Elastic properties of the ferromagnetic heavy fermion system SmOs$_4$Sb$_{12}$

Y Nakanishi$^1$, T Tanizawa$^1$, T Fujino$^1$, P Sun$^1$, M Nakamura$^1$, H Sugawara$^2$, D Kikuchi$^3$, H Sato$^3$ and M Yoshizawa$^1$

$^1$ Graduate School of Engineering, Iwate University, Morioka 020-8551, Japan
$^2$ Faculty of Integrated Arts and Sciences, The University of Tokushima, Tokushima, 770-8502, Japan
$^3$ Department of Physics, Tokyo Metropolitan University, Hachioji, 192-0397, Japan

E-mail: yoshiki@iwate-u.ac.jp

Abstract. Ultrasonic measurements were made on a single crystal of the filled skutterudite compound SmOs$_4$Sb$_{12}$. A remarkable elastic softening toward low temperature was observed in the elastic constants $C_{11}, (C_{11}-C_{12})/2$ and $C_{44}$ as a function of temperature, followed by a sharp drop which is associated with the onset of ferromagnetic ordering, and then display a monotonic increase below $T_c$. The present results indicate that the crystalline electric field (CRF) effect would not support straightforward the observed elastic softening toward low temperature. We suggest that this fact is originated from valence instability of the Sm ion at low temperature in SmOs$_4$Sb$_{12}$. The $4f$ electronic ground state of the Sm ion and its elastic property are discussed.

Filled skutterudite compounds, which are described by $R$Tr$_4$X$_{12}$ ($R =$ lanthanide, alkali metal, alkaline-earth, or actinide; Tr = transition metal, X: pnictogen) have attracted considerable attention because of a rich variety of interesting strongly correlated electron phenomena and potential for thermoelectric applications.[1-5] Among them, Sm-based skutterudite compounds exhibit outstanding features including heavy fermion (HF) behavior, ferromagnetism in SmFe$_4$P$_{12}$ and SmOs$_4$Sb$_{12}$, and metal-insulator transition, multipole ordering in SmRu$_4$P$_{12}$.[6-10] One of the essential ingredients in the physics is the strong hybridization between localized $f$ electrons and conduction bands owing to the large coordination number of X to $R$. These systems provide us novel and unique stages with plural $4f$ electrons. SmOs$_4$Sb$_{12}$ exhibits a ferromagnetic transition below $\sim 2.6$ K. Furthermore, it was found that the electronic specific heat coefficient and the coefficient of the quadratic temperature dependence of electric resistivity are significantly enhanced as $\gamma \sim 0.82$ J/K$^2$mol and $A \sim 0.8 \, \mu\Omega cm$, respectively.[6, 7] It should be noted that the $\gamma$ and $A$ are insensitive to the applied field, in markedly contrast to the strong field dependence observed in the typical Ce-based HF compounds.[11, 12] This fact implies that the formation of HF state is ascribable to a non-magnetic origin. One of the central issues in SmOs$_4$Sb$_{12}$ is how the HF state is formed. The aim of the present work is to evaluate the ground state properties of SmOs$_4$Sb$_{12}$ and to explore the elastic properties by means of ultrasonic measurements.

Ultrasonic measurements are a powerful method to elucidate the ground state multiplet of rare-earth ions split mainly by CEF effect. The macroscopic strain of symmetry $\Gamma$, $\varepsilon_\Gamma$, can couple directly to the quadrupolar operator $Q_\Gamma$. The anomaly of elastic constants in rare-earth compounds with localized $4f$-electrons is explained well with the quadrupolar susceptibility.[13]
The elastic strain induced by the sound wave causes a perturbation on the CEF potential due to the quadrupole-strain interaction \( H_{qs} = -g_q O \varepsilon \), where \( g_q \) is the coupling constant between the quadrupolar moment \( O \) and the symmetric strain \( \varepsilon \). The inter-site quadrupolar interaction is described as \( H_{qq} = -\sum g'_{iq} \langle O_i \rangle O_j \), where \( g'_{iq} \) and \( \langle O_i \rangle \) are the coupling constant and the mean field of the quadrupolar moment, respectively. The temperature dependence of the symmetric elastic constant is described as \( C_\Gamma(T) = C_\Gamma^{0} + N g^2 \chi_\Gamma^{(s)} / (1 - g'_{iq} \chi_\Gamma^{(s)}) \), where \( C_\Gamma^{0}, \chi_\Gamma^{(s)} \) and \( N \) are a background part without quadrupole-strain interaction and quadrupolar susceptibility and the number of Sm ions in unit volume, respectively.

The single crystal of SmOs\(_4\)Sb\(_{12}\) was grown by the Sb-self-flux method using high purity raw materials of 4N (99.99 % pure)-Sm, 4N-Os and 6N-Sb. X-ray powder diffraction pattern shows that no impurity phase was detected, without small amounts of Os and Sb metals of the order of \( \sim 1 \text{ %} \) in volume. The sound wave velocity \( v \) was detected by an ultrasonic apparatus based on the phase-comparison method. The absolute value of the elastic constant could not be estimated explicitly because the thickness of the sample was not enough large to do that. The ultrasonic measurement was performed using a \(^3\)He cryostat with a 14 T superconducting magnet above 0.4 K.

**Figure 1.** Temperature dependence of the elastic constants \( C_{11}, (C_{11} - C_{12})/2 \) and \( C_{44} \) in zero field.

**Figure 2.** Temperature dependence of the elastic constant \( C_{11} \) under selected fields for \( H//\langle 100 \rangle \).

Figure 1 shows the temperature dependence of the elastic constant \( C_{11}, (C_{11} - C_{12})/2 \) and \( C_{44} \). \( C_{11} \) was measured by the longitudinal sound wave with frequencies of 10 - 30 MHz propagated along the \( \langle 100 \rangle \) axis. \( (C_{11} - C_{12})/2 \) and \( C_{44} \) were measured by the transverse sound wave with frequencies of 5 - 15 MHz propagated along the \( \langle 110 \rangle \) axis with the polarization parallel to the \( \langle 1-10 \rangle \) axis and propagated along the \( \langle 100 \rangle \) axis with the polarization parallel to the \( \langle 010 \rangle \) axis, respectively. The elastic constant increases monotonically with decreasing temperature. A remarkable elastic softening was observed below \( \sim 5 \text{ K} \). Besides, a clear increase was observed below \( \sim 15 \text{ K} \) in them, although we don’t mention this anomaly in detail in this article. We will
discuss it based on an off-center oscillation of the Sm ion in a relatively oversized Sb-octahedron in a separated article. Figure 2 shows the temperature dependence of the elastic constant $C_{11}$ under the selected fields along the ⟨100⟩ axis. The sharp drop, most probably due to the ferromagnetic transition gradually shifts to higher temperatures and become smaller with increasing field. It exhibits a gradual change around $T_c$ in slope with increasing field. This behavior is consistent with that of a ferromagnetic transition. It is noted that this transition is less sensitive to the application of field as compared to that of SmFe$_4$P$_{12}$.[10] Figure 3 shows the magnetic phase diagram of SmOs$_4$Sb$_{12}$, as deduced from the first derivative of the elastic constant $(C_{11} - C_{12})/2$ with respect to temperature, $dC/dT$. The phase diagram indicates that the boundary goes up to the higher field side with a positive curvature in higher temperature and becomes obscure above $\sim$ 6K, suggesting ferromagnetic nature. Similar behavior is observed in that of the ferromagnetic HF compound SmFe$_4$P$_{12}$.[10]

Here, let us discuss the obtained results. If the Sm ion has the well-localized 4f electronic state in SmOs$_4$Sb$_{12}$, the $J = 5/2$ multiplet of Sm trivalent splits into a doublet $\Gamma_5$ and a quartet $\Gamma_{67}$ in the $T_h$ site symmetry. There are two CEF level scheme models reported so far. The first model is estimated using the experimentally well-determined CEF parameters for PrOs$_4$Sb$_{12}$ as a quartet $\Gamma_{67}$ ground state and a doublet $\Gamma_5$ excited state separated by $\Delta_{CEF} = 19$ K.[6] On the other hand, another model is proposed by the specific heat measurement as a doublet $\Gamma_5$ ground state and a quartet $\Gamma_{67}$ excited state separated by $\Delta_{CEF} = 38$ K.[7] Apparently, the former model is appropriate to reproduce the experimental results since a elastic softening toward low
temperature is expected in both elastic constants \((C_{11} - C_{12})/2\) and \(C_{44}\) in the case for \(J=5/2\) as demonstrated by the present results. In particular, if one sets in a doublet \(\Gamma_5\) ground state and a quartet \(\Gamma_{67}\) excited state separated by \(\Delta_{CEF}\) a characteristic minimum should be observed in the temperature dependence of \((C_{11} - C_{12})/2\) at a temperature of \(\sim \Delta_{CEF}/2\) as associated with the thermally dependent population of such a two-separated level. The expected minimum in the \((C_{11} - C_{12})/2\) was not observed, indicating inadequacy for explaining the 4\(f\) ground state of the Sm ion in SmOs\(_4\)Sb\(_{12}\). The solid lines shown in Fig. 4 are theoretical results based on the above formula using the former level scheme: \(\Gamma_{67} - \Gamma_5\) (19 K). The fits yield the following values: \(N g\_T^2=9.0 \times 10^{-4}\), \(g\_T=0.02\) K for model A and \(N g\_T^2=10.0 \times 10^{-4}\), \(g\_T=0.02\) K for model B. As can be seen, neither model can reproduce successfully the softening toward \(T_c\) in the temperature dependence of the elastic constants \((C_{11} - C_{12})/2\).

Very recently, the Extended X-ray Absorption Fine Structure (EXAFS) measurement indicated that the mixed valence state of Sm ion was formed in SmOs\(_4\)Sb\(_{12}\).[15] In particular, the valence of the Sm ion decreases gradually from +2.83 to +2.76 with decreasing temperature. This means that Sm\(^{+2}\) state with \(J = 0\) plays an important role in this system as well as Sm\(^{+3}\) state. Probably, the mixture of Sm\(^{+2}\) and Sm\(^{+3}\) leads to failure in the fit to reproduce the experimental results discussed above. This fact seems to lead to a tiny entropy : 2\% of Rln2 and a tiny observed magnetic moment associated with the magnetic ordering.

In summary, we have investigated the elastic properties of SmOs\(_4\)Sb\(_{12}\) in magnetic fields by means of the ultrasonic measurements. The feature would reflect the formation of the itinerant heavy quasiparticles. The low-temperature behavior of the elastic constants can not be explained well only by the proposed CEF models. This fact supports the unstable Sm valence in SmOs\(_4\)Sb\(_{12}\), i.e., a mixed valence state. The same investigation in higher fields is required to clarify the formation mechanism for the HF state of SmOs\(_4\)Sb\(_{12}\).

The measurements have been performed in the Cryogenic Division of the Center for Instrumental Analysis, Iwate University. This work was supported by a Grant-in-Aid for Science Research in Priority Area "Skutterudite" (No. 15072202) and for Young Scientists (No. 16740182) of the Minister of Education, Culture, Sports, Science, and Technology of Japan.

1. Reference

[1] See for example, Proc. Int. Conf. Strongly Correlated Electrons with Orbital Degrees of Freedom, 2002 J. Phys. Soc. Jpn. B 71 Supplement

[2] Torikachvili S M, Chen W J, Dalichaouch Y, Guertin P R, McElfresh W M, Rossel C and Maple B M, 1987 Phys. Rev. B 36 8660

[3] Sato H, Abe Y, Okada H, Matsuda D T, Abe K, Sugawara H and Aoki Y, 2000 Phys. Rev. B 62 15125

[4] Bauer D E, Frederick A N, Ho -C P, Zapf S V and Maple B M, 2002 Phys. Rev. B 65 100506(R)

[5] Sales C B, Mandrus D, Chakoumakos C B, Keppens V, Thompson R J, 1997 Phys. Rev. B 56 15081

[6] Sanada S, Aoki Y, Aoki H, Tsuchiya A, Kikuchi D, Sugawara H and Sato H 2005 J. Phys. Soc. Jpn. B 74 246

[7] Yuhasz M W, Butch P N, Ho -C P, Jeffries R J, Yanagisawa T, Frederick A N, Maple B M, Henkie Z, Pietraszko A, McCall K S, McElfresh W M, Fluss J M 2005 Phys. Rev. B 71 104402

[8] Yoshizawa M, Nakashishi Y, Oikawa M, Sekine C, Shiratori I, Saha R S, Sugawara H and Sato H 2005 J. Phys. Soc. Jpn. B 74 1030

[9] Hachitani K, Kohori Y, Giri R, Sekine C, Shiratori I 2006 Phys. Rev. B 73 052408

[10] Nakashishi Y, Tanizawa T, Fujino T, Sugawara H, Kikuchi D, Sato H and Yoshizawa M, (to be published in J. Phys. Soc. Jpn.)

[11] Bredd D C, Horn S, Steglich F, Lüthi B and Martin M R 1984 Phys. Rev. Lett. 52 1982

[12] Sato K, Fujita T, Maeno Y, Ônuki Y, Komatsubara T and Okutsuka T, 1985 Solid State Commun 56 327

[13] Nakamura S, Goto T, Kunii S, Iwashita K and Tanaki A, 1994 J. Phys. Soc. Jpn. B 63 623

[14] Nakashishi Y, Tanizawa T, Fujino T, Sugawara H, Kikuchi D, Sato H and Yoshizawa M, (in preparation)

[15] Mizumaki M private communication