High Magnetic Field Study of Elastic Constants of the Cage-structure Compound $SmBe_{13}$

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Abstract. Ultrasonic measurements were performed on the cage-structure compound $SmBe_{13}$. We have investigated the magnetic field–temperature phase diagram of this material by using pulsed magnetic fields. We found that the low-temperature magnetic order is suppressed by a magnetic field of 43 T for $H \parallel [001]$, which is smaller than the estimated value from mean-field approximation assuming the Γ_8 quartet crystal-electric-field ground state and simple antiferromagnetic order. We found that the elastic constant C_{44} shows softening below the ordering temperature and has a local minimum below 7 T. These facts suggest that the low-temperature state is not a simple antiferromagnetically ordered state. In addition, no elastic anomaly due to rattling modes was found in the present measurements.

1. Introduction

Sm-based compounds have been studied extensively and a rich variety of physical properties has been found, such as metal-insulator transitions under pressure in SmX (X = Te, Se, S) [1, 2], dense Kondo behavior and unusual magnetic order in $SmSn_3$ and $SmIn_3$ [3], as well as possible topological in-gap surface states in the Kondo insulator SmB_6 [4, 5]. Among them, cage-structure compounds have recently been attracting much attention because of their novel physical properties, for instance, possible octupole order in $SmRu_4P_{12}$ [6], magnetically robust heavy-fermion behavior in $SmOs_4Sb_{12}$ [7], and magnetic-field insensitive magnetic order in $SmTr_2Al_{20}$ (Tr = Ti, V, Cr) [8, 9]. In these materials, strong c-f hybridization and multipole degrees of freedom, which are enhanced by the highly symmetrical cage structure, are considered to play important roles in the physical properties. Furthermore, in cage-structure compounds, large anharmonic vibrations of the guest ion, rattling, have been observed by several measurements, such as an Einstein-phonon contribution in specific heat, an ultrasonic dispersion, and in Raman scattering [10, 11, 12, 13]. The possible contribution of these rattling modes to the magnetically robust heavy-fermion state has also been discussed for $SmOs_4Sb_{12}$ [14].

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$SmBe_{13}$ has the $NaZn_{13}$-type crystal structure (Fm$\overline{3}$c), which is the same as for the heavy-fermion superconductor UBe_{13}. The Sm ion is surround 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 [15].

Recently, our group has succeeded to grow single crystals of $SmBe_{13}$ and performed measurements of magnetization, specific heat, X-ray diffraction (XRD), muon-spin relaxation (μSR) and electrical resistivity. The magnetic susceptibility shows a Curie-Weiss behavior above T_M with positive Weiss temperature, and exhibits an antiferromagnetism (AFM)-like cusp anomaly at T_M [16]. Our recent μSR study confirmed that the low-temperature phase is a magnetically ordered state [17]. In the magnetic-field and temperature dependencies of the magnetization, several anomalies were found below T_M, which suggest existence of subphases below T_M [16]. These facts imply that this material has a complex magnetically ordered state. It should be noted that many $M\mathrm{Be}_{13}$ (M = Gd–Er, and Np) compounds show helical magnetic structures at low temperatures and have positive Weiss temperatures; further, $HoBe_{13}$ has a multi-magnetic phase diagram [18, 19, 20]. Consequently, helical magnetic order is one of the candidates for the low-temperature state of $SmBe_{13}$ [16].

In order to understand this low-temperature state in $SmBe_{13}$, it is necessary to clarify the degrees of freedom of the $4f$ electrons. It is suggested that the valence of the Sm ions in this material is nearly trivalent, and that the $4f$ electrons are well localized even at low temperatures [16]. Thus, it is important to determine the crystalline-electric-field (CEF) level scheme of these localized $4f$ electrons of Sm^{3+}. In a cubic CEF, the sextet ($J = 5/2$) of Sm^{3+} 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 [15, 21]. However, as another possibility, the Γ_8 ground state with a gap of 90 K is proposed from our recent analysis, where the Einstein-phonon contribution with Einstein energy of about 170 K in the specific heat is taken into account properly [16]. 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 observed 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.

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 μm 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).

3. Results

In Figs. 1 and 2, 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 [16], this material does not show any ultrasonic dispersion. One of the possible explanations for the absence of

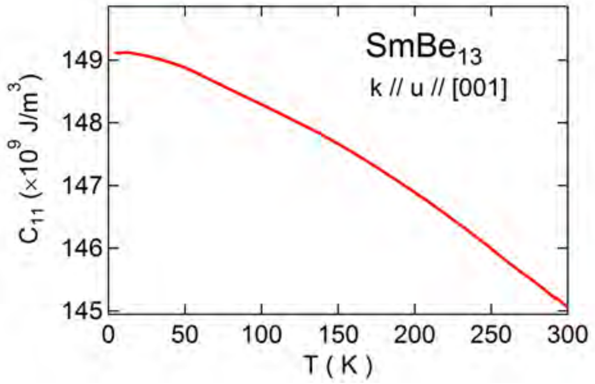

Figure 1. Temperature dependence of C_{11} in zero magnetic field. The wave vector, $\boldsymbol{k}$, and the polarization, $\boldsymbol{u}$, of the sound wave are aligned along [001].

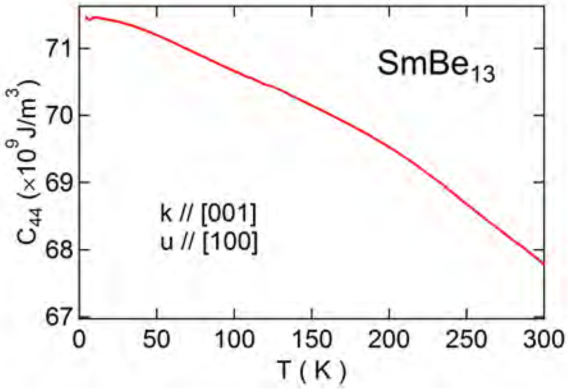

Figure 2. Temperature dependence of C_{44} in zero magnetic field.

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 [11]. Further ultrasonic measurements at higher temperatures would be needed.

Figure 3 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 $T_{\rm M}$ is not very clear. Below 2 T, we define the $T_{\rm M}$ as the temperature at which $\mathrm{d}C_{11}/\mathrm{d}T$ 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 $T_{\rm M}$ is clear above 3 T. Moreover, a difference between zero-field cooling (ZFC) and field cooling (FC) is observed below $T_{\rm Hys}$ in magnetic fields between 2 and 9 T. These facts suggest that there is a subphase below $T_{\rm M}$ above 2 T. The difference between ZFC and FC processes has also been observed in our recent magnetization measurements [16].

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 [22]. 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, Γ_7(0 K)–Γ_8(30 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. 4, $C_{44}(T)$ in various fields is shown. Elastic anomaly in $C_{44}(T)$ at $T_{\rm M}$ is not so clear compared with that of $C_{11}(T)$, and we cannot determine $T_{\rm M}$ from $C_{44}(T)$. The arrows in the figure represent the $T_{\rm M}$ 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 $T_{\rm M}$, 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.

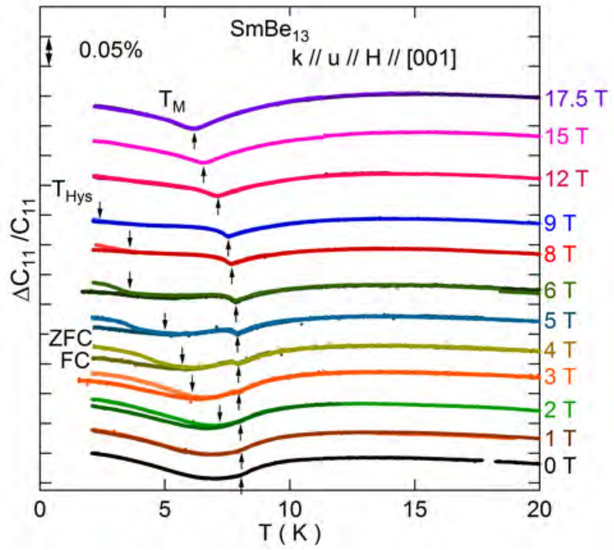

Figure 3. Temperature dependence of C_{11} in various magnetic fields.

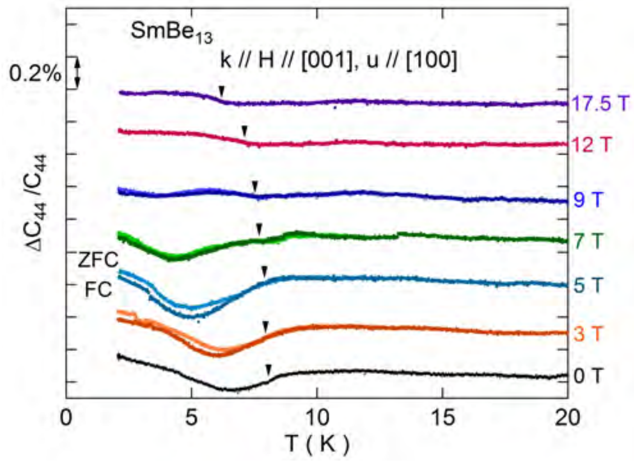

Figure 4. Temperature dependence of C_{44} in various magnetic fields. The arrows indicate $T_{\rm M}$ determined from C_{11}.

In Fig. 5, 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 $H_{\rm M}$ $\approx$ 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 $T_{\rm M}$ in high magnetic fields, this minimum in the pulsed-field data could be due to the phase transition to the paramagnetic state.

Figure 6 shows the H-T phase diagram obtained from our C_{11} data in static and pulsed magnetic fields. As can be seen, $T_{\rm M}$ is clearly reduced with applied magnetic fields. The extrapolated phase boundary from the low-field region nicely merge with the magnetic field, $H_{\rm M}$.

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 [16]. Here, we take into account only the ground-state multiplet of $J = 5/2$, and the Hamiltonian is

$$H = H_{\rm CEF} - K\boldsymbol{J}\cdot\langle\boldsymbol{J}\rangle + g_J\mu_B\boldsymbol{J}\cdot\boldsymbol{H}. \quad (1)$$

The inter-site coupling constant, K, is assumed to be -4 and -3.07 K for free Sm-ions and the Γ_8(0 K)–Γ_7(90 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.*, $H_{\rm CEF} = 0$, 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 Γ_8(0 K)–Γ_7(90 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

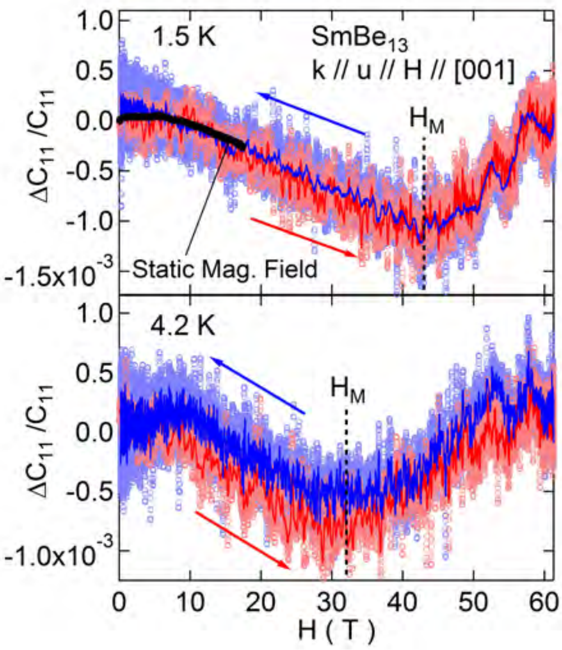

Figure 5. Relative change of C_{11} in pulsed magnetic field. Light-colored circles represent raw data, and deep-colored lines are smoothed curves.

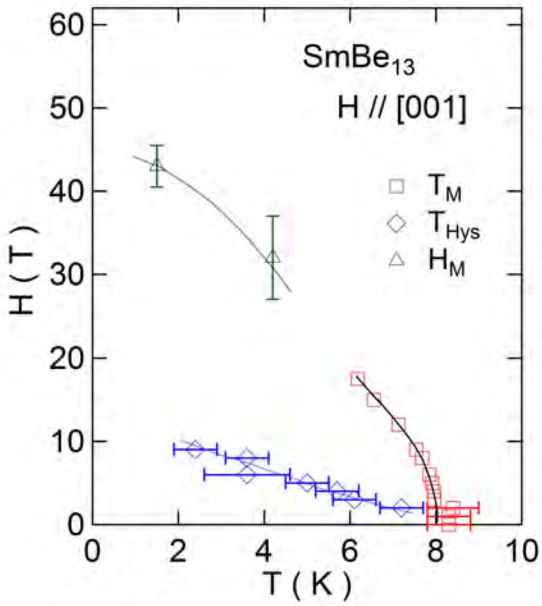

Figure 6. H-T phase diagram obtained from the result of our C_{11} measurements. The lines are guide to the eye.

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 $SmBe_{13}$ 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.

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.

5. Acknowledgment

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References

[1] Jayaraman A, Narayanamurti V, Bucher E and Maines R G 1970 *Phys. Rev. Lett.* **25** 368.
[2] Jayaraman A, Narayanamurti V, Bucher E and Maines R G 1970 *Phys. Rev. Lett.* **25** 1430.
[3] Kasaya M, Liu B, Sera M, Kasuya T, Endoh D, Goto T and Fujimura T 1985 *J. Magn. Magn. Mater.* **52** 289.
[4] A. Menth, E. Buehler, and T. H. Geballe 1969 *Phys. Rev. Lett.* **22** 295.
[5] Dzero M, Sun K, Galitski V and Coleman P 2010 *Phys. Rev. Lett.* **104** 106408.
[6] Aoki Y, Sanada S, Kikuchi D, Sugawara H and Sato H 2008 *Physica* B **403** 1574.
[7] Sanada S, Aoki Y, Aoki H, Tsuchiya A, Kikuchi D, Sugawara H and Sato H 2005 *J. Phys. Soc. Jpn.* **74** 246.
[8] Higashinaka R, Maruyama T, Nakama A, Miyazaki R, Aoki Y and Sato H 2011 *J. Phys. Soc. Jpn.* **80** 093703.
[9] Sakai A and Nakatsuji S 2011 *Phys. Rev.* B **84** 201106(R).
[10] Goto T, Nemoto Y, Sakai K, Yamaguchi T, Akatsu M, Yanagisawa T, Hazama H, Onuki K, Sugawara H and Sato H 2004 *Phys. Rev.* B **69** 180511(R).
[11] Yanagisawa T, Saito H, Hidaka H, Amitsuka H, Araki K, Akatsu M, Nemoto Y, Goto T, Ho P-C, Baumbach R E and Maple M B 2008 *J. Phys. Soc. Jpn.* **77** 074607.
[12] Ogita N, Kondo T, Hasegawa T, Takasu Y, Udagawa M, Takeda N, Ishikawa K, Sugawara H, Kikuchi D, Sato H, Sekine C and Shirotani I 2006 *Physica* B **383** 128.
[13] Matsuhira K, Sekine C, Wakeshima M, Hinatsu Y, Namiki T, Takeda K, Shirotani I, Sugawara H, Kikuchi D and Sato H 2009 *J. Phys. Soc. Jpn.* **78** 124601.
[14] Hattori K, Hirayama Y and Miyake K 2005 *J. Phys. Soc. Jpn.* **74** 3306.
[15] Bucher E, Maita J P, Hull G W, Fulton R C and Cooper A S 1975 *Phys. Rev.* B **11** 440.
[16] Hidaka H to be submitted.
[17] in preparation.
[18] Vigneron F 1991 *Phys. Scr.* **44** 27.
[19] Hiess A, Bonnet M, Burlet P, Ressouche E, Sanchez J -P, Waeren-borgh J C, Zwirner S, Wastin F, Rebizant J, Lander G H and Smith J L 1996 *Phys. Rev. Lett.* **77** 3917.
[20] Dervenagas P, Burlet P, Bonnet M, Bourdarot F, Hiess A, Bud'ko S L, Caneld P C, Lander G H, Kim J S and Stewart G R 2000 *Phys. Rev.* B **61** 405.
[21] Besnus M J, Panissod P, Kappler J P, Heinrich G and Meyer A 1983 *J. Magn. Magn. Mater.* **31–34** 227.
[22] Goto T and Lüthi B 2003 *Adv. Phys.* **52** 67.