Intermediate valence in the filled skutterudite compound $YbFe_4Sb_{12}$

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We have synthesized and characterized $YbFe_4Sb_{12}$, a member of the class of filled skutterudite ($LaFe_4P_{12}$-type) compounds. Measurements of the lattice parameter, magnetization, electrical resistivity, and specific heat suggest that the Yb ions have an intermediate valence and that the effective mass of the conduction electrons is moderately enhanced at low temperatures. The coefficient of the electronic specific heat is estimated to be $\gamma(0) = 140$ mJ mol^{-1} K^{-2}, and we observe a characteristic temperature for the Yb ion valence fluctuations of $T^* \sim 50$ K. No superconductivity was detected down to $T = 0.40$ K. [S0163-1829(98)03733-3]

I. INTRODUCTION

The family of compounds known as the filled skutterudites[1] (space group $Im3$), with the general structural formula MT_4X_{12} (M = alkaline earth, rare earth, actinide; T = Fe, Ru, Os; X = pnictogen: P, As, Sb) exhibits a striking variety of physical properties that are associated in large part with the unusual behavior of the M atoms. Insulating behavior can arise due to an energy gap formed by hybridization of the M atom f level with a broad band of the T_4X_{12} sublattice.[2] Superconductivity,[3–5] ferromagnetism,[2] and a metal-insulator transition[6] have also been observed among various members of the filled skutterudites. Recent work has shown that $CeFe_4Sb_{12}$ exhibits heavy-fermion behavior with moderately high electron effective masses,[7–9] which motivated us to search for similar correlated electron effects in other filled skutterudite compounds. Elements that are known to exhibit such physics in intermetallic compounds include Ce, Pr, Sm, Eu, Tm, Yb, and U, i.e., those which are generally close to an f-electron valence instability. There are many models for this subtle electronic state that are neither localized nor truly itinerant, but a common feature is the existence of a characteristic energy scale k_BT^* that delineates high-temperature magnetic (Curie law) behavior from low-temperature nonmagnetic (Pauli-like) behavior of the f electrons.

There have been no reports of successful synthesis of any filled skutterudites containing heavier rare earths, M = Gd–Lu, and it was conjectured[1] within the context of the MFe_4P_{12} series that the smaller radii of the heavier M^{3+} ions prevent adequate bonding to the lattice. However, Tm and Yb are known to be divalent in some compounds, and the radii of divalent Tm and Yb ions are comparable to those of the trivalent light lanthanides (La–Eu). Hence, we hypothesized that divalent Tm and Yb might stabilize the filled skutterudite structure. Ytterbium is especially interesting as it is the 4 f-hole analog to Ce, and Yb compounds exhibit many of the same Kondo-like properties seen in Ce intermetallics.[10]

In addition to relatively long-standing interest in the correlated electron physics of filled skutterudite compounds, the recent attention these materials have received is largely due to their potential for thermoelectric applications.[11–13] Future measurements of the thermal and transport properties of $YbFe_4Sb_{12}$ will therefore be of great interest in the continuing search for better thermoelectric materials.

II. EXPERIMENTAL DETAILS

Bulk dc magnetization measurements were made using a commercial Quantum Design MPMS magnetometer over the temperature range $2 < T < 300$ K and for values of applied magnetic field H up to 70 kOe. For low-temperature measurements, we employed a Faraday magnetometer equipped with a ^{3}He cryostat with a base temperature of 0.40 K and maximum field of 50 kOe. Transport properties were measured in a commercial Quantum Design PPMS cryostat using a standard four-lead arrangement and an ac resistance bridge operating at 16 Hz with a 1-mA excitation current. The low-temperature specific heat was measured down to 0.55 K in a ^{3}He semiadiabatic calorimeter with a standard heat-pulse technique. The crystal structure and phase purity of the samples were measured using a 9-kW Rigaku powder diffractometer with a rotating copper anode ($\lambda_{\mathrm{Cu}\,K\alpha} = 1.541\,78$ Å). For more accurate determination of the lattice parameter, a silicon standard was used.

Polycrystalline samples of $YbFe_4Sb_{12}$ were prepared from elemental constituents of purity 99.99% or better that were placed in a vacuum-baked graphite crucible in the stoichiometry $Yb_{1.05}Fe_4Sb_{12}$. The crucible was sealed in a fused quartz ampoule under 150 torr of ultrahigh purity argon, and heated in an induction furnace to a maximum temperature of ~950 °C, verified using an optical pyrometer. Powder x-ray diffractometry performed on the as-cast induction-melted samples revealed that they were mixed phase and similar to as-cast $CeFe_4Sb_{12}$,[8] being comprised of Sb, $FeSb_2$, and $YbSb_2$, among other unidentified phases. Annealing the sample at 600 °C under argon for 20 h, however, produced a nearly single-phase skutterudite structure. Weak impurity peaks seen in the powder-diffraction pattern were attributed to trace amounts of $YbSb_2$, $FeSb_2$, and Sb. The annealing temperature of 600 °C was determined to be near optimal, as the sample remained in the as-cast mixed phase for annealing temperatures less than 500 °C, and decomposed to FeSb and other phases upon annealing at 750 °C.

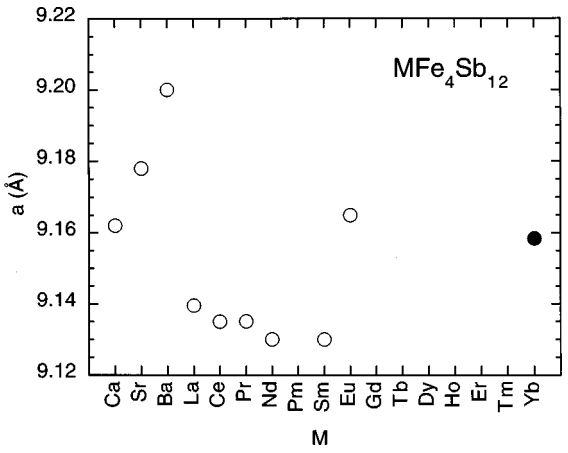

FIG. 1. Cubic lattice parameters in the $M\mathrm{Fe_4Sb_{12}}$ series. For $\mathrm{YbFe_4Sb_{12}}$, $a=9.158\pm0.001$ Å is significantly larger than in $M=$La–Sm and indicates a tendency towards divalent behavior of Yb. The lattice parameters shown as open symbols are quoted from Refs. 14, 18, and 19.

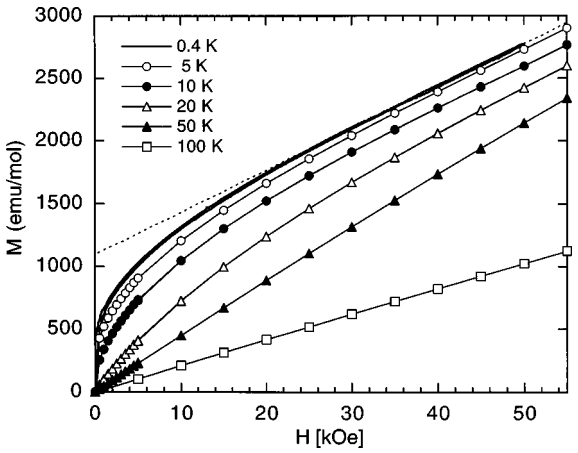

FIG. 2. Isothermal magnetization curves $M(H)$ taken at $T=0.4$ K in a Faraday magnetometer, and at $T=5$, 10, 20, 50, and 100 K in a superconducting quantum interference device magnetometer. The dashed line shows an estimate of the high-field susceptibility $\chi_0=3.45\times10^{-2}$ cm^3 mol^{-1} at $T=0.4$ K.

III. RESULTS AND DISCUSSION

The cubic lattice parameter of $\mathrm{YbFe_4Sb_{12}}$ was determined from x-ray powder diffractometry to be $a=9.158\pm0.001$ Å. In Fig. 1 the lattice parameter of $M\mathrm{Fe_4Sb_{12}}$ is plotted versus M, the alkaline-earth or rare-earth atom. The first observation is that the divalent alkaline earths ($M=$Ca, Sr, Ba) yield larger values of the lattice parameter than the generally trivalent rare earths. Starting with La, one observes the typical reduction of the lattice parameter due to the contraction of the ionic radii of the rare earths with increasing atomic number. However, the cases of $M=$Eu and Yb are clearly anomalous, reflecting their tendency toward divalence or intermediate valence in contrast to the other rare earths in this series that all appear to be trivalent. It is possible that this larger ionic radius stabilizes Yb and Eu in the skutterudite structure, while all other trivalent rare earths in the range $M=$Gd–Tm are too small to be accommodated in the atomic ''cages'' that are formed by the transition metal-pnictogen sublattice. Note that Tm is also divalent in some compounds, yet our attempts to synthesize $\mathrm{TmFe_4Sb_{12}}$ by this same technique were unsuccessful. Synthesis of $\mathrm{YbFe_4P_{12}}$ by a molten metal flux growth technique[1] was also unsuccessful. This is in accord with an earlier observation[14] that the valence of the M ion is strongly influenced by the electronegativity of the pnictogen atom, in that the M valence is higher in the phosphides than in the corresponding antimonides. This could make $\mathrm{YbFe_4P_{12}}$ unstable as the Yb would be trivalent and thus too small to be accommodated in the structure.

Measurements of the magnetic properties of $\mathrm{YbFe_4Sb_{12}}$ are also suggestive of intermediate valence of the Yb ions and did not reveal any evidence of superconductivity down to $T=0.40$ K. Figure 2 shows isothermal magnetization curves $M(H)$ measured at temperatures $0.4<T<100$ K that indicate that the magnetic response of $\mathrm{YbFe_4Sb_{12}}$ may be decomposed into (1) a saturable portion indicative of localized magnetic moments and (2) a susceptibility χ_0 evident at high fields and low temperatures that reflects the Pauli paramagnetism of the conduction electrons. The dashed line in Fig. 2 is an estimate of this latter contribution at $T=0.4$ K, yielding $\chi_0=3.45\times10^{-2}$ cm^3 mol^{-1}. Magnetization data $M(H)$ taken in applied fields up to $H=70$ kOe (not shown) allowed us to estimate this high-field susceptibility, indicated by solid circles in Fig. 3, at temperatures up to $T=10$ K. We were unable to model the saturable portion of the magnetization $M(H)$ as some function $f(H/(T-\Theta))$, where Θ is a constant, suggesting that this material may exhibit some type of magnetic order at low temperatures. The saturation magnetization as estimated from the y-axis intercept of the dashed line in Fig. 2 corresponds to $M_{\mathrm{sat}}=0.2\mu_B$/f.u. Inverse magnetic susceptibility $\chi^{-1}=H/M$ vs T data, taken in an applied field $H=55$ kOe, are shown in the inset of Fig. 3. The susceptibility can be described by a Curie-Weiss law $\chi=N_A\mu_{\mathrm{eff}}^2/3k_B(T-\Theta_{\mathrm{CW}})$ in the temperature range $120<T<300$ K, and yields an effective magnetic moment $\mu_{\mathrm{eff}}=3.09\mu_B$/f.u. and a Curie-Weiss temperature $\Theta_{\mathrm{CW}}=40$ K. The effective moment is intermediate between

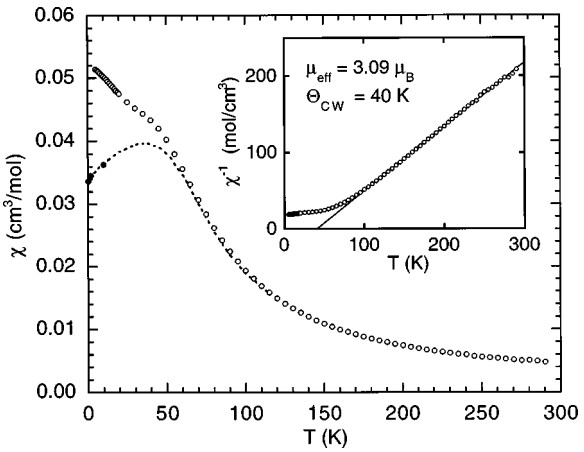

FIG. 3. Magnetic susceptibility $\chi=M/H$ (open circles) at $H=55$ kOe plotted along with the estimated high-field susceptibility χ_0 (filled circles) vs temperature T. The dashed line is the conjectured behavior of $\chi_0(T)$. Inset: inverse magnetic susceptibility $\chi^{-1}=H/M$ vs T. The line shows a fit to a Curie-Weiss law for $120<T<300$ K.

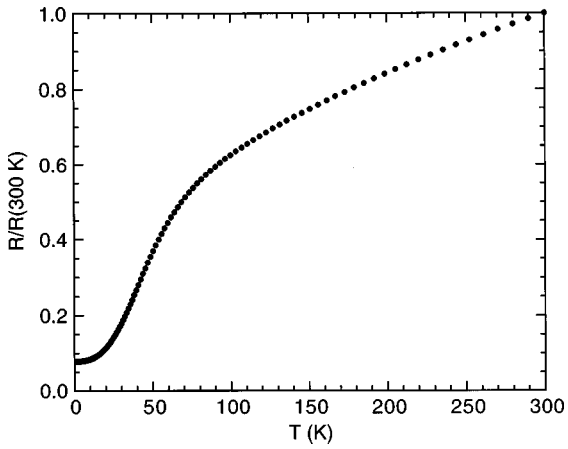

FIG. 4. Electrical resistance measured from 300 K down to 1.8 K. Note the broad shoulder around 70 K.

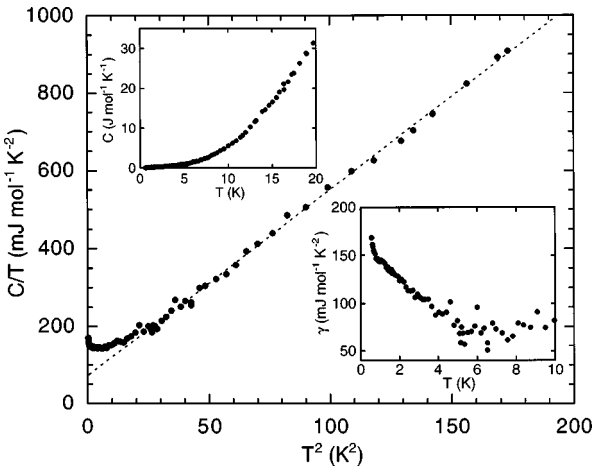

FIG. 5. Specific heat $C(T)$ measured over the range $0.55<T<20$ K (upper inset) and C/T vs T^2 at low temperatures, fitted to $C(T)=\gamma T+\beta T^3$ (dashed line). Below $T=4$ K, C/T approaches a value of 140 mJ mol^{-1} K^{-2}, and an upturn in C/T below $T=1$ K is likely due to a Schottky anomaly. Lower inset: temperature dependence of $\gamma(T)=C/T-\beta T^2$ that exhibits a linear increase below $T\approx 5$ K.

the values for Yb^{3+} ($\mu_{\rm eff}=4.5\mu_B$/f.u. for the free ion) and the nonmagnetic Yb^{2+} ($\mu_{\rm eff}=0$) configurations. In Fig. 3, a comparison of $\chi=M/H$ (open circles) with the high-field susceptibility χ_0 (filled circles) is shown. The dashed line is our conjecture for the behavior of $\chi_0(T)$ as it merges with the $\chi=M/H$ vs T curve near $T=50$ K. Alternatively, our observations of a positive Curie-Weiss temperature, a rounding of the susceptibility near that temperature, and magnetization curves $M(H)$ that do not scale as $H/(T-\Theta)$ could be evidence of ferromagnetic ordering near $T=50$ K. The absence of magnetic hysteresis in low-temperature $M(H)$ measurements (Fig. 2) may be explained by a very low coercive field in the ordered state. A more detailed magnetization study as well as neutron-scattering experiments will shed more light on this unusual magnetic behavior at low temperatures. Nonetheless, the high value of χ_0 at low temperatures points to a large effective mass of the conduction electrons, a finding that is corroborated by electrical-resistivity and specific-heat measurements.

The electrical resistivity of $YbFe_4Sb_{12}$ increases monotonically with temperature up to 300 K, as shown in Fig. 4. We estimate a residual resistivity $\rho_0\approx 9\ \mu\Omega$ cm based on infrared reflectivity measurements.[15] A broad shoulder near $T\sim 50-70$ K was observed in measurements on four separate samples. This shape of the $\rho(T)$ curve is similar to that expected for conduction electrons that scatter into a large narrow feature in the electronic density of states near the Fermi level, which is presumably of f character.[16] The rapid drop in resistivity near 70 K could be a measure of the effective degeneracy of this narrow feature, which may itself be the analogue of an Abrikosov-Suhl resonance for a Kondo lattice of f electrons.

Low-temperature specific-heat data, plotted as C/T vs T^2, for $YbFe_4Sb_{12}$ shown in Fig. 5 indicate a slightly enhanced electronic specific-heat coefficient $\gamma\approx 75$ mJ mol^{-1} K^{-2} in the temperature range $5<T<15$ K, obtained from a fit of the data to the form $C(T)=\gamma T+\beta T^3$, where the latter term is the low-temperature expression for phonons within the Debye model. We estimate the Debye temperature $\Theta_D=(12\pi^4 N_i R/5\beta)^{1/3}$ to be 190 K; here $N_i=17$ is the number of ions per formula unit and R is the universal gas constant. Below $T\approx 5$ K, $\gamma(T)=C/T-\beta T^2$ shows a nearly linear increase with decreasing temperatures to 140 mJ mol^{-1} K^{-2}, as shown in the lower inset of Fig. 5. A sharp upturn occurs below $T\approx 1$ K, and while no accompanying feature in the magnetization indicative of magnetic ordering was seen down to 0.4 K, the feature was modeled as the high-temperature tail of a Schottky anomaly that varies as T^{-2}. We were able to fit the specific heat in the temperature range $T=0.6-1.0$ K to the form $C(T)=\gamma T+DT^{-2}$ with γ and D as adjustable parameters, obtaining $\gamma=140$ mJ mol^{-1} K^{-2}. The Schottky anomaly is possibly due to trace amounts of magnetic impurities in the sample.

The moderate enhancement of the electronic specific heat and the magnetic susceptibility is very similar to other heavy-fermion Yb compounds such as $YbCu_4Ag$ (Ref. 10) and YbCuAl.[17] In order to determine whether the large values of $\chi_0(0)$ and $\gamma(0)$ are associated with itinerant f electrons, we estimated the Wilson-Sommerfeld ratio for $YbFe_4Sb_{12}$:

$$R=\left(\frac{\chi_0(0)}{\gamma(0)}\right)\frac{\pi^2 k_{\rm B}^2}{\mu_{\rm eff}^2}.$$

Using $\mu_{\rm eff}=4.5\mu_B$ appropriate for Yb^{3+} free ions, $\chi_0(0)=3.45\times 10^{-2}$ cm^3 mol^{-1}, and $\gamma(0)=140$ mJ mol^{-1} K^{-2}, we obtain $R=2.62$. This value is in good agreement with $R=2$ expected for a spin-$\frac{1}{2}$ Kondo effect, indicating that the enhancements of χ_0 and γ are due to heavy electrons attributable to either intermediate valent Yb ions or a Kondo lattice of screened Yb^{3+} moments.

In conclusion, we have synthesized the filled skutterudite compound $YbFe_4Sb_{12}$ and have found the cubic lattice parameter to be anomalous with respect to the other predominantly trivalent rare earths M in MFe_4Sb_{12}, which is indicative of an Yb valence intermediate between 2+ and 3+. The magnetic, electrical transport, and thermal properties measured to low temperatures are consistent with heavy-fermion or intermediate-valence behavior associated with the Yb ions. Based on these measurements, we estimate an effective

degeneracy temperature $T^* \sim 50$ K for a narrow *f*-electron feature in the density of states near the Fermi level. Below $T \approx 5$ K, the coefficient of the electronic specific heat increases to $\gamma = 140$ mJ mol^{-1} K^{-2} and the linear magnetic susceptibility saturates to $\chi_0 = 3.45 \times 10^{-2}$ cm^3 mol^{-1}, pointing to a moderately enhanced effective mass of the conduction electrons. Neutron-scattering and high-temperature specific-heat measurements are planned to address the issue of magnetic ordering and assess the thermal parameters of the Yb ion, while Seebeck-coefficient and thermal-conductivity measurements will be performed to determine the thermoelectric figure of merit *ZT*. Clearly, this compound as well as many other members of the filled skutterudites continue to be fascinating subjects of both applied and basic research.

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