



HOKKAIDO UNIVERSITY

Title	Investigation of Localized and Delocalized Character of 4f Electrons in Cage-Structure Compounds
Author(s)	門別, 翔太
Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第12235号
Issue Date	2016-03-24
DOI	https://doi.org/10.14943/doctoral.k12235
Doc URL	https://hdl.handle.net/2115/61690
Type	doctoral thesis
File Information	Shota_Mombetsu.pdf



Doctoral Dissertation

Investigation of Localized and Delocalized Character of 4f Electrons in Cage-Structure Compounds

(カゴ状化合物における 4f 電子の局在・非局在性の研究)

Shota Mombetsu

Graduate School of Science, Hokkaido University

Department of Physics

March 24, 2016

HOKKAIDO UNIVERSITY

DOCTORAL THESIS

Investigation of Localized and Delocalized Character of $4f$ Electrons in Cage-Structure Compounds

Author:
Shota Mombetsu

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

*A thesis submitted in fulfilment of the requirements
for the degree of Doctor (Science)*

in the

Laboratory of magnetism in strongly-correlated electronic systems
Very low temperature group
Department of Physics

March 24, 2016

Investigation of Localized and Delocalized Character of $4f$ Electrons in Cage-Structure Compounds

Shota Mombetsu

February 25, 2016

Contents

1	Introduction	1
1.1	c - f Hybridization and Kondo Physics	2
1.2	c - f Hybridization in Plural $4f$ Electrons	2
1.3	Cage-structure Compound	3
1.4	Motivation	5
2	Physical Property of $\text{SmOs}_4\text{Sb}_{12}$	7
2.1	Previous Reports on Physical Property of $\text{SmOs}_4\text{Sb}_{12}$	8
2.2	Previous Hydrostatic-Pressure Study on $\text{SmOs}_4\text{Sb}_{12}$	12
2.3	Previous Ultrasonic Study on $\text{SmOs}_4\text{Sb}_{12}$	15
3	Ultrasonic Measurement on $\text{SmOs}_4\text{Sb}_{12}$ in Pulsed Magnetic Field	17
3.1	Introduction	18
3.2	Experimental Details	18
3.3	Results and Discussions	19
3.4	Summary	20
4	Ultrasonic Measurement on $\text{SmOs}_4\text{Sb}_{12}$ under Hydrostatic Pressure	25
4.1	Introduction	26
4.2	Experimental Procedure	26
4.3	Results and Discussions	28
4.4	Summary	36
5	Mean-field Analysis	37
5.1	Mean Field Approximation	38
5.2	Result of Mean-field Calculation and discussion of low-temperature ordered state of $\text{SmOs}_4\text{Sb}_{12}$	39
5.3	Mean-Field Calculation for Magnetic Field Dependence of Elastic Constants Regarding Magneto-Elastic Coupling	45
6	Ultrasonic Study on Cage-Structured Compound SmBe_{13}	47
6.1	Introduction	48
6.2	Experimental Details	51
6.3	Results	51
6.4	Summary	56

7	Conclusion	57
A	Appendix	61
A.1	Quadupolar Susceptibility	62

Chapter 1

Introduction

1.1 c - f Hybridization and Kondo Physics

In rare earth based intermetallic compounds, much variety of quantum phenomena has been found, such as heavy-fermion (HF) behavior, multipole order, and unusual superconductivity [1, 2, 3]. The c - f hybridization, *i.e.*, a hybridization between conduction electrons and $4f$ -electrons of rare-earth ions, plays important roles in these materials. The c - f hybridization causes two competitive effects: the Kondo effects and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. By Kondo effect, the magnetic moments of $4f$ electrons are antiferromagnetically screened by the conduction electron's spins below a characteristic temperature, T_K . This many-body singlet state can be described as quasi-particles which have a large effective mass, so-called heavy fermion. Therefore, the characteristic temperature T_K , so-called "Kondo temperature", is taken as a crossover temperature separating localized electron behavior at high temperatures, relative to T_K , from itinerant behavior at low temperatures. On the other hand, RKKY interaction, which is an inter-site interaction between $4f$ -electrons via conduction electrons, causes an ordering of local multipole moments. These two effects are competitive, and the Doniach phase diagram have provided a good explanation for this competitive feature [4]. The strength of c - f hybridization can be controlled by external parameters, such as pressure, magnetic fields, and doping, and this competitive feature have been studied by controlling the magnitude of c - f hybridization. In the case of Ce compounds, a lot of compounds have been studied by applying pressure and doping [3].

In the vicinity of a quantum critical point (QCP), several exotic physical properties have been found, such as non-fermi liquid (NFL) behavior and superconductivity [5, 6, 7]. The mechanism of the superconductivity and the relation between NFL and QCP are still open question. How the electron state changes from the heavy fermion state to a magnetically ordered state is also an open question. There are two possible scenarios. One is that the heavy fermion state continues below the magnetic-order temperatures [8, 9, 10]. The other one is that the heavy fermion disappears when local moment order appears [11].

Although there are still several open questions about this competition, Doniach phase diagram has been a good guide for discussing the physical properties and for a study by tuning strength of c - f hybridization in particular for Ce and Yb compounds [4].

1.2 c - f Hybridization in Plural $4f$ Electrons

"Heavy fermion" compounds with other rare-earth elements have not yet been understood well, and unusual physical properties which are considered to be due to c - f hybridization have been found in Pr- and Sm-based compounds with $4f^2$ (Pr^{3+}) and $4f^5$ configuration, respectively. So far, only a few Pr-based heavy-fermion compounds have been found, such as $\text{PrOs}_4\text{Sb}_{12}$ and $\text{PrV}_2\text{Al}_{20}$ [12, 13]. $\text{PrV}_2\text{Al}_{20}$ has a doublet CEF ground state of Pr ion, which has quadrupolar degrees of freedom but does not have magnetic dipolar degrees of freedom. In this case, a new type of Kondo effect which screens quadrupole degrees of freedom, so-called quadrupole Kondo effect, is expected [14]. Indeed, several experimental results consistency with the theory suggest the existence of quadrupole Kondo effect in $\text{PrV}_2\text{Al}_{20}$. Note that this feature only appears in compounds with ions which possess plural $4f$ electrons, since non-magnetic doublet CEF state can exist only if the number of $4f$ electron is even. There are also only a few examples for Sm-based compounds which show heavy-fermion behavior and/or Kondo-effect-like $\log T$ dependences in electrical resistivity, for example, $\text{SmOs}_4\text{Sb}_{12}$, SmSn_3 , and $\text{SmTr}_2\text{Al}_{20}$ ($\text{Tr} = \text{Ti}, \text{V}, \text{Cr}$) [15, 16, 17, 18]. Unusual field insensitive features of heavy-fermion

state and magnetic order state in $\text{SmTr}_2\text{Al}_{20}$ have been reported. It is still unclear whether the heavy-fermion states in these Sm-based compounds and their origin are the same as that of Ce compounds or not. It should be noted that these heavy-fermion behavior with the elements having plural $4f$ electrons are mostly found in cage-structure compounds. In the next section, we introduce the cage structure and the characteristic features of compounds with this type of crystal structures.

1.3 Cage-structure Compound

Some of compounds have a characteristic crystal structure in which an ion is surrounded by many atoms. Namely, a “cage” consists of many atoms. An ion surrounded by the atomic cage is called guest ion. We call these compounds “cage-structure compounds”.

For example, filled skutterudite compounds have a cage structure, which consists of 8 transition metal and 12 pnictogen atoms. The crystal structure of filled skutterudite compounds is body centered cubic, and the space group is $\text{Im}\bar{3}$. The rare-earth site symmetry is T_h . In Fig. 1.1, we show the crystal structure and the *cage structure* of a filled skutterudite.

The characteristic features of rare-earth based cage-structure compounds are the strong c - f hybridization, the low-lying CEF levels with multipolar degrees of freedom, and the anharmonic vibration of a guest ion, so-called “rattling”. In the cage-structure compounds, competitions among these features with small energy scales is considered to cause a variety of interesting physical properties.

Since a guest ion in an atomic cage has many ligands, which provide $4f$ electron of a guest ion with more possibility to hybridize, strong c - f hybridization is expected in total for cage-structure compound.

$\text{PrOs}_4\text{Sb}_{12}$ is the first example of Pr-based heavy fermion compound. A Pr ion has a lower $4f$ -electron levels compared to a Ce ion; namely, a $4f$ electron of a Pr ion is more localized than that of a Ce ion. Thus the heavy-fermion states, which are seen in Ce-based compounds, seem to be difficult to exist for Pr compounds. Thus, a heavy fermion behavior in a Pr-based compound is quite rare example and would be originate from the strong c - f hybridization due to the cage structure.

If the atomic cage has high symmetry like a sphere, the splitting of $4f$ -energy state of the guest ion would be small. Thus, multipolar degrees of freedom would remain at low temperatures and contribute to physical properties. For example, $\text{PrOs}_4\text{Sb}_{12}$ shows a field-induced antiferro quadrupolar order [19]. In the isostructural family, $\text{PrRu}_4\text{P}_{12}$ is a possible electric-hexadecapolar-order compound [20]. The ordered state of $\text{SmRu}_4\text{P}_{12}$ is considered to be a magnetic octupolar order [21].

Furthermore, in the cage-structure compounds, large anharmonic vibrations of the guest ions, so-called rattling, have been observed by several measurements, such as an Einstein-phonon contribution in the specific heat, the ultrasonic dispersion, and in the Raman scattering [22, 23, 24, 25]. Possible contribution of rattling modes to HF behavior has been theoretically suggested [26, 27].

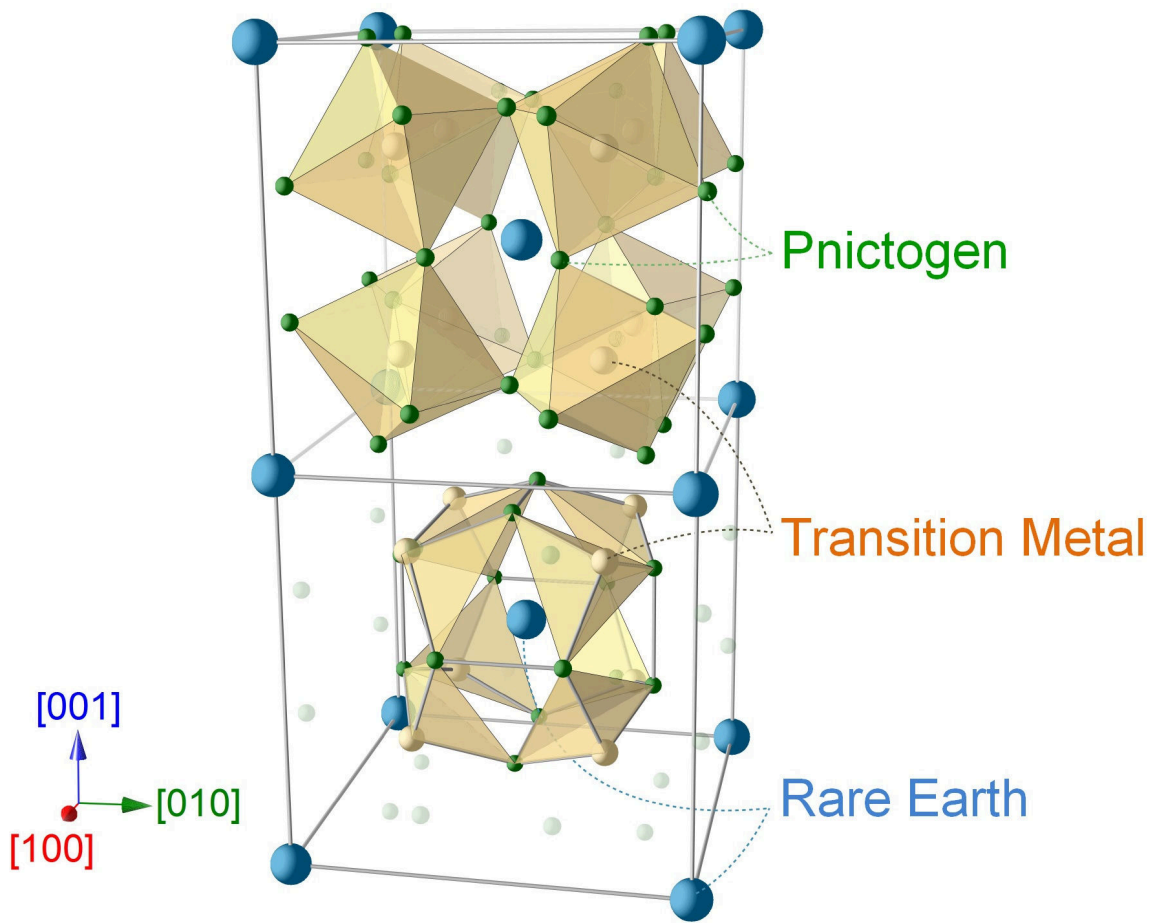


Figure 1.1: Crystal structure of $\text{SmOs}_4\text{Sb}_{12}$ (space group: $\text{Im}\bar{3}$), where two unit cells are described. In the upper cell, an octahedra which consists of Sb atoms around a Os atom is written. In the lower cell, a cage structure which consists of Os and Sb atoms is emphasized.

1.4 Motivation

The heavy fermion compound $\text{SmOs}_4\text{Sb}_{12}$ is one of the good examples for studying the effects of c - f hybridization in Sm compounds. This material shows unusual physical properties at low temperatures as we mention in the next section. The conventional way to study heavy fermion compounds is to control the c - f hybridization by applying external fields, such as hydrostatic pressure. There are some previous hydrostatic-pressure studies on this compound, and a NFL-like behavior and unusual pressure dependence of ordered state have been reported. Although these interesting features have been found in the previous study, it is still not clear how c - f hybridization, multipolar degrees of freedom and/or rattling relate to these features. Moreover the CEF ground state, from which we can know the multipolar degrees of freedom at low temperatures, has not been clarified yet. Thus, to understand the physical properties of these compounds, an observation of multipolar degrees of freedom and/or rattling modes should be studied.

The motivation of this study is

- to clarify the nature of c - f hybridization and its role in unusual physical properties of this material,
- to investigate the possible effect of multipoles on the physical properties of this material,
- to study pressure dependence of rattling and its possible relation to the physical property.

By means of ultrasonic measurement one can observe a response of higher-rank electric multipole moments of local $4f$ -electrons. One can also observe a resonance of rattling modes and ultrasonic strain. Thus, the ultrasonic measurement are suitable way to study such compounds with cage structure. In the present study, we have performed ultrasonic measurements on Sm-based cage-structure compounds under strong external fields.

We start with determining the CEF state. In order to achieve this, we have performed ultrasonic measurements in pulsed magnetic field. Then, we have performed ultrasonic measurements under hydrostatic pressure.

We have studied on another cage-structure compound, SmBe_{13} . This material shows a magnetic order below about 8 K. Some of Sm compounds show magnetic-field insensitive magnetic order as mentioned above. In the case of Sm compounds, a response against magnetic fields is weak due to relatively smaller Lande g factor. Thus, in order to study the magnetic property, high fields would be needed. In the present study, we have performed ultrasonic measurement under pulsed magnetic fields, and we successfully observed elastic anomaly, which would be correspond to the phase transition from magnetically-ordered state to paramagnetic state.

Chapter 2

Physical Property of $\text{SmOs}_4\text{Sb}_{12}$

2.1 Previous Reports on Physical Property of $\text{SmOs}_4\text{Sb}_{12}$

The filled skutterudite compound $\text{SmOs}_4\text{Sb}_{12}$ has attracted much attention because of its unusual physical properties [15, 28]. Figure 2.1 shows the temperature dependence of the specific heat. The upturn toward low temperature below ≈ 0.5 K is due to nuclear spins. By considering this, this results suggest that this compound has a relatively large Sommerfeld coefficient, $\gamma \approx 820 - 880 \text{ mJ mol}^{-1} \text{ K}^{-2}$. Interestingly, this large γ value is hardly affected by magnetic fields up to 8 T (Fig. 2.2) [15]. This robust γ value is in contrast to the magnetically suppressed γ in typical Ce-based heavy-fermion compounds such as CeCu_6 [29]. This suggests that the heavy-fermion state in $\text{SmOs}_4\text{Sb}_{12}$ might have a non-magnetic origin. On the other hand, several phenomena due to anharmonic vibrations of guest ions, so-called rattling, have been observed in this material, such as characteristic peaks in the Raman spectra, a contribution of Einstein mode to the specific heat, and ultrasonic dispersions [24, 25, 30, 38]. A multi-channel Kondo effect due to the coupling between the rattling modes and conduction electrons has been theoretically proposed to explain the magnetically robust heavy-fermion state [26, 27].

The characteristic temperature, T^* , which is related to the crossover temperature of Kondo-like screening due to hybridization, is estimated to be ≈ 20 K [32]. Below T^* , $\text{SmOs}_4\text{Sb}_{12}$ shows a phase transition at $T_C \approx 2.6$ K, accompanied by the appearance of a weak spontaneous magnetic moment of $0.02 - 0.03 \mu_B/\text{Sm-ion}$ [15, 28]. This value is much smaller than the free-ion value of $0.71 \mu_B/\text{ion}$ for Sm^{3+} . Considering an intermediate valence of $\approx +2.76$, as found by X-ray absorption spectroscopy below 20 K [33], the ordered moment should be 0.71×0.76 , since the ground J multiplet of the divalent state is $J = 0$. Thus, the ordered state would not be a simple ferromagnetic order of the magnetic moment of the localized $4f$ electrons. One of the possible explanations is that the low-temperature phase is an itinerant ferromagnetic state [15]. Another possibility would be a contribution of higher-order multipole moments to the low-temperature properties, which has been suggested based on a hydrostatic-pressure study [34].

As mentioned above, this material shows a mixed valence state. Figure 2.3 shows temperature dependence of XAS spectra of $\text{SmOs}_4\text{Sb}_{12}$ [33]. In Fig. 2.4, the temperature dependence of the averaged valence are shown. The averaged valence decrease with decreasing temperature and levels off at around T^* . This fact implies a possible relation between the valence state and appearance of coherent state of $4f$ electrons. Since measurements of XAS spectra corresponds to very fast time-scale measurements, it is difficult to know whether this intermediate valence state is static or not. In order to clarify the dynamics of the valence state of Sm ion, Mössbauer effect measurements would be needed.

To study the role of multipole degrees of freedom in this material, knowledge about the CEF level scheme of Sm^{3+} ion is required. Due to CEFs in the cubic T_h symmetry, the 6-fold degenerate ground-state multiplet $J = 5/2$ of the Sm^{3+} ion splits into a Γ_{67} quartet and a Γ_5 doublet. The Γ_{67} quartet has not only magnetic dipoles but also electric quadrupoles and magnetic octupoles, while the Γ_5 doublet has only magnetic dipole degrees of freedom [2]. As mentioned in Chap. 1, multipolar ordered states have been found in cage-structure compounds. Because of the similar cage-featured crystal structure, it is expected that the unusual physical properties of $\text{SmOs}_4\text{Sb}_{12}$ also originate from higher-order multipoles.

Thus far, two models for the CEF level scheme have been proposed for $\text{SmOs}_4\text{Sb}_{12}$. The $\Gamma_5(0 \text{ K}) - \Gamma_{67}(37 \text{ K})$ model was suggested from specific-heat and electrical resistivity measurements [28]. In Fig. 2.5, temperature dependence of C/T and magnetic entropy are shown. The data of C/T between 3.5 and 20 K were fitted by an equation containing electronic, lattice, and Schottky terms. The best

fit was obtained by scaling the CEF Schottky contribution by 0.58. They explain that the rest of the entropy is lost by appearance of heavy quasi-particles. On the other hand, the $\Gamma_{67}(0\text{ K})\text{--}\Gamma_5(20\text{ K})$ model was suggested on the basis of a point-charge model using extrapolated parameters of $\text{PrOs}_4\text{Sb}_{12}$ [15]. Anisotropic features in the magnetization support a Γ_{67} ground state (Fig. 2.6) [35]. Further, the Γ_{67} CEF ground state is consistent with the fact that the magnetic entropy increases without any tendency of saturation at $R\ln 2$ (Fig. 2.7).

Thus, the CEF ground state has yet to be determined. However, the presence of Kondo-screening below $T^* \approx 20\text{ K}$ and the ferromagnetism below $T_C \approx 2.6\text{ K}$ make it difficult to decide which of CEF energy level schemes is correct by performing measurements at low temperatures and low magnetic fields. It should also be noted that inelastic neutron scattering is challenging for this compound, since naturally abundant Sm atom has a large neutron absorption cross section.

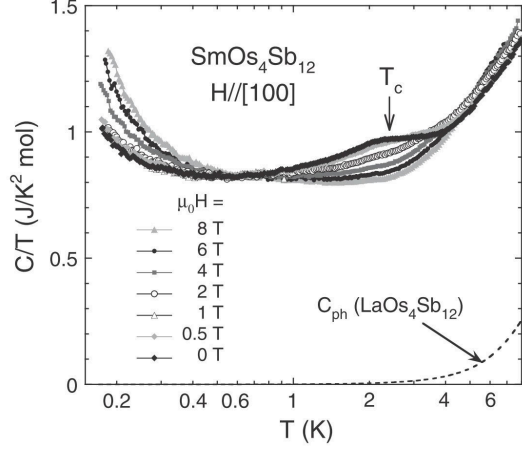


Figure 2.1: Specific heat divided by temperature C/T of $\text{SmOs}_4\text{Sb}_{12}$ measured in different magnetic fields [15].

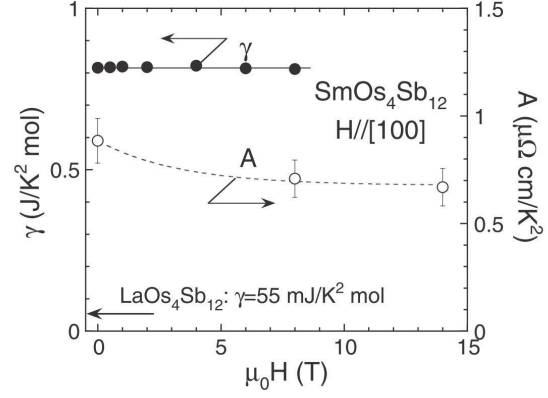


Figure 2.2: Magnetic field dependence of Sommerfeld coefficient, Γ , and quadratic coefficient of electrical resistivity, A , as a function of magnetic field [15].

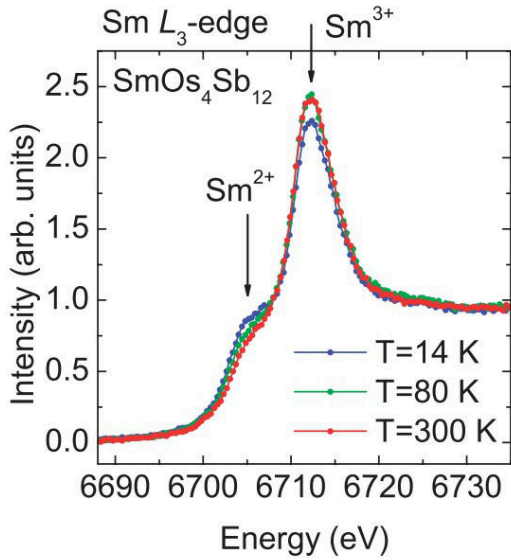


Figure 2.3: Temperature dependence of XAS spectra around Sm L3-edge of $\text{SmOs}_4\text{Sb}_{12}$ [33].

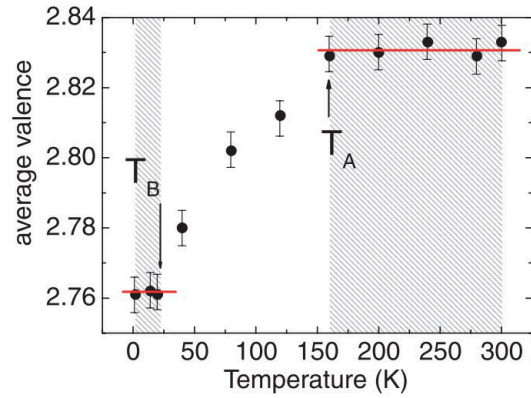


Figure 2.4: Temperature dependence of the averaged valence of Sm ion of $\text{SmOs}_4\text{Sb}_{12}$ [33].

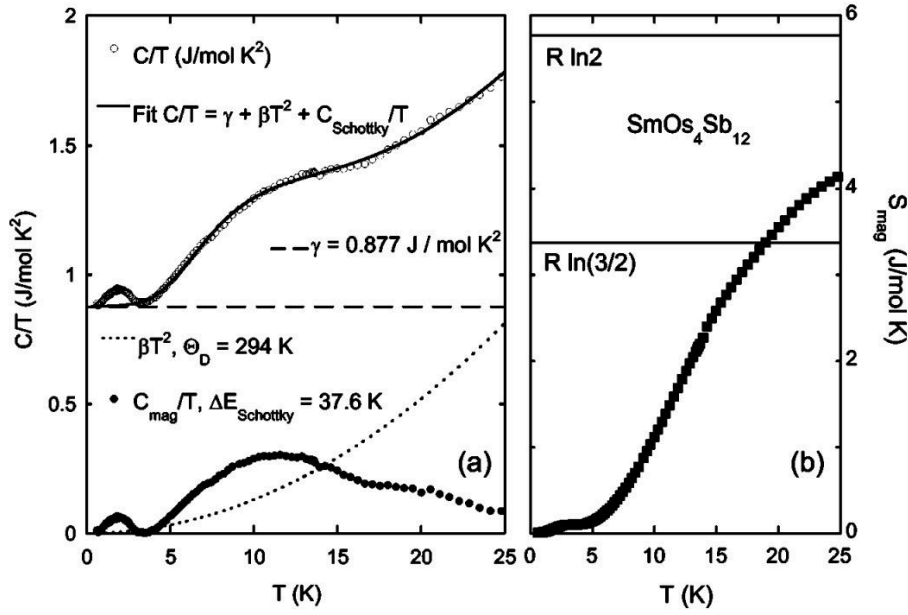


Figure 2.5: (a) Temperature dependence of C/T and a fit to the data (see text). (b) Magnetic entropy of $\text{SmOs}_4\text{Sb}_{12}$ [28].

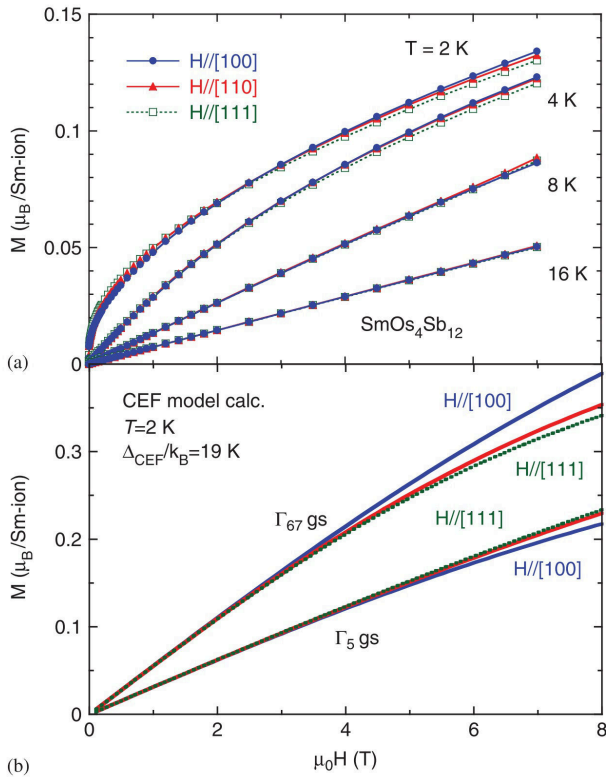


Figure 2.6: (a) Magnetization vs. magnetic field. (b) Calculated magnetization curves for two possible CEF models [35].

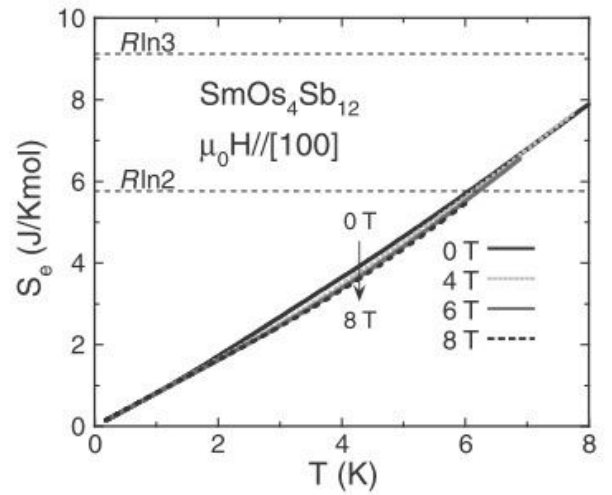


Figure 2.7: Temperature dependence of the magnetic entropy of $\text{SmOs}_4\text{Sb}_{12}$ [15].

2.2 Previous Hydrostatic-Pressure Study on $\text{SmOs}_4\text{Sb}_{12}$

As mentioned above, the filled skutterudite $\text{SmOs}_4\text{Sb}_{12}$ is one of the good candidate to study the c - f hybridization effect of Sm system. For studying such a material, one of the useful ways is a measurement with controlling c - f hybridization by applying pressure. In Fig. 2.8, pressure dependence of T_C and T^* are shown [36]. By applying hydrostatic pressure on $\text{SmOs}_4\text{Sb}_{12}$, T_C increases, while T^* decreases. These opposite tendencies imply an increasing of the localized character of $4f$ electrons [36]. Interestingly, NFL behavior appears in the electrical resistivity between 0.5 GPa to 1.5 GPa (Figs. 2.8, 2.9) [32], while NFL behaviors have typically been found in the vicinity of quantum critical points. In Fig. 2.10, temperature dependence of ac-susceptibility under various pressures is shown [34]. The ac-susceptibility shows a peak at T_C , which suggests a ferromagnetic order. In Fig. 2.11, pressure dependence of the peak value is shown. The peak value increases drastically by applying relatively weak pressure of 0.5 GPa. The disappearance of NQR signal from wide frequency range at around 0.4 GPa, which suggests drastic change of internal magnetic and/or electric field, has also been reported [37]. By applying more pressure, the peak of ac-susceptibility becomes smaller, and seems to disappear at 3.6 GPa. On the other hand, the peak of the specific heat at T_C , $\Delta C/T_C$, becomes larger with increasing pressure, which suggests the ordered state is stabilized (Fig. 2.12) [34].

These facts strongly suggest that the ordered state changes drastically by applying pressure more than 0.5 GPa, and that at high pressures, the ordered state is not a simple magnetic dipolar order but a multipolar order. The possible contribution of multipoles to the physical properties of this compound should be studied by measurements which can observe higher-rank multipoles.

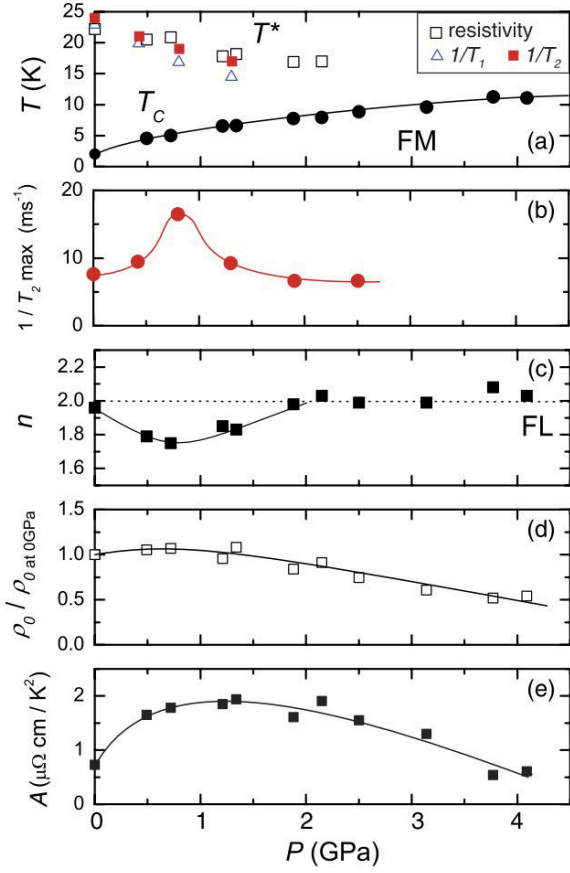


Figure 2.8: (a) Pressure-temperature phase diagram. (b-e) Pressure dependence of the maximum value in $1/T_2$ around T^* , the exponent n , the residual resistivity ρ_0 , and quadratic coefficient of electrical resistivity A [36].

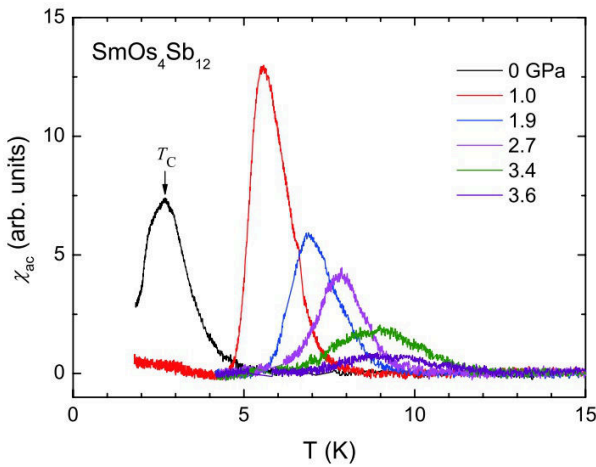


Figure 2.10: Temperature dependence of ac-susceptibility under various pressures [34].

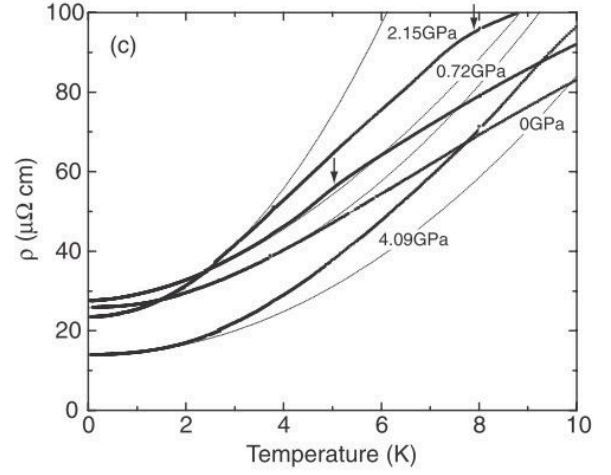


Figure 2.9: Temperature dependence of electrical resistivity ρ under various pressures, displayed with fitting curves, $\rho(T) = \rho_0 + A'T^n$. The kink corresponding to T_C is indicated by arrows [32].

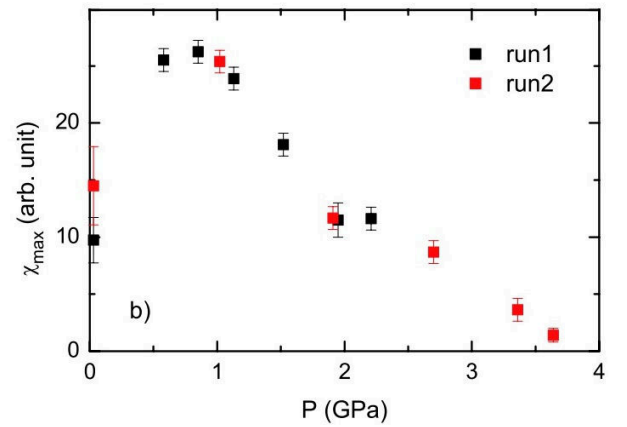


Figure 2.11: Pressure dependence of the peak value of ac-susceptibility at T_C [34].

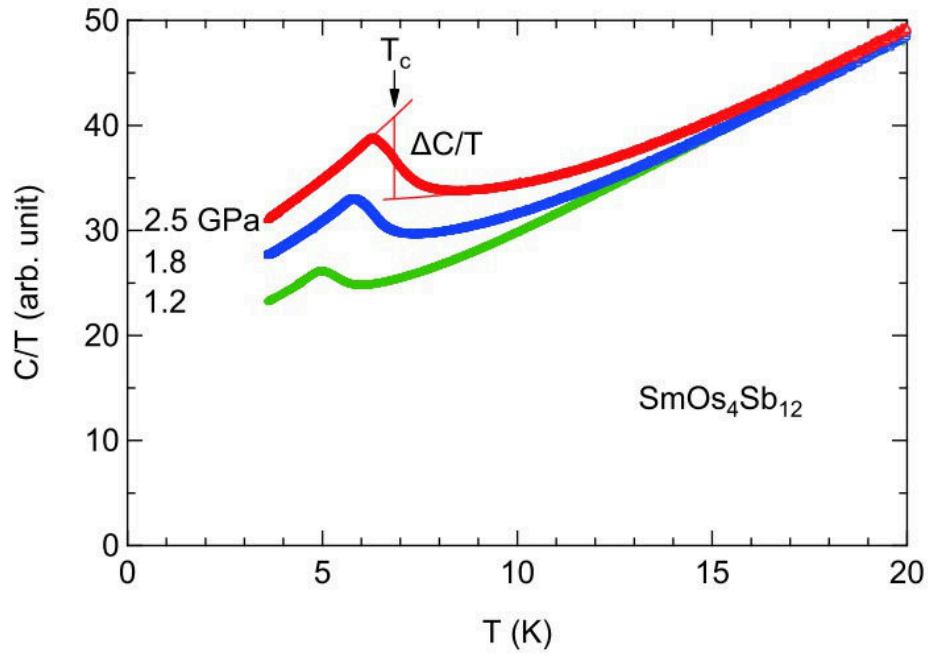


Figure 2.12: Temperature dependence of C/T at several pressures [34].

2.3 Previous Ultrasonic Study on $\text{SmOs}_4\text{Sb}_{12}$

In Fig. 2.13, we show temperature dependence of the elastic constants C_{11} and C_{44} [38]. C_{11} shows two step-like anomalies, which are considered to be due to rattling as mentioned below. C_{44} shows a softening below 80 K and levels off below 20 K. This softening can be explained by strain-quadrupole coupling as we mention in Appendix A. In the inset, measured C_{44} is plotted with fitting curves calculated from assuming the two models. The Γ_5 ground-state model agrees well, while the calculated curve for Γ_{67} ground-state model deviates from the experimental result. Although Γ_{67} model cannot explain the result, it is possible that the c - f hybridization plays a role at low temperatures, which extinguishes the quadrupolar degrees of freedom of the localized $4f$ -electrons. Thus, it is difficult to distinguish which model is suitable for this compound.

In Fig. 2.14, temperature dependences of C_{11} of $\text{ROs}_4\text{Sb}_{12}$ ($R = \text{La, Pr, Nd, Sm}$) measured with various frequencies are shown [38]. Ultrasonic dispersions (UD), *i.e.*, frequency dependent elastic anomalies accompanied by a peak of ultrasonic attenuation, have been observed widely in the family of $\text{ROs}_4\text{Sb}_{12}$. $\text{SmOs}_4\text{Sb}_{12}$ also show ultrasonic dispersions at around 20 K and 55 K. Note that UD is also seen in the C_{11} of non- $4f$ compound $\text{LaOs}_4\text{Sb}_{12}$ and suggests that UDs originate from lattice degrees of freedom. Since anharmonic vibration of guest ion, rattling, is observed in $\text{ROs}_4\text{Sb}_{12}$, these anomalies are considered to be due to resonance of rattling modes and ultrasonic strain. Assuming Arrhenius-type relaxation time, $\tau = \tau_0 \exp(E/k_B T)$, the elastic constant and the attenuation in a ultrasonic dispersion can be described phenomenologically by following Debye-type dispersion,

$$C(\omega) = C_\infty - \frac{C_\infty - C_0}{1 + \omega^2 \tau^2}, \alpha(\omega) = \alpha_0 - \frac{C_\infty - C_0}{2\rho v_\infty^3} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (2.1)$$

where C_∞ and C_0 are high- and low-frequency limit. Two parameter set of activation energy E and the attempt time τ_0 can be determined from Arrhenius plot. We can obtain the relaxation time τ by considering the resonance condition, $\omega\tau = 1$, for each frequency. If we plot $\log\tau$ as a function of $1/T$, so-called Arrhenius plot, we can see linear relation between $\log\tau$ and $1/T$, as described in Fig. 2.14. Then, we can obtain the two parameters, E and τ_0 , from the slope and the ordinate intercept, respectively.

In the previous study on $\text{SmOs}_4\text{Sb}_{12}$, magnetic-field dependence of C_{11} has been reported. Interestingly, the activation energy and the attempt time remain unchanged in magnetic fields of at least 10 T. This magnetically robust feature implies possible relation between the lattice degrees of freedom and the magnetically robust γ . Further study on the ultrasonic response and specific heat in higher magnetic fields would be necessary.

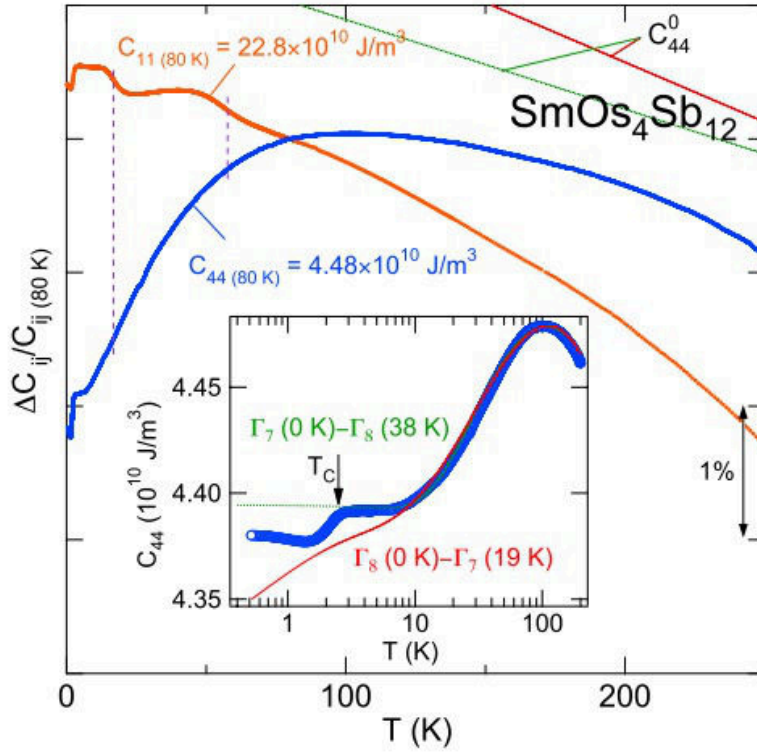
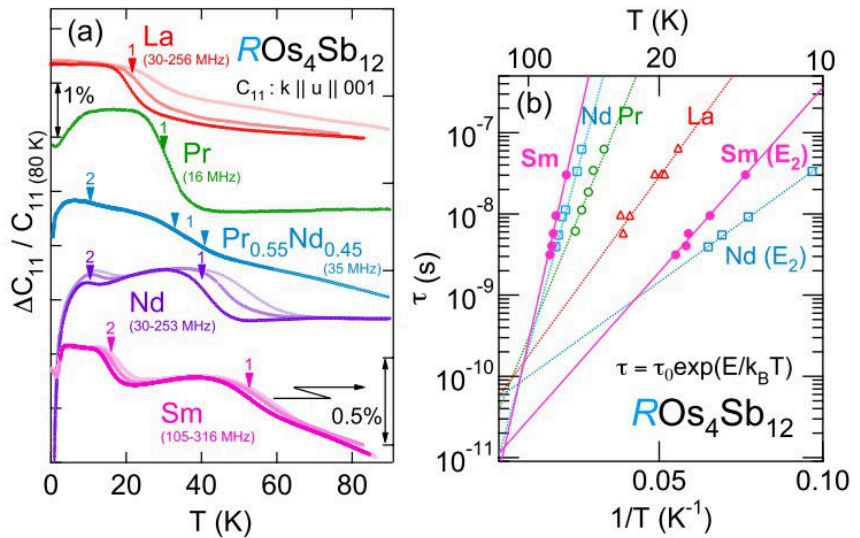


Figure 2.13: Temperature dependence of the elastic constants, C_{11} and C_{44} . In the inset, fitting lines are shown, which are calculated by assuming the two possible CEF models [38].

Figure 2.14: Comparison of UD of $\text{ROs}_4\text{Sb}_{12}$. Temperature dependences of C_{11} of $\text{ROs}_4\text{Sb}_{12}$ with several frequencies are shown. Downward arrow indicate the temperature at which the resonance condition is satisfied. (b) Arrhenius plots of the characteristic temperature and relaxation time of the UD for $\text{ROs}_4\text{Sb}_{12}$ [38].



Chapter 3

Ultrasonic Measurement on $\text{SmOs}_4\text{Sb}_{12}$ in Pulsed Magnetic Field

3.1 Introduction

As mentioned above, one can detect quadrupolar degrees of freedom of localized $4f$ electron. Indeed, ultrasonic measurements have successfully elucidated low-lying CEF states even in several Kondo systems [39, 40]. There are three independent components of elastic strains in the T_h (O_h) symmetry, as listed in Table A.1 of Appendix A, and one can obtain quadrupolar susceptibilities from elastic-constant measurements [41].

One of the possible way to suppress effects of c - f hybridization is applying high magnetic fields. Furthermore, as shown later in Figs. 3.2(b), 3.2(c), 3.3(b), and 3.3(c), the calculated quadrupolar susceptibilities for the two models are clearly different in high magnetic fields. Thus, we can distinguish the CEF ground state by checking whether the elastic constants exhibit an increase or a decrease with increasing magnetic field. Here, we present the results of ultrasonic measurements in pulsed magnetic fields with the conclusion that the CEF ground state in $\text{SmOs}_4\text{Sb}_{12}$ is the Γ_{67} quartet.

3.2 Experimental Details

A single crystal of $\text{SmOs}_4\text{Sb}_{12}$ was grown using the Sb-flux method. The conventional pulse-echo method was employed for the ultrasonic measurements. Pulsed-magnetic field experiments were performed at the Dresden High Magnetic Field Laboratory (Helmholtz-Zentrum Dresden-Rossendorf). The maximum magnetic field was 58.3 T, and the whole pulse duration was ≈ 200 ms (Fig. 3.1). The repetition rate of the ultrasonic pulse was set to 55 kHz. A superconducting magnet was used for static-field measurements up to 17.5 T. Resonance LiNbO_3 transducers were employed for exciting and detecting ultrasonic waves. The ultrasonic frequencies were; 106 MHz for the measurements of C_{11} , 70 MHz for the measurements of C_{44} at 1.5 and 4.2 K, and 19 MHz for the measurement of C_{44} at 8.7 K, in pulsed-magnetic fields. We have not observed any difference between the result for up- and down-sweeps of the pulsed-magnetic field. We conclude that heating of the sample due to eddy currents is negligible.

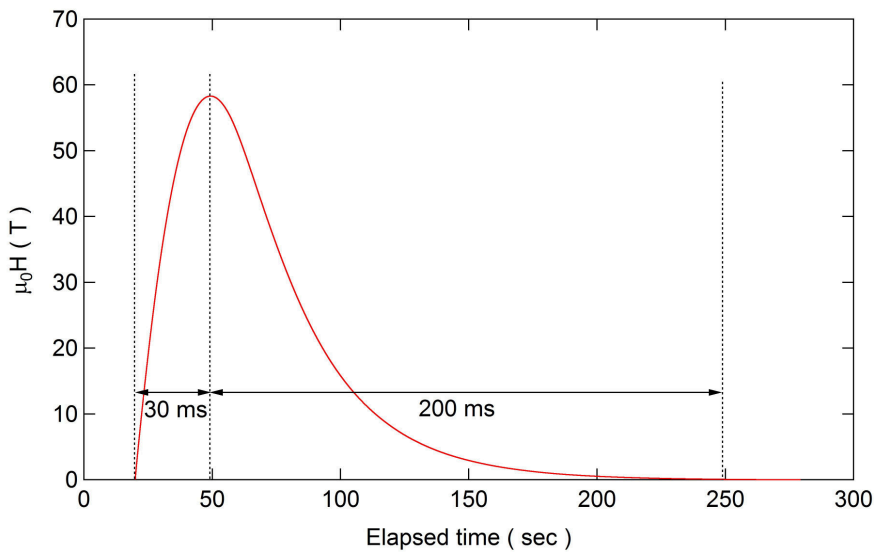


Figure 3.1: (Color online) Profile of the pulsed magnetic field in this study.

3.3 Results and Discussions

Figure 3.2(a) shows the pulsed-field data for C_{44} at various temperatures. This elastic constant exhibits a broad minimum at ≈ 4 and ≈ 10 T for 1.5 and 4.2 K, respectively. This characteristic feature is confirmed by experimental results obtained in static magnetic field and shown as black curves in Fig. 3.2(a). We will discuss the possible origin of this minimum later. At higher magnetic fields, C_{44} again increases with field. These features can be explained by the quadrupolar susceptibility calculated for the Γ_{67} quartet ground state as shown in Fig. 3.2(c). In this case, the magnetic field splits the Kramers doublets of the ground quartet (Zeeman splitting), and the system's quadrupolar degrees of freedom are suppressed. As a result, a reduction of the absolute value of the quadrupolar susceptibility (*i.e.*, an increase of the elastic constants) is expected [Fig. 3.2(c)]. On the other hand, in the case of the Γ_5 doublet ground state, the quadrupolar susceptibility should increase [Fig. 3.2(b)]. Here, the Zeeman splitting produces mixing of the wave functions of the Γ_5 ground state and the excited Γ_{67} quartet state, and the $4f$ -electron system gains quadrupolar degrees of freedom. In Fig. 3.3(a), the relative change of the elastic constant C_{11} is shown. The elastic constant $C_{11} = C_B + \frac{4}{3} \frac{(C_{11}-C_{12})}{2}$ includes not only the bulk modulus C_B , which corresponds to volume change with the Γ_1 symmetry, but also $\frac{(C_{11}-C_{12})}{2}$, which corresponds to the Γ_{23} symmetry, related to the O_2^0 quadrupole. The calculated Γ_{23} -type quadrupolar susceptibilities are shown in Figs. 3.3(b) and (c) for the two different ground states. Here, we compare C_{11} with the calculated quadrupolar susceptibility, $\chi_{\Gamma_{23}}$, assuming that the change of the Γ_{23} component of the elastic constant, $\frac{(C_{11}-C_{12})}{2}$, is dominant. As can be seen, again our high-field experimental results for C_{11} can be explained well by the Γ_{67} ground-state model. In order to estimate the magnetic-field dependence of C_B more precisely, measurements of the thermal expansion in magnetic fields would be necessary.

Next, we discuss the results obtained at low magnetic fields. Here, a local minimum in C_{11} at 4.2 K and a relatively large decrease in C_{44} have been observed [Figs. 3.2(a) and 3.3(a)]. To explain these features, we consider two origins.

The first one is the magneto-elastic coupling due to an induced weak ferromagnetic moment, which is induced spontaneously below $T_C \approx 2.5$ K in zero magnetic field [15, 28]. Since the magnetic field above 10 T polarizes the ferromagnetic moments, we can treat the system as a polarized paramagnetic phase [15]. In this case, we can ignore this magneto-elastic effect and only consider CEF effects above 20 T.

The other possible origin is the Kondo screening, which is due to c - f hybridization and can be suppressed by a magnetic field. In Figs. 3.4(a) and 3.4(b), we compare the magnetic-field and temperature-sweep results in order to estimate the role of the Kondo effect in this system and verify the limit of applicability of a localized electron picture. Figure 3.4(a) represents the magnetic-field dependence (bottom axis) and the temperature dependence (top axis) of the elastic constant C_{44} . Figure 3.4(b) shows the results of the calculation of C_{44} , based on the quadrupolar susceptibility for O_{yz} ($= J_y J_z + J_z J_y$). In our analysis, we took into account the temperature-dependent mixed-valence state by multiplying the quadrupolar susceptibility by the ratio of Sm^{3+} to Sm^{2+} , $r_v = 0.83 - 0.76$. Note that Sm^{2+} ($J = 0$) has no contribution to the quadrupolar susceptibility. The temperature dependence of the average valence of the Sm ions is assumed to be linear between +2.83 at 150 K and +2.76 at 20 K and constant below 20 K in accordance with Ref. 7. The elastic constant $C_{44} = C_{44}^0 - \frac{N g^2 r_v \chi_{\Gamma_4}}{(1 + g' r_v \chi_{\Gamma_4})}$ is calculated with $C_{44}^0 = 4.91 \times 10^{10}$ J/m³, $N = 2.50 \times 10^{27}$ m⁻³, $|g_{\Gamma_4}| = 435$ K and $g'_{\Gamma_4} = -1$ K, where C_{44}^0 , N , g_{Γ_4} , g'_{Γ_4} , r_v , and χ_{Γ_4} are the background elastic constant, the number of magnetic ions per unit volume, the quadrupole-strain coupling constant, the inter-site quadrupole-

quadrupole coupling constant, the ratio of Sm^{3+} , and the quadrupolar susceptibility, respectively. In the calculation of the magnetic-field dependence, we used the averaged valence at zero magnetic field, since there has been no previous report on the magnetic-field dependence of the valence state of Sm ion in $\text{SmOs}_4\text{Sb}_{12}$. Comparing Fig. 3.4(a) and Fig. 3.4(b), the quantitative agreement between both temperature and magnetic-field results is obvious except at low temperatures and low magnetic fields. Below $T^* \approx 20$ K, the experimental data decrease less strongly towards low temperatures, while the decrease in the calculated elastic constant continues below 20 K. As discussed in Ref. 38, this deviation can be explained by a modified quadrupolar susceptibility picture that includes a crossover to a Kondo-singlet state, where $4f$ electrons lose their localized character at low temperature in zero magnetic field. On the other hand, the amount of change in the experimental results of C_{44} is also comparable to that of the calculation for $H > 10$ T and $T > 20$ K. This means that a significant response of quadrupolar degrees of freedom is observed at high fields, while they recover their localized character. Thus, we conclude that the softening and the minima in the elastic constants versus field at low-temperatures can be explained by a combination of the above-mentioned two effects: the recovery of the localized character and the magneto-elastic coupling. In order to carry out a quantitative analysis, measurements of elastic constants with other geometry, such as $(C_{11} - C_{12})/2$, or C_{44} for other magnetic-field directions, would be necessary.

Finally, we discuss how robust the heavy-fermion state is in a magnetic field. According to the above discussion, we conclude that a typical Kondo effect of magnetic origin exists, that is suppressed by magnetic field, *i.e.*, the system recovers the localized character of $4f$ electrons by applying magnetic field. Indeed, the signature of the Kondo effect is also found in NQR measurements [36]. On the other hand, the robustness of the Sommerfeld coefficient has also been reported, which implies that the present compound possesses a magnetically stable heavy-fermion state [15]. This feature is, however, not verified above 8 T. Our ultrasonic results suggest that magnetic fields above 10 T are sufficient to suppress the Kondo effect. To gain more information on the relation between the large γ value and the Kondo-like screened state of this material, further studies, such as magnetization or resistivity measurements in high magnetic field $\mu_0 H > 20$ T would be necessary.

3.4 Summary

We have performed ultrasonic measurements of $\text{SmOs}_4\text{Sb}_{12}$ in pulsed magnetic fields up to 58 T. The magnetic-field dependences of the elastic constants suggest that the present system possesses a Γ_{67} -quartet CEF ground state. In our CEF analysis, we assume a simple localized picture of $4f$ electrons, which describes qualitatively our experimental results obtained above 10 T and at high temperatures as well. Moreover, our results show that the Kondo-like screening due to $c - f$ hybridization dominates the low-temperature and low-magnetic-field physics of $\text{SmOs}_4\text{Sb}_{12}$. We conclude that the system recovers localized character of $4f$ electrons in magnetic fields above 10 T.

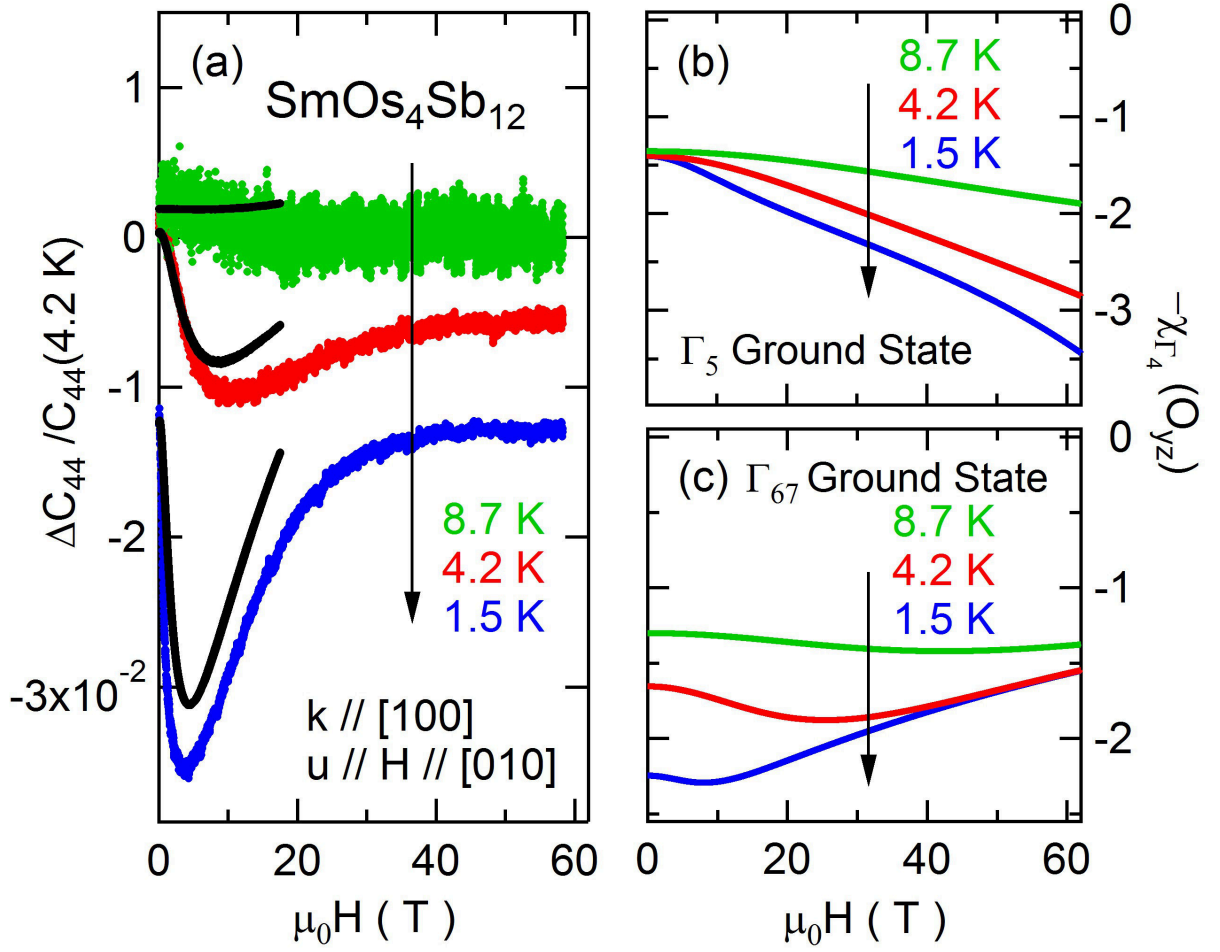


Figure 3.2: (Color online) (a) Relative change of the elastic constant, $\Delta C_{44}/C_{44}$, versus magnetic field. The pulsed-field data ($\mathbf{k} \parallel \langle 100 \rangle$ and $\mathbf{u} \parallel \mathbf{H} \parallel \langle 010 \rangle$, color plots) and static-field data ($\mathbf{H} \parallel \mathbf{k} \parallel \langle 001 \rangle$ and $\mathbf{u} \parallel \langle 010 \rangle$, black curves) are shown. The zero-field values of the experimental results are calculated based on the temperature dependence of C_{44} , which is shown in Fig. 3.4 (a). (b) Magnetic-field dependence of the quadrupolar susceptibility, $\chi_{\Gamma_4}(O_{yz})$, calculated for the Γ_5 ground state and the Γ_{67} first excited state, separated by a gap $\Delta \approx 38$ K. (c) The same as in (b) but for the Γ_{67} ground state and the Γ_5 first excited state separated by $\Delta \approx 20$ K (see text for details).

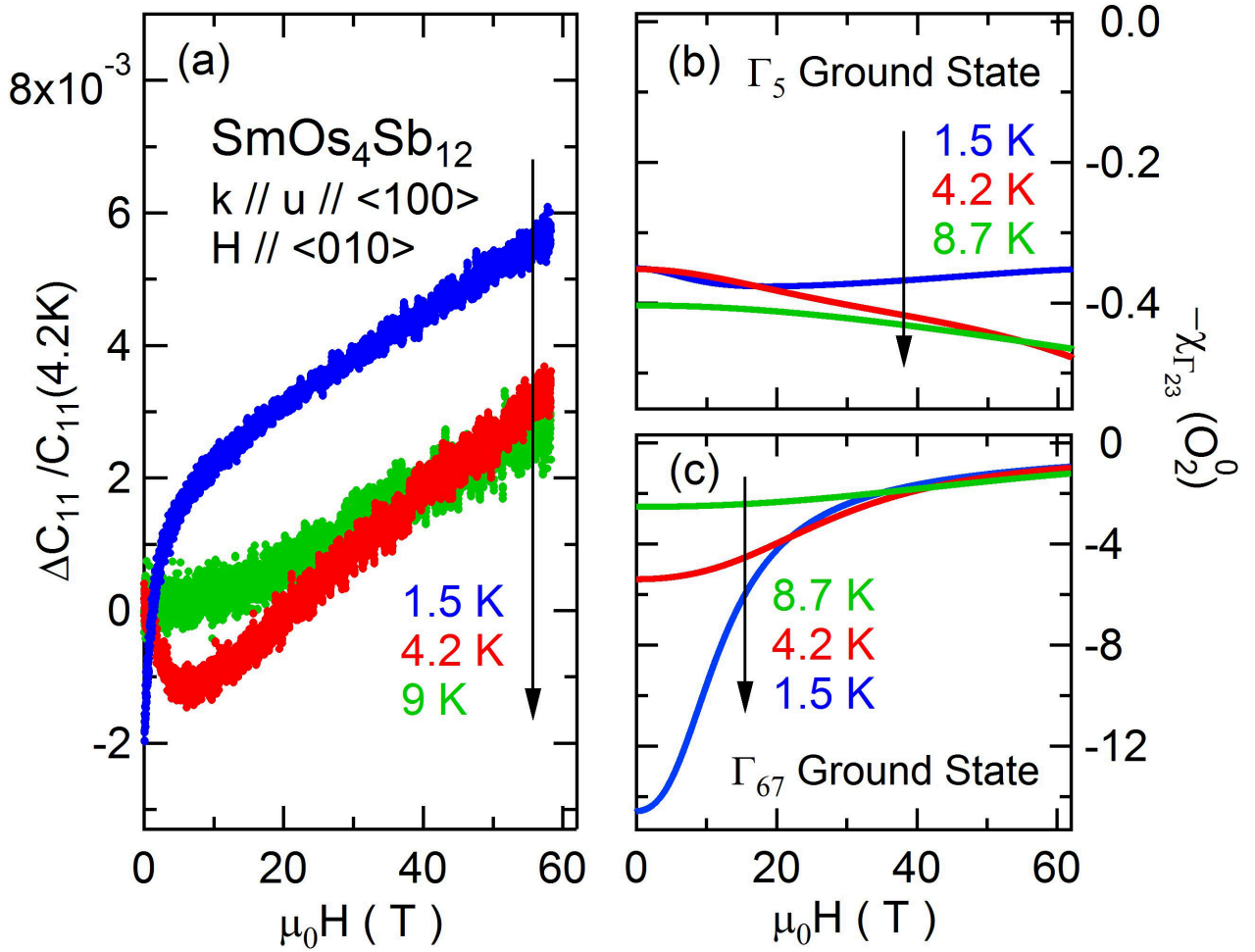


Figure 3.3: (Color online) (a) Relative change of the elastic constant C_{11} versus magnetic field. The zero-field values of the experimental results are calculated based on the temperature dependence of C_{11} reported in Ref. 38. (b) Field dependence of the quadrupolar susceptibility, $\chi_{\Gamma_{23}}(\text{O}_2^2)$, calculated for the Γ_5 ground state and the Γ_{67} first excited state separated by a gap $\Delta \approx 38$ K. (c) The same as in (b) but for the Γ_{67} ground state and the Γ_5 first excited state separated by $\Delta \approx 20$ K (see text for details).

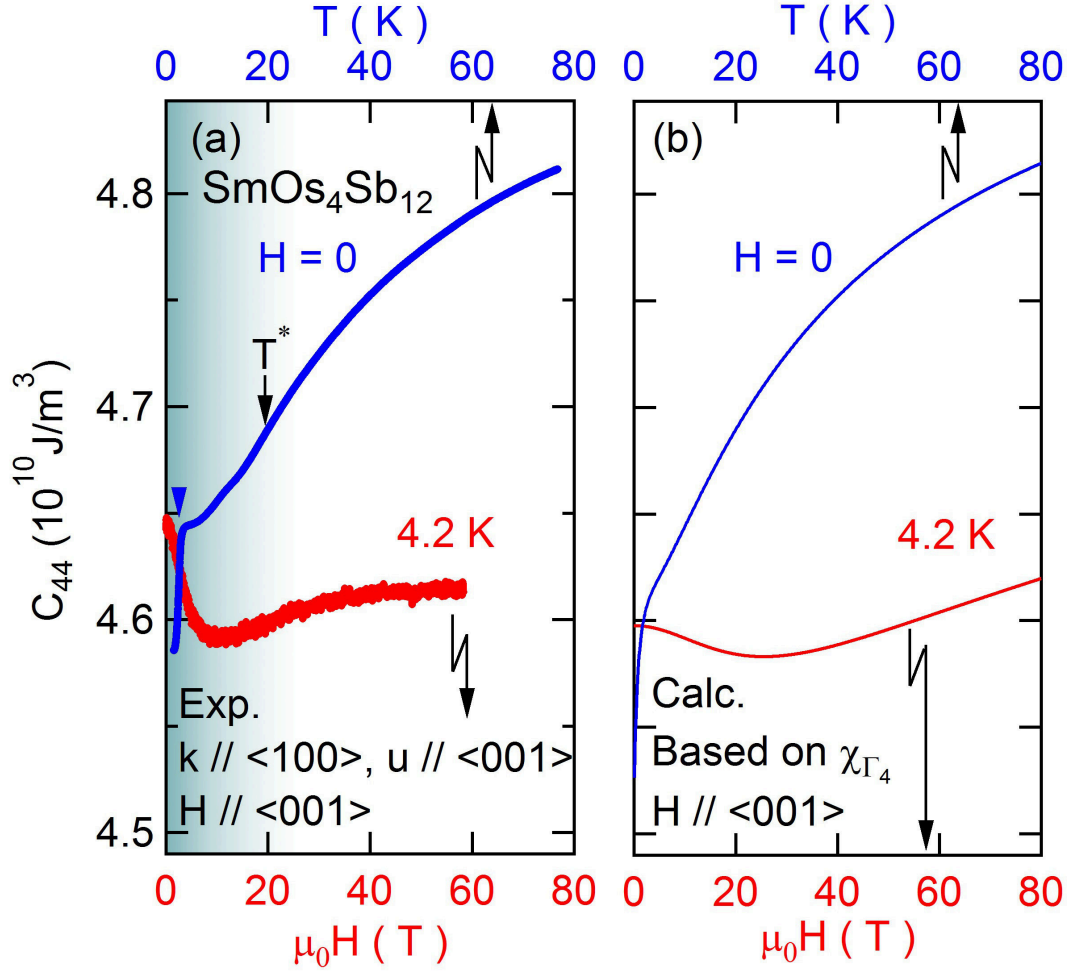


Figure 3.4: (Color online) Red curves show the measured (a) and calculated (b) magnetic field dependence of C_{44} at 4.2 K . Blue curves represent the measured (a) and calculated (b) temperature dependence of C_{44} at 0 T . The calculations are based on the quadrupolar susceptibility for Γ_4 symmetry and a Γ_{67} ground state (see text for details). The colored background region in (a) indicates the temperature and magnetic field regions where $4f$ electrons are considered to be less localized.

Chapter 4

Ultrasonic Measurement on $\text{SmOs}_4\text{Sb}_{12}$ under Hydrostatic Pressure

4.1 Introduction

We have performed ultrasonic measurement under hydrostatic pressure in order to investigate

- how the c - f hybridization is controlled by pressure
- the possible contribution of multipoles to the physical property
- relation between rattling and the $4f$ -electron state

By means of ultrasonic measurements, one can obtain a response of quadrupole moments of localized $4f$ electrons, as we show in the previous chapter. Furthermore, ultrasonic measurement is a powerful tool to detect the electrical fluctuations due to rattling as well as quadrupoles, as we described in Chap. 2. Thus, we can expect that ultrasonic measurements with controlling the strength of c - f hybridization by pressure will provide crucial information for understanding the exotic HF state of this material.

4.2 Experimental Procedure

In order to carry out ultrasonic measurements with high-frequency ultrasonic waves under hydrostatic pressure, two semi-rigid coaxial cables (SC-033/50: Coax Co. Ltd.), which have a diameter of 0.33 mm ϕ for Cu-shield sleeve and Au-deposited W-core cable with diameter of 0.08 mm ϕ for impedance (50 Ω) matching, were installed into the pressure cell. As described in Fig. 4.1, the sample was mounted on the delaminated outer conductor of the coaxial cables, which works as a thermal anchor between the sample and thermometers. The edge of the dielectric (PTFE) and shield tubes (Cu) are sealed with Stycast 1266. By this setup, we have obtained a very clear ultrasonic-echo signal under high pressures at 4.2 K, as shown in Fig. 4.2. In the present study, we have achieved ultrasonic measurements with variable frequencies up to 320 MHz.

A single crystalline $\text{SmOs}_4\text{Sb}_{12}$ grown by Sb-self flux method was used in this study. LiNiO_3 transducers were attached on the sample with superglue (GEL-10: TOAGOSEI Co. Ltd.) to excite and detect ultrasonic waves.

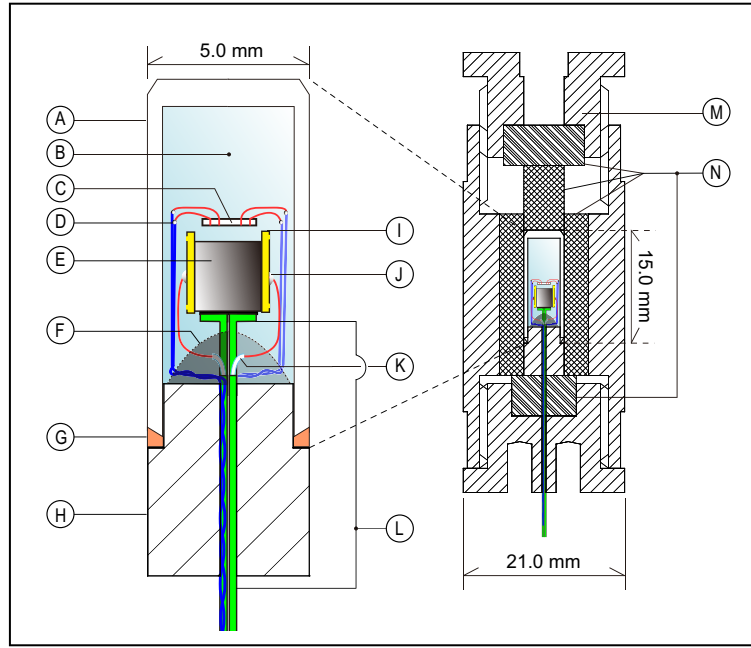


Figure 4.1: Hydrostatic-pressure ultrasonic measurement setup. A: Teflon capsule, B: Daphne 7373 for pressure medium, C: tin stick for a manometer, D: Cu line, E: Sample, F: Stycast 1266, G: CuBe seal ring, H: Body of a CuBe plug, I: LiNbO_3 transducer, J: Ag paste, K: Teflon insulation shield and inner conductor of semi-rigid coaxial cable, L: Cu outer shield of semi-rigid coaxial cable, M: Cu-Be parts (nuts and cylinder), N: WC cylinder and pusher.

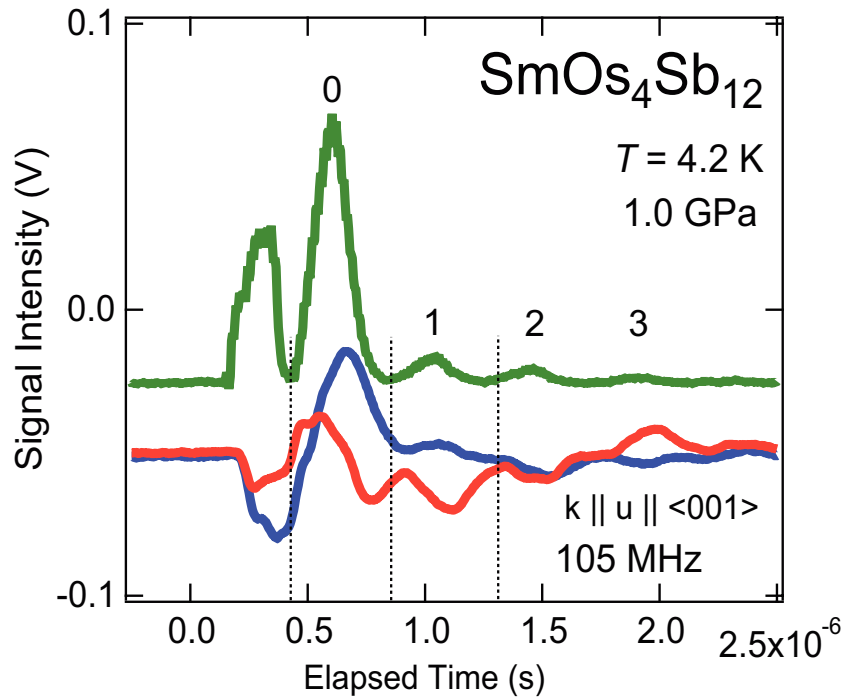


Figure 4.2: Ultrasonic echo signal (Green) and phase signals (Blue and Red) of longitudinal C_{11} mode with 105 MHz at 1 GPa.

4.3 Results and Discussions

Figure 4.3 shows temperature dependence of C_{44} measured at various pressures. The elastic anomalies at T_C are step-like. Thus, we defined T_C as the temperature at which the first differential, dC/dT , has a peak. Below 80 K, C_{44} exhibits a decrease with decreasing temperature, a softening, at all of the pressures. Assuming the Γ_{67} quartet CEF ground state, this softening can be explained by the strain-quadrupole coupling. The black curves in Fig. 4.4 represent calculated relative change of C_{44} . We used the formula $C_{44} = C_{44}^0 - \frac{Ng^2\chi_{\Gamma_4}}{(1+g'\chi_{\Gamma_4})}$, where C_{44}^0 , N , g , χ_{Γ_4} and g' are background elastic constant, the number of magnetic ions per unit volume, the quadrupole-strain coupling constant, the quadrupolar susceptibility and the inter-site quadrupole-quadrupole coupling constant, respectively [41]. Here, we discuss only the relative change of the temperature dependence and will not determine the absolute value of C_{44}^0 and g . The inter-site quadrupole-quadrupole coupling constant, g' , is negative at all of the pressures, which suggests antiferro quadrupolar interaction. g' is -1.55 and -1.5 K at ambient pressure and 0.35 GPa, respectively, and at 0.69 and 0.96 GPa, g' is -0.9 K. The calculated C_{44} based on the quadrupolar susceptibility well reproduces the softening above $T^* \approx 17$ K. On the other hand, below T^* , the result deviates from the calculated curve. This deviation can be explained as follows; $4f$ -electrons gradually lose their localized character with decreasing temperature due to the c - f hybridization, and quadrupolar degrees of freedom are suppressed. Thus, the softening of C_{44} , which is caused by the quadrupole moment of $4f$ electrons and its coupling to the elastic strain with the same symmetry, should be suppressed as the temperature decreases. For the data obtained under hydrostatic pressure of 0.36 GPa, the calculation can reproduce the softening of C_{44} down to 8 K. The temperature, T^* , at which the result deviates from the calculated quadrupolar susceptibility is lower than that at 0 GPa. This fact are consistent with the results of electrical resistivity and NMR measurements under hydrostatic pressure mentioned in chapter 2 [36]. Above 0.7 GPa, the calculation reproduces the whole feature of the C_{44} well down to T_C . Thus, we conclude that $4f$ electrons are well localized above $T_C \approx 4$ K at 0.7 GPa. This fact also suggests that the CEF ground state is Γ_{67} quartet also under high pressure, since the Γ_5 CEF ground state model predicts leveling off of the softening below ≈ 10 K [38].

In Fig. 4.4, we show the temperature dependence of the elastic constant C_{11} measured with 250 MHz under various hydrostatic pressures. At ambient pressure, C_{11} shows an abrupt decreasing at around T_C and shoulder-like anomalies at around 15 and 55 K, which are ultrasonic dispersions (UDs) as described above. A clear pressure dependence of the elastic anomalies of UD can be seen. Between these UD, C_{11} shows a softening. This softening would also be due to the strain-quadrupole coupling. This softening must level off below $T^* \approx 17$ K in the same manner as in C_{44} . The presence of the UD at around 15 K, however, makes it difficult to distinguish the cross-over phenomena. By applying pressure, the softening of C_{11} increases and continues down to T_C and the elastic anomaly at T_C increases drastically, which is again explained by an enhancement of the localized character of $4f$ electrons as discussed in the results of C_{44} . The upturn at around 15 K at ambient pressure is getting smaller by applying pressure and seems to disappear at around 0.65 GPa. Below T_C , C_{11} shows step-like elastic anomalies under pressures greater than 0.65 GPa.

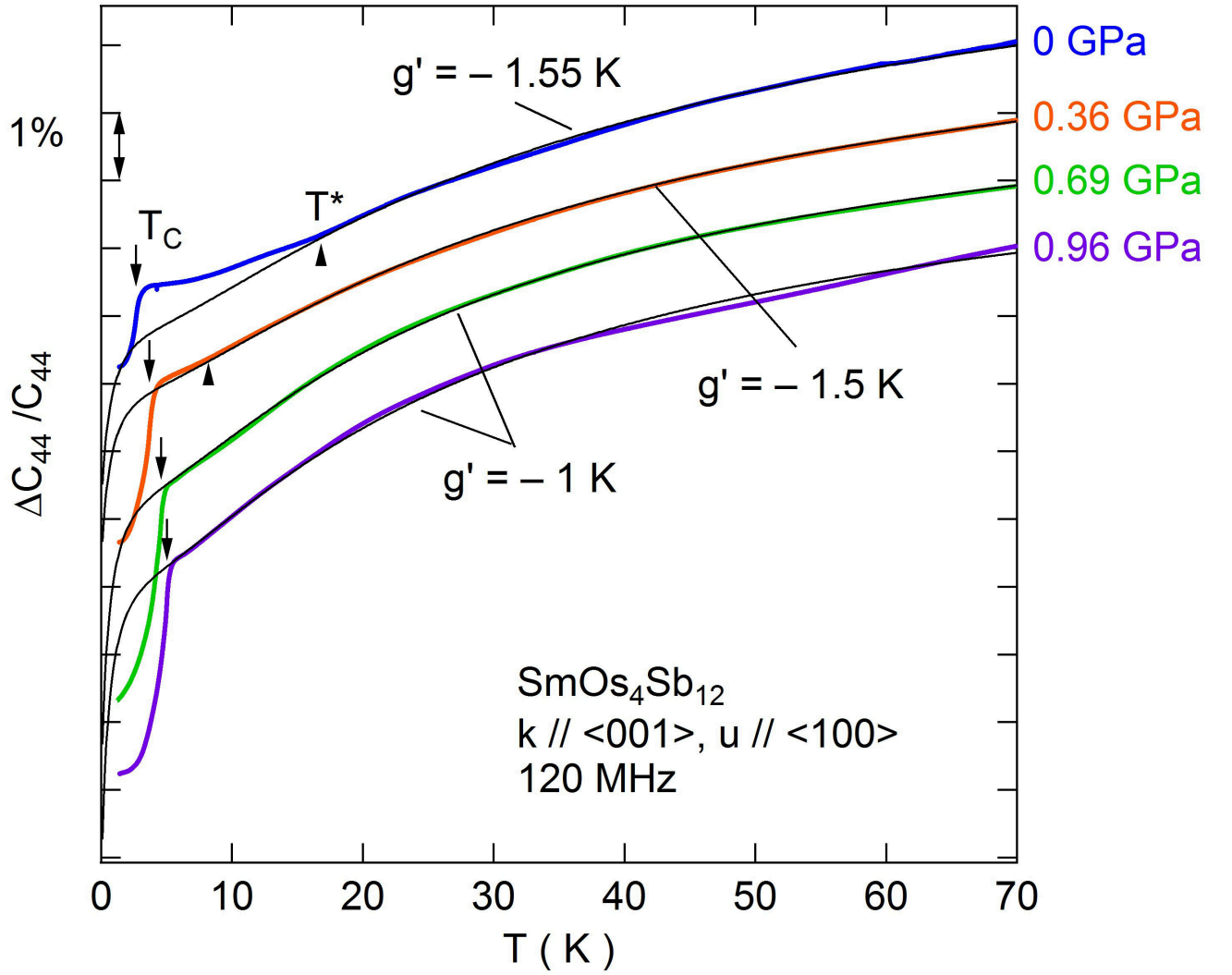


Figure 4.3: Color curves represent the relative change of C_{44} versus temperature at various hydrostatic pressures. Black curves represent the calculated elastic constant based on the localized $4f$ -electron model assuming $\Gamma_{67}(0 \text{ K})$ – $\Gamma_5(20 \text{ K})$. The upward arrows represent the characteristic temperature, T^* , at which the result deviates from the calculation. The downward arrows indicate the ordering temperature, T_C .

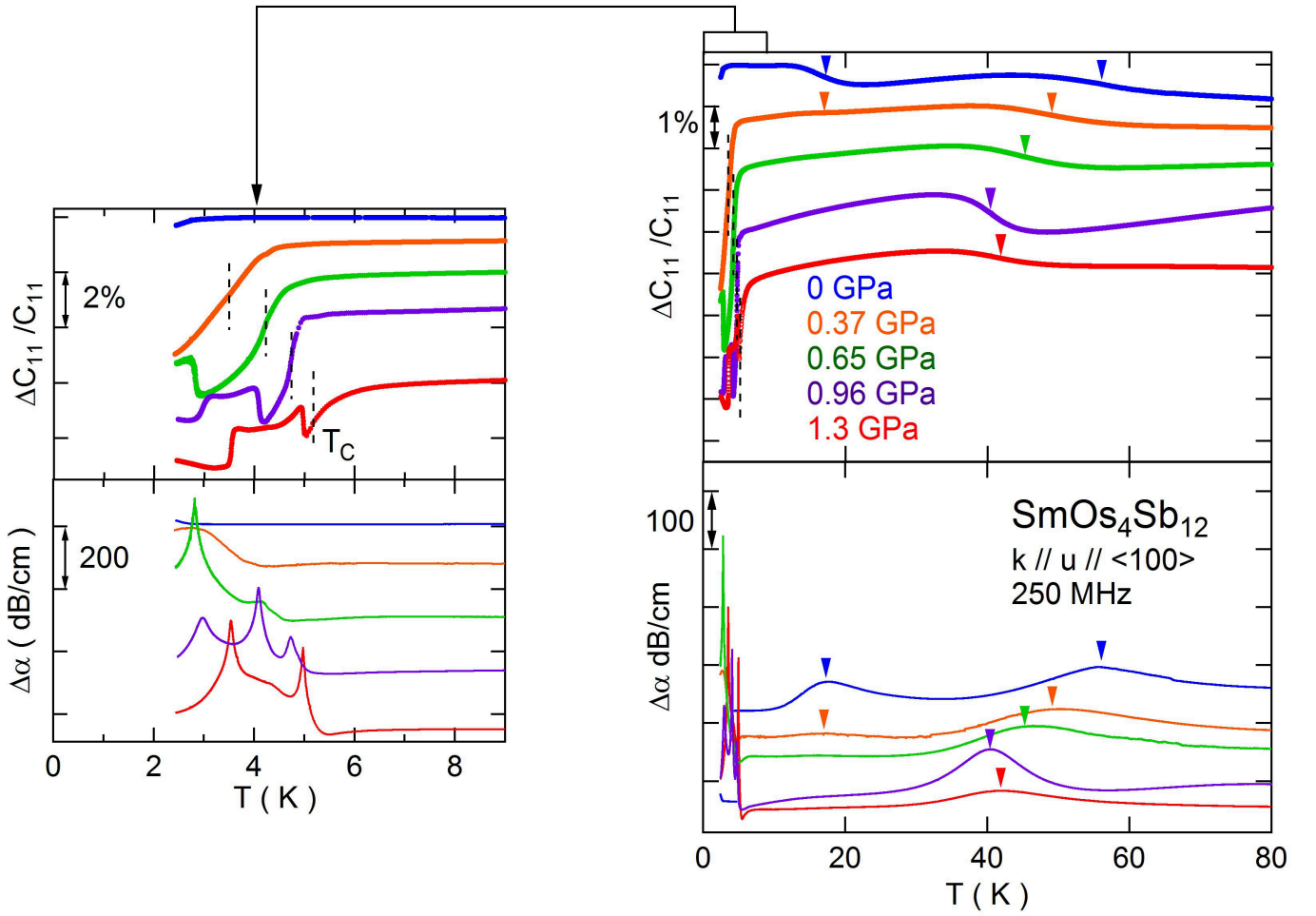


Figure 4.4: Relative change of C_{11} versus temperature measured with 250 MHz at various hydrostatic pressures. The downward arrows indicate the temperatures at which the resonance relation, $\omega\tau = 1$, is satisfied.

In Fig. 4.5, we show a phase diagram and the pressure dependence of the elastic anomaly at T_C , ΔC , of C_{11} and C_{44} . Although both of the elastic constants show a large anomaly at T_C by applying pressure, which would also be explained by an enhancement of the localized character, the enhancement of the elastic anomaly of C_{11} is drastic compared to that of C_{44} . This fact implies a possible coupling between the strain which corresponds to C_{11} and induced quadrupole moments. At ambient pressure a FM order along $\langle 100 \rangle$ has been proposed by muon relaxation scattering [42]. The magnetic dipolar ordering along $[001]$ induces quadrupole moment O_2^0 , which couples to the elastic strain corresponding to the elastic constant C_{11} . Thus, the ordered FM moment would largely be enhanced by applying pressure of 0.4 GPa, and its coupling to the strain would be the origin of the drastic enhancement of the elastic anomaly of C_{11} . This drastic change would have same origin as disappearance of NQR signal in wide range at 0.4 GPa, which has been reported in Ref. 37. Moreover a peak of ac-susceptibility increases rapidly by applying pressure of about 0.5 GPa [34]. These facts imply that the ordered state changes drastically to localized FM order from itinerant FM order by applying pressures greater than about 0.4 GPa. Note that this pressure value is close to the onset of NFL region, which is reported in Ref. 32. Moreover, as can be seen in the phase diagram, the pressure at which T^* becomes lower than T_C seems to correspond to that at which the quadratic term of the electrical resistivity, n , shows a minimum. Thus, these facts suggest that the NFL behavior would have some relation to the change of the localized character of $4f$ electrons.

Here, we comment on the unusual feature of the ordered state at high pressures. In the case of magnetic dipolar order along $[001]$, induced O_2^0 quadrupole moments increase as the ordered magnetic dipole moment increases with decreasing temperature. Thus, quadrupolar degrees of freedom are suppressed, and C_{11} should show a hardening below T_C . This expectation is also derived by a mean-field calculation of the quadrupolar susceptibility, $\chi_{\Gamma_{23}}$, assuming the magnetic order along $[001]$ (see next section). In the case of C_{44} , the Γ_5 -type quadrupolar degrees of freedom are suppressed by the splitting of the $4f$ -energy levels due to magnetic order, and a hardening of C_{44} below T_C is expected by the calculation (see next section). On the other hand, the measured C_{44} does not show hardening below T_C . Although C_{11} shows a small hardening, this hardening is much smaller than that expected by the calculation. Thus, this suppression of the hardening below T_C cannot be explained by simple ferromagnetic dipolar order of localized $4f$ electron. One of the possible explanations is that multipole-multipole interaction would play an important role, which has also been discussed some of other Sm compounds [17]. Another possible origin is some other fluctuations, such as c - f hybridization and/or valence fluctuations.

Next, we describe the pressure dependence of ultrasonic dispersions (UDs). In Fig. 4.6, we show temperature dependence of C_{11} and ultrasonic attenuation, $\Delta\alpha$, at 1.3 GPa measured with various frequencies. As can be seen, a clear UD, *i.e.*, frequency dependent elastic anomaly and ultrasonic absorption, was observed also under the high pressure. To the best of our knowledge, this is the first observation of the frequency dependence of elastic constants with wide frequency range at high pressure. The UD which appears at higher temperatures, UD(high), shifts to lower temperatures with increasing pressure to 0.96 GPa. As can be seen in Fig. 2.14, UD appears at higher temperatures as atomic number increases. Namely, as the ionic radius increases, the temperature at which UD appears shifts to low temperatures. By applying pressure, cage size will decrease, and relative size of the guest ion become larger. Thus, the UD is expected to shift to low temperatures as observed below 0.96 GPa. However, at 1.3 GPa, the elastic anomaly of UD(high) at 250 MHz is broader and appears at higher temperatures. This fact cannot be explained by the analogy above and suggests possible relation between the other parameters, such as recovery of the localized character and change of the valence

state. In Fig. 4.7 (a), we show an Arrhenius plot obtained from C_{11} under several pressures. In Fig. 4.7 (b), obtained parameters from Arrhenius plot are shown. We can see an abrupt increase of the activation energy. This might be due to abrupt change of the anharmonic potential of the guest ion. On the other hand, it is reported that the temperature dependence of averaged valence changes by applying pressure, and the temperature at which averaged valence starts to decrease has a minimum around 1 GPa [43]. The size of an ion strongly depends on the valence. Thus, UD(high) would be affected by this change of the valence state. For further investigation, more measurements of UD and valence state around 1 GPa would be needed.

The UD which appears at lower temperatures, UD(low), gradually disappears with increasing pressure. Interestingly, this UD seems to disappear at the pressure where T^* becomes smaller than T_C . This fact implies a possible relation between UD(low) and the c - f hybridization. In order to check the relation between UD(low) and localized character of $4f$ electrons, ultrasonic measurements of C_{11} in high magnetic fields would be needed, since a recovery of the localized character of $4f$ electrons has been observed in our ultrasonic measurements above 20 T at ambient pressure.

Below T_C , we newly found two step-like elastic anomalies at high pressures, which are accompanied by sharp peaks of ultrasonic absorption. As can be seen in Fig. 4.6, this anomaly is frequency-dependent. Thus, this anomaly would be due to some resonance between ultrasonic strain and phonon modes. Moreover, C_{44} does not show this type of anomalies, *i.e.*, these anomalies are mode selective as with UD(low) and UD(high). Thus, these anomalies seem to have the same origin as the UDs. Assuming the resonance relation, $\omega\tau = 1$, is satisfied at the temperature where a peak of absorption appears, the relaxation time τ seems to diverge between the two anomalies (Fig. 4.8). This fact suggests a freezing of some phonon modes, which couple to Γ_1 and/or Γ_{23} strain waves. We also observed this type of elastic anomaly at 0.96 and 0.65 GPa with 250 MHz as can be seen in Fig. 4.4. Interestingly, this anomaly seems to appear under high pressure where UD(low) disappears. These experimental facts of the frequency-dependent and mode-selective elastic anomalies led us to one simple assumption as follow: the anharmonic potential of the guest Sm ion might change, as the character of $4f$ electrons changes from itinerant to localized character by applying pressure. The origin and tripartite relationship among c - f hybridization, valence fluctuation, local charge fluctuation due to rattling, and multipolar interactions are still open questions. Further measurements at higher pressure in wide temperature and frequency range would be needed to solve issues.

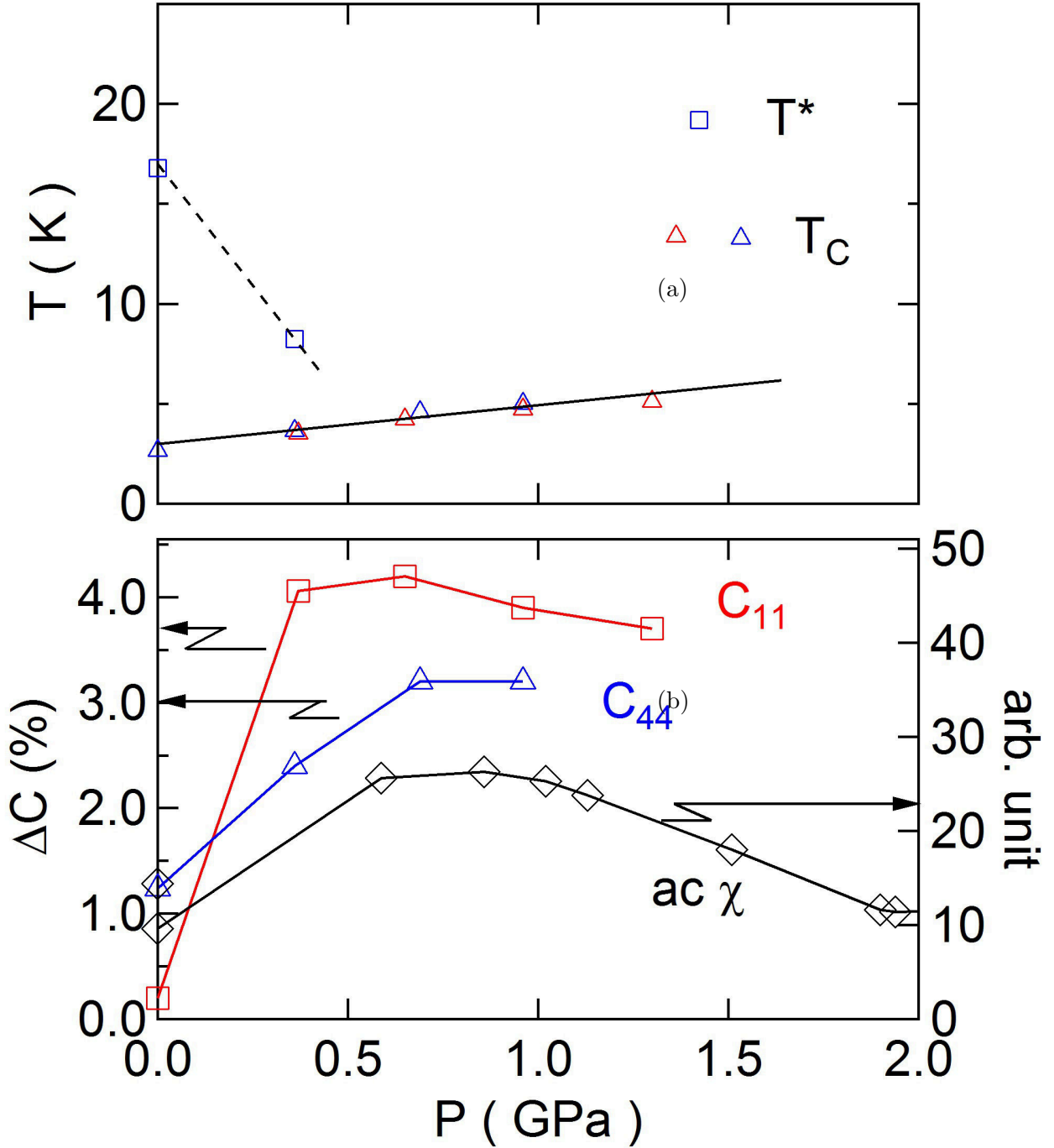


Figure 4.5: (a) T - P Phase diagram of $\text{SmOs}_4\text{Sb}_{12}$. (b) Amount of change in C_{11} (red) and C_{44} (blue) at T_C . Here, we plotted pressure dependence of the peak of ac susceptibility at T_C , which was extracted from Ref. 34, for comparison.

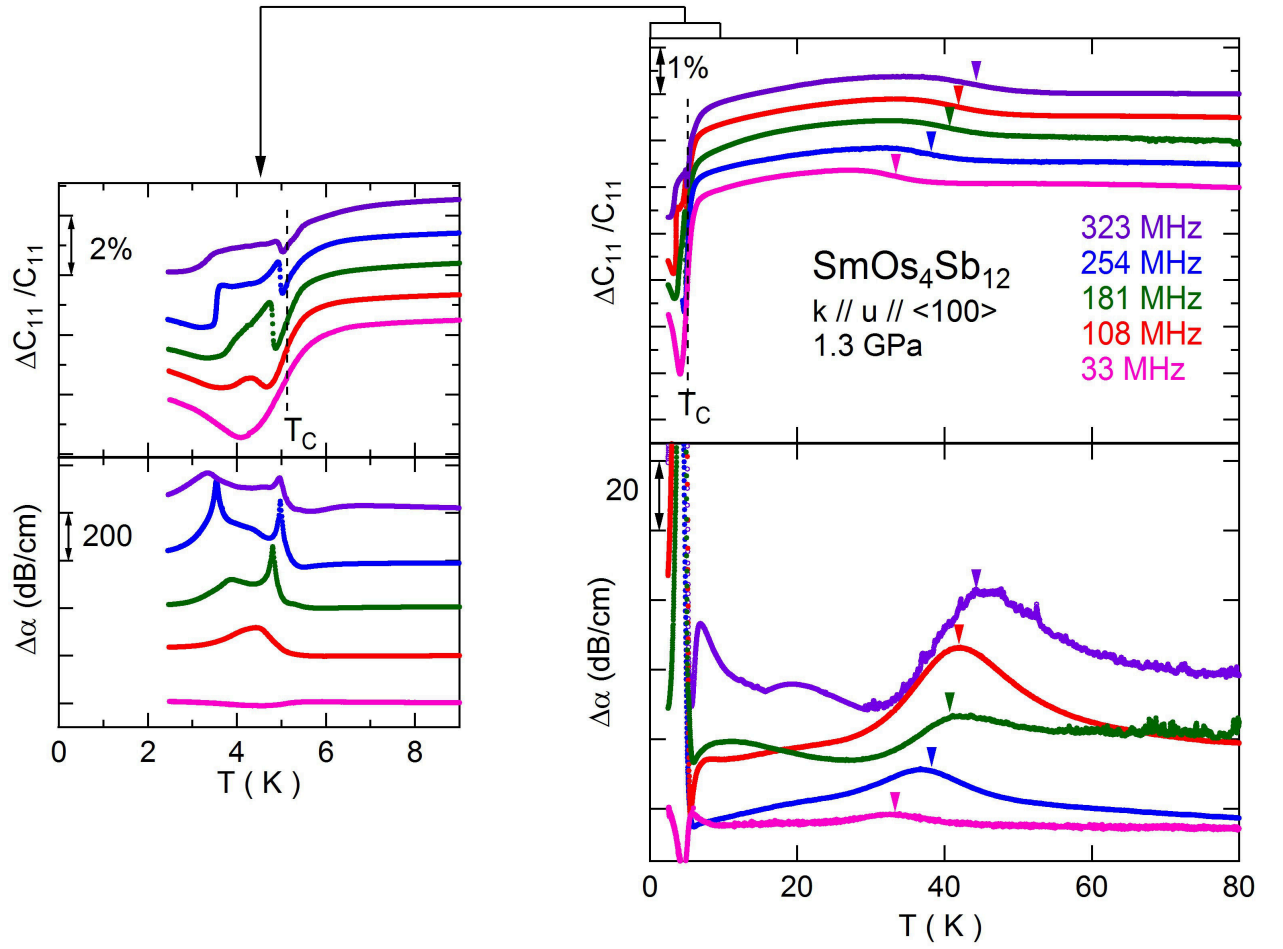


Figure 4.6: Temperature dependence of C_{11} and $\Delta\alpha$ at 1.3 GPa with various frequencies. Downward triangles indicate the temperatures at which the resonance relation, $\omega\tau = 1$, is satisfied.

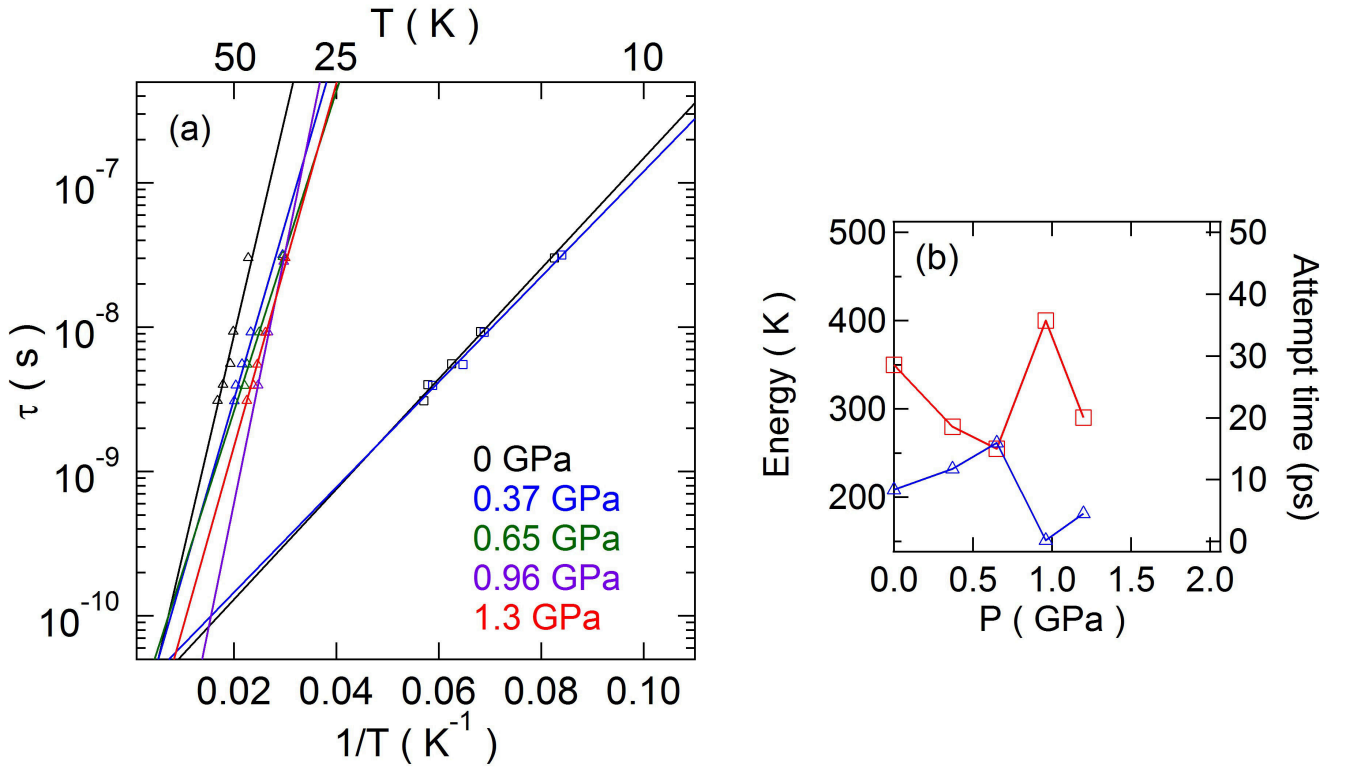


Figure 4.7: (a) Arrhenius plot for UD of $\text{SmOs}_4\text{Sb}_{12}$. (b) Pressure dependence of activation energy and attempt time.

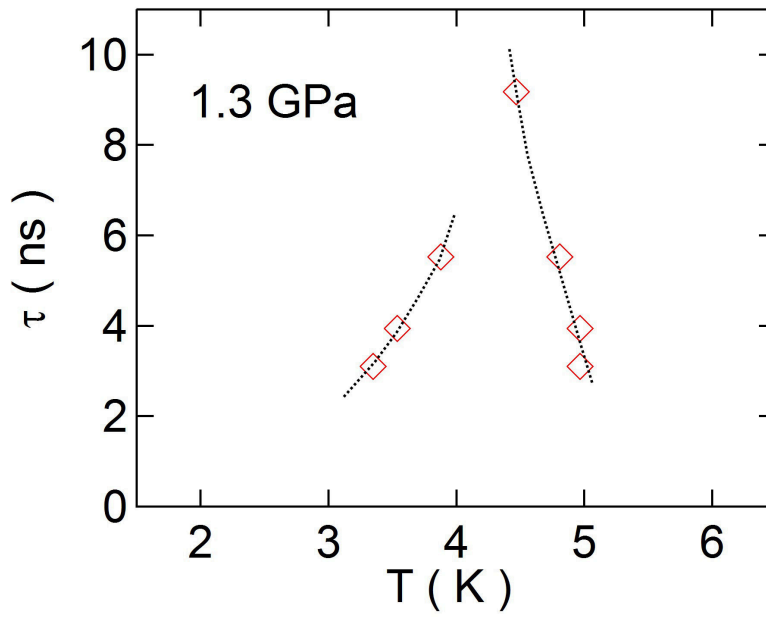


Figure 4.8: Relaxation time τ vs. temperature at 1.3 GPa obtained from peak of the attenuation.

4.4 Summary

In summary, we have achieved high-frequency and high-pressure ultrasonic measurements on the filled skutterudite $\text{SmOs}_4\text{Sb}_{12}$. We have clearly observed a cross over from the itinerant $4f$ -electron region to localized $4f$ -electron region at around 0.7 GPa. We would like to emphasize that this is the first observation of pressure dependence of the character of $4f$ electrons by means of ultrasound. The Γ_{67} CEF ground state and multipolar degrees of freedom of $4f$ electrons in this material are also confirmed. We have also achieved measurements of the ultrasonic frequency dependence of the UDs due to rattling under high pressures. The results imply a possible relation between the local charge fluctuation and the character of $4f$ electronic states of this compound.

Chapter 5

Mean-field Analysis

5.1 Mean Field Approximation

For well localized $4f$ -electron systems, the mean-field approximation has provided crucial information, and many kind of ordered states have been analyzed by this method. For example, CeB_6 shows antiferro quadrupolar (AFQ) order at low temperatures. The AFQ transition temperature increases with increasing magnetic field up to ≈ 40 T. This feature can be reproduced by the calculation by means of mean-field approximation assuming higher-rank octupolar interaction [2]. If only inter-site quadrupole interaction is assumed, the transition temperature would decrease with increasing magnetic fields. When external magnetic fields induce multipole moments in the AFQ ordered state, the interaction between these induced moments reduces the energy of the ordered state. Thus, the AFQ transition temperature would increase by external magnetic field. Not only for the typical compound CeB_6 , multipole interaction also plays important roles in some of the rare-earth compounds [51, 52], and this effect can be analyzed qualitatively by means of mean-field approximation.

The Hamiltonian for the $4f$ -electron state including inter-site multipole interaction is as follows:

$$H = H_{\text{CEF}} + \sum_{\langle i,j \rangle} K^{ij} M_i M_j, \quad (5.1)$$

where H_{CEF} is a crystalline-electric-field term, and the second term is an inter-site multipole-multipole interaction for a multipole moment, M . K^{ij} is a coupling constant for the multipole moments between i and j site. We consider fluctuation,

$$\delta M_i = M_i - \langle M_i \rangle, \quad (5.2)$$

where $\langle \dots \rangle$ means a thermal average. We assume the quadratic term of the fluctuation, $\delta M_i \delta M_j$, to be zero,

$$0 = \delta M_i \delta M_j = (M_i - \langle M_i \rangle)(M_j - \langle M_j \rangle) \quad (5.3)$$

Thus,

$$M_i M_j = M_i \langle M_j \rangle + M_j \langle M_i \rangle - \langle M_i \rangle \langle M_j \rangle \quad (5.4)$$

$$H = H_{\text{CEF}} + \sum_{i,j} K^{ij} M_i \langle M_j \rangle \quad (5.5)$$

Here, we consider two sub-lattices. In this case, the mean-field Hamiltonian can be written as follows,

$$H_A = H_{\text{CEF}} + K^{AB} \langle M \rangle_B M \quad (5.6)$$

$$H_B = H_{\text{CEF}} + K^{AB} \langle M \rangle_A M \quad (5.7)$$

In order to calculate quadrupolar susceptibility, quadrupole-strain interaction is added,

$$H_{\text{QS}} = g_{\Gamma} O_{\Gamma} \varepsilon_{\Gamma}, \quad (5.8)$$

where g_{Γ} , O_{Γ} and ε_{Γ} are the strain-quadrupole coupling constant, quadrupolar operator and strain with a symmetry, Γ . Then the total Hamiltonians for sub-lattice A and B are

$$H_{A(B)} = H_{\text{CEF}} + K^{AB} \langle M \rangle_{B(A)} M + H_{\text{QS}} \quad (5.9)$$

By solving the mean-field equation self-consistently, we will obtain the eigen-energies and eigenvectors, and then we can calculate the thermal average of the quadrupole moment, $\langle O_\Gamma \rangle_{\varepsilon_\Gamma}^{A(B)}$, which include a non-zero strain, ε_Γ . The quadrupolar susceptibility, $\chi_\Gamma^{A(B)}$, which is a linear susceptibility, can be calculated as follow;

$$\chi_\Gamma^{A(B)} = \frac{d}{d\varepsilon_\Gamma} \langle O_\Gamma \rangle_{\varepsilon_\Gamma}^{A(B)} = \lim_{\varepsilon_\Gamma \rightarrow 0} \frac{\langle O_\Gamma \rangle_{\varepsilon_\Gamma}^{A(B)} - \langle O_\Gamma \rangle_0^{A(B)}}{\varepsilon_\Gamma} \quad (5.10)$$

The total susceptibility, χ_Γ , can be obtained by taking average of the susceptibilities of sub-lattices,

$$\chi_\Gamma = \frac{\chi_\Gamma^A + \chi_\Gamma^B}{2} \quad (5.11)$$

When considering uniform order, $A = B$, we will obtain the same result as calculating single sub-lattice.

In the calculation below, ε_Γ was set to be 10^{-4} , and diagonalization was done with an accuracy of $\approx 10^{-10}$. Mean-field equations were solved with an accuracy of $\approx 10^{-8}$.

5.2 Result of Mean-field Calculation and discussion of low-temperature ordered state of $\text{SmOs}_4\text{Sb}_{12}$

$\text{SmOs}_4\text{Sb}_{12}$ shows a phase transition at T_C . As described Chap. 4, under high pressure, elastic constants C_{11} and C_{44} show abrupt decrease at around T_C . Below T_C , C_{11} shows a hardening, while C_{44} seems to be leveling off. Since $4f$ electrons expected to be well localized under high pressure, we discuss the characteristic features of C_{11} at 1.3 GPa and C_{44} at 1 GPa by means of mean-field approximation. Since ac-susceptibility shows a peak at T_C , which suggests ferro magnetic order, there are two possible ordering states in the case of Γ_{67} CEF ground state: a ferro-type magnetic dipole ordered state and a Γ_4 -type ferro octupolar ordered state. Here, we calculate quadrupolar susceptibility for these states.

In the present calculation, We use the following Hamiltonian;

$$H_B = H_{\text{CEF}} + K_{\text{DD}} \langle J \rangle \cdot J + K_{\text{OO}}^\alpha \langle T^\alpha \rangle T^\alpha + K_{\text{OO}}^\beta \langle T^\beta \rangle T^\beta, \quad (5.12)$$

where T^α and T^β are the octupole moments with Γ_4 (Γ_4) and Γ_5 (Γ_4) symmetry of O_h (T_h) point group, respectively. The assumed models in this analysis are listed in Table 5.1.

In Fig. 5.1, we show the calculated quadrupolar susceptibilities for the model (1): “Ferromagnetic dipolar ordered” model. The inter-site dipole-dipole coupling constant, K_{DD} , is set to 2.2 K, and any other multipolar interaction is neglected. In the case of Γ_{67} CEF ground state, the easy axis of magnetic dipole moment is $\langle 100 \rangle$. Thus, the ordered moments are aligned along $\langle 100 \rangle$, and three domain states exist in zero magnetic field in this model. The calculation well reproduces a large jump at the transition temperature, T_o . A hardening down to low temperatures is seen below T_o in the calculated quadrupolar susceptibilities. Since ferro-quadrupole moments of O_2^0 are induced in the case of this magnetic dipolar ordering state, quadrupolar degrees of freedom are suppressed. Thus, the elastic constant, C_{11} , become harder with decreasing temperature due to the freezing of the quadrupole moment, O_2^0 . Although the amount of hardening of experimental result of C_{11} is smaller than that appears in the calculation, the calculation qualitatively agrees with the experimental result. On the other hand, the calculated susceptibility $-\chi_{\Gamma_4}$ is, however, not consistent with the experimental result

Table 5.1: Assumed models in the present mean-field (MF) analysis.

	Order Parameter	Symmetry	MF coefs
(1)	$J_z (J_x, J_y)$	Γ_4	$K_{DD} = 2.2, K_{OO}^\alpha = 0, K_{OO}^\beta = 0$
(2)	$T_x^\alpha + T_y^\alpha + T_z^\alpha$	Γ_4	$K_{DD} = 0, K_{OO}^\alpha = 0.1, K_{OO}^\beta = 0$
(3)	$J_z (J_x, J_y)$	Γ_4	$K_{DD} = 1.8, K_{OO}^\alpha = 0.04, K_{OO}^\beta = 0$
(4)	$T_x^\alpha + T_y^\alpha + T_z^\alpha$	Γ_4	$K_{DD} = 1, K_{OO}^\alpha = 0.09, K_{OO}^\beta = 0$
(5)	$J_z (J_x, J_y)$	Γ_4	$K_{DD} = 2.2, K_{OO}^\alpha = 0, K_{DD}^\beta = 0.05$

of C_{44} below T_C . The calculated C_{44} shows a sharp hardening of C_{44} below T_o , while the measured C_{44} does not show such a hardening. Therefore, we simply conclude that the ordered state under high pressure would not be a simple magnetic dipolar order.

In Fig. 5.2, we show the calculated quadrupole susceptibilities for the model (2): “Ferromagnetic octupolar order”¹. Here, the inter-site octupole-octupole coupling constant, K_{OO}^α , is set to be 0.1 K and any other multipolar interactions are neglected. The easy axis of the octupole moment is $\langle 111 \rangle$ in the case of Γ_{67} CEF ground state, and the most plausible order parameter predicted from the present mean-field analysis is $T_x^\alpha + T_y^\alpha + T_z^\alpha$. In this case, although there are four domains in zero magnetic field, the contribution of each domain state to the susceptibility is the same. In this state, the ferromagnetic dipolar ordering along $\langle 111 \rangle$ and ferro-type ordering of the quadrupole moment, $O_{yz} + O_{zx} + O_{xy}$ are induced. A jump is seen at T_o in both of the quadrupolar susceptibilities. Compared to $-\chi_{\Gamma_4}$, the jump of $-\chi_{\Gamma_{23}}$ is relatively smaller. By applying pressure 4*f*-electrons become more localized, and the response would be larger. Thus, these calculated results for model (2) seem to be inconsistent with the fact that C_{11} shows a relatively large elastic anomaly at T_C under pressure, where 4*f*-electrons are considered to be well localized. A clear increase of $-\chi_{\Gamma_4}$ below T_C is also inconsistent with the result.

Next, we will show a result of a calculation including plural coupling constants. In Fig. 5.3, we show the calculated quadrupole susceptibilities for the model (3): “primary dipole-order” in which inter-site dipole-dipole and octupole-octupole interactions are assumed. The jump at T_C is again reproduced well. Compared to the quadrupolar susceptibility calculated for the model (1) (Fig. 5.1), the hardening of C_{44} below T_o is rather suppressed in the model (3). Furthermore, the calculated curve for the mono-domain state of J_x order is quite similar to the experimental results. Thus, the suppression of the hardening of the elastic constants, which was observed in the ultrasonic measurements under pressures, may be due to Γ_4 -type magnetic octupole interaction. Although this calculation can explain the experimental result qualitatively, there is a quantitative disagreement with the result. Although C_{11} shows hardening below T_o as expected by the calculation, the hardening of the measured C_{11} is smaller than the calculation. C_{11} is still softer below T_o than that above T_o , while the calculation expects that C_{11} become harder than that above T_o . This fact implies that there are other fluctuations which cause the suppression of the hardening below T_C .

In Fig. 5.4, we show the calculated quadrupole susceptibilities for the model (4); “primary octupole-order” in which inter-site dipole-dipole and octupole-octupole interactions are assumed. A large decrease of $-\chi_{\Gamma_{23}}$ is seen at T_C , which is consistent with the experimental results. On the other hand, a clear hardening is seen in the calculated $-\chi_{\Gamma_4}$, which is inconsistent with the experimental results.

In Fig. 5.5, we show the calculated quadrupole susceptibilities for the model (5): “primary dipole-order” in which inter-site dipole-dipole and T_β octupole-octupole interactions are assumed. The jump at T_C is again reproduced well. The calculated Γ_4 type quadrupolar susceptibility reproduces the experimental results of C_{44} well. Furthermore, a suppression of the hardening of C_{11} below T_C is also expected in this model. Thus, this results suggests that an inter-site T_β octupolar interaction play a role in the ferromagnetically ordered state.

In summary, the magnetically ordered state of $\text{SmOs}_4\text{Sb}_{12}$ was analyzed by means of mean-field approximation, where we assume localized $4f$ -electron model. The calculation assuming ferromagnetic dipolar order and octupolar interaction, *i.e.*, model (3), quantitatively reproduces the characteristic features of the temperature dependence of the elastic constants. These analyses suggest that the ordered state is not a simple ferromagnetic order, and that there are inter-site octupole-octupole interactions and/or some other fluctuation.

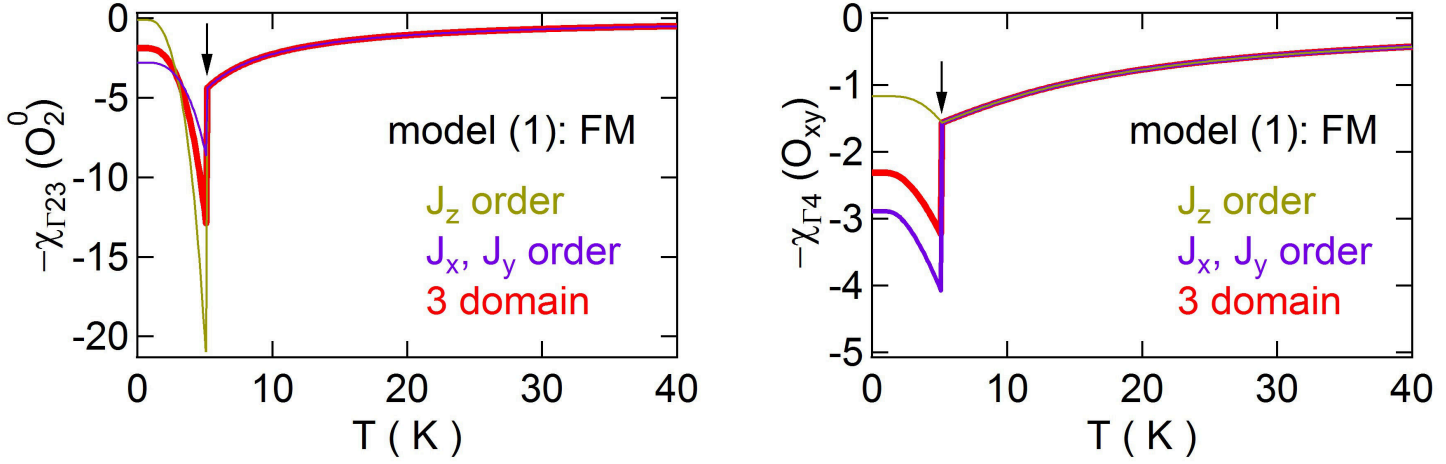


Figure 5.1: Temperature dependence of the quadrupole susceptibilities, $-\chi_{\Gamma 23}$ and $-\chi_{\Gamma 4}$, for the ferromagnetic dipolar-order model.

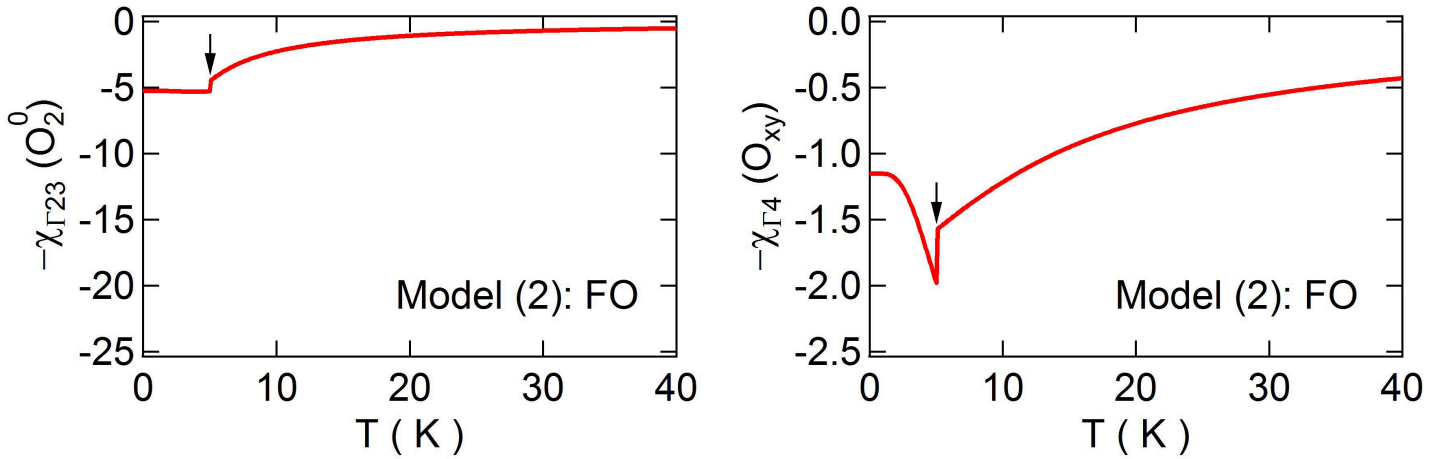


Figure 5.2: Temperature dependence of the quadrupole susceptibilities, $-\chi_{\Gamma 23}$ and $-\chi_{\Gamma 4}$, for the ferromagnetic octupolar-order model.

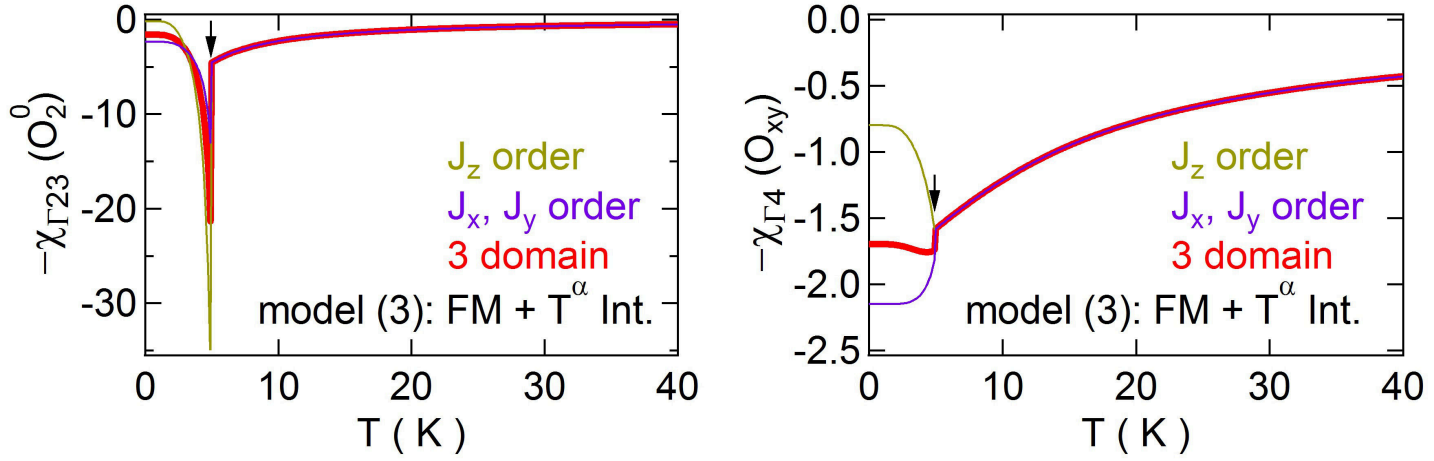


Figure 5.3: Temperature dependence of the quadrupole susceptibilities, $-\chi_{\Gamma 23}$ and $-\chi_{\Gamma 4}$, for the ferro-type magnetic dipolar-order model including ferro-type inter-site octupolar interaction.

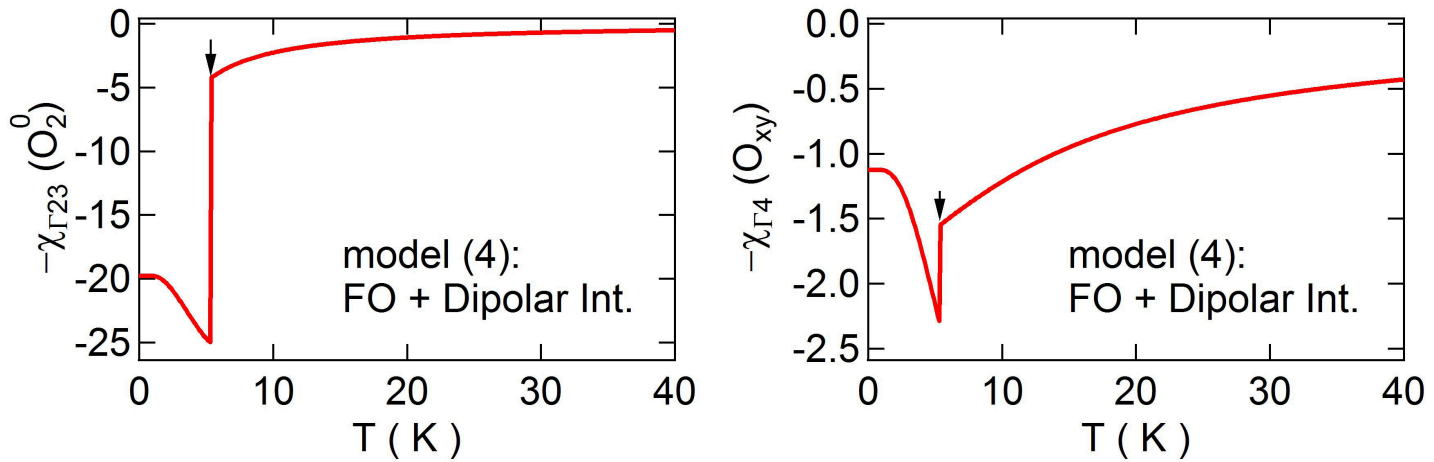


Figure 5.4: Temperature dependence of the quadrupole susceptibilities, $-\chi_{\Gamma 23}$ and $-\chi_{\Gamma 4}$, for the ferro-type magnetic dipolar-order model including ferro-type including inter-site ferromagnetic interaction.

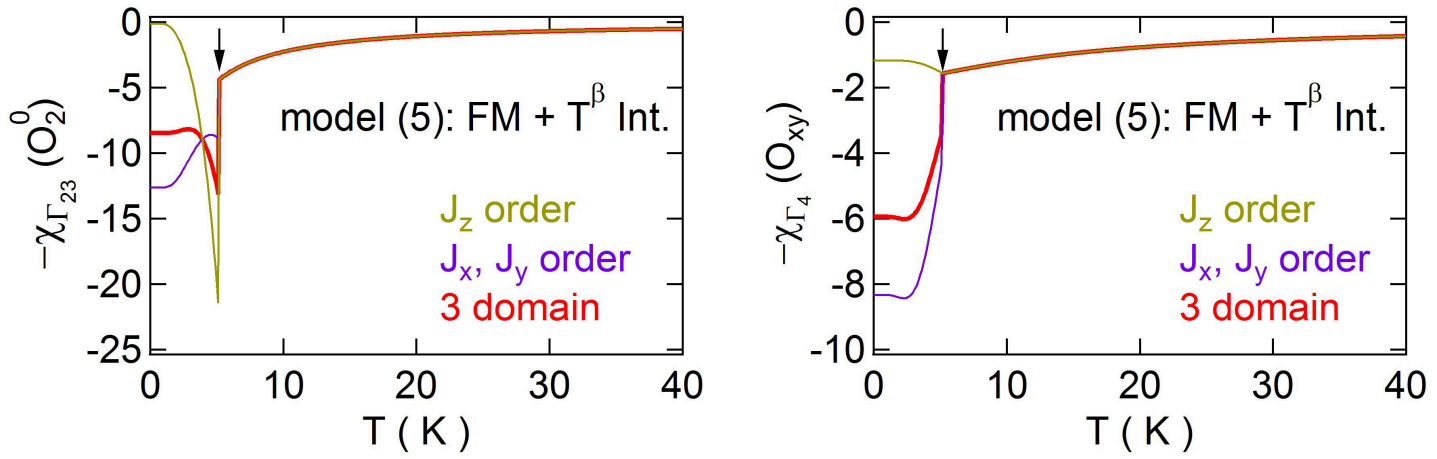


Figure 5.5: Temperature dependence of the quadrupole susceptibilities, $-\chi_{\Gamma_{23}}$ and $-\chi_{\Gamma_4}$, for the ferro-type magnetic dipolar-order model including ferro-type inter-site T^β octupolar interaction.

5.3 Mean-Field Calculation for Magnetic Field Dependence of Elastic Constants Regarding Magneto-Elastic Coupling

In the Chap. 3, we discussed the origin of the softening and the minimum in magnetic-field dependence of the elastic constants of $\text{SmOs}_4\text{Sb}_{12}$ at 4.2 K, and we referred to two possible causes: suppression of Kondo effect and magneto-elastic coupling due to ferromagnetic order. Since $\text{SmOs}_4\text{Sb}_{12}$ shows ferromagnetic order at low temperatures, the ferromagnetic-interaction between $4f$ -electrons and induced quadrupole moment would affect the elastic constant.

In order to estimate this magneto elastic coupling, we calculate the elastic constants by means of mean-field approximation. The Hamiltonian is

$$H = H_{\text{CEF}} - K_{\text{D}}\langle J \rangle J + g_J \mu_{\text{B}} J \cdot H \quad (5.13)$$

In Fig. 5.6, we show the calculated quadrupolar susceptibility. In this calculation, the coupling constant, K_{D} , was set to be 1.2, and $T_{\text{C}} \approx 2.5$ K. As can be seen, FM interaction possibly causes a softening and a minimum at low field. This model also seems to be consistent with an increase of the softening in magnetic-field dependence with decreasing temperature. However, there is no minimum in calculated $-\chi_{\Gamma_4}$ at 1.5 K, while the measured C_{44} has a minimum. Although this model cannot directly explain the magnetic field dependence of C_{44} , the result of the calculation implies a possible contribution of FM interaction to the softening and minimum in the measured C_{44} .

Note that in this calculation, we assumed localized $4f$ model; namely, we ignored c - f hybridization. Thus, only if the Kondo effect is suppressed by magnetic fields, this magneto-elastic response due to localized $4f$ electrons appears.

In this section, we confirmed that a FM interaction, as well as the suppression of the Kondo effect, can cause a softening and a minimum at a low magnetic field in magnetic field dependence. In order to estimate which effect is dominant at low magnetic fields, ultrasonic measurements with another field direction would be needed.

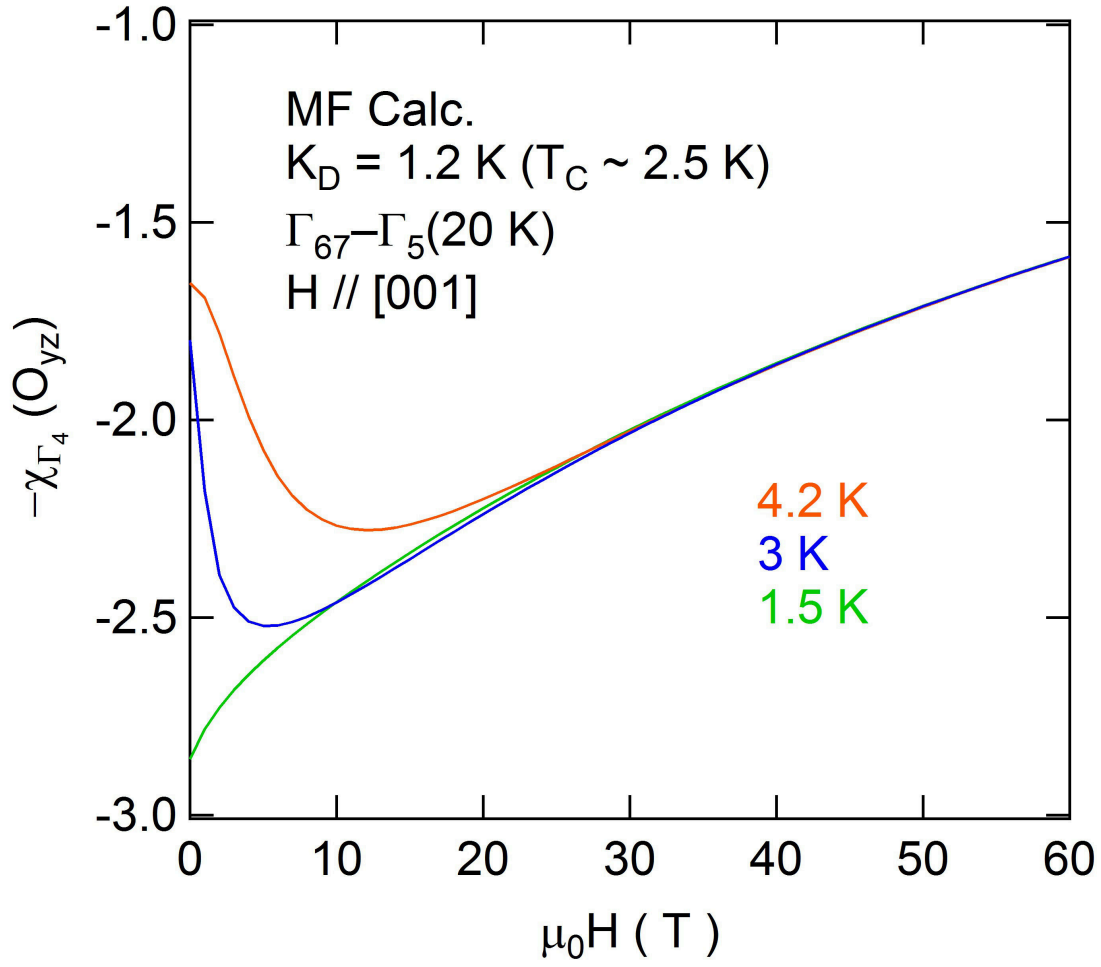


Figure 5.6: Magnetic field dependence of the quadrupole susceptibility at several temperatures, $-\chi_{\Gamma_4}$, calculated assuming ferro-type magnetic dipolar inter-site interaction.

Chapter 6

Ultrasonic Study on Cage-Structured Compound SmBe_{13}

6.1 Introduction

SmBe₁₃ has the NaZn₁₃-type crystal structure (Fm $\bar{3}$ c), which is the same as for the heavy-fermion superconductor UBe₁₃ (Fig. 6.1). The Sm ion is surrounded by a cage structure which consists of 24 Be atoms. This material shows a phase transition at $T_M \approx 8.8$ K, which was revealed by specific-heat measurements using a polycrystalline sample [44].

Recently, our group has succeeded to grow single crystals of SmBe₁₃ and performed measurements of magnetization, specific heat, X-ray diffraction (XRD), muon-spin relaxation (μ SR) and electrical resistivity. In Fig. 6.2, temperature dependence of the magnetic susceptibility is displayed. The magnetic susceptibility shows a Curie-Weiss behavior above T_M with positive Weiss temperature of +10.8 K, and exhibits an antiferromagnetism (AFM)-like cusp anomaly at T_M [45]. Our recent μ SR study confirmed that the low-temperature phase is a magnetically ordered state [46]. In the magnetic-field and temperature dependencies of the magnetization (Fig. 6.3), several anomalies were found below T_M , which suggest existence of subphases below T_M [45]. These facts imply that this material has a complex magnetically ordered state. The phase diagram is shown in Fig. 6.4. It should be noted that many $M\text{Be}_{13}$ ($M = \text{Gd-Er}$, and Np) compounds show helical magnetic structures at low temperatures and have positive Weiss temperatures; further, HoBe₁₃ has a multi-magnetic phase diagram [47, 48, 49]. Consequently, helical magnetic order is one of the candidates for the low-temperature state of SmBe₁₃ [45].

In order to understand this low-temperature state in SmBe₁₃, it is necessary to clarify the degrees of freedom of the $4f$ electrons. Figure 6.5 displays temperature dependence of $4f$ -electronic contribution to the specific heat of SmBe₁₃ obtained by assuming that the contributions of conduction electrons and phonon are same as LaBe₁₃. The $4f$ -electronic entropy calculated from $C_{4f}(T)$ is also shown in Fig. 6.5. We can see that the $4f$ -electronic entropy reaches $R\ln 6$ at around 80 K, which is the expected value for Sm³⁺. This fact suggests that the $4f$ electrons are well localized in Sm³⁺ ion and that the CEF splitting is less than 80 K. In Fig. 6.5, calculated curves of the specific heat assuming three CEF models are also shown. In a cubic CEF, the sextet ($J = 5/2$) of Sm³⁺ splits into a Γ_7 doublet and a Γ_8 quartet. Thus far, the Γ_7 doublet was assumed to be the ground state with a gap of 12.5 and 30 K to the first excited quartet, estimated by use of specific-heat and magnetization measurements, respectively [44, 50]. However, as another possibility, the Γ_8 ground state with a gap of 90 K is proposed from our recent analysis. Thus, it is desirable to confirm the CEF level scheme by other measurements.

In the present study, we have investigated the phase boundary of the low-temperature phase using pulsed magnetic fields. Since the Sm ion has a relatively small Landé g -factor, high-field measurements are necessary to study the low-temperature state. Indeed, in these measurements, we could clearly observe an elastic anomaly at 43 T and 1.5 K. By ultrasonic measurements in static magnetic fields, we also investigated the CEF level scheme and magnetic-field dependence of the transition temperature, T_M .

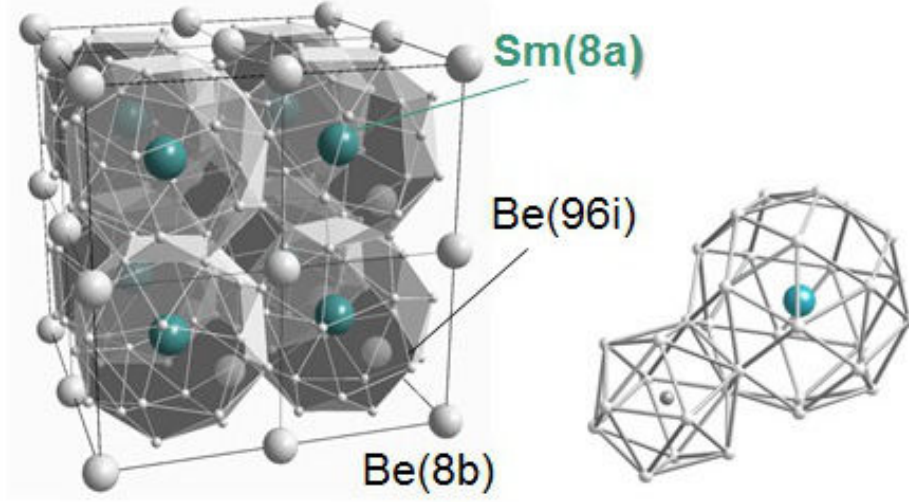


Figure 6.1: (Color online) Crystal structure of SmBe_{13} (left) and the cage structures around a Sm ion and a Be atom (right).

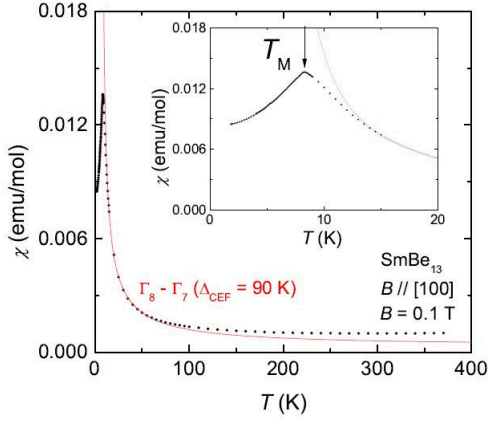


Figure 6.2: Temperature dependence of the magnetic susceptibility of SmBe_{13} . The red solid curve represents a mean-field calculation of the magnetic susceptibility obtained by assuming the CEF level scheme of $\Gamma_8(0 \text{ K}) - \Gamma_7(90 \text{ K})$ and a temperature-independent term.

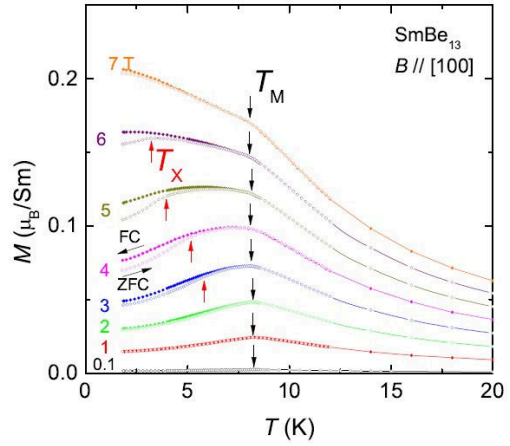


Figure 6.3: Temperature dependence of the magnetization of SmBe_{13} measured in various magnetic fields.

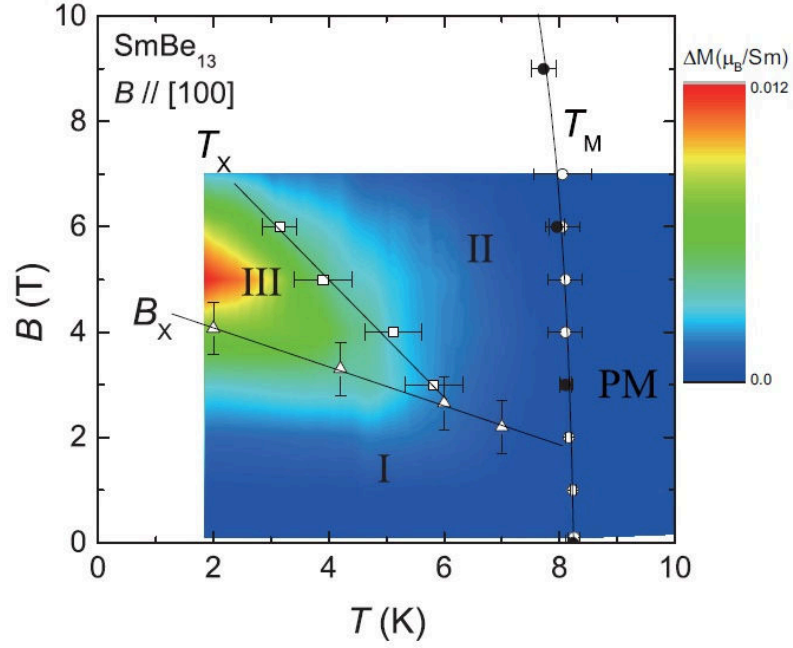


Figure 6.4: (Color online) Magnetic field-temperature phase diagram of SmBe_{13} for $\mathbf{B} \parallel [001]$. A contour plot of the difference between the ZFC-M and FC-M (ΔM) is displayed as background.

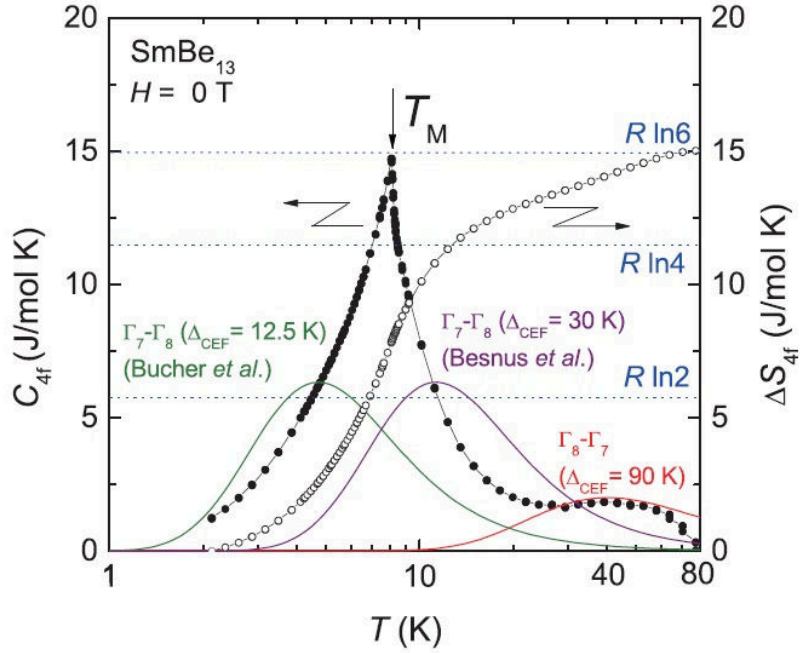


Figure 6.5: (Color online) Temperature dependence of the $4f$ -electronic contribution to the specific heat (left axis) and the $4f$ -electronic entropy (right axis) in SmBe_{13} .

6.2 Experimental Details

A single-crystalline SmBe_{13} sample grown by an Al-flux method was used in the present study. The sample was annealed at 700°C for 2 weeks. Ultrasonic measurements were carried out by means of the conventional pulse-echo method. Ultrasonic waves were excited by LiNbO_3 transducers of $100\ \mu\text{m}$ thickness, which were attached on the polished surfaces of the sample. The ultrasonic frequencies of longitudinal C_{11} and transverse C_{44} modes were 108 MHz (3rd harmonics) and 20 MHz (fundamental frequency), respectively. The measurements in static magnetic fields were carried out by using a superconducting magnet. Pulsed magnetic fields up to 61.3 T were generated by a magnet at the Dresden High Magnetic Field Laboratory (Helmholtz-Zentrum Dresden-Rossendorf).

6.3 Results

In Figs. 6.6 and 6.7, we show the temperature dependence of the elastic constants, $C_{11}(T)$ and $C_{44}(T)$, in zero magnetic field. For both modes, no clear anomaly is observed from 300 K down to T_M . Although an Einstein mode has been observed in specific heat [45], this material does not show any ultrasonic dispersion. One of the possible explanations for the absence of ultrasonic dispersions is that the Einstein mode does not couple to the acoustic phonon. Another possibility is that such a dispersion exists only above the present temperature range, *i.e.*, above room temperature. Actually, the Einstein energy of about 170 K is higher than that of filled-skutterudites, which show some ultrasonic dispersions due to rattling [38]. Further ultrasonic measurements at higher temperatures would be needed.

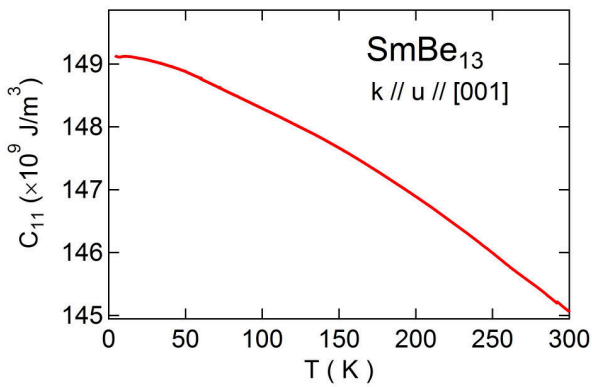


Figure 6.6: Temperature dependence of C_{11} in zero magnetic field. The wave vector, $\mathbf{k}$, and the polarization, $\mathbf{u}$, of the sound wave are aligned along [001].

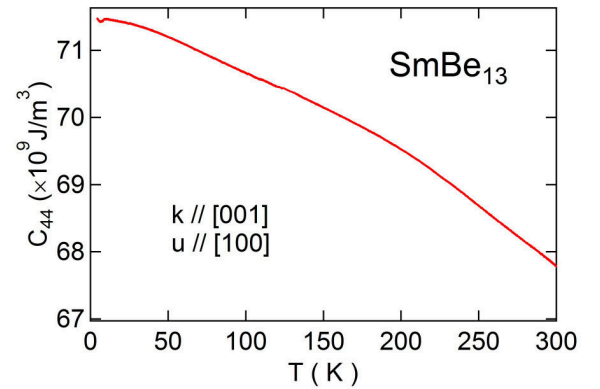


Figure 6.7: Temperature dependence of C_{44} in zero magnetic field. The wave vector, $\mathbf{k}$ is along [001], and the polarization of the sound wave, $\mathbf{u}$, is aligned along [100].

Figure 6.8 shows $C_{11}(T)$ in various magnetic fields for $H \parallel [001]$. In zero magnetic field, $C_{11}(T)$ shows a softening below 14 K. In low magnetic field, elastic anomaly at T_M is not very clear. Below 2 T, we define the T_M as the temperature at which dC_{11}/dT takes a local maximum, and the error bar is defined as the full width at half maximum. On the other hand, the elastic anomaly at T_M is clear above 3 T. Moreover, a difference between zero-field cooling (ZFC) and field cooling (FC) is observed below T_{Hys} in magnetic fields between 2 and 9 T. These facts suggest that there is a subphase below T_M above 2 T. The difference between ZFC and FC processes has also been observed in our recent magnetization measurements [45].

Here, we consider the origin of the softening of $C_{11}(T)$ below 14 K. This softening could be explained by strain-quadrupole coupling, since the $4f$ electrons of Sm^{3+} can have quadrupole degrees of freedom [41]. Since the Γ_8 quartet has quadrupole degrees of freedom, a softening toward low temperatures is expected in the case of a Γ_8 quartet CEF ground state. Thus, a Γ_8 ground state is one of the possible CEF models. It is also possible that the elastic constant show a softening in the case of a Γ_7 doublet ground state with a small gap of about 12.5 K to the Γ_8 quartet excited state. On the other hand, $\Gamma_7(0 \text{ K})$ – $\Gamma_8(30 \text{ K})$ is inconsistent with our result, because in this case the elastic constant is expected to have a local minimum at around 15 K and should not show a softening below 15 K.

In Fig. 6.9, $C_{44}(T)$ in various fields is shown. Elastic anomaly in $C_{44}(T)$ at T_M is not so clear compared with that of $C_{11}(T)$, and we cannot determine T_M from $C_{44}(T)$. The arrows in the figure represent the T_M determined from $C_{11}(T)$. $C_{44}(T)$ also shows softening at low temperatures. Compared to the softening of $C_{11}(T)$, the softening starts rapidly near T_M , which suggests that this softening is caused by the phase transition and/or precursory phenomenon of the phase transition, *i.e.*, short-range ordering. This softening of $C_{44}(T)$ is enhanced in a magnetic field of about 5 T, where the difference between ZFC and FC in $C_{11}(T)$ is largest, and suppressed at higher magnetic fields. This significant change in the behavior of $C_{44}(T)$ also implies a modulation of the low-temperature ordered state by the magnetic field.

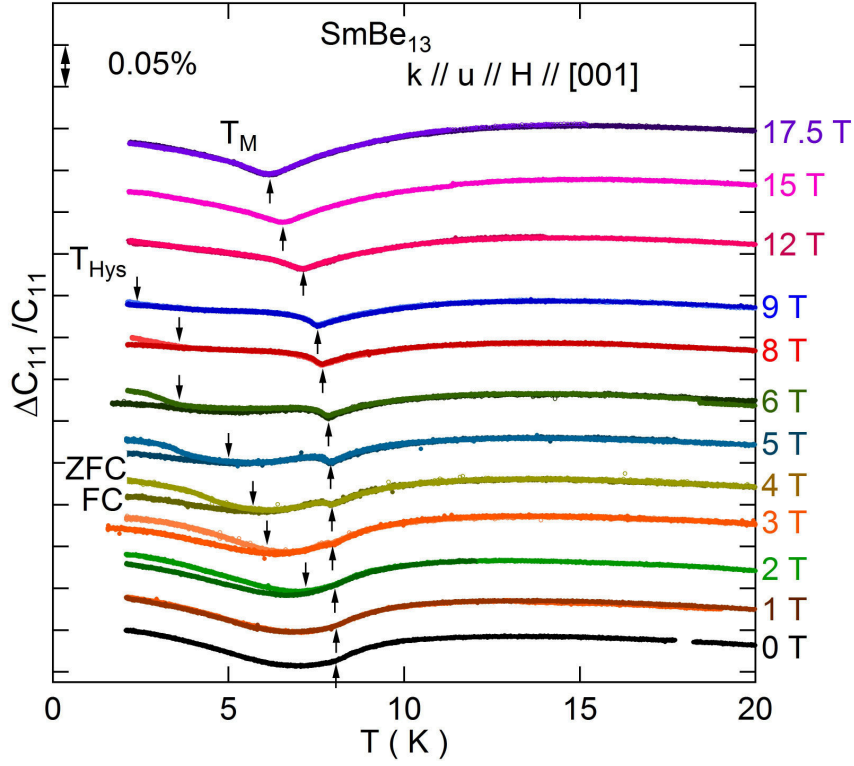


Figure 6.8: (Color online) Temperature dependence of C_{11} in various magnetic fields.

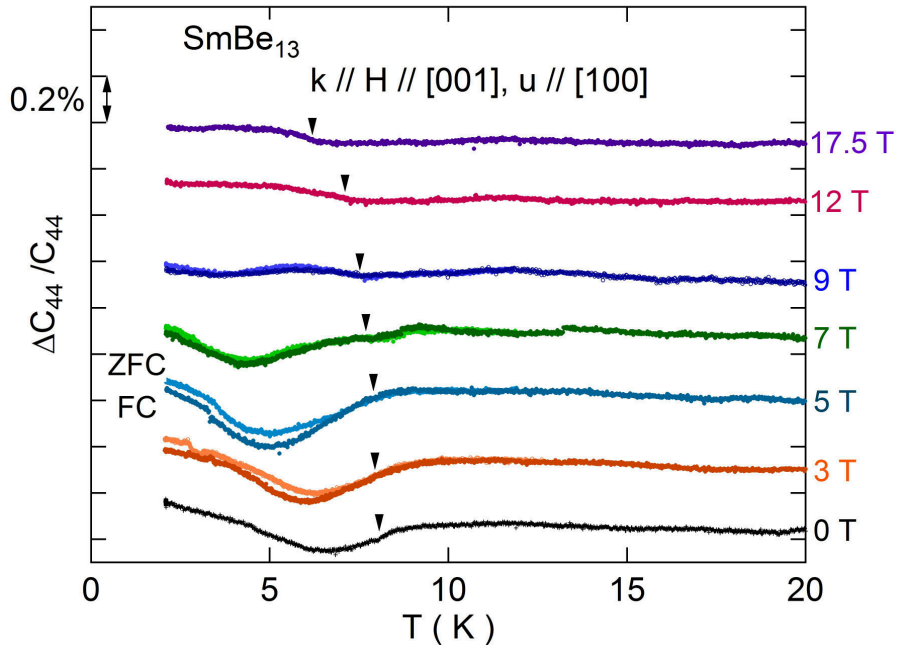


Figure 6.9: (Color online) Temperature dependence of C_{44} in various magnetic fields. The arrows indicate T_M determined from C_{11} .

In Fig. 6.10, we show the relative change of $C_{11}(H)$ observed in pulsed magnetic fields. Note that the absolute value of the elastic constant is always the same before and after pulsed magnetic fields. Thus, eddy-current heating is negligible. At 1.5 K, $C_{11}(H)$ exhibits a minimum at $H_M \approx 43$ T as indicated by a dashed line. A broad minimum is also seen at around 32 T in the data obtained at 4.2 K. Since the temperature dependence of the elastic constant, $C_{11}(T)$, has a local minimum at T_M in high magnetic fields, this minimum in the pulsed-field data could be due to the phase transition to the paramagnetic state.

Figure 6.11 shows the H - T phase diagram obtained from our C_{11} data in static and pulsed magnetic fields. As can be seen, T_M is clearly reduced with applied magnetic fields. The extrapolated phase boundary from the low-field region nicely merge with the magnetic field, H_M .

Next, we show a model calculation of the phase-transition fields for AFM order by means of a mean-field approximation. Since Sm ions locate at 8a sites, which are the lattice points of a simple cubic structure when only Sm ions are considered, we assume G-type AFM state of simple cubic structure, *i.e.*, the directions of neighboring magnetic moments are opposite with each other. In our calculation, we consider that the $4f$ electrons are well localized at Sm^{3+} , which is confirmed by our recent physical property measurements [45]. Here, we take into account only the ground-state multiplet of $J = 5/2$, and the Hamiltonian is

$$H = H_{\text{CEF}} - K\mathbf{J} \cdot \langle \mathbf{J} \rangle + g_J \mu_B \mathbf{J} \cdot \mathbf{H}. \quad (6.1)$$

The inter-site coupling constant, K , is assumed to be -4 and -3.07 K for free Sm-ions and the $\Gamma_8(0\text{ K})$ – $\Gamma_7(90\text{ K})$ CEF-state case, respectively, which cause a transition at about 8 K in each case. By computing the self-consistent equation in the case of applying magnetic fields along $[001]$, we obtained following results. In the case of free Sm^{3+} ions, *i.e.*, $H_{\text{CEF}} = 0$, AFM moments are aligned perpendicular to external magnetic fields, and a magnetic field of 75 T is estimated to suppress the AFM at 1.5 K. In the case of the $\Gamma_8(0\text{ K})$ – $\Gamma_7(90\text{ K})$ CEF state, magnetic moments are aligned along the easy axis $\langle 100 \rangle$, and a magnetic field of 57 T would be needed to break the AFM order.

These estimated values of magnetic field regarding to the upper phase boundary of G-type AFM phase are larger than the present experimental result of 43 T. This mismatch between the experimentally and theoretically obtained upper-phase boundary implies that the actual ordered state of SmBe₁₃ in high magnetic fields for $H \parallel [001]$ is not a simple G-type AFM state. It is also possible that multipole degrees of freedom play also a role at high magnetic fields, since the $4f$ -electron system has multipole degrees of freedom in the case of Γ_8 CEF ground state. For further discussion, measurements in pulsed magnetic fields aligned along other axes would be necessary.

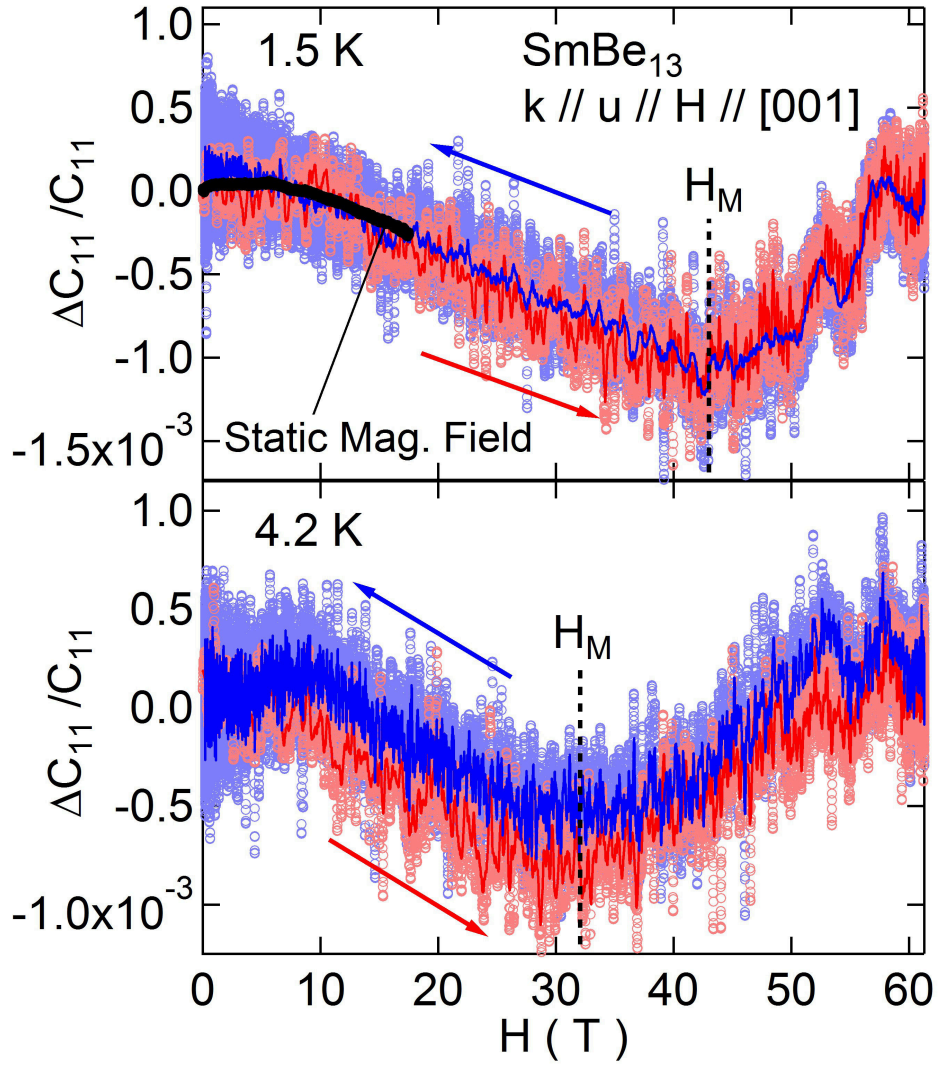


Figure 6.10: (Color online) Relative change of C_{11} in pulsed magnetic field. Light-colored circles represent raw data, and deep-colored lines are smoothed curves.

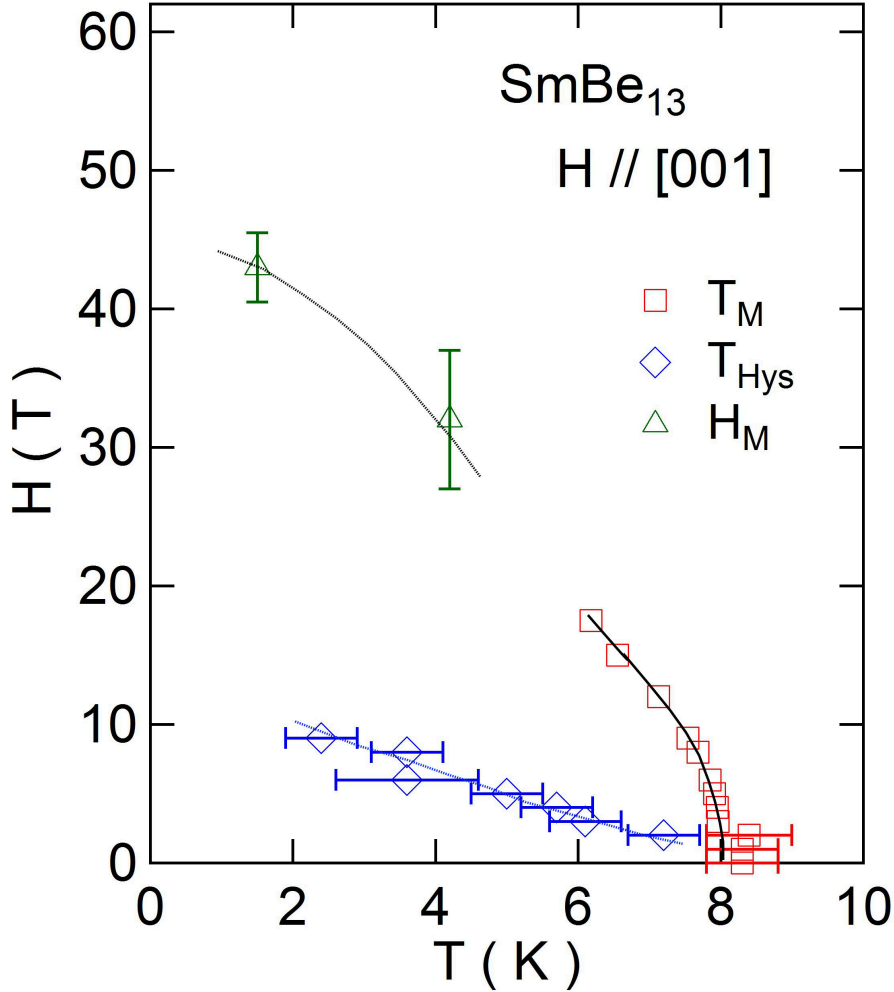


Figure 6.11: (Color online) H - T phase diagram obtained from the result of our C_{11} measurements. The lines are guide to the eye.

6.4 Summary

We have performed ultrasonic measurements for a single-crystalline SmBe_{13} in static and pulsed magnetic fields in order to shed more light on the low-temperature magnetic order of this compound. We have observed an elastic anomaly at 43 T at 1.5 K, which could be an upper phase boundary of the magnetically ordered state. The relative weakness of the low-temperature phase against magnetic fields, compared to results using mean-field calculations, strongly suggests that the ordered state is not simple AFM. By measurements in static fields, some indication for the existence of a subphase at lower temperatures was found, which has also been suggested by magnetization measurements.

Chapter 7

Conclusion

We have performed ultrasonic measurements on heavy-fermion compound $\text{SmOs}_4\text{Sb}_{12}$. The important point of the present study is an usage of outer parameters: high magnetic field and hydrostatic pressure. By high magnetic field study, we have observed response of localized $4f$ electrons beyond the delocalized state of $4f$ electrons due to c - f hybridization. The important facts which have been obtained in this study are,

- The crystalline-electric-field ground state would be Γ_{67} quartet.
- Magnetic fields of more than 10 T for $H \parallel [001]$ would be sufficient to suppress c - f hybridization, and this feature suggests an existence of typical Kondo effect.

Thus, we conclude that the CEF ground state has multipolar degrees of freedom. We have also clarified that strong c - f hybridization, which extinguish the multipolar degrees of freedom, exists in low-temperature and low magnetic-field region.

By hydrostatic pressure study, we have obtained following results and possible explanations for several features under high pressure reported in the previous studies, such as large increase of the peak of ac-susceptibility and sudden appearance of NFL behavior far from a quantum critical point.

- $4f$ electrons would become localized by applying hydrostatic pressure, and $4f$ electrons have quadrupolar degrees of freedom down to T_C above 0.7 GPa.
- The result suggest that the ordered state changes from a delocalized (itinerant) to a localized magnetic moments order at 0.4 GPa. This fact can explain the drastic change of ac-susceptibility at around 0.5 GPa, which has previously reported.
- These facts above imply a possible relation between this drastic change of the character of $4f$ electrons and the appearance of non-Fermi-liquid-like behavior observed electrical resistivity measurements.
- From the analysis using mean-field approximation, it is suggested that the characteristic feature, such as an abrupt decrease of elastic constant, can be explained by magneto-elastic coupling. The analysis also suggest that possible existence of multipole-multipole interaction in the ordered state.
- Possible relation between rattling and $4f$ -electron state is suggested.
- C_{11} shows a frequency dependent elastic anomaly below T_C at high pressure, and this anomaly would have same origin as the ultrasonic dispersions which can be observed at ambient pressure.

In the present study, we could clarify multipolar degrees of freedom even at high pressures. At high pressure, $4f$ electrons become well localized and these degrees of freedom would active even at low temperatures. Thus, considering with previous report, this fact suggest an occurrence of a multipolar order at high pressures. For further investigation, ultrasonic study under higher pressure and magnetic fields would be needed.

Although possible relation between rattling modes and $4f$ -electron state was suggested by the present study, further measurements of C_{11} mode under pressure is necessary. Since c - f hybridization is suppressed by applying high magnetic field, we can investigate this relation by measuring ultrasonic dispersions in higher magnetic fields.

Finally, we would like to emphasize that this is the first observation of the crossover of $4f$ -electron state from delocalized to localized state under magnetic fields and hydrostatic pressures by means of ultrasound. Since the magnetization become larger with decreasing temperature due to ferromagnetic order in $\text{SmOs}_4\text{Sb}_{12}$, it is difficult to observe the crossover by magnetization measurements. Thus, it is proved that ultrasonic method, which can observe higher-rank multipoles even under high magnetic fields and pressures, is powerful method to observe the crossover effect.

Appendix A

Appendix

A.1 Quadrupolar Susceptibility

The response of quadrupole moments can be detected by means of ultrasound, since quadrupole moments couple to strains induced by ultrasound. Here, we introduce quadrupolar susceptibilities. The procedure for calculating quadrupolar susceptibility can be understood by an analogy from a magnetic susceptibility. In the calculation below, we consider only ground multiplet of J multiplets.

We introduce a small strain to calculate a susceptibility. A strain changes crystalline electric field, and for small strain,

$$\delta H = \frac{dV_{\text{CEF}}}{d\varepsilon}\varepsilon + O(\varepsilon^2) \quad (\text{A.1})$$

This change can be written by using the Hatching's operators and a coupling constant, g . Then, by using a symmetrized strain, a strain-quadrupole interaction term can be written as follows,

$$H_{\text{QS}} = g_{\Gamma} O_{\Gamma} \varepsilon_{\Gamma}, \quad (\text{A.2})$$

where Γ is a label for a symmetry. The elastic strain couples to the quadrupole moment with the same symmetry. The quadrupole moments and related strains for cubic symmetry are listed in Table A.1. Thus, total Hamiltonian is,

$$H = H_{\text{CEF}} + H_{\text{QS}} \quad (\text{A.3})$$

The free energy and the partition function are

$$F = \frac{1}{2} C_{\Gamma}^0 \varepsilon^2 - N k_{\text{B}} T \ln Z \quad (\text{A.4})$$

$$Z = \sum_i \exp(-E_i / k_{\text{B}} T), \quad (\text{A.5})$$

where i represents an eigenstate, and we take sum of all of the eigenstates. N is the number of magnetic ions per unit volume. The elastic constant can be calculated as follows:

$$C = \lim_{\varepsilon_{\Gamma} \rightarrow 0} \frac{\partial^2 F}{\partial \varepsilon_{\Gamma}^2} = C_{\Gamma}^0 - N g_{\Gamma}^2 \chi_{\Gamma}(T), \quad (\text{A.6})$$

where C_0 is a background elastic constant, such as contribution of phonon. $\chi_{\Gamma}(T)$ is the quadrupolar susceptibility.

$$-g_{\Gamma}^2 \chi_{\Gamma}(T) = \left\langle \frac{\partial^2 E_i}{\partial \varepsilon_{\Gamma}^2} \right\rangle - \frac{1}{k_{\text{B}} T} \left\{ \left\langle \left(\frac{\partial E_i}{\partial \varepsilon_{\Gamma}} \right)^2 \right\rangle - \left(\left\langle \frac{\partial E_i}{\partial \varepsilon_{\Gamma}} \right\rangle \right)^2 \right\} \quad (\text{A.7})$$

By considering second perturbation with respect to the strain, the energy can be written as follows,

$$E_i(\varepsilon_{\Gamma}) = E_i^0 + \langle i | H_{\text{QS}} | i \rangle + \sum_{j \neq i} \frac{|\langle j | H_{\text{QS}} | i \rangle|^2}{E_j^0 - E_i^0} = E_i^0 - g_{\Gamma} \varepsilon_{\Gamma} \langle i | O_{\Gamma} | i \rangle + g_{\Gamma}^2 \varepsilon_{\Gamma}^2 \sum_{j \neq i} \frac{|\langle j | H_{O_{\Gamma}} | i \rangle|^2}{E_j^0 - E_i^0}, \quad (\text{A.8})$$

where $\langle \dots \rangle$ means a thermal average. Thus, the first term of (A.7) comes from the cross term of the quadrupole operator O_{Γ} , and the second term comes from the diagonal term. The first term corresponds to a Van Vleck term of the magnetic susceptibility, and the second term, which is proportional

Table A.1: Quadrupoles, symmetrized strains, and corresponding elastic constants are categorized with T_h symmetry (O_h symmetry).

Symmetry	Quadrupole	Strain	Elastic Constant
Γ_1		$\varepsilon_B = (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})/\sqrt{3}$	$C_B = (C_{11} + 2C_{12})/3$
$\Gamma_{23} (\Gamma_3)$	O_0^2, O_2^2	$(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})/\sqrt{6}, (\varepsilon_{yy} - \varepsilon_{xx})/\sqrt{2}$	$(C_{11} - C_{12})/2$
$\Gamma_4 (\Gamma_5)$	O_{yz}, O_{zx}, O_{xy}	$\varepsilon_{yz}, \varepsilon_{zx}, \varepsilon_{xy}$	C_{44}

to the inverse of temperature, corresponds to a Curie term. Note that the Curie term has a negative sine. Thus, if the electron system has a quadrupolar degrees of freedom, the elastic constant would show a decrease towards low temperatures, which is called elastic softening.

Next, we consider inter-site quadrupole-quadrupole interaction between neighboring two sites, α and β ,

$$- \sum_{\alpha \neq \beta} K_{QQ} O_{\Gamma}^{\alpha} O_{\Gamma}^{\beta}, \quad (\text{A.9})$$

where K_{QQ} is a coupling constant. In the case of positive sine, this coupling is ferro type, and vice versa. By using mean-field approximation, we can write this term,

$$H_{QQ} = -g'_{\Gamma} \langle O_{\Gamma} \rangle O_{\Gamma}, \quad (\text{A.10})$$

where we again define the coupling constant, g'_{Γ} . Then, if we consider a linear susceptibility, we can calculate the elastic constant as (A.7), and we will obtain,

$$C_{\Gamma}(T) = C_{\Gamma}^0 - \frac{N g_{\Gamma}^2 \chi_{\Gamma}(T)}{1 - g'_{\Gamma} \chi_{\Gamma}(T)} \quad (\text{A.11})$$

Bibliography

- [1] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43** (1979) 1892.
- [2] R. Shiina, H. Shiba, and P. Thalmeier: J. Phys. Soc. Jpn. **66** (1997) 1741.
- [3] Y. Ōnuki, R. Settai, K. Sugiyama, T. Takeuchi, T. C. Kobayashi, Y. Haga, and E. Yamamoto, J. Phys. Soc. Jpn. **73** (2004) 769.
- [4] S. Doniach, in Valence Instabilities and Related Narrow Band Phenomena, ed. R. D. Parks (Plenum, New York, 1977) p. 169.
- [5] D. Jaccard, K. Behnia, and J. Sierro, Phys. Lett A **163** (1992) 475.
- [6] E. Vargoz, P. Link, and D. Jaccard, Physica B **230 – 232** (1997) 182.
- [7] H. Hegger, C. Petrovic, E. G. Moshopoulou, M. F. Hundley, J. L. Sarrao, Z. Fisk, and J. D. Thompson, Phys. Rev. Lett. **84** (2000) 4986.
- [8] T. Moriya and J. Kawabata, J. Phys. Soc. Jpn. **34** (1973) 639.
- [9] J. A. Hertz, Phys. Rev. B **14** (1976) 1165.
- [10] J. Millis and P. A. Lee, Phys. Rev. B **35** (1987) 3394
- [11] P. Coleman, C. Pépin, Q. Si, and R. Ramazashvili, J. Phys. Condens. Matter **13** (2001) R723.
- [12] E.D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B **65** (2002) 100506(R).
- [13] A. Sakai, K. Kuga, and S. Nakatsuji, J. Phys. Soc. Jpn. **80** (2011) 063701.
- [14] D. L. Cox, Phys. Rev. Lett. **59** (1987) 1240.
- [15] S. Sanada, Y. Aoki, H. Aoki, A. Tsuchiya, D. Kikuchi, H. Sugawara, and H. Sato: J. Phys. Soc. Jpn. **74** (2005) 246.
- [16] M. Kasaya, B. Liu, M. Sera, T. Kasuya, D. Endoh, T. Goto, and T. Fujimura, J. Magn. Magn. Mater. **52** (1985) 289.
- [17] R. Higashinaka, T. Maruyama, A. Nakama, R. Miyazaki, Y. Aoki, and H. Sato, J. Phys. Soc. Jpn. **80** (2011) 093703.
- [18] A. Sakai and S. Nakatsuji, Phys. Rev. B **84** (2011) 201106(R).

- [19] M. Kohgi, K. Iwasa, M. Nakajima, N. Metoki, S. Araki, N. Bernhoeft, J.-M. Mignot, A. Gukasov, H. Sato, Y. Aoki, and H. Sugawara, J. Phys. Soc. Jpn. **72** (2003) 1002.
- [20] T. Takimoto, Physica B **378 – 380** (2006) 252.
- [21] Y. Aoki, S. Sanada, D. Kikuchi, H. Sugawara, and H. Sato, Physica B **403** (2008) 1574.
- [22] T. Goto, Y. Nemoto, K. Sakai, T. Yamaguchi, M. Akatsu, T. Yanagisawa, H. Hazama, K. Onuki, H. Sugawara, and H. Sato, Phys. Rev. B **69** (2004) 180511(R).
- [23] T. Yanagisawa, 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. **77** (2008) 074607.
- [24] N. Ogita, T. Kondo, T. Hasegawa, Y. Takasu, M. Udagawa, N. Takeda, K. Ishikawa, H. Sugawara, D. Kikuchi, H. Sato, C. Sekine, and I. Shirotni, Physica B **383** (2006) 128.
- [25] K. Matsuhira, C. Sekine, M. Wakeshima, Y. Hinatsu, T. Namiki, K. Takeda, I. Shirotni, H. Sugawara, D. Kikuchi, and H. Sato, J. Phys. Soc. Jpn. **78** (2009) 124601.
- [26] K. Hattori, Y. Hirayama, and K. Miyake, J. Phys. Soc. Jpn. **74** (2005) 3306.
- [27] T. Hotta, J. Phys. Soc. Jpn. **78** (2008) 073707.
- [28] W. M. Yuhasz, N. A. Frederick, P.-C. Ho, N. P. Butch, B. J. Taylor, T. A. Sayles, M. B. Maple, J. B. Betts, A. H. Lacerda, P. Rogl, and G. Giester, Phys. Rev. B **71** (2005) 104402.
- [29] G. R. Stewart, B. Andraka, C. Quitmann, B. Treadway, Y. Shapira, and E. J. McNiff, Jr., Phys. Rev. B **37** (1988) 3344.
- [30] S. Tsutsui, H. Kobayashi, J. P. Sutter, H. Uchiyama, A. Q. R. Baron, Y. Yoda, D. Kikuchi, H. Sugawara, C. Sekine, I. Shirotni, A. Ochiai, and H. Sato, J. Phys. Soc. Jpn. **77**, Suppl. A (2008) 257.
- [31] T. Hotta, J. Phys. Soc. Jpn. **78** (2008) 073707.
- [32] H. Kotegawa, H. Hidaka, Y. Shimaoka, T. Miki, T. C. Kobayashi, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **74** (2005) 2173.
- [33] M. Mizumaki, S. Tsutsui, H. Tanida, T. Uruga, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **76** (2007) 053706.
- [34] T. C. Kobayashi, K. Miyazawa, K. Tabira, Y. Ikeda, S. Araki, H. Kotegawa, H. Sugawara, D. Kikuchi, and H. Sato, J. Phys. Soc. Jpn. **80** (2011) SA034.
- [35] Y. Aoki, S. Sanada, H. Aoki, D. Kikuchi, H. Sugawara, and H. Sato, Physica B **378-380** (2006) 54.
- [36] H. Kotegawa, H. Hidaka, T. C. Kobayashi, D. Kikuchi, H. Sugawara, and H. Sato, Phys. Rev. Lett. **99** (2007) 156408.
- [37] H. Kotegawa, K. Tabira, Y. Irie, H. Hidaka, T. C. Kobayashi, D. Kikuchi, K. Tanaka, S. Tatsuoka, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **77** Suppl. A (2008) 90.

- [38] T. Yanagisawa, 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.
- [39] S. Nakamura, T. Goto, S. Kunii, K. Iwashita, and A. Tamaki, J. Phys. Soc. Jpn. **63** (1994) 623.
- [40] T. Goto, Y. Nemoto, K. Onuki, K. Sakai, T. Yamaguchi, M. Akatsu, T. Yanagisawa, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **74** (2005) 263.
- [41] T. Goto and B. Lüthi, Adv. Phys. **52** (2003) 67.
- [42] Y. Aoki, W. Higemoto, Y. Tsunashima, Y. Yonezawa, K. H. Satoh, A. Koda, T. U. Ito, K. Ohishi, R. H. Heffner, D. Kikuchi, and H. Sato, Physica B **404** (2009) 757.
- [43] S. Tsutsui, N. Kawamura, M. Mizumaki, N. Ishimatsu, H. Maruyama, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **82** (2013) 023707.
- [44] E. Bucher, J. P. Maita, G. W. Hull, R. C. Fulton, and A. S. Cooper, Phys. Rev. B **11** (1975) 440.
- [45] H. Hidaka, to be submitted.
- [46] H. Hidaka, in preparation.
- [47] F. Vigneron, Phys. Scr. **44** (1991) 27.
- [48] A. Hiess, M. Bonnet, P. Burlet, E. Ressouche, J.-P. Sanchez, J. C. Waeren-borgh, S. Zwirner, F. Wastin, J. Rebizant, G. H. Lander, and J. L. Smith, Phys. Rev. Lett. **77** (1996) 3917.
- [49] P. Dervenagas, P. Burlet, M. Bonnet, F. Bourdarot, A. Hiess, S. L. Bud'ko, P. C. Caneld, G. H. Lander, J. S. Kim, and G. R. Stewart, Phys. Rev. B **61** (2000) 405.
- [50] M. J. Besnus, P. Panissod, J. P. Kappler, G. Heinrich, and A. Meyer, J. Magn. Magn. Mater. **31–34** (1983) 227.
- [51] T. Goto, T. Watanabe, S. Tsuduku, H. Kobayashi, Y. Nemoto, T. Yanagisawa, M. Akatsu, G. Ano, O. Suzuki, N. Takeda, A. Dönni, and H. Kitazawa, J. Phys. Soc. Jpn. **78** (2009) 024716.
- [52] H. Takaguchi, Y. Hayashi, T. Matsumura, K. Umeo, M. Sera, and A. Ochiai, J. Phys. Soc. Jpn. **84** (2015) 044708.