High-pressure synthesis of new filled skutterudite compounds SrT4As12 (T = Fe, Ru, Os)

メタデータ	言語: English 出版者: Japan Society of Applied Physics 公開日: 2018-08-23 キーワード (Ja): キーワード (En): 作成者: 西根, 康平, 川村, 幸裕, 林, 純一, 関根, ちひろ メールアドレス: 所属:
URL	http://hdl.handle.net/10258/00009678

High-pressure synthesis of new filled skutterudite compounds $\mathrm{Sr}T_4\mathrm{As}_{12}$ (T = Fe, Ru, Os)

Kohei Nishine*, Yukihiro Kawamura, Junichi Hayashi, and Chihiro Sekine*

Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

*E-mail: 15043051@mmm.muroran-it.ac.jp; sekine@mmm.muroran-it.ac.jp

We have succeeded in synthesizing samples of new filled skutterudite compounds $\mathrm{Sr}T_4\mathrm{As}_{12}$ (T=Fe, Ru, and Os) using a high-pressure synthesis technique. These compounds have lattice constants of 8.351, 8.521, and 8.561 Å, respectively. The physical properties of the compounds are reported for the first time. The temperature dependences of the electrical resistivity for $\mathrm{Sr}T_4\mathrm{As}_{12}$ (T=Fe, Ru, and Os) exhibit metallic behaviors. The electrical resistivity and magnetic measurements indicates that $\mathrm{SrOs_4As_{12}}$ is a new superconductor with a transition temperature of 4.8 K. A broad maximum of magnetic susceptibility at around 50 K and a large electronic specific heat coefficient of 58 mJ $\mathrm{mol^{-1}\,K^{-2}}$ suggest that $\mathrm{SrFe_4As_{12}}$ is a nearly ferromagnetic metal with spin fluctuations of Fe 3d electrons.

1. Introduction

The filled skutterudite compounds AT_4X_{12} (A = alkali metal, alkaline earth metal, lanthanide (Ln), and actinide; T = Fe, Ru, Os, and Pt; X = P, As, Sb, and Ge) crystallize in a body-centered cubic structure with the space group $Im\bar{3}$ (T^5_h, No. 204) 1, 2). Filled skutterudite compounds, especially compounds including Ln, have attracted considerable attention owing to their wide variety of strongly correlated electron behaviors 3, 4), such as anomalous metal-insulator transition 5, 6), multipole ordering 7-11), and unconventional superconductivity 12, 13). The various attractive features in these systems are believed to be mainly due to the large hybridization between the f electrons of Ln and the p electrons of X. The d electrons of Fe, Ru, and Os atoms should also play important roles in the physical properties. However, the roles have not been well understood yet. Matsuoka *et al.* reported that filled skutterudite compounds including the alkaline earth metal AFe$_4$Sb$_{12}$ (A = Ca, Sr, and Ba) reveal the strong ferromagnetic spin fluctuations of Fe 3d electrons and the properties of nearly ferromagnetic metals 14). Furthermore, AOs$_4$Sb$_{12}$ (A=Sr and Ba) shows the characteristics of enhanced Pauli paramagnets where Os 5d electrons play important roles 15). The filled skutterudite compounds including alkaline earth metal could be a favorable system for systematically investigating the effect of d electrons in skutterudite systems because alkaline earth ions carry no magnetic moments. However, only preliminary studies have been conducted on the properties of P- and As-based compounds including alkaline earth metal because the compounds are difficult to prepare. A high-pressure synthesis method is adequate for preparing As-based skutterudite compounds 16, 17). Actually, new As-based alkaline-earth-filled skutterudite compounds such as $BaFe_4As_{12}$ and $BaRu_4As_{12}$ have been synthesized using a multianvil high-pressure apparatus 18, 19). Recently, the magnetic properties of $BaFe_4As_{12}$ prepared under high pressures have been reported 20). $BaFe_4As_{12}$ shows the feature of a nearly ferromagnetic metal. In this study, we focused on As-based filled skutterudite compounds including Sr as part of our search for new materials using a high-pressure synthesis technique.

2. Experimental methods

The polycrystalline compounds SrT_4As$_{12}$ (T=Fe, Ru, and Os) were prepared at high temperatures and high pressures using a Kawai-type double-stage multianvil high-pressure apparatus [21]. We used eight tungsten carbide cubes with a truncated edge length of 11 mm as second-stage anvils. The sample container, made of magnesia (MgO + 5% Cr_2O_3), was transformed into an octahedron with an edge length of 18 mm. The starting materials were placed in 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)-Sr chip, 4N-Fe, 4N-Ru, 4N-Os, and 6N-As powders at 4 GPa. The reaction temperature was 830-900 °C. The prepared samples were characterized by powder X-ray diffraction using Co $K\alpha_1$ radiation and silicon as a standard. Resistivity was measured by a standard dc four-probe method. Magnetization and dc magnetic susceptibility were measured by a superconducting quantum interference device magnetometer (Quantum Design MPMS). Specific heat measurement was carried out by a thermal relaxation method (Quantum Design PPMS).

3. Results and discussion

Figure 1 shows the powder X-ray diffraction patterns of the new filled skutterudite compounds $\mathrm{Sr}T_4\mathrm{As}_{12}$ (T=Fe, Ru, and Os) synthesized at 4 GPa. Although a small amount of impurity phase [$T\mathrm{As}_2$ (T = Fe, Ru, and Os)] was detected, most of the observed diffraction peaks were indexable using the skutterudite structure. The lattice constants of the compounds determined by a least-squares fit to the data were 8.351, 8.521, and 8.561 Å, respectively. Figure 2 shows the lattice constants of the new filled skutterudite compounds $\mathrm{Sr}T_4\mathrm{As}_{12}$ (T = Fe, Ru, and Os) along with the values reported earlier for $\mathrm{Ba}T_4\mathrm{As}_{12}$ (T = Fe and Ru) and the rare-earth filled skutterudite arsenides $LnT_4\mathrm{As}_{12}$ [18, 19, 22-24]. Starting with La, there is a typical reduction in lattice constant owing to the contraction of the trivalent ionic radii of the lanthanides with increasing atomic number. The small lattice constants of Ce compounds are due to a 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 large lattice constants of $\mathrm{Ba}T_4\mathrm{As}_{12}$ (T = Fe and Ru) and $\mathrm{Sr}T_4\mathrm{As}_{12}$ (T = Fe, Ru, and Os) are considered to be due to the divalent ions of alkaline earth metals.

Figure 3 shows the temperature dependences of electrical resistivity $\rho(T)$ for $\mathrm{Sr}T_4\mathrm{As}_{12}$

(T = Fe, Ru, and Os). $\rho(T)$ exhibits a positive temperature dependence, such as that observed in, typical metals below room temperature. Figure 4 shows the temperature dependence of the relative electrical resistivity $[\rho(T)–\rho_0]/\rho_{290\ \mathrm{K}}$ for SrT_4As$_{12}$ (T = Fe, Ru, and Os). ρ_0 and $\rho_{290\ \mathrm{K}}$ are the residual resistivity (1.85, 1.12, and 0.21 mΩcm) and the resistivity at T = 290 K, respectively. $SrRu_4As_{12}$ shows no anomaly down to 2 K. On the other hand, a broad shoulder in $\rho(T)$ was observed for $SrFe_4As_{12}$ and $SrOs_4As_{12}$. In contrast with the monotonic decrease in $\rho(T)$ for $SrRu_4As_{12}$, a strong curvature in $\rho(T)$ was observed for $SrFe_4As_{12}$ and $SrOs_4As_{12}$. The behavior of $SrFe_4As_{12}$ seems to be a common feature among the alkaline-earth filled skutterudite compounds including Fe, such as $BaFe_4As_{12}$ and AFe$_4$Sb$_{12}$ (A = Ca, Sr, and Ba) [14, 20]. The curvature in $\rho(T)$ for $SrFe_4As_{12}$ is stronger than that for an isostructural compound $BaFe_4As_{12}$ [20]. This suggests that the effect of 3d electron spin fluctuation in $SrFe_4As_{12}$ could be larger than that in $BaFe_4As_{12}$. On the other hand, the strong curvature of $SrOs_4As_{12}$ may be due to a strong electron–phonon interaction, which was discussed for AOs$_4$Sb$_{12}$ (A = Ca, Sr, and Ba) [15]. Matsuoka *et al*. proposed that the strong electron–phonon interaction in the presence of tunneling states of A^{2+} ions in the $[Os_4Sb_{12}]^{2-}$ cage is the origin of a similar shoulder observed in the resistivity of AOs$_4$Sb$_{12}$ (A = Ca, Sr, and Ba) [15]. Figure 5 shows the $\rho(T)$ of $SrOs_4As_{12}$ at low temperatures. A sharp drop of $\rho(T)$ was observed below 4.8 K. Figure 6 shows the temperature dependence of the dc susceptibility measured at B = 0.001 T for $SrOs_4As_{12}$. The susceptibility of the arsenide sharply decreases at around 4.8 K. The hysteresis between zero-field cooling (ZFC) and field cooling (FC) indicates that the arsenide is a type-II superconductor.

Figures 7 and 8 show the magnetic properties of $SrFe_4As_{12}$. The magnetic behavior of $SrFe_4As_{12}$ is similar to that of $BaFe_4As_{12}$ [20]. The magnetic parameters of $SrFe_4As_{12}$ are summarized in Table I with those of $BaFe_4As_{12}$ and Sb-based compounds as references. The temperature dependences of the magnetic susceptibility $\chi(T)$ and inverse magnetic susceptibility $\chi^{-1}(T)$, measured at B = 1 T, are depicted in Fig. 7. At high temperatures above 150 K, the linear slope of $\chi^{-1}(T)$ yields an effective magnetic moment of 1.36 μ_B/Fe and a Weiss temperature θ_p of 36 K. In contrast with the large negative θ_p (-57 K) for $BaFe_4As_{12}$ [20], $SrFe_4As_{12}$ has a positive θ_p, while the effective magnetic moments of both compounds are almost the same. The magnetization data of $SrFe_4As_{12}$ up to 7 T at 2 K are depicted in Fig. 8. The magnetization increases linearly with magnetic field. At 7 T, the observed magnetic moment is 0.045 μ_B/Fe. This value is approximately twice as large as that of $BaFe_4As_{12}$. The small observed magnetic moment at a high magnetic field compared with the effective magnetic moment is also a common feature among the alkaline-earth filled skutterudite compounds including Fe. This indicates that the system is considered as an itinerant magnetic metal. A broad maximum is also observed for $SrFe_4As_{12}$ at around 50K as shown in Fig. 7. A similar behavior is observed for $BaFe_4As_{12}$ and AFe_4Sb_{12} (A = Ca, Sr, and Ba) 14, 20). The peak of $SrFe_4As_{12}$ is prominent compared with that of $BaFe_4As_{12}$. This tendency is the same as that observed in Sb-based compounds 14). Such a broad maximum was found in nearly ferromagnetic compounds such as Co-based Laves phase compounds, which exhibit a metamagnetic transition 25). Therefore, high-field magnetization measurements are required in clarifying this point.

The temperature dependence of specific heat $C(T)$ for $SrFe_4As_{12}$ at zero field is shown in Fig. 9. The $C(T)$ data exhibit no anomaly due to any phase transitions down to 2 K. Figure 10 shows a plot of $C(T)/T$ versus T^2 at low temperatures. The $C(T)/T$ data of $SrFe_4As_{12}$ can be expressed as $C(T)/T = \gamma + \beta T^2$ with the electronic specific heat coefficient γ = 58 mJ mol^{-1} K^{-2} and Debye temperature $\Theta_D = (12\pi 4nR/5\beta)^{1/3}$ = 360 K, where R is the gas constant and n = 17. For many filled skutterudite compounds, the lattice specific heat is modeled by a combination of the usual Debye mode and an Einstein mode due to rattling 26). Figure 11 shows the temperature dependence of $(C - \gamma T)/T^3$ for $SrFe_4As_{12}$ along with the data of $BaFe_4As_{12}$ (taken from Ref. 20). We can easily see the contribution of the Einstein mode in this plot. The Einstein specific heat leads to a broad maximum in $(C - \gamma T)/T^3$ at Θ_E /4.92, where Θ_E is the Einstein temperature. We estimated Θ_E = 133 K for $SrFe_4As_{12}$. For $BaFe_4As_{12}$, a broad maximum related to the Einstein mode was not observed 20). The results could be closely related to the difference between the ionic radii of Ba and Sr. Namely, a smaller Sr ion shows a random motion in the large space inside the cage. On the other hand, there is no space to move inside the cage in $BaFe_4As_{12}$. The thermal parameters of $SrFe_4As_{12}$ are also summarized in Table I together with those of $BaFe_4As_{12}$ and Sb-based compounds as reference compounds.

4. Conclusions

Using a high-pressure synthesis technique, we have succeeded in synthesizing the new skutterudite compounds SrT_4As$_{12}$ (T=Fe, Ru, and Os) with lattice constants of 8.351, 8.521, and 8.561 Å, respectively. SrOs$_4$As$_{12}$ was found to be a new superconductor at around 4.8 K. The magnetic susceptibility of SrFe$_4$As$_{12}$ shows a broad peak at around 50 K and a large electronic specific heat coefficient is observed for the compound. The results suggest that SrFe$_4$As$_{12}$ is a nearly ferromagnetic metal with spin fluctuations of Fe 3d electrons similar to BaFe$_4$As$_{12}$. The new synthesized As-based filled skutterudite compounds including Sr could be favorable systems for systematically investigating the effect of d electrons in skutterudite systems. Furthermore, EuFe$_4$As$_{12}$ with divalent Eu^{2+} ions was reported to exhibit a ferrimagnetic-like phase transition with an extremely high transition temperature of 152 K 27). The exchange interaction between the 3d electrons of Fe and the 4f electrons could be essential to the ordering in this compound. Therefore, SrFe$_4$As$_{12}$ and BaFe$_4$As$_{12}$ with divalent ions, without 4f electrons, are important reference compounds for elucidating the origin of the magnetic properties of EuFe$_4$As$_{12}$ in detail.

Acknowledgment

This work was supported by JSPS KAKENHI Grant Number 23340092.

References

1) W. Jeitschko and D. Braun, Acta Crystallogr., Sect. B **33**, 3401 (1977).

2) E. Bauer, A. Grytisiv, Xing-Qiu Chen, N. Melnychenko-Koblyuk, G. Hilscher, H. Kaldarar, H. Michor, E. Royanian, G. Giester, M. Rotter, R. Podloucky, and P. Rogl, Phys. Rev. Lett. **99**, 217001 (2007).

3) See Proc. Int. Conf. New Quantum Phenomena in Skutterudite and Related Systems, J. Phys. Soc. Jpn. **77**, Suppl. A (2008).

4) H. Sato, H. Sugawara, Y. Aoki, and H. Harima, in *Handbook of Magnetic Materials*, ed. K. H. J. Buschow (North-Holland, Amsterdam, 2009) Vol. 18, Chap. 1.

5) C. Sekine, T. Uchiumi, I. Shirotani, and T. Yagi, Phys. Rev. Lett. **79**, 3218 (1997).

6) C. Sekine, T. Uchiumi, I. Shirotani, and T. Yagi, in *Science and Technology of High Pressure*, ed. M. H. Manghnani, W. J. Nellis, and M. F. Nicol (Universities Press, Hyderabad, 2000) p. 826.

7) M. Yoshizawa , Y. Nakanishi, M. Oikawa, C. Sekine, I. Shirotani, S. R. Saha, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **74**, 2141 (2005).

8) M. Yoshizawa, Y. Nakanishi, T. Kumagai, M. Oikawa, C. Sekine, and I. Shirotani, J. Phys. Soc. Jpn. **73**, 315 (2004).

9) Y. Kuramoto, Prog. Theor. Phys. Suppl. **176**, 77 (2008).

10) A. Kiss and Y. Kuramoto, J. Phys. Soc. Jpn. **78**, 124702 (2009).

11) R. Shiina, J. Phys. Soc. Jpn. **82**, 083713 (2013).

12) E. D. Bauer, N. A. Frederick, P. -C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B **65**, 100506 (2002).

13) Y. Aoki, T. Tayama, T. Sakakibara, K. Kuwahara, K. Iwasa, M. Kohgi, W. Higemoto, D.E. MacLaughlin, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **76**, 051006 (2007).

14) E. Matsuoka, K. Hayashi, A. Ikeda, K. Yanaka, T. Takabatake, and M. Matsumura, J. Phys. Soc. Jpn. **74**, 1382 (2005).

15) E. Matsuoka, S. Narazu, K. Hayashi, K. Umeo, and T. Takabatake, J. Phys. Soc. Jpn. **75**, 014602 (2006).

16) T. Namiki, Y. Aoki, H. Sato, C. Sekine, I. Shirotani, T. D. Matsuda, Y. Haga, and T. Yagi, J. Phys. Soc. Jpn **76**, 093704 (2007).

17) C. Sekine, R. Abe, K. Takeda, K. Matsuhira, and M. Wakeshima, Physica B **403**, 856

(2008).

18) K. Takeda, K. Ito, J. Hyashi, C. Sekine, and T. Yagi, J. Phys. Soc. Jpn. **80**, SA029 (2011).

19) K. Takeda, N. Hoshi, J. Hayashi, C. Sekine, S. Kagami, I. Shirotani, and T. Yagi, J. Phys.: Conf. Ser. **215**, 012130 (2010).

20) C. Sekine, T. Ishizaka, K. Nishine, Y. Kawamura, J. Hayashi, K. Takeda, H. Gotou and Z. Hiroi, Phys. Procedia **75**, 383 (2015).

21) C. Sekine, T. Kawata, Y. Kawamura, and T. Yagi, J. Korean Phys. Soc. **63**, 359 (2013).

22) D. J. Braun and W. Jeitchko, J. Solid State Chem. **32**, 357 (1980).

23) W. Jeitchko, A. J. Foecker, D. Paschke, M. V. Dewalsky, C. B. H. Evers, B. Kunnen, A. Lang, G. Kotzyba, U. C. Rodewald, and M. H. Moller, Z. Anorg. Allg. Chem. **626**, 1112 (2000).

24) A. Rudenko, Z. Henkie, and T. Cichorek, Solid State Commun. **242**, 21 (2016).

25) H. Yamada, Phys. Rev. B **47**, 11211 (1993).

26) 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**, 124601 (2009).

27) C. Sekine, K. Akahira, K. Ito, and T. Yagi, J. Phys. Soc. Jpn. **78**, 093707 (2009).

Figure Captions

Fig. 1. (Color online) Powder x-ray diffraction patterns of SrT_4As$_{12}$ (T = Fe, Ru, and Os) prepared under high pressures.

Fig. 2. (Color online) Lattice constants of SrT_4As$_{12}$ (T = Fe, Ru, and Os) and BaT_4As$_{12}$ (T = Fe and Ru) and rare-earth filled skutterudite arsenides LnT_4As$_{12}$ (Ln = rare-earth elements; T = Fe, Ru, and Os).

Fig. 3. (Color online) Temperature dependence of electrical resistivity ρ(T) of SrT_4As$_{12}$ (T = Fe, Ru, and Os).

Fig. 4. (Color online) Temperature-dependent part $\rho(T)$-ρ_0 of electrical resistivity for SrT_4As$_{12}$ (T = Fe, Ru, and Os), normalized at 290K.

Fig. 5. (Color online) Temperature dependence of electrical resistivity $\rho(T)$ of SrOs$_4$As$_{12}$ at low temperatures.

Fig. 6. (Color online) ZFC and FC dc magnetic susceptibility χ at 0.001 T for SrOs$_4$As$_{12}$.

Fig. 7. (Color online) Magnetic susceptibility χ and inverse magnetic susceptibility χ^{-1} versus temperature for SrFe$_4$As$_{12}$ at 1 T.

Fig. 8. (Color online) Magnetization for SrFe$_4$As$_{12}$ at 2 K.

Fig. 9. (Color online) Temperature dependence of the specific heat C for $SrFe_4As_{12}$.

Fig. 10. (Color online) T^2 dependence of C/T for $SrFe_4As_{12}$.

Fig. 11. (Color online) Temperature dependence of the specific heat for $SrFe_4As_{12}$ and $BaFe_4As_{12}$. The data are displayed in the form of $(C-\gamma T)/T^3$. The data of $BaFe_4As_{12}$ were taken from Ref. 20.

Fig.1. (Color Online)

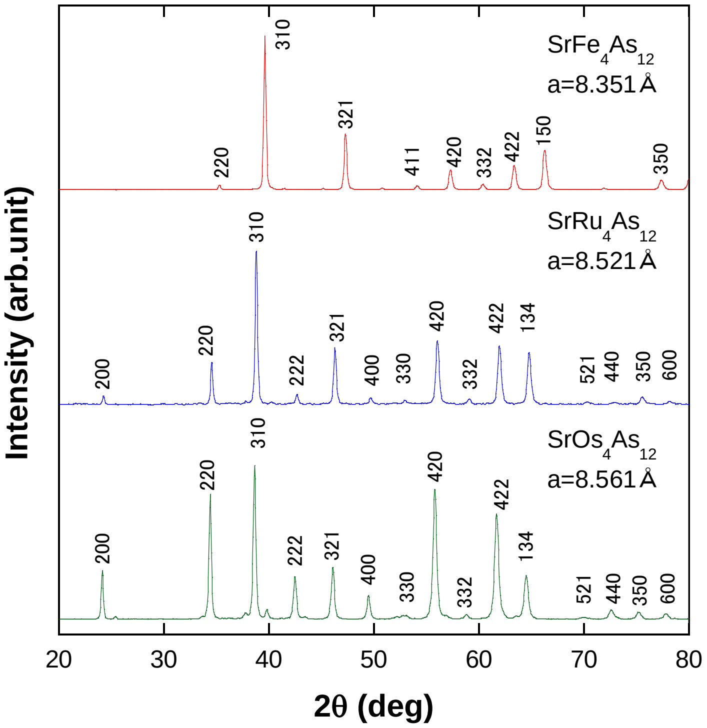

Fig.2. (Color Online)

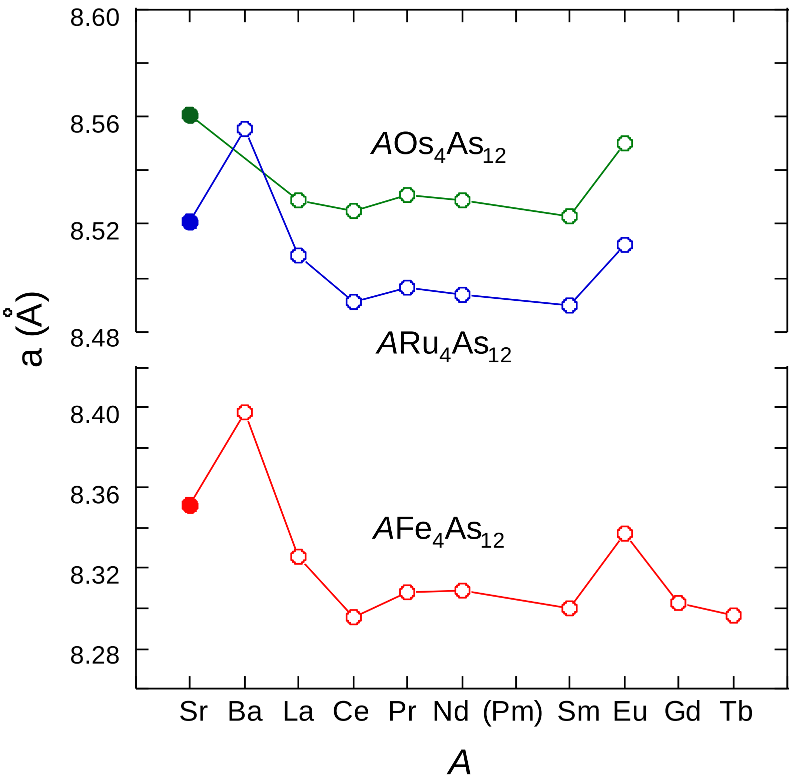

Fig.3. (Color Online)

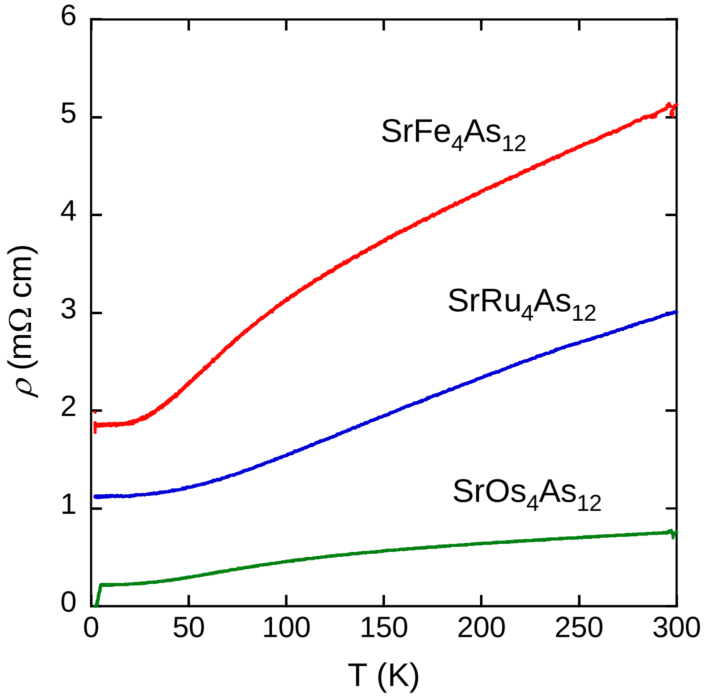

Fig.4. (Color Online)

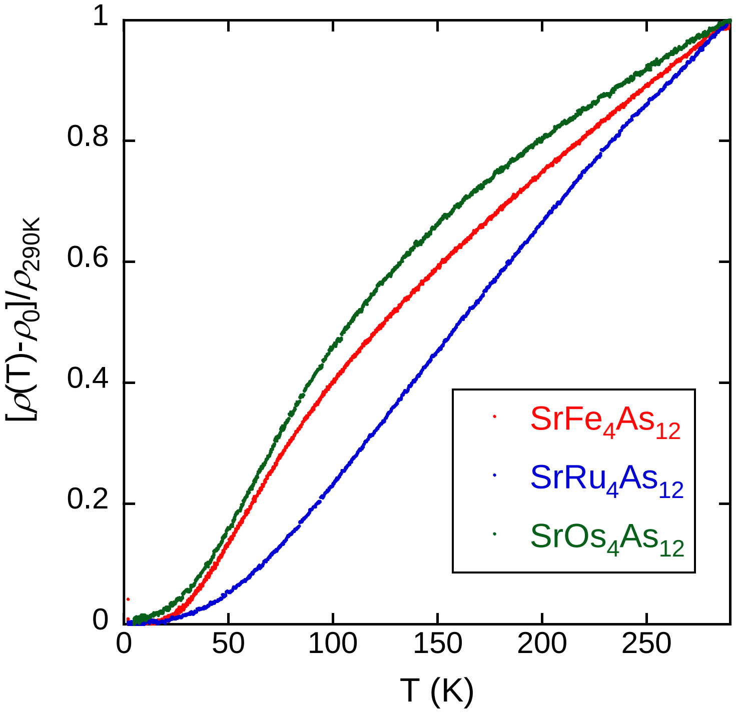

Fig.5.

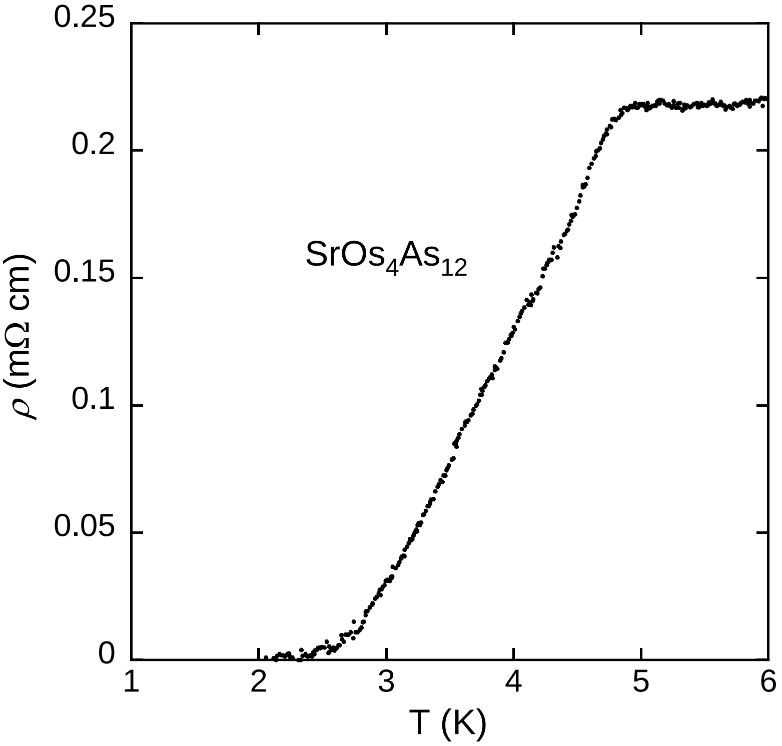

Fig.6. (Color Online)

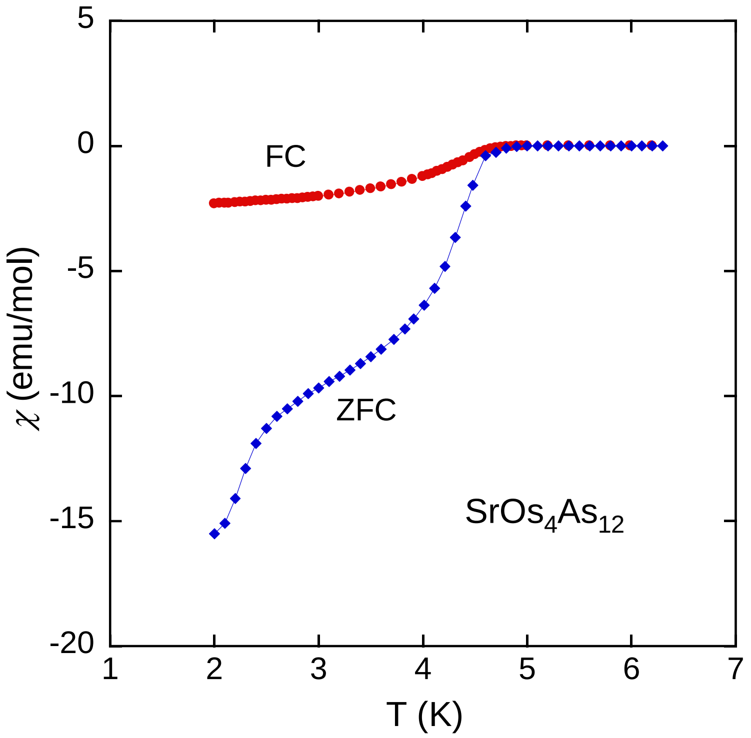

Fig.7. (Color Online)

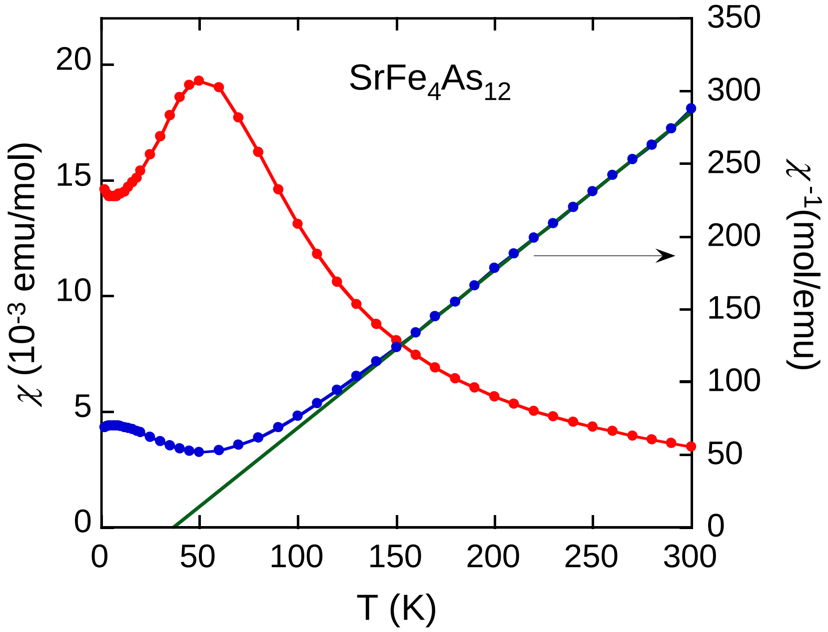

Fig.8.

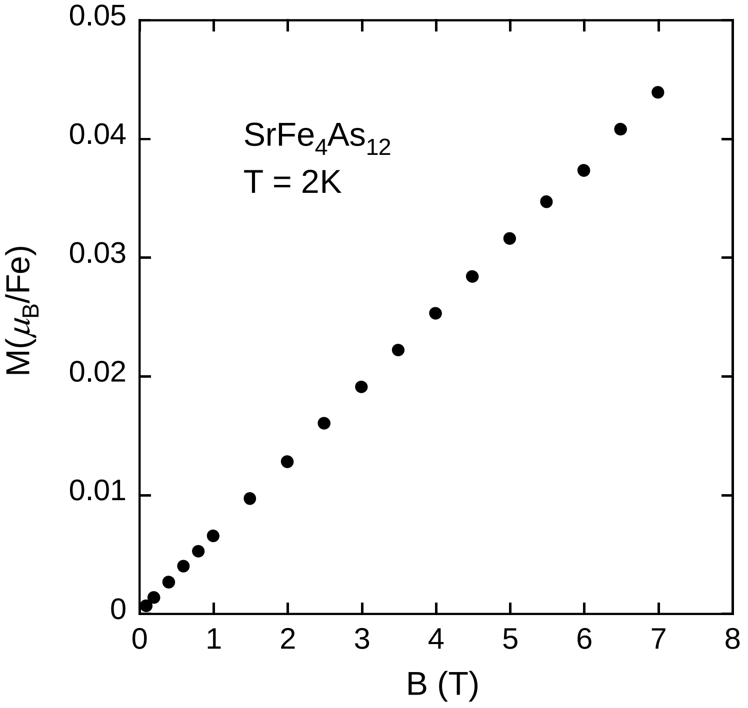

Fig.9.

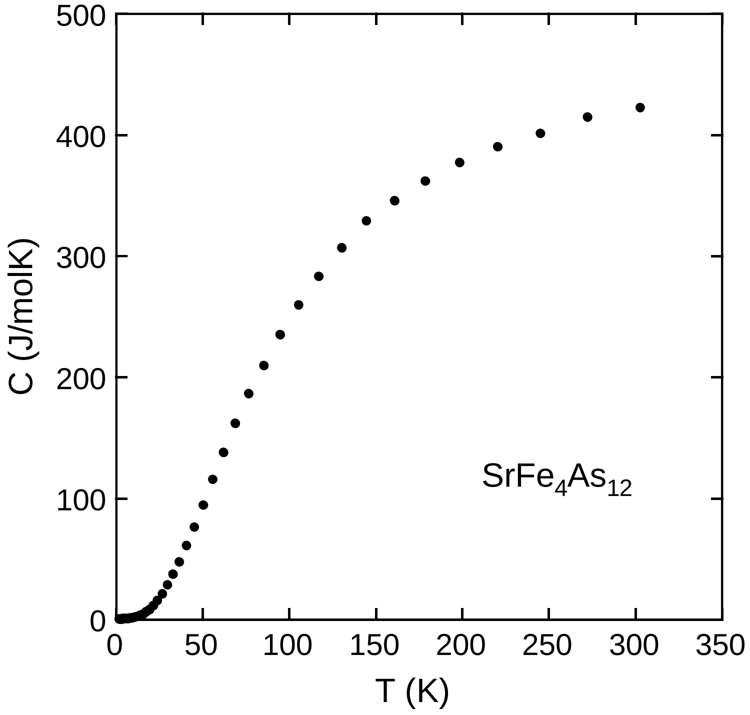
500
400
300
200
100
0
C (J/molK)
0
50
100
150
200
250
300
350
T (K)
$SrFe_4As_{12}$

Fig.10.

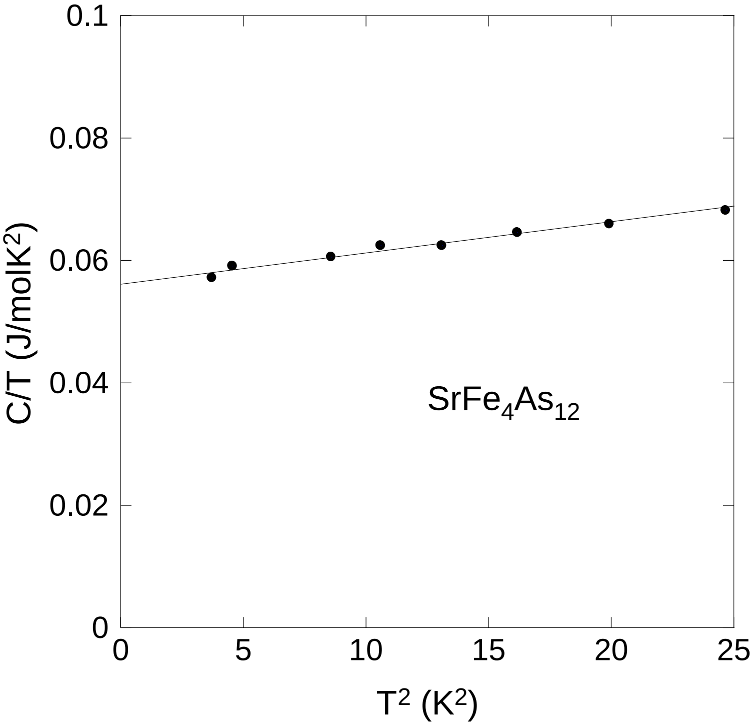

Fig.11. (Color Online)

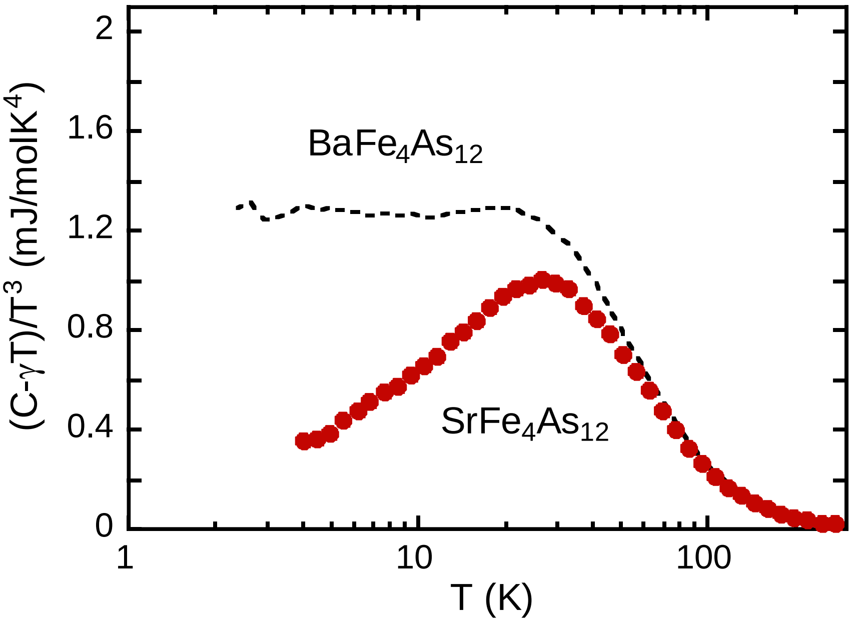

Table I. Magnetic and thermal parameters of $SrFe_4As_{12}$, $BaFe_4As_{12}$, and Sb-based compounds as reference compounds (μ_{eff}: effective magnetic moment, θ_P: Weiss temperature, γ: electronic specific heat coefficient, Θ_D: Debye temperature, and Θ_E: Einstein temperature).

Compound	μ_{eff} (μ_B)	θ_P (K)	γ (mJ/molK^2)	Θ_D (K)	Θ_E (K)	Reference
$SrFe_4As_{12}$	1.36	36	58	360	133	This work
$BaFe_4As_{12}$	1.46	-57	62	295	-	20
$SrFe_4Sb_{12}$	1.47	53	87	279	103	14, 15
$BaFe_4Sb_{12}$	1.50	31	104	298	108	14, 15