Investigation of ferromagnetic filled skutterudite compound EuFe$_4$As$_{12}$

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Abstract. A variety of thermodynamic and transport measurements were performed on As-based filled skutterudite compound EuFe$_4$As$_{12}$ prepared under high pressure. EuFe$_4$As$_{12}$ was reported to exhibit a ferromagnetic-like phase transition with an unexpectedly high transition temperature of 152 K. In order to investigate the field dependence of the transition in the arsenide, specific heat measurements under magnetic fields up to 8 T have been carried out. The ferromagnetic-like transition is clearly visible as a peak of the specific heat at 0 T. The anomaly for the phase transition was found to become broad and shift to higher temperature with applying magnetic field. This behavior is consistent with a ferromagnetic ordering. Furthermore, the excess magnetic entropy suggests a possibility of the magnetic contribution of the [Fe$_4$As$_{12}$] polyanions. We will discuss the magnetic ordering state from a viewpoint of the interaction of Eu 4f moments with the ferromagnetic [Fe$_4$As$_{12}$] host lattice. From the measurements of thermoelectric properties, the dimensionless figure of merit ZT was evaluated as 0.007 at room temperature.

1. Introduction
Filled skutterudite compounds $MT_4X_{12}$ ($M$ = alkali metal, alkaline earth and lanthanide; $T$ = Fe, Ru and Os; $X$ = P, As and Sb) have received considerable attention owing to their potential use as improved, next-generation thermoelectric materials [1, 2, 3]. The $M$ ions, located inside the cages formed by twelve $X$ ions, are believed to show random motion (rattling) around the equilibrium positions. Then, the rattling produces a large phonon scattering, reducing the lattice thermal conductivity. Owing to the reduced thermal conductivity, filled skutterudite compounds show excellent thermoelectric performance. Furthermore, these compounds, particularly P- and Sb-based compounds, exhibit a wide variety of strongly correlated electron behaviors, such as unconventional superconductivity, anomalous metal–insulator transition and multipole ordering [4, 5]. On the other hand, the properties of As-based filled skutterudite compounds have not been studied so far because the As-based compounds are quite difficult to prepare. However, As-based filled skutterudite compounds are important for systematic research on skutterudite family. High-pressure synthesis using pressures above 4 GPa is a powerful technique for preparing As-based filled skutterudite compounds. In fact, we have succeeded in synthesizing samples of new As-based filled skutterudite compounds $MT_4As_{12}$ ($M$=Eu, Gd and Tb, $T$=Fe, Ru, and Os) using the high-pressure synthesis technique [6, 7].

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New As-based filled skutterudite compound EuFe$_4$As$_{12}$ was reported to exhibit a ferromagnetic-like phase transition with an unexpectedly high transition temperature of 152 K [6]. The larger lattice constant than that expected from the lanthanide contraction in trivalent ion and the effective magnetic moment (6.9 $\mu_B$/Eu) of the compound suggest that Eu ions in the compound are in divalent or mixed-valent state. Furthermore, the reciprocal susceptibility $\chi^{-1}$ of EuFe$_4$As$_{12}$ has a nonlinear temperature dependence and magnetization measurements of the compound show that its magnetic moment is about 4.5 $\mu_B$/Eu at 2 K, which is much less than the magnetic moment ($7\mu_B$/Eu) expected for Eu$^{2+}$. These results imply that EuFe$_4$As$_{12}$ has a canted ferromagnetic or ferrimagnetic structure below 152 K. Similar behaviors are also observed in a ferrimagnetic compound EuFe$_4$Sb$_{12}$ [8, 9, 10]. In this study, we report further results for EuFe$_4$As$_{12}$.

2. Experimental

Single-phase polycrystalline samples of EuFe$_4$As$_{12}$ and an isomorphous reference compound LaFe$_4$As$_{12}$ were synthesized using a cubic-anvil high-pressure apparatus. The samples were prepared by reacting stoichiometric amounts of 3N (99.9% pure)-Eu and La chips, 4N-Fe and 6N-As powders at 4 GPa. The reaction temperature was 800 °C. The samples were characterized by powder X-ray diffraction using Co K$_\alpha1$ radiation and silicon as a standard. Most of the observed diffraction lines were indexable using the skutterudite structure for both compounds. The lattice constants of EuFe$_4$As$_{12}$ and LaFe$_4$As$_{12}$ determined by a least-squares fit to the data were 8.3373 Å and 8.3252 Å, respectively. These values are in reasonable agreement with those in the previous reports [6, 11, 12].

Resistivity was measured by a standard dc four-probe method. The Seebeck coefficient and thermal conductivity were measured by a thermal transport system (PPMS; Quantum Design). The specific heat C(T) in magnetic fields up to 8T was measured by a thermal relaxation method (PPMS; Quantum Design).

3. Results and discussion

3.1. Specific heat

Figure 1 shows temperature dependence of specific heat C(T)/T for EuFe$_4$As$_{12}$ and LaFe$_4$As$_{12}$ at zero field. The ferromagnetic-like transition of EuFe$_4$As$_{12}$ is clearly visible as a peak of the specific heat C(T). The Curie temperature $T_C$ is estimated to be 152 K from the midpoint of the jump in C(T). The value is consistent with the previous report [6]. We estimated the electronic specific heat coefficients $\gamma$ of LaFe$_4$As$_{12}$ and EuFe$_4$As$_{12}$ from plots of C(T)/T versus $T^2$. LaFe$_4$As$_{12}$ exhibits an itinerant-electron weak ferromagnetic order at 5.3 K [12, 13]. Therefore, for LaFe$_4$As$_{12}$, the C(T)/T data between 6 K and 9 K above the ferromagnetic transition, were fitted by C(T)/T = $\gamma + \beta T^2$ (Debye T$^3$ law); Debye temperature $\Theta_D = (12\pi^4 nR/5\beta)^{1/3}$, where R is the gas constant and n = 17. Thus, we obtained $\gamma = 135$ mJ/molK$^2$ and $\Theta_D = 420$ K, as previously reported [13, 14]. For EuFe$_4$As$_{12}$, the electronic specific heat coefficient $\gamma$ is estimated to be $\sim 100$ mJ/molK$^2$ as an extrapolation of C(T)/T to $T = 0$ K. We estimated the magnetic contribution to the specific heat $C_{mag}$ of EuFe$_4$As$_{12}$ by subtracting the lattice specific heat of LaFe$_4$As$_{12}$. The magnetic entropy $S_{mag}$ was derived from the temperature integral of $C_{mag}$/T. The line is $S_{mag}$ in Fig. 1 (the right axis). $S_{mag}$ continuously increases and a kink at $T_C$ reflects the ordering temperature. The release of entropy at this temperature is about 29 J/molK, larger than expected for Eu ions in nearly divalent state ($J = 7/2, S = R \ln(2J + 1) = 17.28$ J/molK). The excess entropy could be attributed to differences in the phonon spectra (Debye Temperature and the contribution of Einstein specific heat due to the rattling motion). Another possibility could be differences in the magnetic contribution of the [Fe$_4$As$_{12}$] polyanions.
Then, we made a \((C - \gamma T)/T^3\) versus T plot of EuFe\(_4\)As\(_{12}\) (Fig. 2) in order to investigate the contribution of rattling motion of the Eu ion inside the As-cage, to the lattice specific heat. The lattice specific heat for filled skutterudites is generally described by Debye specific heat and Einstein specific heat due to rattling \[14\]. The Einstein specific heat leads to a broad maximum in \((C - \gamma T)/T^3\) at \(\sim \Theta_E/4.92\), where \(\Theta_E\) is the Einstein temperature. Therefore, we can obtain \(\Theta_E\) from the maximum temperature \(T_{\text{max}}\) in \((C - \gamma T)/T^3\). Figure 2 shows the temperature dependence of \((C - \gamma T)/T^3\) for EuFe\(_4\)As\(_{12}\) and a Debye model \((\Theta_D = 320 \text{ K})\) by the solid line. The data for EuFe\(_4\)As\(_{12}\) seem to be described by only Debye specific heat. A broad maximum due to Einstein specific heat was not observed. This result suggests that rattling motion of Eu ion is not prominent.

In order to investigate the field dependence of the transition on EuFe\(_4\)As\(_{12}\), specific heat measurements under magnetic fields up to 8 T have been carried out. Figure 3 shows the temperature dependence of the specific heat \(C(T)\) for EuFe\(_4\)As\(_{12}\) under magnetic fields. The anomaly for the phase transition around 152 K at zero field was found to become broad and shift to higher temperature with applying magnetic field. This behavior is consistent with a ferromagnetic ordering.
3.2. Thermoelectric properties

Furthermore, in order to evaluate the thermoelectric performance of EuFe$_4$As$_{12}$, we have measured the electrical resistivity $\rho$, the Seebeck coefficient $S$ and the thermal conductivity $\kappa$ of EuFe$_4$As$_{12}$. Figure 4 shows the temperature dependences of the electrical resistivity $\rho(T)$ and the Seebeck coefficient $S(T)$ of EuFe$_4$As$_{12}$. The overall behavior of the compound indicates a metallic state, as previously reported [6]. The $\rho(T)$ shows a pronounced kink around $T_C=152$ K, corresponding to the ferromagnetic-like transition. The $S(T)$ is positive over the entire temperature range. From room temperature, $S(T)$ gradually decreases with decreasing temperature. The curve of $S(T)$ changes from positive curvature to negative curvature below $T_C$.

Figure 5 shows the thermal conductivity $\kappa$ of EuFe$_4$As$_{12}$. The kink around 150 K is due to the onset of the ferromagnetic-like phase transition. The total thermal conductivity is given by $\kappa=\kappa_E+\kappa_L$ where $\kappa_E$ represents the electronic part and $\kappa_L$ the lattice contribution. We estimated the lattice thermal conductivity $\kappa_L=\kappa-\kappa_E$, where the electronic thermal conductivity $\kappa_E$ was calculated using the Wiedemann-Franz law ($\kappa_E=L_0\rho/T$), $L_0=2.44 \times 10^{-8}$ V$^2$/K$^2$ is Lorenz number and $\rho$ is the electrical resistivity. The $\kappa_L(T)$ for EuFe$_4$As$_{12}$ shows a maximum around 100 K, which is characteristic of $\kappa_L(T)$ for a crystalline solid. The value of $\kappa_L$ is 52
Figure 5. Temperature dependence of thermal conductivity $\kappa$ for EuFe$_4$As$_{12}$. The lattice contribution $\kappa_L$ and the electronic contribution $\kappa_E$ to the total thermal conductivity are also shown.

mW/cmK at 300 K, which is larger than those of CeFe$_4$As$_{12}$ (38 mW/cmK) and CeFe$_4$Sb$_{12}$ (14 mW/cmK) [15]. The large lattice thermal conductivity is consistent with the missing of Einstein specific heat. We estimated the power factor $S^2/\rho = 1.7 \times 10^{-4}$ W/mK$^2$ at room temperature. The dimensionless thermoelectric figure of merit $ZT(=S^2T/\rho\kappa)$ for EuFe$_4$As$_{12}$ was estimated to 0.007 at 300 K.

4. Summary

The study of thermal and transport properties was performed on As-based filled skutterudite compound EuFe$_4$As$_{12}$ prepared under high pressure. The Curie temperature $T_C$ was found to become broad and shift to higher temperature with applying magnetic field. This behavior is consistent with a ferromagnetic ordering. Several experimental results suggest that Eu ions in EuFe$_4$As$_{12}$ are in divalent or mixed-valent state. The magnetic configuration of Eu$^{2+}$ is the same as Gd$^{3+}$ ($J = S = 7/2$, $L = 0$). Therefore, Gd systems are good reference compounds. Recently, GdFe$_4$As$_{12}$ was reported to exhibit a ferromagnetic-like phase transition at 56 K [7]. Table 1 lists the magnetic parameters of EuFe$_4$As$_{12}$ and GdFe$_4$As$_{12}$. Although the effective magnetic moments $\mu_{eff}$ and the magnetization $m_s$ at 2K, 1T of EuFe$_4$As$_{12}$ are smaller than those of GdFe$_4$As$_{12}$, the $T_C$ of EuFe$_4$As$_{12}$ is about three times as high as that of GdFe$_4$As$_{12}$. The unexpectedly high transition temperature $T_C$ of 152K in EuFe$_4$As$_{12}$ could be due to the magnetic ordering of the Eu$^{2+}$ 4f moment with the Fe 3d moment with antiferromagnetic coupling. Furthermore, the comparison between Eu and Gd compounds suggests that the [Fe$_4$As$_{12}$]$^{2-}$ polyanion tends to induce an Fe moment more easily than the [Fe$_4$As$_{12}$]$^{3-}$ polyanion.

In order to elucidate the origin of the magnetic properties of EuFe$_4$As$_{12}$ in detail, we need to obtain more direct information on the valence of Eu ion in EuFe$_4$As$_{12}$ and the magnetic structure of this system. Therefore, measurements of neutron scattering, x-ray absorption near-edge spectroscopy and x-ray magnetic circular dichroism are currently in progress.

The thermoelectric performance of EuFe$_4$As$_{12}$ was also evaluated. The low figure of merit $ZT$ is mainly related to the large lattice thermal conductivity $\kappa_L$. The reason for the large $\kappa_L$ could be due to insufficient rattling effect by the large Eu$^{2+}$ ion inside the As cage.
Table 1. Ferromagnetic transition temperatures $T_C$, effective magnetic moments $\mu_{\text{eff}}$, Weiss temperatures $\theta_p$ and magnetization $m_s$ at 2K, 1T of EuFe$_4$As$_{12}$ and GdFe$_4$As$_{12}$.

| Compound        | $T_C$(K) | $\mu_{\text{eff}}$(µB) | $\theta_p$(K) | $m_s$(µB) | Ref. No. |
|-----------------|----------|------------------------|---------------|-----------|----------|
| EuFe$_4$As$_{12}$ | 152      | 6.93                   | 46            | 4.5       | 6        |
| GdFe$_4$As$_{12}$ | 56       | 8.09                   | 23            | 5.3       | 7        |

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