Magnetic properties of new filled skutterudite compounds GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$

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Abstract. New As-based filled skutterudite compounds GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ have been synthesized under high pressure. The samples have a cubic structure with lattice parameters $a=8.3024$ Å, and $8.2961$ Å, respectively. Both compounds show metallic behavior and a pronounced kink at low temperature in the temperature dependence of resistivity. Magnetic measurements reveal that GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ exhibit a ferromagnetic-like phase transition at 56K and 38K, respectively. The unexpectedly high transition temperatures could be related to the interaction of Gd (or Tb) 4f moments with Fe 3d moments.

1. Introduction

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\cite{1}, non-Fermi liquid behavior\cite{2, 3}, anomalous metal–insulator transition\cite{4}, and multipole ordering\cite{5}. 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)\cite{6}, canted ferromagnetic or ferrimagnetic phase transition in EuFe$_4$As$_{12}$\cite{7}. 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 using pressure above 4 GPa is a powerful technique for preparing As-based skutterudite compounds. We have succeeded in synthesizing samples of new As-based filled skutterudite compounds GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ using the high-pressure synthesis technique. In this paper, we report the magnetic properties of GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ for the first time.

2. Experimental

Polycrystalline GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ were prepared at high temperatures and high pressures using a wedge-type cubic anvil high-pressure apparatus. The sample cell assembly for the preparation of the As-based filled skutterudite compounds is similar to that used for the high-pressure synthesis of P-based filled skutterudite compounds\cite{8}. The compounds were prepared by reacting stoichiometric amounts of 3N (99.9% pure)-Gd, Tb chips, 4N-Fe, and 6N-As powders at 4 GPa. The reaction temperatures were between 840 and 850°C. The prepared samples were characterized by powder x-ray diffraction using CoK$_{\alpha 1}$ 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.

3. Results and discussion

Figure 1 shows an x-ray diffraction pattern of the new filled skutterudite GdFe$_4$As$_{12}$ prepared at high pressures. Most of the observed diffraction lines were indexable using the skutterudite structure though small amount of impurity phases (FeAs$_2$, metallic As) were detected. The lattice constant determined by a least-squares fit to the data was 8.3024 Å. The x-ray diffraction pattern of the new compound TbFe$_4$As$_{12}$ also indicates that the main phase consists of the filled skutterudite with less than 5 wt% impurity phases of FeAs$_2$ or metallic As. The lattice constant of TbFe$_4$As$_{12}$ was determined in the same manner and found to be 8.2961 Å.

Figure 1. X-ray diffraction pattern of the new filled skutterudite compound GdFe$_4$As$_{12}$.

Figure 2 plots the lattice constants of the new filled skutterudite compounds GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ along with the values reported earlier for the filled skutterudite arsenides LnFe$_4$As$_{12}$[7]. Starting with La, there is a typical reduction in lattice constant due to the contraction of the trivalent ionic radii of the lanthanides with increasing atomic number. This indicates that Gd and Tb ions are in a trivalent state. The small lattice constants of Ce compounds are due to strong c-f hybridization. The large lattice constants of the Eu compounds suggest that Eu ions are in a divalent or mixed-valence state. The same tendency of the lattice constant was observed in P-based filled skutterudite compounds [9].

Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi$ and the inverse magnetic susceptibility $\chi^{-1}$ at 1T for GdFe$_4$As$_{12}$. The inset of Fig. 3 shows the temperature dependence of $\chi$ below 100K at 0.01T. A large increase in $\chi(T)$ below 56K indicates a ferromagnetic-like transition. Figure 4 shows the temperature dependence of $\chi$ and $\chi^{-1}$ at 1T for TbFe$_4$As$_{12}$. The inset of Fig. 4 shows the low temperature region of $\chi$ at 0.05T. TbFe$_4$As$_{12}$ also exhibits a large increase in $\chi(T)$ below 38K indicating ferromagnetism. $\chi(T)$ of GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ follows the Curie–Weiss law above 150K. Least-squares fits yield effective moments of 8.09 $\mu_B$/Gd and 9.76 $\mu_B$/Tb for GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$, respectively. These effective moments are close to the expected values for trivalent ions of $\mu_{eff} = 7.94 \mu_B$/Gd and 9.72$\mu_B$/Tb.

Magnetization measurements at 2 K on GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ reveal a feature due to spontaneous magnetization (Fig. 5). The magnetization increases with increasing fields, reaching 6$\mu_B$/Gd and 4.6$\mu_B$/Tb at 5 T. The saturation magnetization should reach 7 $\mu_B$/Gd...
Figure 3. Magnetic susceptibility $\chi$ and inverse magnetic susceptibility $\chi^{-1}$ vs temperature at 1T for GdFe$_4$As$_{12}$. The inset shows the low-temperature region of $\chi$ at 0.01T.

Figure 4. Magnetic susceptibility $\chi$ and inverse magnetic susceptibility $\chi^{-1}$ vs temperature at 1T for TbFe$_4$As$_{12}$. The inset shows the low-temperature region of $\chi$ at 0.05T.

Figure 5. Magnetization for GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ at 2 K.

Figure 6. Temperature dependence of electrical resistivity $\rho/\rho_{273K}$ for GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ normalized at 273 K.

and $9\mu_B$/Tb. The significantly small experimental values of the magnetization and relatively high transition temperatures suggest that these compounds have ferrimagnetic or canted ferromagnetic ground state. The nonlinear, s-like shape of $\chi^{-1}$ also supports this scenario. EuFe$_4$Sb$_{12}$ with high transition temperature $T_C$ of 85K has been found to be ferrimagnetic in which Fe and Eu moments are ordered with antiferromagnetic coupling[12].

Figure 6 shows the temperature dependence of the electrical resistivity $\rho(T)/\rho_{273K}$ for GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ normalized at 273K. The overall behaviors of these compounds indicate metallic states. The $\rho(T)$’s of these compounds show a pronounced kink around $T_C=56$ and 38K, corresponding to the ferromagnetic-like transitions.

4. Summary
We have studied the physical properties of new filled skutterudite compounds GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$. Magnetic measurements reveal that GdFe$_4$As$_{12}$ and TbFe$_4$As$_{12}$ exhibit a ferromagnetic-like transition at 56K and 38K. The magnetic properties of GdFe$_4$As$_{12}$ and
Table 1. Transition temperatures to the ordered state \( T_{TR} \) (\( T_C \): ferromagnetic order, \( T_N \): antiferromagnetic order), effective magnetic moments \( \mu_{eff} \), and Weiss temperatures \( \theta_p \) of \( \text{LnT}_4\text{X}_{12} \) (\( \text{Ln}=\text{Gd}, \text{Tb}, \ T=\text{Fe}, \text{Ru}, \text{and Os}; \ X=\text{P}, \text{and As} \)).

| Compounds   | \( T_{TR}(K) \) | \( \mu_{eff}(\mu_B) \) | \( \theta_p(K) \) | Ref. No. |
|-------------|-----------------|-------------------------|------------------|----------|
| \( \text{GdFe}_4\text{P}_{12} \) | 23              | 7.90                    | 17.5             | 9        |
| \( \text{GdRu}_4\text{P}_{12} \) | 22              | 8.04                    | 23               | 10       |
| \( \text{GdOs}_4\text{P}_{12} \) | 5               | 8.54                    | 2.9              | 8        |
| \( \text{GdFe}_4\text{As}_{12} \) | 56              | 8.09                    | 23               | This study |
| \( \text{TbFe}_4\text{P}_{12} \) | 10              | 9.48                    | 10               | 11       |
| \( \text{TbRu}_4\text{P}_{12} \) | 20              | 9.76                    | 8                | 10       |
| \( \text{TbOs}_4\text{P}_{12} \) | No              | 10.86                   | 3                | 9        |
| \( \text{TbFe}_4\text{As}_{12} \) | 38              | 9.76                    | 16               | This study |

\( \text{TbFe}_4\text{As}_{12} \) are summarized in Table 1 along with those of filled skutterudite phosphides with Gd and Tb. Fe and Os compounds show a ferromagnetic transition except for \( \text{TbOs}_4\text{P}_{12} \), which remains paramagnetic down to 2K. On the other hand, Ru compounds show an antiferromagnetic transition. The positive Weiss temperatures for these compounds suggests that basically there are ferromagnetic correlations in this system. In the absence of other effects, e.g., Fermi surface instability or multipole interaction, these compounds are expected to show ferromagnetic ordering. The unexpectedly high transition temperatures of \( \text{GdFe}_4\text{As}_{12} \) and \( \text{TbFe}_4\text{As}_{12} \) could be due to the interaction between Gd (or Tb) 4f moments and Fe 3d moments. To elucidate this point, element-specific magnetic measurements are needed.

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Thank you very much for positive evaluation of our study.

>P.1, Line 26, Abstract: Authors should specify that the metallic behavior and the kink is observed
>in the temperature dependence of resistivity

1) We have added the phrase “in the temperature dependence of resistivity” to the third line sentence in Abstract.

> P3: Fig. 3 and Fig. 4 Captions: Indicate the magnetic field for the main figures.

2) We have added the phrase “at 1T” in the figure captions.

> Please indicate in text whether the samples are single- or poly- crystalline.

3) We have added the word “Polycrystalline” to the first sentence in the chapter of “Experimental”.

> The nonlinear, s-like shape of the inverse susceptibility also provides support for ferrimagnetism or
> canted ferromagnetism. Adding a note to this effect near line 46 (page 3) would bolster your claim
> concerning the nature of the ordered state.

4) We have added the sentence “The nonlinear, s-like shape of $\chi^{-1}$ also supports this scenario.” near line 46 (page 3).

With the best wish
The authors