Crystalline Electric Field and Kondo Effect in SmOs$_4$Sb$_{12}$

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Our ultrasound results obtained in pulsed magnetic fields show that the filled-skutterudite compound SmOs$_4$Sb$_{12}$ has the $\Gamma_6^+$ quartet crystalline-electric-field ground state. This fact suggests that the multipolar degrees of freedom of the $\Gamma_6^+$ quartet play an important role in the unusual physical properties of this material. On the other hand, the elastic response below $\approx 20$ T cannot be explained using the localized 4$f$-electron model, which does not take into account the Kondo effect or ferromagnetic ordering. The analysis result suggests the presence of a Kondo-like screened state at low magnetic fields and its suppression at high magnetic fields above 20 T even at low temperatures.

The filled-skutterudite compound SmOs$_4$Sb$_{12}$ has attracted much attention because of its unusual physical properties.$^{1,2}$ Namely, this compound shows a relatively large Sommerfeld coefficient, $\gamma \approx 820 \sim 880 \text{ mJ mol}^{-1} \text{ K}^{-2}$, which is hardly affected by magnetic fields of up to 8 T.$^1$ This robust $\gamma$ is in contrast to the magnetically suppressed $\gamma$ in typical Ce-based heavy-fermion compounds such as CeCu$_6$.$^3$ This suggests that the heavy-fermion state in SmOs$_4$Sb$_{12}$ is of non-magnetic origin. On the other hand, several phenomena due to the anharmonic vibrations of guest ions, so called rattling, have been observed in this material.$^{4,7}$ A multichannel 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.$^{8,9}$ The characteristic temperature $T^*$, which is related to the crossover temperature of Kondo-like screening due to hybridization, is estimated to be $\approx 20$ K.$^{10}$ Below $T^*$, SmOs$_4$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$\sim$0.03 $\mu_B$/Sm-ion$^{1,2}$ which is much smaller than the free-ion value of 0.71 $\mu_B$/ion for Sm$^{3+}$, even considering an intermediate valence of $\approx +2.76$, as found by X-ray absorption spectroscopy below 20 K.$^{11}$ One of the possible explanations is that the low-temperature phase is an itinerant ferromagnetic state.$^1$ Another possible explanation would be a contribution of higher-order multipole moments to the low-temperature properties, which has been suggested on the basis of a hydrostatic-pressure study.$^{12}$

In some Sm-based cage-structured compounds with a cubic symmetry and a quartet ground state, such as SmRu$_4$P$_{12}$ and SmTi$_2$Al$_3$, the possible effects of multipolar degrees of freedom have been discussed.$^{13,14}$ In several Pr-based filled-skutterudite compounds with a pseudodegenerate crystalline-electric-field (CEF) ground state, such as PrRu$_4$P$_{12}$, multipole ordering has been suggested.$^{15}$ Because of the similar cage-featured crystal structure (Fig. 1), it is expected that the unusual physical properties of SmOs$_4$Sb$_{12}$ also originate from higher-order multipoles.

To study the role of multipolar degrees of freedom in this material, we have performed an ultrasound study in pulsed magnetic fields.$^{16}$ This type of experiment is particularly sensitive to the elastic characteristic of rare earth compounds, and thus it provides a unique tool to explore the nature of multipolar contributions in SmOs$_4$Sb$_{12}$.

![Image](https://example.com/fig1.png)

**Fig. 1.** (Color online) Crystal structure of SmOs$_4$Sb$_{12}$ (space group: Im3), where two unit cells are described. In the upper cell, an octahedra that consists of Sb atoms around an Os atom is shown. In the lower cell, a cage structure that consists of Os and Sb atoms is emphasized.

### Table 1. Quadrupoles, symmetrized strains, and corresponding elastic constants are categorized with $T_6$ symmetry ($O_h$ symmetry).

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Quadrupole</th>
<th>Strain</th>
<th>Elastic Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>$\varepsilon_B = \varepsilon_{zz} + \varepsilon_{yy}$</td>
<td>$\varepsilon_{zz}$</td>
<td>$C_B = \frac{C_{11} + 2C_{12}}{3}$</td>
</tr>
<tr>
<td>$\Gamma_23$ ($\Gamma_3$)</td>
<td>$O^1_2$, $O_2^1$</td>
<td>$\frac{2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy} - \varepsilon_{kk}}{\sqrt{6}}$, $\frac{\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}}{\sqrt{3}}$</td>
<td>$C_{11} - C_{12}$</td>
</tr>
<tr>
<td>$\Gamma_4$ ($\Gamma_5$)</td>
<td>$O_{zz}$, $O_{xx}$, $O_{yy}$</td>
<td>$\varepsilon_{zz}$, $\varepsilon_{xx}$, $\varepsilon_{yy}$</td>
<td>$C_{44}$</td>
</tr>
</tbody>
</table>
Owing to the possible presence of the strong screening of quadrupole moments below $T^*$. In this study, we focus on the quadrupolar susceptibility of SmOs$_4$Sb$_{12}$ at high magnetic fields to determine the CEF states without the effect of the Kondo-like screening. As will be shown later in Figs. 2(b), 2(c), 3(b), and 3(c), the calculated quadrupolar susceptibilities are clearly different between the two models at high magnetic fields. Thus, we can distinguish the CEF ground state by checking whether the elastic constants increase or 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 SmOs$_4$Sb$_{12}$ is the $\Gamma_{67}$ quartet.

A single crystal of SmOs$_4$Sb$_{12}$ was grown by 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 $\approx 200$ ms. 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 results for up and down sweeps of the pulsed magnetic field. We conclude that the heating of the sample due to eddy currents is negligible.

Figure 2(a) shows the pulsed field data for $C_{44}$ at various temperatures. This elastic constant exhibits a broad minimum at $\approx 4$ and $\approx 10$ T for 1.5 and 4.2 K, respectively. This characteristic feature is confirmed by experimental results obtained in a static magnetic field and shown as black curves in Fig. 2(a). We will discuss the possible origin of this minimum in a later section.

**Fig. 2.** (Color online) (a) Relative change in the elastic constant, $\Delta C_{44}/C_{44}$, versus magnetic field. The pulsed field data (k || [100] and $\mu$ || $H$ || [010], color plots) and static field data ($H$ || k || [001] and $\mu$ || [010], black curves) are shown. The zero-field values of the experimental results are calculated on the basis of the temperature dependence of $C_{44}$, which is shown in Fig. 4(a).

**Fig. 3.** (Color online) (a) Relative change in the elastic constant $C_{11}$ versus magnetic field. The zero-field values of the experimental results are calculated on the basis of the temperature dependence of $C_{11}$ reported in Ref. 7. (b) Magnetic field dependence of the quadrupolar susceptibility $\chi_{Q}(0^2)$, calculated for the $\Gamma_5$ ground state and the $\Gamma_5$ first excited state separated by a gap $\Delta \approx 38$ K. (c) The same as in (b) but for the $\Gamma_{67}$ ground state and the $\Gamma_5$ first excited state separated by $\Delta \approx 20$ K (see text for details).
with the calculated quadrupolar susceptibility \( \Gamma \) the bulk modulus (b) magnetic field dependences of \( \Gamma \) pendence of fields. Here, a local minimum in expansion in magnetic fields are necessary. The calculations are based on the quadrupolar susceptibility for \( \Gamma_\text{t} \) symmetry and a \( \Gamma_{67} \) 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.

At higher magnetic fields, \( C_{44} \) increases with increasing magnetic field. This feature can be explained by the quadrupolar susceptibility calculated for the \( \Gamma_{67} \) quartet ground state as shown in Fig. 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 in the absolute value of the quadrupolar susceptibility (i.e., an increase in the elastic constants) is expected [Fig. 2(c)]. On the other hand, in the case of the \( \Gamma_5 \) doublet ground state, the quadrupolar susceptibility should increase [Fig. 2(b)]. Here, the Zeeman splitting causes the mixing of the wave functions of the \( \Gamma_5 \) ground state and the excited \( \Gamma_{67} \) quartet state, and the 4f-electron system gains quadrupolar degrees of freedom. In Fig. 3(a), the relative change in the elastic constant \( C_{11} \) is shown. The elastic constant \( C_{11} = C_B + \frac{4}{3}(C_{11} - C_{12}) \) includes not only the bulk modulus \( C_B \), which corresponds to volume change with the \( \Gamma_1 \) symmetry, but also \( \frac{4}{3}(C_{11} - C_{12}) \), which corresponds to the \( \Gamma_{23} \) symmetry, related to the \( O^0 \) quadrupole. The calculated \( \Gamma_{23} \)-type quadrupolar susceptibility is shown in Figs. 3(b) and 3(c) for the two different ground states. Here, we compare \( C_{11} \) with the calculated quadrupolar susceptibility \( \chi_{23} \), assuming that the change in the \( \Gamma_{23} \) component of the elastic constant, \( \frac{4}{3}(C_{11} - C_{12}) \), is dominant. As can be seen, again our high-field experimental results for \( C_{11} \) can be explained well by the \( \Gamma_{67} \) ground-state model. To estimate the magnetic field dependence of \( C_B \) more precisely, measurements of the thermal expansion in magnetic fields are 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. 2(a) and 3(a)]. To explain these features, we consider two origins. The first one is the magnetoelastic coupling due to an induced weak ferromagnetic moment, which is induced spontaneously below \( T_C \approx 2.5 \) K at zero magnetic field. Since a magnetic field above 10 T polarizes the ferromagnetic moments, we can treat the system as a polarized paramagnetic phase. In this case, we can neglect this magnetoelastic effect and consider only 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. 4(a) and 4(b), we compare the magnetic field and temperature sweep results to estimate the role of the Kondo effect in this system and to verify the limit of applicability of a localized electron picture. Figure 4(a) shows the magnetic field dependence (bottom axis) and temperature dependence (top axis) of the elastic constant \( C_{44} \). Figure 4(b) shows the results of the calculation of \( C_{44} \). The calculated \( C_{44} \) at 4.2 K and a relative change in the elastic constant, \( \chi_{23} \), is shown. The colored background indicates the temperature and magnetic field regions where 4f electrons are considered to be less localized.
pressed by magnetic fields, i.e., the system recovers the localized character of 4f electrons by applying magnetic fields. Indeed, the signature of the Kondo effect has also been found in NQR measurements. On the other hand, the robustness of the Sommerfield coefficient has also been reported, which implies that the present compound possesses a magnetically stable heavy-fermion state. This feature is, however, not verified above 8 T. Our ultrasonic results suggest that magnetic fields above 20 T are sufficient to suppress the Kondo effect. To gain more information on the relationship between the large γ and the Kondo-like screened state of this material, more studies, such as magnetization or resistivity measurements in the high magnetic field μ₀H > 20 T are necessary.

In summary, we have performed ultrasonic measurements of SmOs₄Sb₁₂ in pulsed magnetic fields of up to 58 T. The magnetic field dependences of the elastic constants suggest that the present system possesses a Γ₆₇ quartet CEF ground state. In our CEF analysis, we assume a simple localized picture of 4f electrons, which qualitatively describes our experimental results obtained above 20 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 SmOs₄Sb₁₂. We conclude that the system recovers the localized character of 4f electrons at magnetic fields above 20 T.

Acknowledgments We acknowledge the support of the HLD at HZDR, member of the European Magnetic Field Laboratory (EMFL). Research at HZDR was supported by JSPS KAKENHI Grant No. 26400342 and the Strategic Young Researcher Overseas Visits Program for Accelerating Brain Circulation from the Japan Society for the Promotion of Science. Single-crystal growth and characterization at UCSD were supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering under Grant No. DEFG02-04-ER46105. Research at California State University, Fresno is supported by NSF DMR-1506677.