Journal of Physics: Conference Series **592** (2015) 012033 doi:10.1088/1742-6596/592/1/012033

Magnetic Properties of Filled Skutterudite $EuFe_4As_{12}$ under Pressure

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Abstract. We have investigated the effect of pressure on magnetic ordering of $EuFe_4As_{12}$ by measuring magnetization. The magnetization under pressure is measured by incorporating ceramic opposed anvil pressure cell into MPMS. The ferromagnetic-like ordering temperature T_C, which is 152 K at ambient pressure, increases by applying pressure. The increase rate of T_C against pressure (dT_C/dP) is almost the same value at each field i.e., 5.5 K/GPa for H = 0.1 T and 5.2 K/GPa for H = 1T. The dT_C/dP is almost constant up to 4 GPa, the maximum pressure of this study. On the other hand, the value of magnetization at ordering phase monotonically decreases with increasing pressure.

1. Introduction

The filled skutterudite inter-metallic compounds with the chemical formula LnT_4X_{12} (Ln = Lanthanide, T = Transition metal, X = Pnictogen) show characteristic strongly correlated electronic behavior such as heavy fermion[1], non-fermi liquid behavior[2], quadrupole ordering[3], metal-insulator transition[4], and magnetic ordering. Among lots of filled skutterudite compounds which show magnetic ordering, $EuFe_4X_{12}$ (X=P, As, Sb) show ferromagnetic ordering at exceptionally high temperature. $EuFe_4P_{12}$ shows ferromagnetic order below $T_C \sim 99$ K[5]. $EuFe_4As_{12}$ shows ferromagnetic-like order below $T_C \sim 152$ K[6]. $EuFe_4Sb_{12}$ shows ferromagnetic-like order below $T_C \sim 88$ K[7]. These T_Cs are very high, comparing to T_Cs of other Eu based skutterudite compounds such as $EuRu_4X_{12}$ ($T_C \sim 18$ K for X=P and $T_C \sim 3.3$ K for X=Sb), $EuOs_4X_{12}$ ($T_C \sim 15$ K for X=P and $T_C \sim 9$ K for X=Sb). The mechanism of this high T_C is fascinating. In this paper we focus on $EuFe_4As_{12}$, which has the highest ordering temperature.

One of the origin of magnetic ordering is the magnetic moments of Eu^{2+}. Although the lattice constants of $LnFe_4As_{12}$ monotonically decreases with increasing atomic number due to the contraction of the trivalent ionic radii of the lanthanides, that of $EuFe_4As_{12}$ is larger than that expected. This indicates the valence of Eu ion of $EuFe_4As_{12}$ is in divalent or in mixed valence state. Eu^{2+} has magnetic moment in the inter-metallic compounds, while Eu^{3+} does not. Thus, 4f electron in Eu^{2+} is one of the origin of magnetic ordering. On the other hand, the magnetic moment of this compound is 4.5 μ_B/Eu at 2 K, which is much less than the theoretical value of divalent Eu of 7 μ_B/Eu^{2+}. Thus, Eu in $EuFe_4As_{12}$ might be deviated from Eu^{2+} and expected to be in the valence fluctuation regime. In addition, $LaFe_4As_{12}$ also shows ferromagnetic transition at $T_C \sim 5.2$ K[8]. La does not have 4f electron which is the origin of magnetic moment in the intermetallic compounds. Thus the magnetic moment should be attributed to Fe moment in $LaFe_4As_{12}$, which implies that one of the magnetic moment is attributed to Fe moment even in $EuFe_4As_{12}$.

As we have discussed, both Eu and Fe have magnetic moment. The unexpectedly high T_C might due to the interaction of fluctuating 4f moment in Eu ion with Fe moment. In order to investigate the interaction between Eu ion and Fe moment, it is important to clarify the magnetic properties of $EuFe_4As_{12}$ under pressure. Among EuT_4X_{12} (T = Fe, Ru, Os, X = P, As, Sb), the sole report of the measurement under pressure is about $EuFe_4Sb_{12}$. The Curie temperature T_C monotonically increases with pressure at a rate of $dT_C/dP \sim 5$ K/GPa[9]. They proposed that the positive dT_C/dP is a hint to the localized moment behavior of the Eu ion and that pressure drives the magnetic ions closer together and enhance RKKY interaction and T_C. Investigating physical properties of $EuFe_4As_{12}$ under pressure and comparing that of $EuFe_4Sb_{12}$ is one of the keys to clarify the origin of the high T_C. In this paper, we report the magnetic properties of $EuFe_4As_{12}$ under pressure.

2. Experiment

$EuFe_4As_{12}$ samples were synthesized under high-pressure and high-temperature using a wedge-type cubic anvil high-pressure apparatus. Details are described in our previous paper[6] The samples were characterized by powder x-ray diffraction using Co $K\alpha_1$ radiation and silicon as a standard. The magnetization under pressure was measured by MPMS incorporated with opposed ceramic anvil pressure cell[10]. We used two types of anvils and gaskets for opposed anvil pressure cell. One is parts for pressure up to 2 GPa labeled #1; Anvil culet size, inner diameter of gasket, and thickness of gasket are ϕ1.8 mm, ϕ0.9 mm, and 0.9 mm, respectively. The other is parts for pressure up to 4 GPa named #2; Anvil culet size, inner diameter of gasket, and thickness of gasket are ϕ1.0 mm, ϕ0.5 mm, and 0.5 mm, respectively. Glycerin was used as pressure medium, in which hydrostatic pressure can be realized below 6 GPa[11]. Pressures were calibrated with transition temperature of superconductivity on Pb.

3. Results

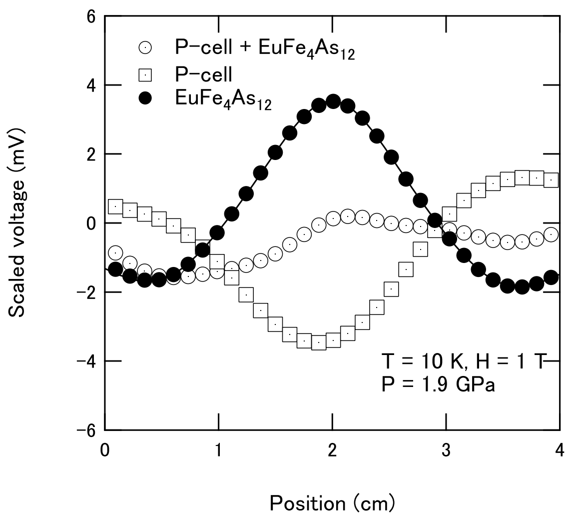

Figure 1. Responses of the scaled SQUID voltage of $EuFe_4As_{12}$ with pressure cell at 1.9 GPa, 10 K(open circle) and that of pressure cell at 0 GPa, 10 K(open square). Closed circle represents the subtracted data. The solid line is the fitting curve for getting magnetization.

Figure 1 shows raw data of $EuFe_4As_{12}$ at 10 K under the pressure of 1.9 GPa and at the field of 1 T. We measured (A) $EuFe_4As_{12}$ with pressure cell at each pressure and (B) vacant pressure cell at ambient pressure. The gasket is too thin to change the environment around pressure cell in every pressure. Thus, we can consider the data of vacant pressure cell at ambient pressure as background of the measurement under every pressure. The SQUID signal of $EuFe_4As_{12}$ is got by subtracting (B) from (A)((A)-(B)). Although the signal of (A) or (B) is asymmetric and bad quality, the signal of (A)-(B) is almost ideal shape. The magnetization was calculated by the fitting shown in line in Figure 1. This procedure is applied to measurements at each temperature in order to get magnetization.

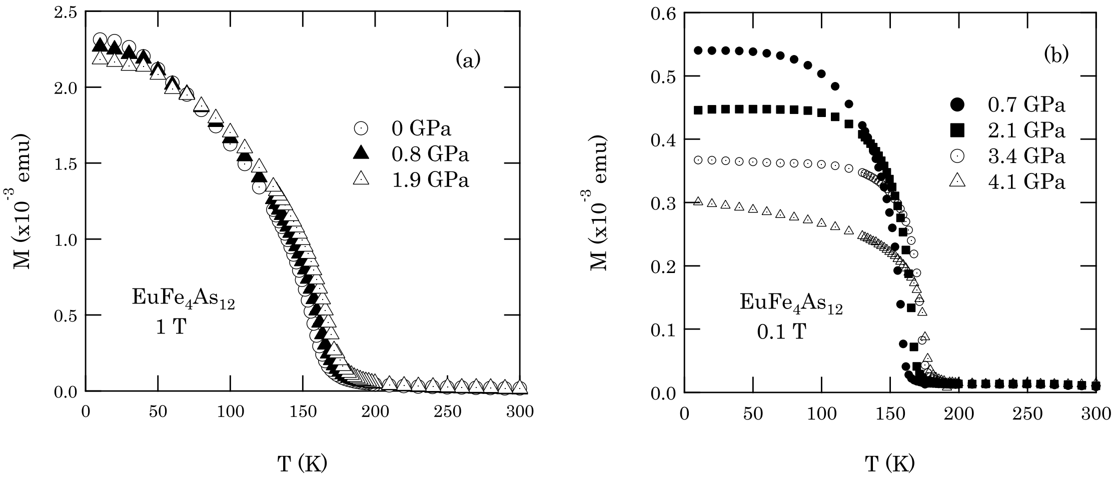

Figure 2. (a) Temperature dependence of magnetization on $EuFe_4As_{12}$ at H = 1 T measured under the pressure of 0 GPa(open circle), 0.8 GPa(closed triangle), and 1.9 GPa(open triangle). (b) Temperature dependence of magnetization on $EuFe_4As_{12}$ at H = 0.1 T under the pressure of 0.7 GPa (closed circle), 2.1 GPa (closed square), 3.4 GPa (open circle), and 4.1 GPa (open triangle).

Figure 2 (a) shows the temperature dependence of magnetization on $EuFe_4As_{12}$ at H = 1 T under the pressure of 0 GPa, 0.8 GPa, and 1.9 GPa with using parts #1. We have successfully measured up to 1.9 GPa of $EuFe_4As_{12}$ by using #1. Figure 2 (b) shows the temperature dependence of magnetization on $EuFe_4As_{12}$ at the field of 0.1 T under pressure with using parts #2. At the lowest pressure 0.7 GPa, magnetization is almost independent of temperature above 180 K. Below 180 K, magnetization increases with decreasing temperature. The value of increase rate of magnetization (dM/dT) is maximum with dM/dT $\sim$ -3.3 x 10^{-5} emu/K around 160 K. Below 160 K, the value of dM/dT gradually decreases and goes constant value at the lowest temperature. The maximum value of magnetization is 40 times larger than that of paramagnetic region. This behavior is typical ferromagnetic order and is consistent with the previous report which is measured at ambient pressure. Here we note that signal to noise ratio (S/N) is not enough to discuss Curie-Weiss behavior at paramagnetic region, because the sample size in this pressure cell is limited and much smaller than commonly used piston cylinder cell. We define the starting temperature of the rapid increase as T_C. In both measurements, the T_C increases with pressure. On the other hand, the value of magnetization at the ground state gradually decreases at 1 T and drastically decreases at 0.1 T by applying pressure.

Figure 3 shows the pressure dependence of T_C on $EuFe_4As_{12}$ at H = 0.1 T and at H = 1 T. T_C increases with pressure in both measurements. The increase rate of T_C against pressure

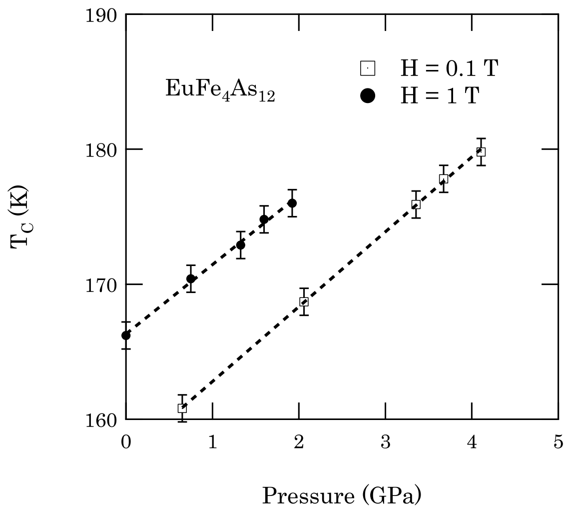

Figure 3. Pressure dependence of ferromagnetic ordering temperature (T_C) on $EuFe_4As_{12}$ at H = 0.1 T (square) and at H = 1 T (Circle)

dT_C/dP is 5.5 K/GPa for H = 0.1 T and 5.2 K/GPa for H = 1T. As it can be seen from the pressure dependence of T_C at H = 0.1 T, the increase rate is almost constant up to 4.1 GPa, the maximum pressure of this measurement. The value of T_C defined in measurements at H = 0.1 T is different from that in measurements at H = 1 T. This is attributed to the definition of T_C. The range of rapid increase around T_C broadens with applying field. That is why T_C, defined by the starting point of rapid increase, increases with magnetic field. The dT_C/dP of these measurements are almost the same as that of $EuFe_4Sb_{12}$. The T_C increases monotonically with dT_C/dP = 5 GPa[9]. This is almost the same value as our result, which implies that the mechanism of ferromagnetic-like order on $EuFe_4As_{12}$ and $EuFe_4Sb_{12}$ might be the same.

Figure 4 shows the pressure dependence of magnetization at 10 K at various conditions. At H = 0.1 T, the magnetization decreases with pressure in a rate of 13 %/GPa by using parts of #1 and 11 %/GPa by using parts of #2. At H = 1 T, the magnetization decreases with pressure in a rate of 3 %/GPa by using parts #1 and 9 %/GPa by using parts #2. Although the decrease rate is depend on the condition of measurements, the magnetization at ordered state monotonically decreases by applying pressure.

4. Discussion

We found the magnitude of magnetization at ordered state reduces and T_C increases by applying pressure. This magnetic transition is reported as canted-ferromagnetic or ferrimagnetic ordering because the temperature dependence of inverse magnetic susceptibility at paramagnetic region deviates from Curie Weiss law[6]. If we assume that this is ferrimagnetic order, there are two scenarios to explain our results, First scenario is changing the magnitude of magnetic moment. In general, ferrimagnetic structure consists of large magnetic moment and opposite small magnetic moment. If the magnetic moment of smaller one is enhanced by applying pressure, the interaction between large magnetic moment and small magnetic moment increases and T_C increases. On the other hand, the magnitude of magnetization reduces because the magnetic structure approaches from ferrimagnet to antiferromagnet. Second scenario is changing the valence of Eu ion. Eu ion can become Eu^{3+} or Eu^{2+} and the former is more stable than the latter under high pressure. This is because ionic size of Eu^{3+} is smaller than that of Eu^{3+}. Eu^{3+} does not have magnetic

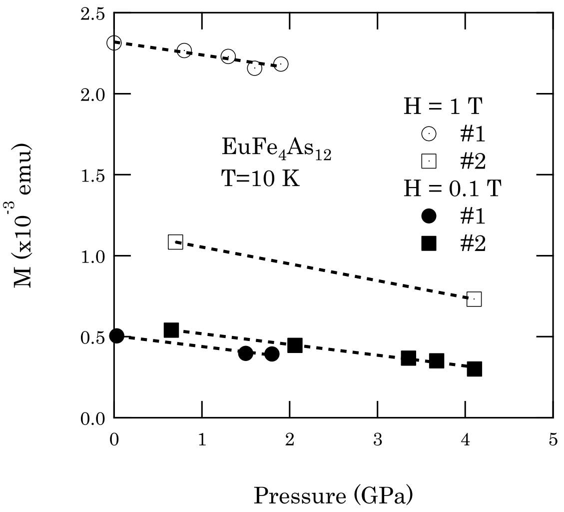

Figure 4. Pressure dependence of magnetization at 10 K under H = 1 T with parts #1 (open circle) and parts #2 (open square) and that under H = 0.1 T with parts #1 (closed circle) and parts #2 (closed square). Parts #1 and parts #2 are described at Experiment section.

moment, whereas Eu^{2+} has the magnetic moment of 7.94 μ_B/Eu^{2+} in a free ion state. If the average valence of Eu ion increases and the magnitude of magnetic moment decreases, the magnetization would be reduced. On the other hand, the interaction of the two moment is enhanced because of the contraction of volume at high pressure. Then, T_C increases with pressure. Although we have proposed two scenarios, our results do not deny the possibility of canted-ferromagnetic structure. To clarify the change of magnetic structure under pressure, magnetic structure at ambient pressure should be solved by neutron diffraction measurement.

5. Summary

We have succeeded in measuring magnetization under pressure up to 4.1 GPa. The magnetization increases drastically below the ferromagnetic-like ordering temperature T_C. The T_C monotonically increases with pressure at a rate of 5.5 K/GPa for H = 0.1 T and 5.2 K/GPa for H = 1T. On the other hand, the value of magnetization at low temperatures decreases with increasing pressure.

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