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|-----------------|-----------------------------------------------------------------------------------------------------------------------------|
| Journal or publication title | Physics Procedia                                                                                                       |
| Volume          | 75                                                                                                                          |
| Year            | 2015                                                                                                                         |
| URL             | http://hdl.handle.net/10258/00009044                                                                                       |
| doi             | info:10.1016/j.phpro.2015.12.046                                                                                           |
Magnetic properties of new filled skutterudite compound BaFe$_4$As$_{12}$

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Abstract

The magnetic, electrical and thermal properties of a new As-based alkaline-earth-filled skutterudite compound BaFe$_4$As$_{12}$ prepared under high pressure have been studied at low temperatures. The temperature dependence of the electrical resistivity for BaFe$_4$As$_{12}$ 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$_4$As$_{12}$ is a nearly ferromagnetic metal with spin fluctuations of Fe 3$d$ electrons.

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

1 Introduction

The filled skutterudite compounds MT$_4$X$_{12}$ ($M$= 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 ($T_h$; 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$_4$As$_{12}$ (Ln = La, Pr) [5, 6], Kondo semiconducting behavior in CeT$_4$As$_{12}$ (T=Fe, Ru, and Os) [7-10], itinerant-electron weak ferromagnetism in LaFe$_4$As$_{12}$ [11, 12] and canted ferromagnetic or ferrimagnetic phase transition in EuFe$_4$As$_{12}$ [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 \( \text{BaFe}_4\text{As}_{12} \)
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
\( \text{BaFe}_4\text{As}_{12} \) was refined by the Rietveld analysis of the powder x-ray diffraction data at ambient
pressure. \( \text{BaFe}_4\text{As}_{12} \) 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 \( \text{BaFe}_4\text{As}_{12} \) 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 \( \text{BaFe}_4\text{As}_{12} \) reveals a metallic behavior. In this paper, we report the magnetic and thermal
properties for \( \text{BaFe}_4\text{As}_{12} \) for the first time.

2 Experimental

Polycrystalline samples of \( \text{BaFe}_4\text{As}_{12} \) were prepared at high temperatures and high pressures.
\( \text{BaFe}_4\text{As}_{12} \) 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\(_2\)O\(_3\)), 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 \( \chi \) and the inverse magnetic susceptibility \( \chi^{-1} \) for \( \text{BaFe}_4\text{As}_{12} \) at 1 T.](image-url)
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$_4$As$_{12}$ prepared at high pressure indicates that the main phase consists of the filled skutterudite compound with less than 5 wt% 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 $\chi$ and the inverse magnetic susceptibility $\chi^{-1}$ for BaFe$_4$As$_{12}$ are presented in Fig. 1. The high-temperature data for BaFe$_4$As$_{12}$ above 150 K can be described by the Curie-Weiss law with the effective magnetic moment of 2.96 $\mu_B$/f.u. (1.46 $\mu_B$/Fe) and Weiss temperature $\theta_p$ of -57 K. A large negative $\theta_p$ is also observed for a weak itinerant-electron ferromagnet LaFe$_4$As$_{12}$ [11, 12]. The magnetization curve of BaFe$_4$As$_{12}$ at 2 K increases linearly with increasing field up to 7 T, where the largest value is only 0.02 $\mu_B$/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.

A broad maximum is observed around 50 K (Fig. 1). A similar behavior is observed for BaFe$_4$Sb$_{12}$ [15, 16]. Such a broad maximum in $\chi$ 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$_4$As$_{12}$ at 2 K.](image)
negative $\theta$ is unclear in this system at present.

Figure 3 shows the temperature dependence of the relative electrical resistivity $[\rho(T) - \rho_0]/\rho_{300K}$ for BaFe$_4$As$_{12}$. $\rho_0$ and $\rho_{300K}$ 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$_4$As$_{12}$, normalized at 300 K.

Figure 4: Temperature dependence of the specific heat $C$ for BaFe$_4$As$_{12}$. 
A small deviation from a T-linear behavior in ρ(T) was observed and ρ(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 MFe4Sb12 (M = Ca, Sr, and Ba) [15, 16]. Figure 4 shows temperature dependence of specific heat C(T) for BaFe4As12 at zero field. Any anomalies were not observed down to 2 K. We estimated the electronic specific heat coefficient γ for BaFe4As12 from plot of C(T)/T versus T2 (Fig. 5). The C(T)/T data between 2 K and 5 K were fitted by C(T)/T = γ + βT2; Debye temperature ΘD = (12π4nR/5β)1/3, where R is the gas constant and n = 17. Thus, we obtained γ = 62 mJ/molK2 and ΘD = 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 - γT)/T3 versus T of BaFe4As12 and LaFe4As12 (Fig. 6). The data for LaFe4As12 are taken from Ref. 18. The Einstein specific heat leads to a broad maximum in (C- γT)/T3 at ΘE/4.92, where ΘE is the Einstein temperature. Therefore, we can obtain ΘE from the maximum temperature Tmax in (C- γT)/T3. LaFe4As12 exhibits a large broad maximum around 23 K (ΘE = 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 BaFe4As12. Therefore, the data for BaFe4As12 seem to be described by only Debye specific heat. The solid line in Fig. 6 shows the result calculated by a Debye model (ΘD = 295 K). This result suggests that rattling motion of Ba ions is not prominent in the As-cages of BaFe4As12. The x-ray analysis exhibits that the thermal equivalent isotropic parameter (Beq) of Ba in BaFe4As12 is a quite small value (0.4 Å2) [14]. The value is much smaller than those (1.3~1.4 Å2) of CeRu4As12 and GdFe4As12 [19, 20].
This result is consistent with no observation of Einstein specific heat for BaFe$_4$As$_{12}$. It is thought that there is no space where relatively large Ba divalent ions exhibit a rattling motion in the As-cages.

4 Summary

We studied the magnetic and thermal properties for a new filled skutterudite compound BaFe$_4$As$_{12}$ prepared at high pressure. The magnetic and thermal parameters of BaFe$_4$As$_{12}$ 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 suggest that BaFe$_4$As$_{12}$ 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. A s-based filled skutterudite compound EuFe$_4$As$_{12}$ 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$_4$As$_{12}$] polyanion tends to induce Fe moment more easily than the [Fe$_4$Sb$_{12}$] polyanion in skutterudite system. Therefore, as a reference compound without 4f electrons, BaFe$_4$As$_{12}$ with divalent Ba$^{2+}$ ions is also an important system for investigating the effect of 3d electrons on the magnetic properties of EuFe$_4$As$_{12}$.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 23340092) of the Japan Society for the Promotion of Science.

References

[1] W. Jeitschko and D. Braun: Acta Crystallogr., Sect. B 33 (1977) 3401.
[2] B. C. Sales, D. Mandrus, and R. K. Williams: Science 272 (1996) 1325.
[3] G. S. Nolas, J. L. Cohn, G. A. Slack, and S. B. Schujman: Appl. Phys. Lett. 73 (1998) 178.
[4] H. Sato, H. Sugawara, Y. Aoki, and H. Harima, Handbook of Magnetic Materials, ed. K. H. J. Buschow (North-Holland, Amsterdam, 2009) Vol. 18, p. 1.
[5] I. Shirotani, T. Uchiumi, K. Ohno, C. Sekine, Y. Nakazawa, K. Kanoda, S. Todo, and T. Yagi: Phys. Rev. B 56 (1997) 7866.
[6] T. Namiki, Y. Aoki, H. Sato, C. Sekine, I. Shirotani, T. D. Matsuda, Y. Haga, and T. Yagi: J. Phys. Soc. Jpn. 76 (2007) 093704.
[7] F. Grandjean, A. Gerard, D. J. Braun, and W. Jeitschko: J. Phys. Chem. Solids 45 (1984) 877.
[8] C. Sekine, N. Hoshi, K. Takeda, T. Y. Oshida, I. Shirotani, K. Matsuhira, M. Wakeshima, and Y. Hinatsu: J. Magn. Magn. Mater. 310 (2007) 260.
[9] C. Sekine, R. Abe, K. Takeda, K. Matsuhira, and M. Wakeshima: Physica B 403 (2008) 856.
[10] C. Sekine, T. Kawata, Y. Kawamura, and T. Yagi: J. Korean Phys. Soc. 63 (2013) 359.
[11] S. Tatsuoka, H. Sato, K. Tanaka, M. Ueda, D. Kikuchi, H. Aoki, T. Ikono, K. Kuwahara, Y. Aoki, H. Sugawara, and H. Harimas: J. Phys. Soc. Jpn. 77 (2008) 033701.
[12] B. Nowak, O. Zogał, A. Pietraszko, R. E. Baumbach, M. B. Maple, and Z. Henkie: Phys. Rev. B 79 (2009) 214411.
[13] C. Sekine, K. Akahira, K. Ito, and T. Yagi: J. Phys. Soc. Jpn. 78 (2009) 093707.
[14] K. Takeda, K. Ito, J. Hayashi, C. Sekine, T. Yagi: J. Phys. Soc. Jpn. 80 (2011) SA029.
[15] E. Matsuoka, K. Hayashi, A. Ikeda, K. Tanaka, T. Takabatake, and M. Matsumura: J. Phys. Soc. Jpn. 74 (2005) 1382.
[16] E. Matsuoka, S. Narazu, K. Hayashi, K. Umeo, and T. Takabatake: J. Phys. Soc. Jpn. 75 (2006) 014602.
[17] H. Yamada: Phys. Rev. B 47 (1993) 11211.
[18] K. Matsuhira, C. Sekine, M. Wakeshima, Y. Hinatsu, T. Namiki, K. Takeda, I. Shirotani, H. Sugawara, D. Kikuchi, and H. Sato: J. Phys. Soc. Jpn. 78 (2009) 124601.
[19] K. Takeda, J. Hayashi, N. Hoshi, C. Sekine and I. Shirotani: J. Phys. Soc. Jpn. 77 Suppl. A (2008) 324.
[20] K. Takeda, Y. Kawamura, K. Ito, J. Hayashi, K. Matsui, H. Nakane, and C. Sekine: JPS Conf. Proc. 3 (2014) 017019.