ELSEVIER

Physica B 259–261 (1999) 8–9

PHYSICA B

Strongly correlated electron phenomena in filled skutterudite compounds

M.B. Maple[a,*], N.R. Dilley[a], D.A. Gajewski[a], E.D. Bauer[a], E.J. Freeman[a], R. Chau[a], D. Mandrus[b], B.C. Sales[b]

[a]*Department of Physics-0319 and Institute for Pure and Applied Physical Sciences, University of California, San Diego, 9500 German Drive, La Jolla, CA 92093-0319, USA*

[b]*Oak Ridge National Laboratory, Oak Ridge, TN, USA*

Abstract

We report on a search for intermediate valence and heavy fermion behavior in filled skutterudite compounds. The compound $YbFe_4Sb_{12}$ was synthesized and, to our knowledge, is the first example of a filled skutterudite of a heavy lanthanide. Transport, magnetic, and thermal measurements on $CeFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ indicate that these materials have a moderately heavy fermion ground state. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Skutterudite; Heavy fermion; Strongly correlated electrons

The class of compounds known as "filled" skutterudites crystallize in the cubic $LaFe_4P_{12}$ structure and exhibit a variety of correlated electron phenomena including superconductivity [1], magnetic order [2,3], small gap semiconducting behavior [2], and intermediate valence [2]. Recently, indications of heavy fermion behavior in the electrical resistivity and magnetic susceptibility, accompanied by a significantly enhanced Seebeck coefficient, were observed in metallic $CeFe_4Sb_{12}$ [4,5]. In this paper, we report the initial findings of a search for intermediate valence and heavy fermion behavior in filled skutterudite compounds RT_4Pn_{12} (R = Ce, Pr, Eu, Yb; T = Fe, Ru; Pn = P, Sb). This search yielded a new compound, $YbFe_4Sb_{12}$, which, to our knowledge, is the first example of a filled skutterudite of a heavy lanthanide [6]. Transport, magnetic, and thermal measurements on $CeFe_4Sb_{12}$ and $YbFe_4Sb_{12}$, reported herein, indicate that these materials have a moderately heavy fermion ground state. The observation of heavy fermion behavior in isostructural compounds of Ce, whose 4f-shell contains up to one electron, and its 4f-hole counterpart Yb, whose 4f-shell contains up to one hole, could shed light on strongly correlated electron phenomena in f-electron materials. More detailed accounts of this work can be found in Refs. [6,7].

Electrical resistivity ρ of $CeFe_4Sb_{12}$, plotted as a function of temperature and normalized to 300 K, is shown by the solid circles in the top portion of Fig. 1a. The drop in resistivity below $T \sim 150$ K is indicative of the onset of Kondo coherence seen in many heavy fermion materials; the slight upturn in $\rho(T)$ below 30 K may be a separate Kondo effect associated with an impurity phase. Magnetic susceptibility measurements made on $CeFe_4Sb_{12}$ are shown in the bottom portion of Fig. 1a, where the ratio χ of the magnetic moment M to the applied magnetic field H measured in a field of $H = 10$ kOe is represented by open circles, while the value of the slope of $M(H)$ isotherms at high fields is indicated by filled circles. This latter quantity is a measure of the Pauli susceptibility which is reflective of the itinerant electron effective mass. Extraction of the linear magnetic susceptibility from the $M(H)$ isotherms required a subtraction of the saturable portion of the magnetization due to localized magnetic moments which was modeled as a function of H/T (see Ref. [7] for details). The Curie-like increase in M/H data at low temperatures can be attributed to local

* Corresponding author. Fax: +1 619 534 1241; e-mail: mbmaple@ucsd.edu.

0921-4526/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0921-4526(98)00629-2

moment magnetism which may or may not be intrinsic to $CeFe_4Sb_{12}$. However, the high-field slope is nearly constant in temperature and extrapolates to a value of $\chi_0 = 8 \times 10^{-3}$ cm^3/mol at $T = 0$ K. Low-temperature specific heat C data for $CeFe_4Sb_{12}$, plotted as C/T versus T^2, are shown in the inset of Fig. 1a, and indicate moderately enhanced electronic effective masses with an electronic specific heat coefficient $\gamma = C/T$ which increases to near 180 mJ mol^{-1} K^{-2} below $T \approx 5$ K. The specific heat is further enhanced and goes through a peak at 1.5 K which may be due to magnetic ordering of an impurity phase. To corroborate the enhanced effective masses of charge carriers inferred from both specific heat and magnetization measurements, we estimated the Wilson–Sommerfeld ratio $R = (\chi_0/\gamma)(\pi^2 k_B^2/\mu_{eff}^2)$, where the effective moment $\mu_{eff} = 3.8\mu_B$ was obtained from a high-temperature fit of the $\chi(T)$ data to a Curie–Weiss law and R should be of order unity for a heavy fermion system ($R = 2$ for a spin-$\frac{1}{2}$ Kondo system). We obtain a value of $R = 1.5$ which supports the conjecture that $CeFe_4Sb_{12}$ is a heavy fermion material at low temperatures.

Powder X-ray diffraction measurements on $YbFe_4Sb_{12}$ yield an anomalously large lattice parameter of $a = 9.158$ Å which indicates that the Yb ions are divalent or mixed valent, as opposed to the light rare earths R = La–Sm that are trivalent in the RFe_4Sb_{12} series. Electrical resistivity measurements, shown in the upper portion of Fig. 1b, reveal a broad shoulder near $T = 100$ K. In this same temperature region, the magnetic susceptibility, defined as $\chi = M/H$ and indicated by the open circles in the lower portion of Fig. 1b, deviates from the Curie–Weiss behavior (linear fits of $\chi^{-1}(T)$ yield a Curie–Weiss temperature $\Theta_{CW} = 40$ K and $\mu_{eff} = 3.1\ \mu_B$) observed at high temperatures. Based on measurements of the high-field slope of $M(H)$ isotherms below $T = 10$ K (solid circles), we have estimated the form of the Pauli susceptibility (dashed line) as it merges with $\chi = M/H$ data at higher temperatures. The inset of Fig. 1b shows low-temperature specific heat data for $YbFe_4Sb_{12}$ which indicate that the electronic specific heat coefficient increases below $T \approx 5$K and saturates to $\gamma(T = 0) = 140$ mJ mol^{-1} K^{-2}. Finally, we evaluated the Wilson ratio for $YbFe_4Sb_{12}$ using $\chi_0(0) = 3.45 \times 10^{-2}$ cm^3 mol^{-1} and $\mu_{eff} = 4.5\mu_B$ appropriate for Yb^{3+} free ions, and obtained $R = 2.62$, suggesting that this material exhibits a heavy fermion ground state.

In conclusion, a comparative study of the filled skutterudite compounds $CeFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ shows that they exhibit strikingly similar heavy electron phenomena at low temperatures. Future studies will focus on the unusual magnetism of these materials by means of chemical substitution experiments and use of techniques such as neutron scattering and infrared spectroscopy.

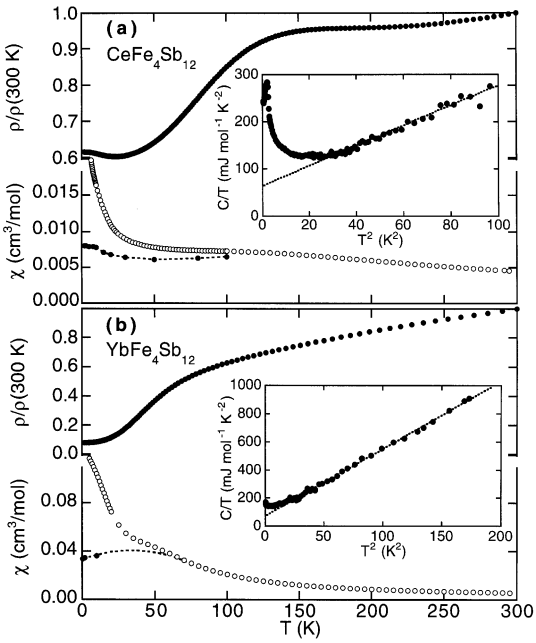

Fig. 1. (a) Electrical resistivity (upper y-axis), magnetic susceptibility (lower y-axis) and specific heat (inset) of $CeFe_4Sb_{12}$. (b) Results from similar measurements for $YbFe_4Sb_{12}$. See text for discussion.

Research at UCSD was supported by US DOE Grant. No. DE-FG03-86ER-45230 and US NSF Grant. No. DMR-97-05454, and at ORNL by US DOE Contract No. DE-AC05-96OR22464 and a Cooperative Research and Development Agreement with Marlow Industries, Contract CRADA 94-0324.

References

[1] G.P. Meisner, G.R. Stewart, M.B. Maple, in: U. Eckern, A. Schmid, W. Weber, H. Wühl (Eds.), LT-17 Elsevier, Amsterdam, 1984, p. 711.
[2] G.P. Meisner, M.S. Torikachvili, K.N. Yang, M.B. Maple, R.P. Guertin, J. Appl. Phys. 57 (1985) 3073.
[3] M.S. Torikachvili, C. Rossel, M.W. McElfresh, M.B. Maple, R.P. Guertin, G.P. Meisner, J. Magn. Magn. Mater. 54–57 (1986) 365.
[4] D.T. Morelli, G.P. Meisner, J. Appl. Phys. 77 (1995) 3777.
[5] B.C. Sales, D. Mandrus, R.K. Williams, Science 272 (1996) 1325.
[6] N.R. Dilley, E.J. Freeman, E.D. Bauer, M.B. Maple, Phys. Rev. B 58 (1998) 6287.
[7] D.A. Gajewski, N.R. Dilley, E.D. Bauer, E.J. Freeman, R. Chau, M.B. Maple, D. Mandrus, B.C. Sales, A.H. Lacerda, J. Phys.: Condens. Matter 10 (1998) 6973.