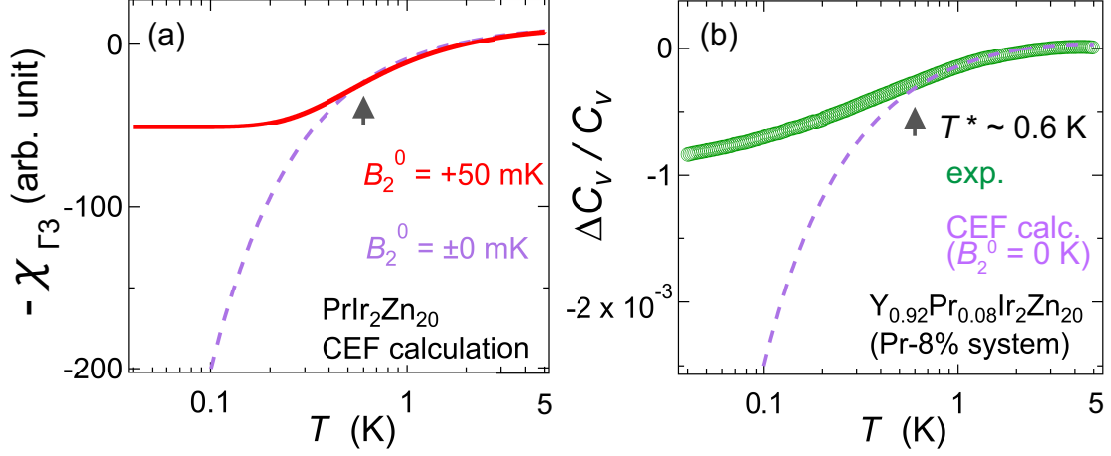


Figure 11.2: (a) Calculation results of the temperature dependence of the Γ_3 -type quadrupolar susceptibility with $B_2^0 = 50$ mK. (b) Experimental results of the relative change of the Γ_3 -symmetrical elastic constant on the Pr-8% system.

Additionally, we performed the analysis assuming that tetragonal distortion has spatial distribution. For the analysis, we assumed that a probability of B_2^0 follows a normal distribution described as

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{(x - \mu)^2}{2\sigma^2} \right].$$

σ corresponds to the width of the distribution, and μ corresponds to the center position. Here, μ is fixed to zero. Figure 11.3(b) shows Γ_3 -type quadrupolar susceptibilities with $\sigma \neq 0$. We analyzed the data in the range $-5\sigma < B_2^0 < 5\sigma$ as shown in Fig. 11.3(a).

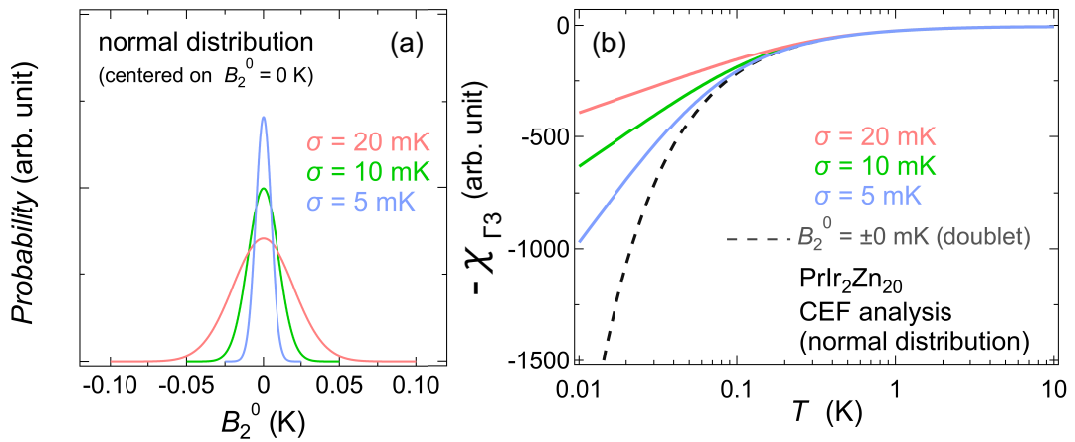


Figure 11.3: (a) Probability of the normal distribution in the case of $\sigma = 5, 10, 20$ mK. (b) Calculation results of the Γ_3 -type quadrupolar susceptibility with σ .

Figure 11.4 shows a comparison between (a) the calculation with $\sigma = 20$ mK and (b) the experimental result of the Pr-3.4% system in which the logarithmic elastic behavior is observed at low temperatures [43]. σ is set to 20 mK to match the characteristic temperature $T^* \sim 0.3$ K obtained by the experiment. In contrast to the case of constant B_2^0 , the calculated quadrupolar susceptibility exhibits an elastic softening down to the lowest temperature. As shown in Fig. 11.4(a), the Γ_3 -type quadrupolar susceptibility is roughly proportional to $+\ln T$ as predicted by single-site quadrupolar Kondo model. Therefore, it is difficult to exclude the possibility that the observed logarithmic behavior in the Pr-3.4% system [43] originates from the atomic disorder.

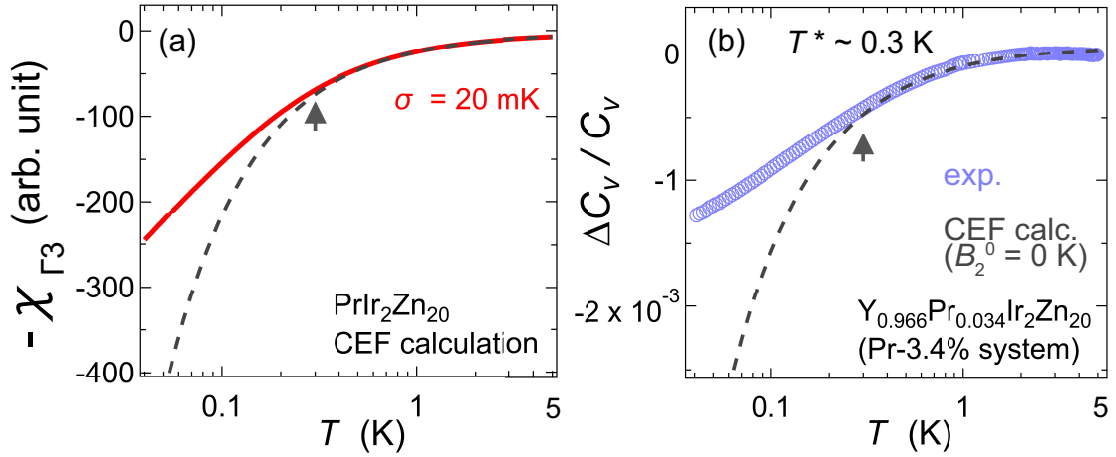


Figure 11.4: (a) Calculation results of the temperature dependence of the Γ_3 -type quadrupolar susceptibility with $\sigma = 20$ mK. (b) Experimental results of the relative change of the Γ_3 -symmetrical elastic constant on the Pr-3.4% system [43].

As shown in the present discussion, the elastic response due to a CEF effect could be modified by the atomic disorder. In the main text, we discussed the elastic behavior at low temperature assuming that Γ_3 doublet is degenerated completely, however, the present analysis suggests that it is possible that an atomic disorder arising from the elemental substitution is also important in understanding the elastic constant at very low temperature. To verify this possibility, we consider that it would be valuable to perform the experiments under uniaxial pressure because uniaxial pressure could lower the symmetry. It is necessary to reveal how the elastic behavior in the present system is modified splitting of the non-Kramers Γ_3 doublet.

Published Works

- Papers (Regarding as Doctoral Dissertation)

1. **R. Hibino**, T. Yanagisawa, Y. Mikami, H. Hidaka, H. Amitsuka, S. Zherlitsyn, J. Wosnitza, Y. Yamane, and T. Onimaru, “Elemental Dilution Effect on the Elastic Response due to a Quadrupolar Kondo Effect of the Non-Kramers Systems $Y_{1-x}Pr_xIr_2Zn_{20}$ ”, J. Phys. Soc. Jpn. **92**, 074708 (2023).
2. **R. Hibino**, T. Yanagisawa, Y. Mikami, H. Hidaka, H. Amitsuka, S. Zherlitsyn, J. Wosnitza, Y. Yamane, and T. Onimaru, “Change in the Ground State of $Y_{1-x}Pr_xIr_2Zn_{20}$ due to a Quadrupolar Kondo Effect with Pr Concentration x ”, JPS Conf. Proc. **38**, 011089 (2023).

- Papers (Other Topics)

1. C. Tabata, F. Kon, K. Ota, **R. Hibino**, Y. Matsumoto, H. Amitsuka, H. Nakao, Y. Haga, and K. Kaneko, “Magnetic order in honeycomb layered $U_2Pt_6Ga_{15}$ studied by resonant x-ray and neutron scattering”, Phys. Rev. B **109**, 134403 (2024).
2. K. Ushida, T. Yanagisawa, **R. Hibino**, M. Matsuda, H. Hidaka, H. Amitsuka, G. Knebel J. Flouquet, and D. Aoki, “Lattice Instability of UTe_2 Studied by Ultrasonic Measurements”, JPS Conf. Proc. **38**, 011021 (2023).
3. M. Matsuda, T. Yanagisawa, **R. Hibino**, F. Kon, H. Hidaka, and H. Amitsuka, “Elastic Properties and Crystalline-Electric-Field Effects of UIr_2Si_2 ”, JPS Conf. Proc. **38**, 011075 (2023).
4. F. Kon, C. Tabata, **R. Hibino**, H. Hidaka, T. Yanagisawa, H. Nakao, and H. Amitsuka, “Correlation between antiferromagnetic and charge-density-wave order in UPt_2Si_2 studied by resonant X-Ray scattering”, SciPost Physics Proc. **11**, 011 (2023).
5. D. I. Gorbunov, **R. Hibino**, Y. Skourski, T. Yanagisawa, A. V. Andreev, S. Zherlitsyn, and J. Wosnitza, “Elastic response of $U_3Cu_4Ge_4$ to spontaneous and field-induced phase transitions”, Phys. Rev. B **106**, 144403 (2022).

REFERENCES

- [1] 糟谷忠雄: 日本物理学会誌 **42** (1987) 722.
- [2] H. Kusunose: J. Phys. Soc. Jpn. **77** (2008) 064710.
- [3] S. Hayami and H. Kusunose: J. Phys. Soc. Jpn. **87** (2018) 033709.
- [4] H. Yamauchi, H. Onodera, K. Ohoyama, T. Onimaru, M. Kosaka, M. Ohashi, and Y. Yamaguchi: J. Phys. Soc. Jpn. **68** (1999) 2057.
- [5] D. Mannix, Y. Tanaka, D. Carbone, N. Bernhoeft, and S. Kunii: Phys. Rev. Lett. **95** (2005) 117206.
- [6] J. P. Franck, F. D. Manchester, and D. L. Martin: Proc. Roy. Soc. A **263** (1961) 494.
- [7] J. Kondo: Progress of Theoretical Physics **32** (1964) 37.
- [8] K. Yosida: Phys. Rev. **147** (1966) 223.
- [9] T. Komatsubara, N. Sato, S. Kunii, I. Oguro, Y. Furukawa, Y. Onuki, and T. Kasuya: Journal of Mag. Mag. Mat. **31-34** (1983) 368.
- [10] A. Sumiyama, Y. Oda, H. Nagano, Y. Ōnuki, K. Shibutani, and T. Komatsubara: J. Phys. Soc. Jpn. **55** (1986) 1294.
- [11] P. Nozières and A. Blandin: Journal de Physique **41** (1980) 193.
- [12] P. D. Sacramento and P. Schlottmann: Phys. Rev. B **43** (1991) 294.
- [13] D. L. Cox: Phys. Rev. Lett. **59** (1987) 1240.
- [14] 楠瀬博明: 物性研究 **70** (1998) 242.
- [15] C. L. Seaman, M. B. Maple, B. W. Lee, M. S. T. S. Ghamaty, J. S. Kang, L. Z. Liu, J. W. Allen, and D. L. Cox: Phys. Rev. Lett. **67** (1991) 2882.
- [16] H. Amitsuka, T. Hidano, T. Honma, H. Mitamura, and T. Sakakibara: Physica B: Condens. Matter **186-188** (1993) 337.

- [17] F. G. Aliev, S. Vieira, R. Villar, and V. V. Moshchalkov: J. Phys.: Condens. Matter **8** (1996) 9807.
- [18] A. Tsuruta and K. Miyake: J. Phys. Soc. Jpn. **84** (2015) 114714.
- [19] A. Tsuruta and K. Miyake: J. Phys. Commun. **6** (2022) 025006.
- [20] Y. Yamane, T. Onimaru, K. Wakiya, K. T. Matsumoto, K. Umeo, and T. Takabatake: Phys. Rev. Lett. **121** (2018) 077206.
- [21] M. S. Torikachvili, S. Jia, E. D. Mun, S. T. Hannahs, R. C. Black, W. K. Neils, D. Martien, S. L. Bud'ko, and P. C. Canfield: Proc. Natl. Acad. Sci. USA **104** (2007) 9960.
- [22] R. Yamamoto, M. D. Le, D. T. Adroja, Y. Shimura, T. Takabatake, and T. Onimaru: Phys. Rev. B **107** (2023) 075114.
- [23] K. Momma and F. Izumi: J. Appl. Crystallogr. **44** (2011) 1272.
- [24] T. Onimaru, K. T. Matsumoto, Y. F. Inoue, K. Umeo, T. Sakakibara, Y. Karaki, M. Kubota, and T. Takabatake: Phys. Rev. Lett. **106** (2011) 177001.
- [25] T. Onimaru, N. Nagasawa, K. T. Matsumoto, K. Wakiya, K. Umeo, S. Kittaka, T. Sakakibara, Y. Matsushita, and T. Takabatake: Phys. Rev. B **86** (2012) 184426.
- [26] A. Sakai, K. Kuga, and S. Nakatsuji: J. Phys. Soc. Jpn. **81** (2012) 083702.
- [27] M. Tsujimoto, Y. Matsumoto, T. Tomita, A. Sakai, and S. Nakatsuji: Phys. Rev. Lett. **113** (2014) 267001.
- [28] T. Onimaru and H. Kusunose: J. Phys. Soc. Jpn. **85** (2016) 082002.
- [29] I. Ishii, H. Muneshige, S. Kamikawa, T. K. Fujita, T. Onimaru, N. Nagasawa, T. Takabatake, and T. Suzuki: Phys. Rev. B **87** (2013) 205106.
- [30] I. Ishii, H. Muneshige, Y. Suetomi, T. K. Fujita, T. Onimaru, K. T. Matsumoto, T. Takabatake, K. Araki, M. Akatsu, Y. Nemoto, T. Goto, and T. Suzuki: J. Phys. Soc. Jpn. **80** (2011) 093601.
- [31] M. Koseki, Y. Nakanishi, K. Deto, G. Koseki, R. Kashiwazaki, F. Shichinomiya, M. Nakamura, M. Yoshizawa, A. Sakai, and S. Nakatsuji: J. Phys. Soc. Jpn. **80** (2011) SA049.
- [32] A. Sakai and S. Nakatsuji: J. Phys. Soc. Jpn. **80** (2011) 063701.
- [33] K. Iwasa, H. Kobayashi, T. Onimaru, K. T. Matsumoto, N. Nagasawa, T. Takabatake, S. Ohira-Kawamura, T. Kikuchi, Y. Inamura, and K. Nakajima: J. Phys. Soc. Jpn. **82** (2013) 043707.

- [34] T. Onimaru, K. T. Matsumoto, Y. F. Inoue, K. Umeo, Y. Saiga, Y. Matsushita, R. Tamura, K. Nishimoto, I. Ishii, T. Suzuki, and T. Takabatake: J. Phys. Soc. Jpn. **79** (2010) 033704.
- [35] T. Tayama, T. Sakakibara, K. Kitami, M. Yokoyama, K. Tenya, H. Amitsuka, D. Aoki, Y. Ōnuki, and Z. Kletowski: J. Phys. Soc. Jpn. **70** (2001) 248.
- [36] K. Iwasa, K. T. Matsumoto, T. Onimaru, T. Takabatake, J.-M. Mignot, and A. Gukasov: Phys. Rev. B **95** (2017) 155106.
- [37] T. Ikeura, T. Matsubara, Y. Machida, K. Izawa, N. Nagasawa, K. T. Matsumoto, T. Onimaru, and T. Takabatake: JPS Conf. Proc. **3** (2014) 011091.
- [38] T. Onimaru, K. Izawa, K. T. Matsumoto, T. Yoshida, Y. Machida, T. Ikeura, K. Wakiya, K. Umeo, S. Kittaka, K. Araki, T. Sakakibara, and T. Takabatake: Phys. Rev. B **94** (2016) 075134.
- [39] S. Kittaka, T. Onimaru, K. T. Matsumoto, and T. Sakakibara: Phys. Rev. B **110** (2024) L081106.
- [40] S. Mühlbauer, B. Binz, F. Jonietz, C. Pfleiderer, A. Rosch, A. Neubauer, R. Georgii, and P. Böni: Science **323** (2009) 915.
- [41] P. W. Anderson, B. I. Halperin, and C. M. Varma: Philos. Mag. **25** (1972) 1.
- [42] W. A. Phillips: J. Low Temp. Phys. **7** (1972) 351.
- [43] T. Yanagisawa, H. Hidaka, H. Amitsuka, S. Zherlitsyn, J. Wosnitza, Y. Yamane, and T. Onimaru: Phys. Rev. Lett. **123** (2019) 067201.
- [44] A. Wörl, M. Garst, Y. Yamane, S. Bachus, T. Onimaru, and P. Gegenwart: Phys. Rev. Research **4** (2022) L022053.
- [45] N. C. Baenziger and R. E. Rundle: Acta Crystallographica **2** (1949) 258.
- [46] M. W. Mcelfresh, J. H. Hall, R. R. Ryan, J. L. Smith, and Z. Fisk: Acta Crystallographica Section C **46** (1990) 1579.
- [47] B. Renker, F. Gompf, J. Suck, H. Rierschel, P. Frings, and J. Beuers: Phys. Rev. B **32** (1985) 1859.
- [48] H. Hidaka, R. Nagata, C. Tabata, Y. Shimizu, N. Miura, T. Yanagisawa, and H. Amitsuka: Phys. Rev. Materials **2** (2018) 053603.
- [49] H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith: Phys. Rev. Lett. **50** (1983) 1595.
- [50] H. R. Ott, H. Rudigier, T. M. Rice, K. Ueda, Z. Fisk, and J. L. Smith: Phys. Rev. Lett. **52** (1984) 1915.

- [51] M. B. Maple, J. W. Chen, S. E. Lambert, Z. Fisk, J. L. Smith, and H. R. Ott: Phys. Rev. Lett. **54** (1985) 477.
- [52] C. Tien and I. M. Jiang: Phys. Rev. B **40** (1989) 229.
- [53] J. E. Soniera, R. H. Heffner, G. D. Morris, D. E. MacLaughlin, O. O. Bernale, J. Cooley, J. L. Smith, and J. D. Thompson: Physica B: Condens. Matter **326** (2003) 414.
- [54] D. Einzel, P. J. Hirschfeld, F. Gross, B. S. Chandrasekhar, K. Andres, H. R. Ott, J. Beuers, Z. Fisk, and J. L. Smith: Phys. Rev. Lett. **56** (1986) 2513.
- [55] D. E. MacLaughlin, C. Tien, W. G. Clark, M. D. Lan, Z. Fisk, J. L. Smith, and H. R. Ott: Phys. Rev. Lett. **54** (1985) 1833.
- [56] B. Golding, D. J. Bishop, B. Batlogg, Z. F. W. H. Haemmerle, J. L. Smith, and H. R. Ott: Phys. Rev. Lett. **55** (1985) 2479.
- [57] Y. Shimizu, S. Kittaka, T. Sakakibara, Y. Haga, E. Yamamoto, H. Amitsuka, Y. Tsutsumi, and K. Machida: Phys. Rev. Lett. **114** (2015) 147002.
- [58] R. Felten, F. Steglich, G. Weber, H. Rietschel, F. Gompf, B. Renker, and J. Beuers: Europhysics Lett. **2** (1986) 323.
- [59] E. A. Knetsch, G. J. Nieuwenhuys, J. A. Mydosh, R. H. Heffner, and J. L. Smith: Physica B **186-188** (1993) 251.
- [60] M. Lang, R. Helfrich, F. Kromer, C. Langhammer, F. Steglich, G. R. Stewart, and J. S. Kim: Physica B: Condens. Matter **259-261** (1999) 608.
- [61] B. Golding, B. Batlogg, D. J. Bishop, W. H. Haemmerle, Z. Fisk, J. L. Smith, and H. R. Ott: Proc. of 2nd Intl. Conf. on Phonon Physics (1985) 406.
- [62] P. Gegenwart, C. Langhammer, R. Helfrich, N. Oeschler, M. Lang, J. S. Kim, G. R. Stewart, and F. Steglich: Physica C **408-410** (2004) 157.
- [63] S. Yotsuhashi, K. Miyake, and H. Kusunose: J. Phys. Soc. Jpn. **71** (2002) 389.
- [64] S. Nishiyama, H. Matsuura, and K. Miyake: J. Phys. Soc. Jpn. **79** (2010) 104711.
- [65] Y. Shimizu, A. Pourret, G. Knebel, A. Palacio-Morales, and D. Aoki: Phys. Rev. B **92** (2015) 241101(R).
- [66] J. A. Detwiler, G. M. Schmiedeshoff, N. Harrison, A. H. Lacerda, J. C. Cooley, and J. L. Smith: Phys. Rev. B **61** (2000) 402.
- [67] H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith: Phys. Rev. B **31** (1985) 1651.
- [68] F. Kromer, R. Helfrich, M. Lang, F. Steglich, C. Langhammer, A. Bach, T. Michels, J. S. Kim, and G. R. Stewart: Phys. Rev. Lett. **81** (1998) 4476.

- [69] Y. Yamane, T. Onimaru, K. Uenishi, K. Wakiya, K. T. Matsumoto, K. Umeo, and T. Takabatake: *Physica B: Condens. Matter* **536** (2018) 40.
- [70] B. Lüthi: *Physical Acoustics in the Solid State* (Springer, Berlin, Heidelberg, 2005).
- [71] K. Araki, Y. Nemoto, M. Akatsu, S. Jumonji, T. Goto, H. S. Suzuki, H. Tanida, and S. Takagi: *Phys. Rev. B* **84** (2011) 045110.
- [72] T. Goto, Y. Nemoto, K. Sakai, T. Yamaguchi, T. M. Akatsu, Yanagisawa, H. Hazama, K. Onuki, H. Sugawara, and H. Sato: *Phys. Rev. B* **69** (2004) 180511(R).
- [73] Y. Nemoto, T. Yamaguchi, T. Horino, M. Akatsu, T. Yanagisawa, and T. Goto: *Phys. Rev. B* **68** (2003) 184109.
- [74] R. Lea, M. J. M. Leask, and W. P. Wolf: *J. Phys. Chem. Solids* **23** (1962) 1381.
- [75] M. T. Hutchings: *Solid State Phys.* **16** (1964) 227.
- [76] T. Yanagisawa, Y. Ikeda, H. Saito, H. Hidaka, H. Amitsuka, K. Araki, M. Akatsu, Y. Nemoto, T. Goto, P. C. Ho, R. E. Baumbach, and M. B. Maple: *J. Phys. Soc. Jpn.* **80** (2011) 043601.
- [77] I. Ishii, T. Fujita, I. Mori, H. Sugawara, M. Yoshizawa, and T. Suzuki: *J. Phys. Soc. Jpn.* **77** (2008) Suppl. A, 303.
- [78] D. J. Braun and W. Jeitschko: *J. Less-Common Met.* **72** (1980) 147.
- [79] V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos, R. C. P. Dai, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington: *Nature* **395** (1998) 876.
- [80] K. Araki, T. Goto, K. Mitsumoto, Y. Nemoto, M. Akatsu, H. S. Suzuki, H. Tanida, S. Takagi, S. Yasin, S. Zherlitsyn, and J. Wosnitza: *J. Phys. Soc. Jpn.* **81** (2012) 023710.
- [81] K. Wakiya, T. Onimaru, S. Tsutsui, K. T. Matsumoto, N. Nagasawa, A. Q. R. Baron, T. Hasegawa, N. Ogita, M. Udagawa, and T. Takabatake: *J. Phys. Conf. Ser.* **592** (2015) 012024.
- [82] K. Wakiya, T. Onimaru, S. Tsutsui, T. Hasegawa, K. T. Matsumoto, Y. Yamane, N. Nagasawa, A. Q. R. Baron, N. Ogita, M. Udagawa, and T. Takabatake: *J. Phys. Soc. Jpn.* **90** (2021) 024602.
- [83] T. Hasegawa, N. Ogita, and M. Udagawa: *J. Phys.: Conf. Ser.* **391** (2012) 012016.

- [84] H. Tanida, H. S. Suzuki, S. Takagi, H. Onodera, and K. Tanigaki: J. Phys. Soc. Jpn. **75** (2006) 073705.
- [85] T. Hotta: Phys. Rev. Lett. **96** (2006) 197201.
- [86] T. Hotta: J. Phys. Soc. Jpn. **76** (2007) 023705.
- [87] K. Araki: Doctoral Thesis, Niigata Univ. (2012).
- [88] M. Matsushita, J. Sakaguchi, Y. Taga, M. Ohya, S. Yoshiuchi, H. Ota, Y. Hirose, K. Enoki, F. Honda, K. Sugiyama, M. Hagiwara, K. Kindo, T. Tanaka, Y. Kubo, T. Takeuchi, R. Settai, and Y. Ōnuki: J. Phys. Soc. Jpn. **80** (2011) 074605.
- [89] I. Ishii: Private Communication (2024).
- [90] S. Yotsuhashi and H. Maebashi: J. Phys. Soc. Jpn. **71** (2002) 1705.
- [91] H. Kusunose: J. Phys. Soc. Jpn. **85** (2016) 064708.
- [92] T. Onimaru, T. Sakakibara, A. Harita, T. Tayama, D. Aoki, and Y. Ōnuki: J. Phys. Soc. Jpn. **73** (2004) 2377.
- [93] 鬼丸孝博: 物性研究 **97(4)** (2012) 764.
- [94] K. Hattori: Private Communication (2024).
- [95] A. de Visser, N. H. van Dijk, K. Bakker, J. J. M. Franse, A. Lacerda, J. Flouquet, Z. Fisk, and J. L. Smith: Phys. Rev. B **45** (1992) 2962.
- [96] K. Hasselbach, L. Taillefer, and J. Flouquet: Phys. Rev. Lett. **63** (1989) 93.
- [97] M. Sigrist: Progress of Theoretical Physics **107** (2002) 917.
- [98] S. Ghosh, A. Shekhter, F. Jerzembeck, N. Kikugawa, D. A. Sokolov, M. Brando, A. P. Mackenzie, C. W. Hicks, and B. J. Ramshaw: Nature Physics **17** (2021) 199.
- [99] S. Benhabib, C. Lupien, I. Paul, L. Berges, M. Dion, M. Nardone, A. Zitouni, Z. Q. Mao, Y. Maeno, A. Georges, L. Taillefer, and C. Proust: Nature Physics **17** (2021) 194.
- [100] Y. Shimizu, A. Pourret, G. Knebel, A. Palacio-Morales, and D. Aoki: Phys. Rev. B **92** (2015) 241101(R).
- [101] H. Hidaka: Private Communication (2024).
- [102] R. Felten, G. W. F. Steglich, H. Rietschel, F. Gompf, B. Renker, and J. Beuers: Europhys. Lett. **2** (1986) 323.
- [103] T. Goto, Y. Nemoto, T. Yamaguchi, M. Akatsu, T. Yanagisawa, O. Suzuki, and H. Kitazawa: Phys. Rev. B **70** (2004) 184126.