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 \(\Gamma_5\) 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 Sm\(_X\) (\(X = \text{Te, Se, S}\)) \([1, 2]\), 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 SmRut\(_4\)P\(_{12}\) \([6]\), magnetically robust heavy-fermion behavior in SmOs\(_4\)Sb\(_{12}\) \([7]\), and magnetic-field insensitive magnetic order in Sm\(_{2}\)Al\(_{20}\) (\(T_r = \text{Ti, V, Cr}\)) \([8, 9]\). 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\(_4\)Sb\(_{12}\) \([14]\).

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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 ($\mu$SR) 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 $\mu$SR 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 MB$_{13}$ ($M$ = 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 4$f$ electrons. It is suggested that the valence of the Sm ions in this material is nearly trivalent, and that the 4$f$ 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 4$f$ electrons of Sm$^{3+}$. In a cubic CEF, the sextet ($J = 5/2$) of Sm$^{3+}$ splits into a $\Gamma_7$ doublet and a $\Gamma_8$ quartet. Thus far, the $\Gamma_7$ 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 $\Gamma_8$ 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$^\circ$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 $\mu$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).

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
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 $T_M$ 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 [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 $\Gamma_8$ quartet has quadrupole degrees of freedom, a softening toward low temperatures is expected in the case of a $\Gamma_8$ quartet CEF ground state. Thus, a $\Gamma_8$ 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 $\Gamma_7$ doublet ground state with a small gap of about 12.5 K to the $\Gamma_8$ 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. 4, $C_{44}(T)$ 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.
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 $H_M$ $\approx$ 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 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 [16]. Here, we take into account only the ground-state multiplet of $J = 5/2$, and the Hamiltonian is

$$H = H_{CEF} - K\langle J \rangle + g\mu_B J \cdot H.$$  \hspace{0.5cm} (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., $H_{CEF} = 0$, 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 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 4$f$-electron system has multipole degrees of freedom in the case of $\Gamma_8$ 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.

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