Magnetic properties of new filled skutterudite compound BaFe4As12

Magnetic properties of new filled skutterudite compound $BaFe_4As_{12}$

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Abstract

The magnetic, electrical and thermal properties of a new As-based alkaline-earth-filled skutterudite compound $BaFe_4As_{12}$ prepared under high pressure have been studied at low temperatures. The temperature dependence of the electrical resistivity for $BaFe_4As_{12}$ reveals a metallic behavior. Any anomalies accompanied by phase transition were not observed down to 2K. A broad maximum of magnetic susceptibility around 50 K and a large electronic specific heat coefficient of 62 mJ/molK^2 suggest that $BaFe_4As_{12}$ is a nearly ferromagnetic metal with spin fluctuations of Fe 3d electrons.

Keywords: skutterudite, magnetic susceptibility, high-pressure synthesis, nearly ferromagnetic metal

1 Introduction

The filled skutterudite compounds MT_4X_{12} (M= alkali metal, alkaline earth and lanthanide; T=Fe, Ru and Os; X= P, As and Sb) crystallize with a body-centered cubic structure of space group Im-3 (T^5_h, No. 204) [1]. The M ions are located inside the cages formed by twelve X ions, and the M ions are believed to show random motion (rattling) around the equilibrium positions [2, 3]. Thus, it produces a large phonon scattering, reducing the lattice thermal conductivity. Owing to the reduced thermal conductivity, filled skutterudite compounds show excellent thermoelectric performance. Furthermore, the filled skutterudite compounds, particularly P- and Sb-based compounds, have attracted much attention of their wide variety of strongly correlated electron behaviors, such as unconventional superconductivity, non-Fermi liquid behavior, anomalous metal-insulator transition, and multipole ordering [4]. As-based filled skutterudite compounds also should be important for systematically investigating skutterudite systems. In fact, several compounds exhibit exotic properties, including superconductivity in $LnRu_4As_{12}$ (Ln = La, Pr) [5, 6], Kondo semiconducting behavior in CeT_4As_{12} (T=Fe, Ru, and Os) [7-10], itinerant-electron weak ferromagnetism in $LaFe_4As_{12}$ [11, 12] and canted ferromagnetic or ferrimagnetic phase transition in $EuFe_4As_{12}$ [13]. However, only preliminary studies

have been conducted on the properties of As-based compounds because the compounds are quite difficult to prepare. High-pressure synthesis is a powerful technique for preparing As-based skutterudite compounds. New As-based alkaline-earth-filled skutterudite compound $BaFe_4As_{12}$ prepared under high pressure has been reported, recently [14]. Powder x-ray diffraction patterns were studied at ambient pressure and at high pressures using synchrotron radiation. A crystal structure of $BaFe_4As_{12}$ was refined by the Rietveld analysis of the powder x-ray diffraction data at ambient pressure. $BaFe_4As_{12}$ had a cubic structure with lattice parameter 8.3975 Å. The atomic position of As site was determined as (0, 0.3474, 0.1534). The volume vs. pressure curve for this arsenide was investigated at room temperature. The cell volume of $BaFe_4As_{12}$ decreased smoothly with increasing pressure up to 10 GPa. A bulk modulus was estimated from the volume vs. pressure curve fitted by a Birch equation of state. The bulk modulus was 107 GPa. The temperature dependence of the electrical resistivity for $BaFe_4As_{12}$ reveals a metallic behavior. In this paper, we report the magnetic and thermal properties for $BaFe_4As_{12}$ for the first time.

2 Experimental

Polycrystalline samples of $BaFe_4As_{12}$ were prepared at high temperatures and high pressures. $BaFe_4As_{12}$ was synthesized using a KAWAI-type double-stage multi-anvil high-pressure apparatus. We used eight tungsten carbide cubes with a truncated edge length of 11 mm as the second stage anvils. The sample container, made of magnesia (MgO + 5% Cr_2O_3), was transformed into an octahedron of 18 mm on the stage. The starting materials were put into a crucible made of boron nitride (BN). The crucible, with a graphite heater surrounded with a zirconia (ZrO_2) thermal insulator was inserted into the magnesia octahedron. The samples were prepared by reacting stoichiometric amounts of 3N (99.9% pure)-Ba chips, 4N-Fe and 6N-As powders at 4 GPa. The reaction temperature was 820-830 °C. The prepared samples were characterized by powder x-ray diffraction using Co $K\alpha_1$
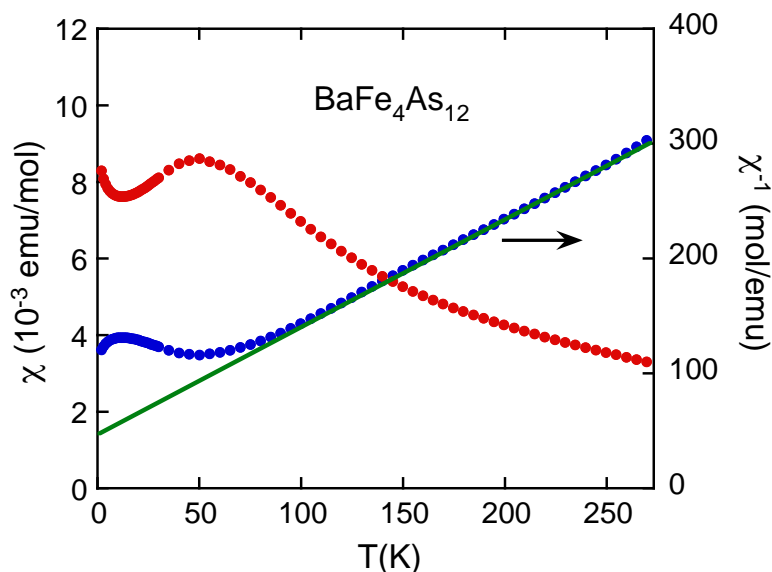

Figure 1: Temperature dependence of the magnetic susceptibility χ and the inverse magnetic susceptibility χ^{-1} for $BaFe_4As_{12}$ at 1 T.

radiation and silicon as a standard.

Resistivity was measured by a standard dc four-probe method. Magnetization and dc magnetic susceptibility were measured with a Quantum Design MPMS superconducting quantum interference device magnetometer. Specific heat measurement was carried out by a thermal relaxation method (Quantum Design PPMS).

3 Results and Discussion

The x-ray diffraction pattern of the polycrystalline sample for $BaFe_4As_{12}$ prepared at high pressure indicates that the main phase consists of the filled skutterudite compound with less than 5wt% impurity phase (metallic As). The lattice constant determined by a least-squares fit to the data was 8.3960 Å (compared with 8.3975 Å in Ref. [14]).

The temperature dependence of the magnetic susceptibility χ and the inverse magnetic susceptibility χ^{-1} for $BaFe_4As_{12}$ are presented in Fig. 1. The high-temperature data for $BaFe_4As_{12}$ above 150 K can be described by the Curie-Weiss law with the effective magnetic moment of 2.96 μ_B/f.u. (1.46 μ_B/Fe) and Weiss temperature θ_p of -57 K. A large negative θ_p is also observed for a weak itinerant-electron ferromagnet $LaFe_4As_{12}$ [11, 12]. The magnetization curve of $BaFe_4As_{12}$ at 2 K increases linearly with increasing field up to 7 T, where the largest value is only 0.02 μ_B/Fe (Fig. 2). This extremely small moment compared with the effective magnetic moment means that the Curie-Weiss behavior is due to the itinerant magnetism of Fe $3d$ electrons. It is noticed that a broad maximum is observed around 50 K (Fig. 1). A similar behavior is observed for $BaFe_4Sb_{12}$ [15, 16]. Such a broad maximum in χ was found in the nearly ferromagnetic compounds like Co-based Laves phase compounds, which exhibit a metamagnetic transition [17]. However, the reason for the large
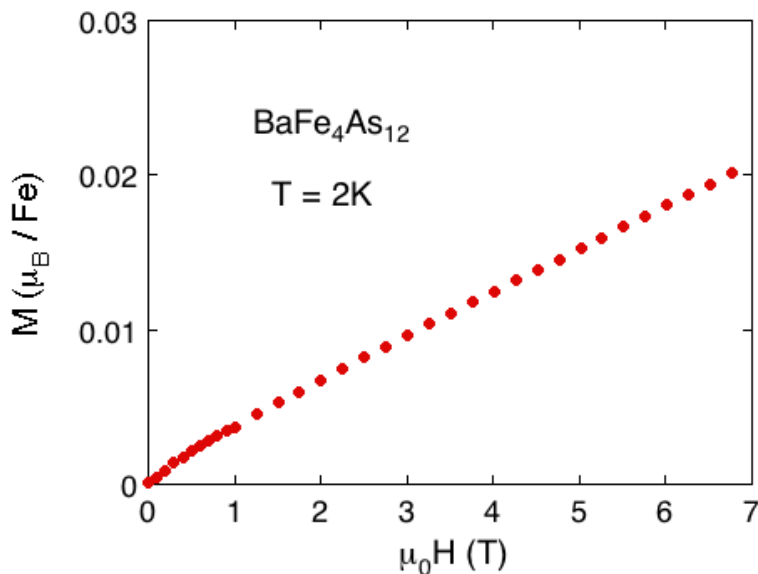

Figure 2: Magnetization for $BaFe_4As_{12}$ at 2 K.

negative θ_p is unclear in this system at present.

Figure 3 shows the temperature dependence of the relative electrical resistivity $[\rho(T)\text{-}\rho_0]/\rho_{300K}$ for $BaFe_4As_{12}$. ρ_0 and ρ_{300K} are the residual resistivity and the value of resistivity at $T = 300$ K, respectively. The overall behavior of the compound indicates a metallic state like as previous report
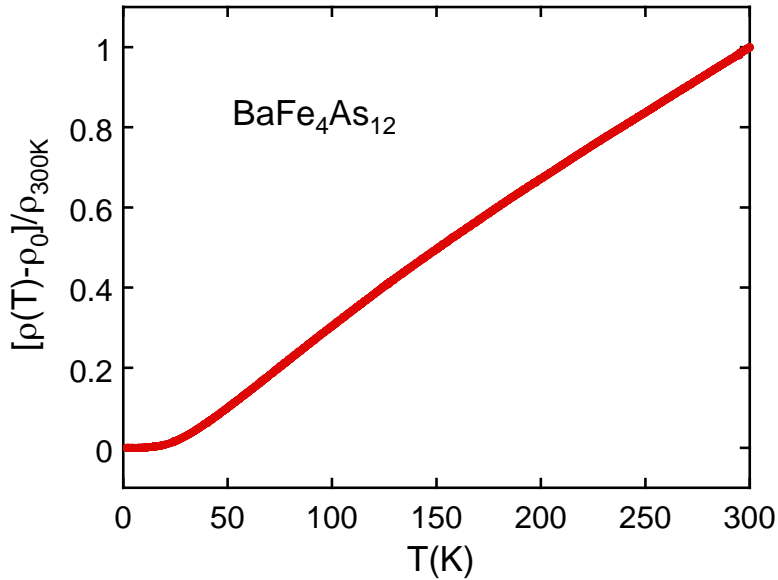

Figure 3: Temperature-dependent part $\rho(T) - \rho_0$ of electrical resistivity for $BaFe_4As_{12}$, normalized at 300 K.
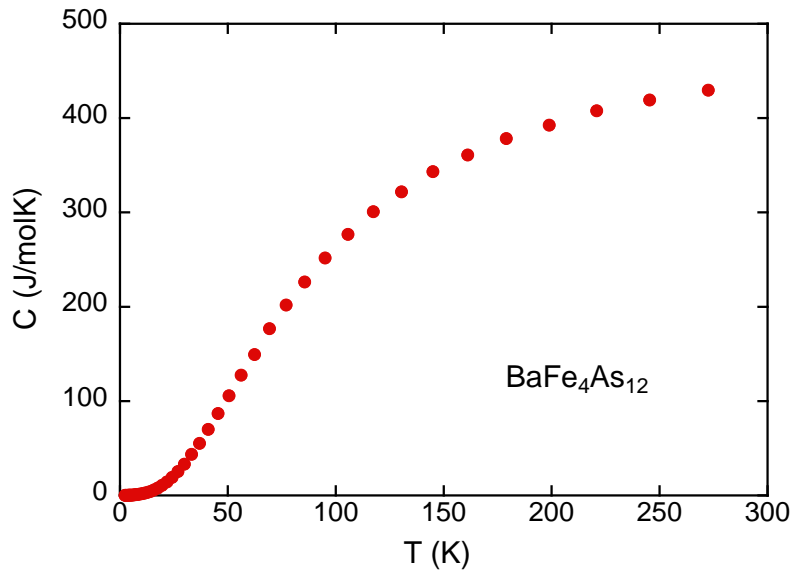

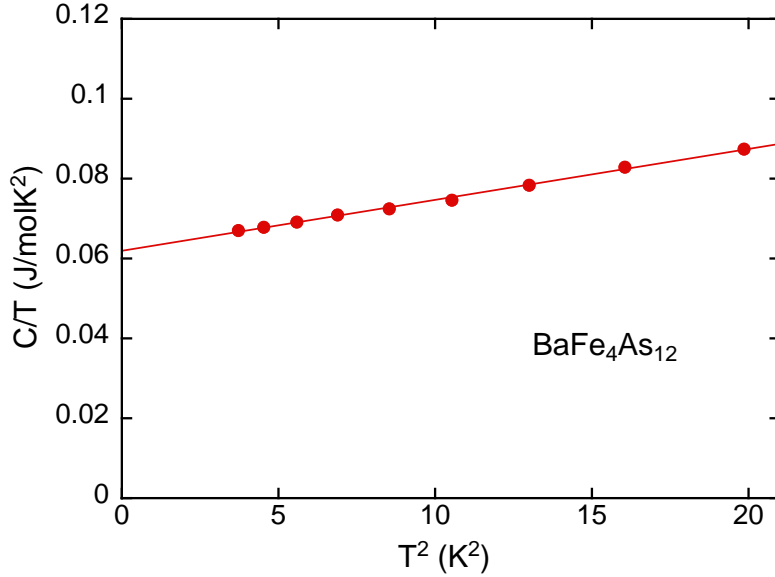**Figure 4:** Temperature dependence of the specific heat C for $BaFe_4As_{12}$.

Figure 5: T^2-dependence of C/T for $BaFe_4As_{12}$.

[14]. A small deviation from a T-linear behavior in $\rho(T)$ was observed and $\rho(T)$ shows the quadratic-like temperature dependence below about 10 K. The behavior could be attributed to the scattering of conduction electrons by the ferromagnetic spin fluctuations of the Fe $3d$ narrow band, such as those in alkaline-earth-filled skutterudite compounds MFe_4Sb_{12} (M=Ca, Sr, and Ba) [15, 16]. Figure 4 shows temperature dependence of specific heat $C(T)$ for $BaFe_4As_{12}$ at zero field. Any anomalies were not observed down to 2 K. We estimated the electronic specific heat coefficient γ for $BaFe_4As_{12}$ from plot of $C(T)/T$ versus T^2 (Fig. 5). The $C(T)/T$ data between 2 K and 5 K were fitted by $C(T)/T = \gamma + \beta T^2$; Debye temperature $\Theta_D = (12\pi 4nR/5\beta)^{1/3}$, where R is the gas constant and $n = 17$. Thus, we obtained $\gamma = 62$ mJ/molK^2 and $\Theta_D = 295$ K.

The lattice specific heat for filled skutterudite compounds is generally described by Debye specific heat and Einstein specific heat due to rattling. In order to investigate the contribution of rattling motion of the Ba ion inside the As-cage to the lattice specific heat, we plots $(C - \gamma T)/T^3$ versus T of $BaFe_4As_{12}$ and $LaFe_4As_{12}$ (Fig. 6). The data for $LaFe_4As_{12}$ are taken from Ref. 18. The Einstein specific heat leads to a broad maximum in $(C - \gamma T)/T^3$ at $\Theta_E/4.92$, where Θ_E is the Einstein temperature. Therefore, we can obtain Θ_E from the maximum temperature T_{max} in $(C - \gamma T)/T^3$. $LaFe_4As_{12}$ exhibits a large broad maximum around 23 K ($\Theta_E = 113$ K), which is a commonly observed feature in filled skutterudites. On the other hand, a broad maximum due to Einstein specific heat was not observed for $BaFe_4As_{12}$. Therefore, the data for $BaFe_4As_{12}$ seem to be described by only Debye specific heat. The solid line in Fig. 6 shows the result calculated by a Debye model ($\Theta_D = 295$ K). This result suggests that rattling motion of Ba ions is not prominent in the As-cages of $BaFe_4As_{12}$. The x-ray analysis exhibits that the thermal equivalent isotropic parameter (B_{eq}) of Ba in $BaFe_4As_{12}$ is a quite small value (0.4 Å^2) [14]. The value is much smaller than those (1.3~1.4 Å^2) of $CeRu_4As_{12}$ and $GdFe_4As_{12}$ [19, 20].

This result is consistent with no observation of Einstein specific heat for $BaFe_4As_{12}$. It is thought that there is no space where relatively large Ba divalent ions exhibit a rattling motion in the As-cages.
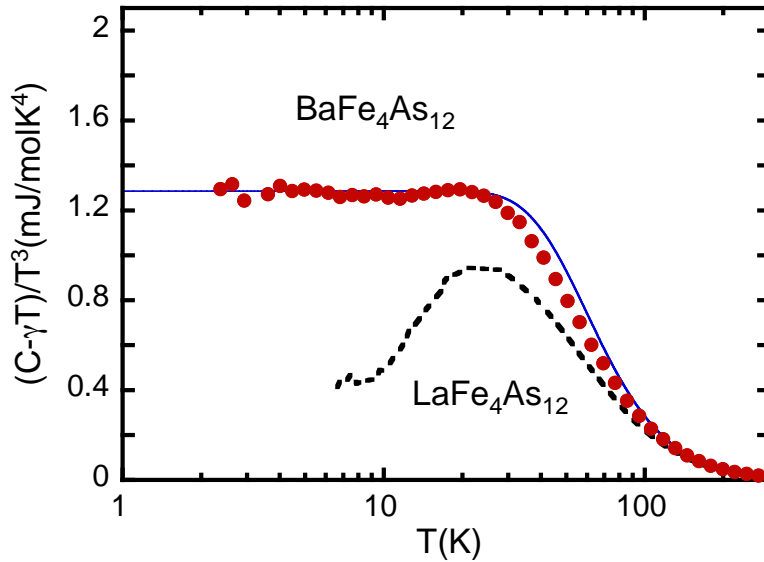

Figure 6: Temperature dependence of the specific heat for $BaFe_4As_{12}$ and $LaFe_4As_{12}$. The data are displayed in the form of $(C - \gamma T)/T^3$. The solid line is the result calculated by Debye model.

Table I. Magnetic and thermal parameters of $BaFe_4As_{12}$ and reference compounds. μ_{eff}, θ_p, γ, Θ_D and Θ_E are effective magnetic moment, Weiss temperature, electronic specific heat coefficient, Debye temperature and Einstein temperature, respectively.

Compounds	μ_{eff} (μ_B/Fe)	θ_p (K)	γ (mJ/molK^2)	Θ_D (K)	Θ_E (K)	Ref.
$BaFe_4As_{12}$	1.46	-57	62	295	-	this work
$LaFe_4As_{12}$	0.95, 0.96	-70, -48	78	421	113	[11], [12], [18]
$BaFe_4Sb_{12}$	1.50	31	104	298	108	[15], [16]

4 Summary

We studied the magnetic and thermal properties for a new filled skutterudite compound $BaFe_4As_{12}$ prepared at high pressure. The magnetic and thermal parameters of $BaFe_4As_{12}$ are summarized in Table I with the reference compounds. The temperature dependence of the magnetic susceptibility shows a broad peak around 50 K. A large electronic specific heat coefficient is observed. The results suggests that $BaFe_4As_{12}$ is a nearly ferromagnetic metal with spin fluctuations of Fe 3d electrons and

the compound is an itinerant-electron metamagnet. In order to confirm this point, high-field magnetization measurements are currently in progress. As-based filled skutterudite compound $EuFe_4As_{12}$ with divalent Eu^{2+} ions exhibits a ferrimagnetic-like phase transition with the unexpectedly high transition temperature of 152K [13]. The exchange interaction between the $3d$ electrons of Fe and the $4f$ electrons could be essential to the ordering in this compound. Furthermore, the $[Fe_4As_{12}]$ polyanion tends to induce Fe moment more easily than the $[Fe_4Sb_{12}]$ polyanion in skutterudite system. Therefore, as a reference compound without $4f$ electrons, $BaFe_4As_{12}$ with divalent Ba^{2+} ions is also an important system for investigating the effect of $3d$ electrons on the magnetic properties of $EuFe_4As_{12}$.

Acknowledgments

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