(PS7)

Thermoelectric and Magnetic Properties of $\mathbf{BaFe_{4-x}Co_xSb_{12}}$

K. Tanaka[1], E. Matsuoka[1], K. Hayashi[1], A. Ikeda[1], and T. Takabatake[1,2]

[1]Department of Quantum Matter, ADSM, and [2]Materials Science Center, N-BARD, Hiroshima University, Higashi-Hiroshima, 739-8530

Recently, alkaline-earth filled AFe_4Sb_{12} (A = Ca, Sr, Ba) have been found to be nearly ferromagnetic metals [1]. All three compounds show a maximum in both the magnetic susceptibility and thermopower at 50 K, and a large electronic specific heat coefficient of 100 mJ/mol K^2. Furthermore, a remanent moment of the order of 10^{-3} μ_B/Fe was observed below 54, 48, and 40 K for A = Ca, Sr, and Ba, respectively. The volume fraction of the ferromagnetic component was estimated to be 10-20% by zero-field μSR measurements. These observations indicated that the ground state of AFe_4Sb_{12} (A = Ca, Sr, Ba) is intermediate between an itinerant ferromagnetic state in $NaFe_4Sb_{12}$ with a monovalent filler ion [2] and an enhanced paramagnetic state in $LaFe_4Sb_{12}$with a trivalent filler ion [3].

We report here the effect of Co substitution for Fe in $BaFe_{4-x}Co_xSb_{12}$ on the magnetic and thermoelectric properties. The thermoelectric properties will be discussed in comparison with those of $CeFe_{4-x}Co_xSb_{12}$ [4,5,6], in which system the dimension-less figure of merit ZT for x = 1 exceeds 1 at 700 K [6]. The samples of $BaFe_{4-x}Co_xSb_{12}$(x=0, 1, 2, 2.5, 3) in both powder and pellet forms were prepared by the method reported in ref. [1]. For transport property measurements, high density pellets were made by a spark-plasma sintering (SPS) technique. The typical density of samples sintered at 743 K under a pressure of 400 MPa for 30 min. was 94% of the theoretical value. Electron-probe microanalysis showed that the filling factor of Ba decreases from 0.97 for $x = 0$ to 0.60 $x = 3$ while the Co content is close to the nominal value x. The lattice parameter gradually decreases from 9.20 Å for $x = 0$ to 9.10 Å for $x = 3$.

The Curie-Weiss behavior in magnetic susceptibility χ for $x = 0$ changes to a paramagnetic behavior upon increasing x, as shown in Fig. 1. When x exceeds 2.5, χ at 300 K becomes negative. This change from a nearly ferromagnetic state to a diamagnetic state is caused by electron doping upon Co substitution for Fe, which should result in a decrease in the electron density of states at the Fermi level.

The decrease in carrier density with increasing x is manifested in the strong enhancement of the electrical resistivity ρ (not shown). For $x = 0$, $\rho(T)$ has a shoulder at 70 K, which is a result of scattering of conduction electrons by spin fluctuations of Fe 3d electrons [1]. The shoulder disappears for $x = 1$. The value at 290 K is increased by one order of magnitude from 0.37 mΩcm for $x = 0$ to 4.2 mΩcm for $x = 3$. The $\rho(T)$ for $x = 2.5$ retains a metallic behavior but $\rho(T)$ for $x = 3$ is almost independent of temperature.

The thermopower $S(T)$ for $x = 0$ exhibits a local maximum at 50 K, which was attributed to the effect of spin fluctuations [1]. As is shown in Fig. 2, the maximum disappears for x = 1, and $S(T)$ linearly increases with temperature up to 500 K. The sign of S changes from positive for $x = 2.5$ to negative for $x = 3.0$. This coincides with the reverse of the sign in $\chi(T)$ shown in Fig. 1. This means that the dominant charge carrier changes from holes to electrons upon increasing x from $x = 2.5$ to 3.0. Since $CoSb_3$ is a narrow-gap semiconductor [7], the number of holes introduced by Fe substitution in $Fe_{4-x}Co_xSb_{12}$ would be 4-x per formula unit and the number of electrons introduced by filling of Ba^{2+} in $Ba_yFe_{4-x}Co_xSb_{12}$ would be $2y$. Both carriers may be compensated when 4-x equals $2y$, if the band structure does not change so much by the substitution and filling. This simple picture is consistent with the compensation found in the sample $Ba_{0.66}Fe_{1.5}Co_{2.5}Sb_{12}$.

The thermal conductivity $\kappa(T)$ for $x = 0$ exhibits a maximum of 58 mW/Kcm at 30 K. Although the maximum value is rather small, the appearance of such a maximum is characteristic of a crystal. With increasing x, the maximum is gradually smeared out but the value at 150 K is unchanged. The loss of the maximum can be attributed to the mass and strain fluctuations associated with the randomness in the Fe-Co sublattice, as was proposed for $\mathrm{CeFe}_{4-x}\mathrm{Co}_x\mathrm{Sb}_{12}$ [5].

With the knowledge of the sets of data $\rho(T)$, $S(T)$, and $\kappa(T)$ for $\mathrm{BaFe}_{4-x}\mathrm{Co}_x\mathrm{Sb}_{12}$, we estimated the dimension-less figure of merit ZT. The value of ZT at 300 is 0.05 for $x = 0$, and decreases with increasing x. The values of ZT are less than 0.2 reported for $\mathrm{Ce}_{0.9}\mathrm{Fe}_3\mathrm{CoSb}_{12}$ [6]. This is primary due to the fact that S(300 K) of 60-70 μV/K in the Ba system is less than 100 μV/K in the Ce system.

[1] E. Matsuoka et al., cond-mat/0412094.
[2] A. Leithe-Jasper *et al.*, Phys. Rev. Lett. **91** (2003) 037208.
[3] D. Ravot, *et al.*, J. Alloys Comp. **323-324** (2001) 389.
[4] B. S . Sales, D. Mandrus, and R.K. Williams, Science **272** (1996) 1325.
[5] B. Chen *et al.*, Phys. Rev. B **55** (1997) 1476.
[6] S. C. Sales *et al.*, Phys. Rev. B **56** (1997) 15081.
[7] J. O Sofo and G. D. Mahan, Phys. Rev. B **58** (1998) 15 620.

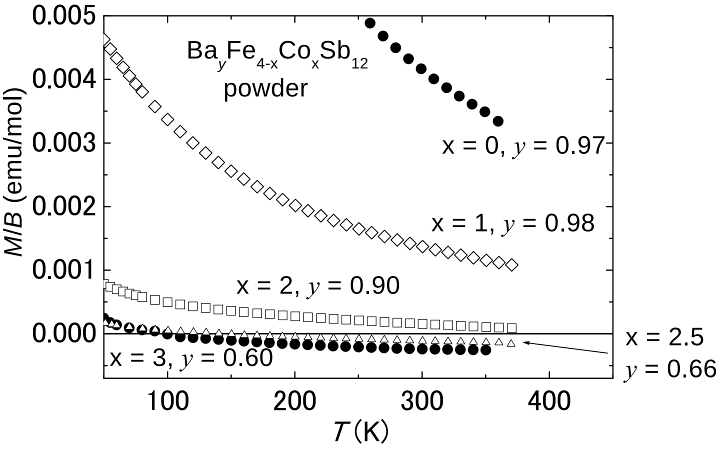

Figure 1: Magnetic susceptibility vs. temperature for $\mathrm{Ba}_y\mathrm{Fe}_{4-x}\mathrm{Co}_x\mathrm{Sb}_{12}$.

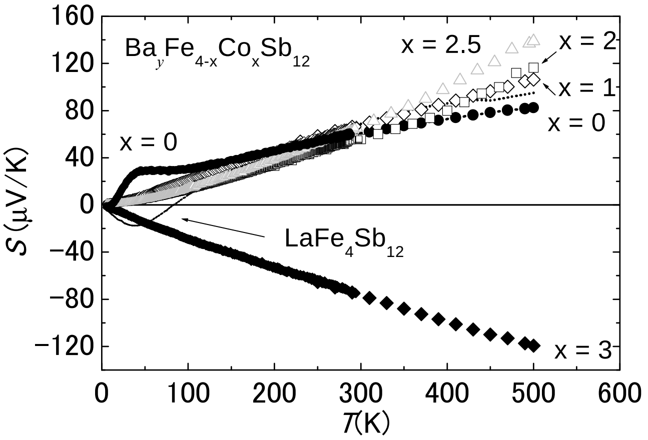

Figure 2: Thermopower vs. temperature for $\mathrm{Ba}_y\mathrm{Fe}_{4-x}\mathrm{Co}_x\mathrm{Sb}_{12}$.