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Heavy fermion behaviour of the cerium-filled skutterudites $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$

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Abstract. The low temperature properties of polycrystalline samples of the filled skutterudites $\text{CeFe}_4\text{Sb}_{12}$, $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, as well as the unfilled skutterudites $\text{Fe}_{0.05}\text{Co}_{0.95}\text{Sb}_3$ and CoSb_3 , have been investigated by means of electrical resistivity, specific heat and magnetic susceptibility measurements. The resistivity of $\text{CeFe}_4\text{Sb}_{12}$ exhibits a rather abrupt drop-off with decreasing temperature near 100 K; this drop-off temperature increases with increasing applied hydrostatic pressure, which is reminiscent of the onset of coherence in so-called Kondo lattice materials. The compounds $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ exhibit values of the electronic specific heat coefficient and Pauli susceptibility at low temperature which are enhanced over those of the lanthanum-filled and unfilled skutterudites. These quantities yield a Wilson ratio of order unity, which indicates that they both correspond to the properties of itinerant electrons. These transport, magnetic and thermodynamic properties suggest a moderately heavy fermion ground state in $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$.

1. Introduction

Heavy fermion materials refer to a growing class of intermetallic compounds whose low temperature properties are characterized by an effective mass m^* of the order of 10^2 – 10^3 times the free electron mass (for reviews of heavy fermion systems, see [1–4]). These compounds, which usually contain a rare earth or actinide element with a partially filled 4f- or 5f-electron shell, exhibit large values of the electronic specific heat coefficient $\gamma = C_p/T$ (as large as several $\text{J mol}^{-1} \text{K}^{-2}$) and Pauli susceptibility as $T \rightarrow 0$. Based on measurements of the magnetic susceptibility and electrical resistivity, Morelli and Meisner [5] estimated that the γ of $\text{CeFe}_4\text{Sb}_{12}$ could reach $\sim 1 \text{ J mol}^{-1} \text{K}^{-2}$ at low temperature, which would place it into the heavy fermion classification of metals. Chen *et al* [6] and Danebrock *et al* [7] concluded from their magnetic susceptibility measurements that cerium may exhibit intermediate valence behaviour at low temperature in $\text{CeFe}_4\text{Sb}_{12}$, while Sales *et al* [8] claim that cerium is trivalent in this compound but that effects of hybridization caused by the proximity of the 4f level to the Fermi energy are evident at low temperature. Measurements of the unit cell volume of the $\text{RFe}_4\text{Sb}_{12}$ series by Evers *et al*

[9] indicate that cerium is nearly trivalent in this compound, at least near room temperature. In this paper, we present low temperature measurements of the electrical resistivity, specific heat and magnetization of polycrystalline samples of the cerium-filled skutterudites $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$. For comparison, these measurements were also performed on the lanthanum-filled skutterudite $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and the unfilled skutterudites $\text{Co}_4\text{Sb}_{12}$ and $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$. (Note that while these chemical formulae for the unfilled skutterudites should technically be written in reduced form, e.g., CoSb_3 , in this paper the formulae will be written and all of the measured quantities quoted in units of ‘per mol formula’, where the formula will be normalized to 12 Sb atoms, in order to compare the molar properties of the filled and unfilled skutterudites.)

While the focus of this paper is heavy fermion behaviour, it is interesting to note that $\text{Ce}_{1-y}\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ has received attention in the literature recently as a candidate for use in thermoelectric devices [5, 6, 8, 10–13]. The compound $\text{Ce}_{1-y}\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ is a member of the so-called ‘filled skutterudite’ class of materials with the general formula RM_4X_{12} , where $\text{R} = \text{La, Ce, Pr, Nd or Eu}$; $\text{M} = \text{Fe, Ru or Os}$ and $\text{X} = \text{P, As or Sb}$. The binary, or ‘unfilled’, skutterudite crystal structure AB_3 consists of a simple cubic sublattice of the transition metal (A) atoms ($\text{A} = \text{Ir, Rh or Co}$), and square planar rings of four pnictogen (group VA) atoms ($\text{B} = \text{Sb, As or P}$) with the rings oriented along the (100), (010) or (001) crystallographic directions. The ‘filled’ skutterudites are obtained by introducing rare earth R atoms into this structure, which are positioned in the two remaining ‘holes’ in the unit cell [14]. The R atoms have been found to ‘rattle’ inside an oversized atomic cage in this structure [12], which strongly reduces the thermal conductivity of this material, but preserves the favourable electrical transport properties. The filled skutterudites are thus preferable over the unfilled skutterudites for use in thermoelectric devices. In addition, Morelli and Meisner speculated [5] that the heavy-fermion-like behaviour in $\text{CeFe}_4\text{Sb}_{12}$ at low temperature could also contribute to the relatively large values of the dimensionless figure of merit ZT that has been observed for this compound, considering that it is a metal (materials with a large value of ZT are viable for use in thermoelectric devices). If this speculation is correct, then the study of heavy fermion materials could be very useful in the search for promising materials for use in thermoelectric devices.

2. Experimental details

Polycrystalline samples of $\text{R}_{1-y}\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ ($\text{R} = \text{Ce, La}$) were prepared at Oak Ridge National Laboratory (ORNL) using a process described elsewhere [8]. The samples that were used in this study were made by hot-pressing a ball milled fine powder of the pre-reacted material into a dense polycrystalline solid with densities between 75% and 95% of the theoretical x-ray density. X-ray diffraction measurements of $\text{CeFe}_4\text{Sb}_{12}$, $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ revealed only trace amounts of the impurity phase FeSb_2 . Specific heat measurements were performed in a ^3He semiadiabatic calorimeter from 0.5 K to 10 K using a heat pulse technique. Electrical resistivity measurements were made with an ac resistance bridge operating at 16 Hz, using a standard four-wire technique. The resistivity was measured under hydrostatic pressures up to 17 kbar in a beryllium–copper piston–cylinder clamp device, where the pressure was inferred from the inductively measured superconducting transition of a Pb manometer [15]. The dc magnetization was measured using a commercial SQUID magnetometer from 1.8 K to 300 K, and using a UCSD-built ^3He Faraday magnetometer from 0.4 K to 10 K.

3. Results

3.1. Electrical resistivity

The electrical resistivity ρ of $\text{CeFe}_4\text{Sb}_{12}$ at applied hydrostatic pressures up to 15.7 kbar is shown in figure 1(a). The resistivity is relatively large and nearly temperature independent from room temperature down to ~ 150 K, and then drops off rather abruptly near 100 K. The shape of this curve is reminiscent of heavy fermion compounds such as CeAl_3 [2], and is therefore interpreted as the onset of coherence in the cerium ion sublattice. This drop-off shifts to higher temperatures with increasing applied hydrostatic pressure, which is presumably brought about by an increasing hybridization between the conduction band and 4f band with increasing pressure. A similar pressure dependence of a Kondo coherence feature has been reported for UBe_{13} [16]. The resistivity passes through a minimum near 25 K, and then saturates to a constant with a temperature dependence of approximately T^3 . Thus, the quadratic temperature dependence of the resistivity that is often observed at low temperature in heavy fermion compounds such as CeAl_3 is not observed in $\text{CeFe}_4\text{Sb}_{12}$, possibly because it is obscured by the upturn in $\rho(T)$ at low temperature. This minimum could be the result of a Kondo effect caused by magnetic impurities. The temperature dependence of $\rho(T)$ at ambient pressure is nearly identical for several resistivity samples which were cut from the same ingot; this at least indicates that the ORNL samples are homogeneous. Note that the resistivity was measured at zero pressure, then at successively higher pressure, and, finally again at zero pressure by releasing the pressure in the clamp (denoted as '0*' in figure 1(a)). The resistivity for the two runs at zero pressure differ from each other, which indicates that some degradation of the electrical contacts occurred during the pressure experiments. However, the zero-pressure data sets can be scaled onto each other by a multiplicative constant, which indicates that the change simply corresponds to a change in the electrical leads and/or geometry of the sample. Since this effect tends to increase the resistivity at all temperatures, it cannot explain the negative pressure dependence of the resistivity below 150 K, and therefore does not change our interpretation of the behaviour of the coherence temperature. Above approximately 150 K, however, some of the positive pressure dependence of the resistivity could be attributed to changes in the geometry of the electrical leads and/or sample.

The resistivity of these samples of $\text{CeFe}_4\text{Sb}_{12}$ fabricated at ORNL are to be compared with the results of Morelli and Meisner on a sample of $\text{CeFe}_4\text{Sb}_{12}$ that they synthesized in an induction furnace [5]. Morelli and Meisner reported a similar temperature dependence of the resistivity of $\text{CeFe}_4\text{Sb}_{12}$ above 50 K, but they observed a kink and a sharp downturn in the resistivity near $T = 15$ K, which they believe to be associated with magnetic ordering. In the $\text{Ce}_{1-y}\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ samples discussed in this paper, all of which were prepared at ORNL using a procedure described in [8], we did not see any evidence of a phase transition or magnetic ordering at 15 K from our resistivity, magnetization or specific heat measurements. However, a sample of $\text{CeFe}_4\text{Sb}_{12}$, synthesized at UCSD in an induction furnace as in [5], does exhibit evidence of magnetic ordering at 15 K. The UCSD samples have a comparable amount of FeSb_2 to the sample of Morelli and Meisner according to x-ray diffraction, but both of these samples contain a higher level of impurities than the samples fabricated at ORNL for use in this study. X-ray diffraction measurements did not reveal the presence of any crystalline CeSb , which orders magnetically near 16 K; nor did Morelli and Meisner report any evidence of CeSb from x-ray diffraction. While we cannot eliminate the possibility that the feature at 15 K in samples made at UCSD and by Morelli and Meisner is due to magnetic ordering, this feature was not seen in the ORNL

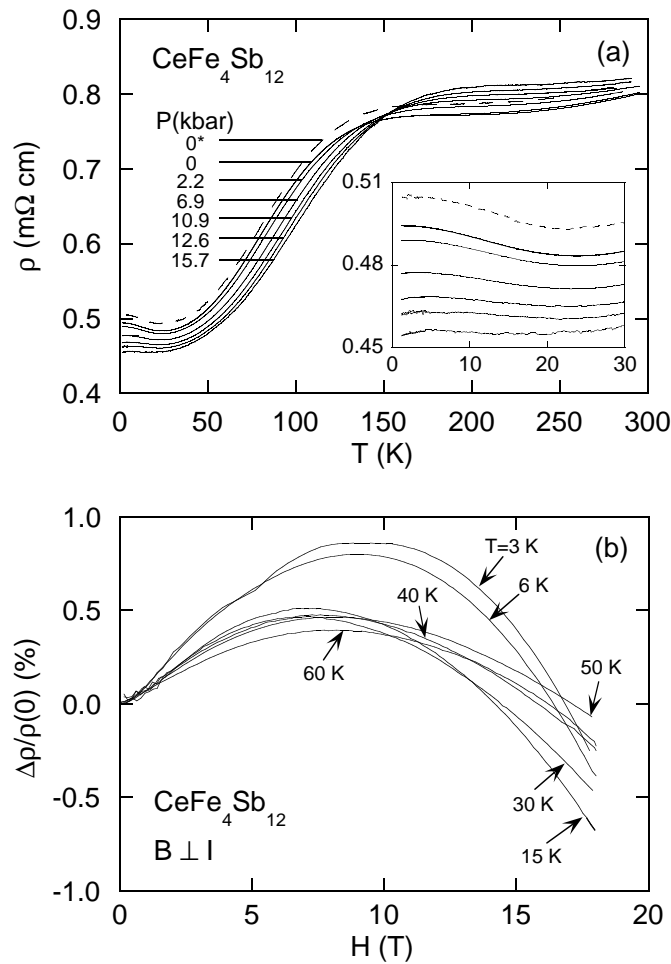


Figure 1. (a) Electrical resistivity ρ against temperature T for $\text{CeFe}_4\text{Sb}_{12}$ at various applied hydrostatic pressures between 0 and 15.7 kbar. 0* refers to a measurement performed at ambient pressure after the measurements under pressure were completed. See text for details. Inset: magnified view of low temperature data. (b) Magnetoresistance $\Delta\rho/\rho(0) = 100(\rho(H) - \rho(0))/\rho(0)$ isotherms from $T = 3$ K to 60 K of $\text{CeFe}_4\text{Sb}_{12}$, with the field applied perpendicular to the applied current.

samples, and is therefore probably due to CeSb , FeSb_2 or some other impurity phase in the samples.

The magnetoresistance $\Delta\rho/\rho(0) = 100(\rho(H) - \rho(0))/\rho(0)$ of $\text{CeFe}_4\text{Sb}_{12}$ is shown in figure 1(b) in applied magnetic fields up to 18 tesla and temperatures from 3 K to 60 K, with the magnetic field applied in a perpendicular direction to the applied current. For applied fields less than approximately 1 tesla, the magnetoresistance has positive curvature; while at higher values of applied field, and it has negative curvature, and varies approximately as H^2 , but does not scale with H/T . The magnetoresistance changes sign from positive to negative at high magnetic fields, for all of the temperatures at which the measurements were performed (note that the small cusp in the $T = 3$ K data set near $H = 6$ T was not observed in a similar experiment on another sample in a different

experimental apparatus, and may be an experimental artifact). We do not know of any heavy fermion compounds which exhibit similar behaviour, and cannot offer a comprehensive explanation for these results at this time, but simply present the data. We can only speculate that two or more mechanisms may be contributing to the magnetoresistance, such as the Kondo effect, field-induced magnetic ordering and/or Fermi surface effects. Measurements on a single crystal of this sample may help to clarify these issues.

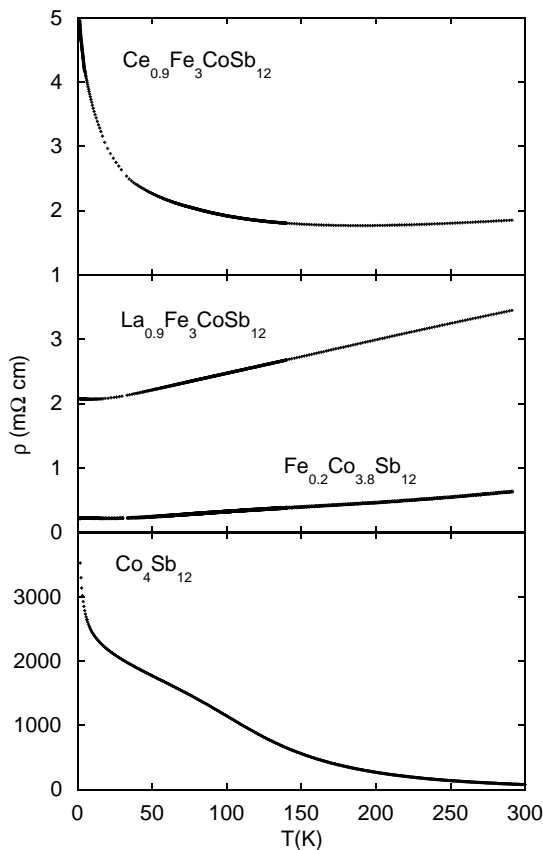


Figure 2. Electrical resistivity ρ against temperature T for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12}$ at ambient pressure.

As shown in figure 2, the resistivity of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ exhibits a shallow minimum near 175 K, and then increases with decreasing temperature down to the lowest measured temperature ($T = 1.4$ K). Since the charge carrier density of this compound is comparable to that of $\text{CeFe}_4\text{Sb}_{12}$ according to Chen *et al* [6], $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ is most likely metallic, and the upturn in the resistivity at low temperature can be ascribed to nearly single-ion Kondo scattering of the conduction electrons by the cerium ions. Indeed, Sales *et al* [8] reported that the resistivity of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ increases with increasing temperature from 300 K to 1000 K, which is consistent with metallic behaviour. Presumably, there is no coherence feature in the resistivity of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ because the cerium sublattice is disordered by incomplete filling of cerium and/or iron–cobalt site disorder. Similar behaviour has been seen in CePd_3 as reported by Kappler *et al* [17], who found that the substitution of 19% yttrium for cerium in CePd_3 destroys the coherence feature in CePd_3 , and yields a resistivity

which increases with decreasing temperature. Finally, it is noteworthy that the behaviour of the cerium-filled skutterudites is very different than that of the metallic filled skutterudite $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, and the unfilled skutterudites $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12}$, which exhibit ordinary metallic and semiconducting behaviour, respectively, as shown in figure 2.

3.2. Specific heat

The specific heat C_p versus temperature T for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$, $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12}$ is shown in figure 3. Since there is a feature in the specific heat of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ near 1.5 K, but none in $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ or $\text{Co}_4\text{Sb}_{12}$, the feature could be due to a small amount of cerium- or iron-based magnetic impurity phase in these samples. The specific heat of two pieces of $\text{CeFe}_4\text{Sb}_{12}$ which were cut from the same ingot both exhibit an anomaly near $T = 1.5$ K, and nearly identical temperature dependences, which indicates again that the samples are homogeneous. The specific heat of $\text{CeFe}_4\text{Sb}_{12}$ yields an integrated entropy of only 10% of $R \ln(2)$ up to 5 K, which is too small to ascribe this feature to a crystal field multiplet of the cerium ions or to an $S = 1/2$ Kondo peak. While we do not know of any intermetallic phase or cerium oxide that may have formed in this compound with an ordering temperature near 1.5 K, the magnetization of a sample of $\text{CeFe}_4\text{Sb}_{12}$, measured down to $T = 0.4$ K using a Faraday magnetometer, exhibits a small hysteresis loop that seems to disappear above ~ 1.5 K. The saturation magnetization $M^{sat} = 100$ emu (mol formula) $^{-1}$ associated with this hysteresis loop would correspond to approximately $0.02 \mu_B$ /cerium. These magnetization measurements did not reveal any diamagnetic signal due to superconductivity or kink that could be associated with antiferromagnetic ordering down to 0.4 K. However, antiferromagnetic ordering cannot be ruled out at this point; the origin of the peak in the specific heat should be investigated further by performing specific heat measurements in magnetic fields and/or using other techniques such as neutron scattering.

The electron and phonon contributions to the specific heat were estimated by performing least-squares fits to $C_p/T = \gamma + \beta T^2$, where γ is the electronic specific heat coefficient and

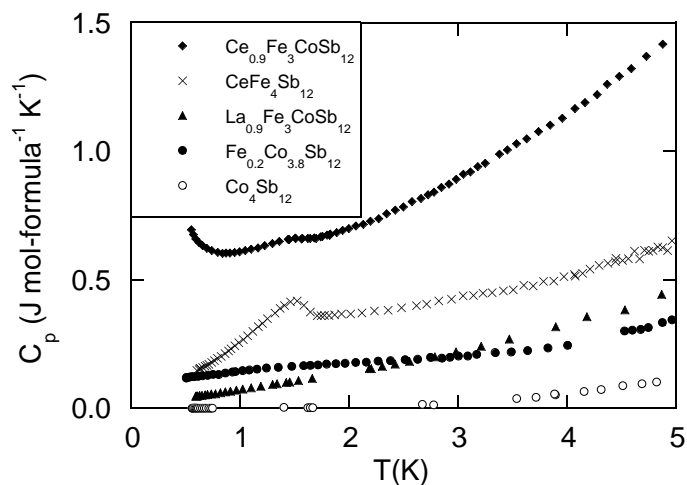


Figure 3. Specific heat C_p versus temperature T for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$, $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12}$.

$\beta = 12\pi^4 r R / (5\Theta_D^3)$ is the low temperature Debye phonon contribution, r is the number of atoms per formula unit, R is the universal gas constant and Θ_D is the Debye temperature; the fits are shown as solid and dashed lines in figure 4, which shows plots of C_p/T versus T^2 , and the fitting parameters are listed in table 1. The low temperature fit (0.5–5 K) for $\text{Co}_4\text{Sb}_{12}$, shown as a dashed line in figure 4, yields $\Theta_D^L \sim 325$ K which is comparable to $\Theta_D \sim 308$ K for IrSb_3 measured by Slack and Tsoukala [18], and $\gamma^L \sim 0$ which is consistent with a low concentration of charge carriers. The low temperature fit (1.5–5 K, discounting the upturn in C_p/T near $T = 1.5$ K, which could be due to a magnetic impurity phase) for $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ yields $\Theta_D^L \sim 298$ K, which agrees well with resonant ultrasound measurements [12] and may be used as an estimate of the Debye temperature of the filled skutterudites, and $\gamma^L \sim 28$ mJ (mol formula) $^{-1}$ K $^{-2}$, which is characteristic of an ordinary metal.

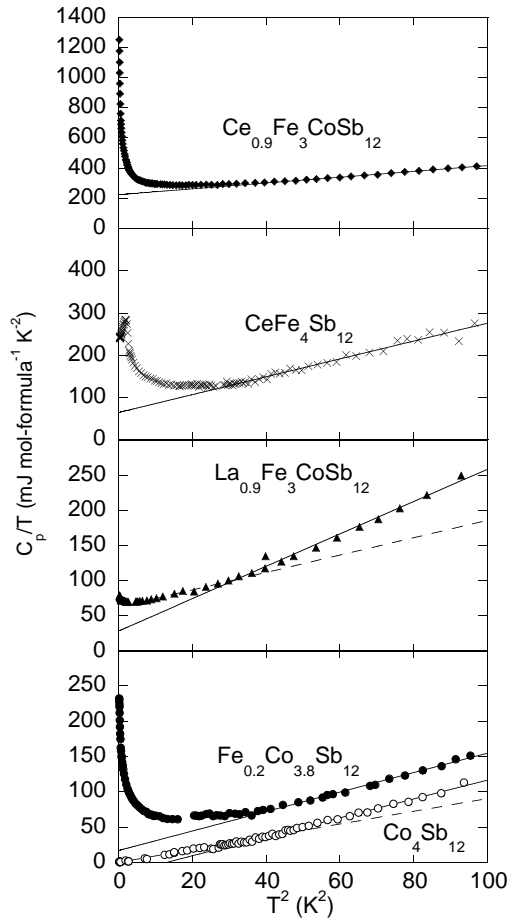


Figure 4. Specific heat C_p data for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$, $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12}$ plotted as C_p/T versus temperature T^2 . See text for details.

Since the specific heat data of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ could not be fitted at low temperature due to the low temperature upturn in C_p/T , the data for all of the samples were fitted from $40 \text{ K}^2 \leq T^2 \leq 100 \text{ K}^2$ ($6.3 \text{ K} \leq T \leq 10 \text{ K}$) for

consistency; these fit parameters Θ_D^H and γ^H are listed in table 1, and the fits are shown as solid lines in figure 4. Fitting over this temperature range yields values for Θ_D^H and γ^H which may be lower than the true values (using this temperature range for $\text{Co}_4\text{Sb}_{12}$ yields $\Theta_D^H \sim 285$ K, and $\gamma^H < 0$ which is obviously nonphysical), but is useful to compare the phonon behaviour in the unfilled and cerium-filled skutterudites. The Θ_D^H of $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ is nearly the same as that of $\text{Co}_4\text{Sb}_{12}$, but the electronic contribution to the specific heat of $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ is typical of metals such as copper (γ^H is estimated as ~ 1 mJ (gm atom) $^{-1}$ K $^{-2}$ for $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$). This indicates that substituting iron for cobalt in $\text{Co}_4\text{Sb}_{12}$ produces holes in the valence band (consistent with the results of Chen *et al* [6]), without affecting the phonon structure to a first approximation. The low temperature upturn in C_p/T of $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$, which looks like a broad local maximum in C_p versus T (see figure 3), is probably magnetic in origin; $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ contains no elements with f electrons, and is thus not expected to display heavy fermion behaviour. As shown in table 1, the Debye temperatures of the filled skutterudites $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$ and $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ are comparable to each other, and lower than those of the unfilled skutterudites, which indicates that the rare earth ions are contributing a phonon-like term to the specific heat. This could indicate that cerium is ‘rattling’ inside an atomic cage like that reported for $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ [12]; however, neutron scattering measurements should be performed on this compound to verify this hypothesis.

As shown in table 1, the value of the electronic specific heat coefficient γ^H of the cerium-filled skutterudites $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ extrapolated from high temperature is many times larger than that of typical metals as well as the lanthanum-filled and unfilled skutterudites, which is indicative of moderately heavy fermion behaviour. Below approximately $T = 5$ K, C_p/T increases with decreasing temperature above the $\gamma^H T + \beta T^3$ behaviour extrapolated from higher temperature for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$, as shown in figure 4. For $\text{CeFe}_4\text{Sb}_{12}$, C_p/T increases with decreasing temperature down to 1.5 K, reaching a maximum value of 290 mJ mol $^{-1}$ K $^{-2}$, then decreases and appears to saturate at a value of ~ 240 mJ mol $^{-1}$ K $^{-2}$ at 0.5 K. For $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, C_p/T increases with decreasing temperature down to the lowest measured temperature of 0.5 K, reaching a value of approximately 1.4 J mol $^{-1}$ K $^{-2}$. The general shape of these curves is similar to that observed in cerium- and uranium-based heavy fermion materials such as CeAl_3 and UPt_3 [2], which has been interpreted as an enhancement of the effective electron mass at low temperature. However, an unambiguous determination of the electronic specific heat coefficient γ at $T = 0$ is made difficult by the presence of the small feature in the specific heat of these samples near 1.5 K (see figure 3) and the upturn in the specific heat of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ at low temperature. Measurements to lower temperature and/or under applied magnetic field could help to resolve whether these large values of C_p/T at low temperature may be attributed to an enhancement of the effective mass, or to contributions from one or more phase transitions at low temperature due to magnetic ordering or impurity phases.

3.3. Magnetic susceptibility

The inverse magnetic susceptibility $(M_{meas}/H)^{-1}$ (not shown) nominally follows a Curie–Weiss law near room temperature, but exhibits significant curvature below $T \sim 300$ K, which could indicate crystal field and/or intermediate valence effects. Least-squares fits of $(M_{meas}/H)^{-1}$ from $T = 150$ K to 300 K to a Curie–Weiss law $(M_{meas}/H)^{-1} = (T + \theta)/C$, where $C = N_A \mu_{eff}^2 / (3k_B)$, μ_{eff} is the effective moment in Bohr magnetons, and θ is the Curie–Weiss temperature, yield $\mu_{eff} = 3.8\mu_B$ and $\theta = -124$ K for $\text{CeFe}_4\text{Sb}_{12}$, and

Table 1. Fitting parameters from fits to specific heat data. Θ_D^H and γ^H were obtained by fitting from 6.3 K to 10 K, while Θ_D^L and γ^L were obtained by fitting from 0.5 K to 5 K. See text for details.

Compound	Θ_D^H (K)	Θ_D^L (K)	γ^H (mJ (mol formula) ⁻¹ K ⁻²)	γ^L (mJ (mol formula) ⁻¹ K ⁻²)
Ce _{0.9} Fe ₃ CoSb ₁₂	257		223	
CeFe ₄ Sb ₁₂	250		63.8	
La _{0.9} Fe ₃ CoSb ₁₂	242	298	28.2	62.1
Fe _{0.2} Co _{3.8} Sb ₁₂	282		16.8	
Co ₄ Sb ₁₂	285	325	-17.6	0.0

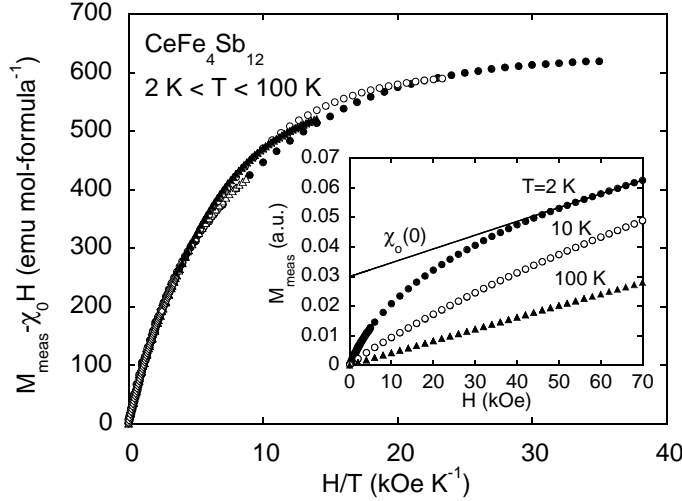


Figure 5. Measured magnetization M_{meas} minus $\chi_0 H$ versus H/T isotherms for 11 temperatures between 2 K and 100 K for CeFe₄Sb₁₂. Inset: M_{meas} versus H for three representative temperatures and $\chi_0(T = 2 \text{ K})$.

$\mu_{eff} = 2.6\mu_B$ and $\theta = -46 \text{ K}$ for Ce_{0.9}Fe₃CoSb₁₂ (these values are listed in table 2); these results are comparable to those obtained in other studies [5, 6, 8]. Since $\theta \propto T_K$ for Kondo systems, the higher θ of CeFe₄Sb₁₂ compared to Ce_{0.9}Fe₃CoSb₁₂ is consistent with the higher value of T_K as estimated from the value of the low temperature Pauli susceptibility. Chen *et al* [6] speculated that the large effective moment observed for CeFe₄Sb₁₂ (compare this value with the free ion value for Ce³⁺, $\mu_{eff} = 2.54\mu_B$) could be the result of local moment magnetism of the (Fe₄Sb₁₂)⁴⁻ polyanions.

In order to estimate the Pauli susceptibility of the conduction electrons in samples of CeFe₄Sb₁₂ and Ce_{0.9}Fe₃CoSb₁₂, the dc magnetization M was measured as a function of applied magnetic field H at constant temperature down to $T = 2 \text{ K}$ and analysed according to the following procedure. The measured magnetization was modelled as the sum of two terms: $M_{meas} = \chi_0 H + M_{imp}(H/T)$, where the intrinsic susceptibility χ_0 is assumed to be independent of H and is used as a measure of the Pauli susceptibility (this assumption is valid provided that $\mu H \ll k_B T_K$, where T_K is the Kondo temperature; this is true in this system, as will be discussed below); and M_{imp} is the contribution from local magnetic moments which saturates at high values of applied field, and is assumed to be a function of H/T . The Pauli susceptibility at the lowest temperature $\chi_0(T = 2 \text{ K})$ was estimated as

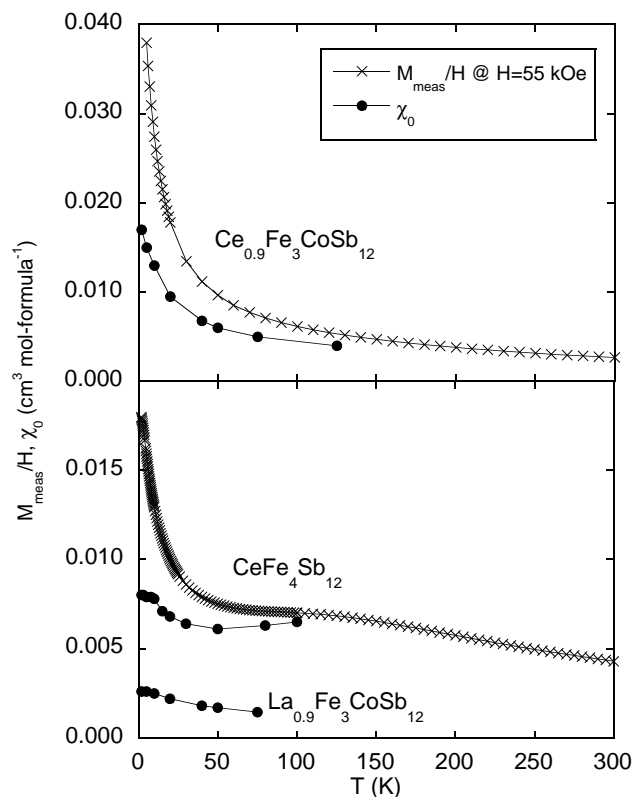


Figure 6. Linear high-field susceptibility χ_0 and magnetization M divided by magnetic field H versus temperature T for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$ and $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ (M/H for $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ is not shown for clarity). See text for discussion.

the intercept of a plot of M/H versus H^{-1} extrapolated to the limit of $H^{-1} \rightarrow 0$. $\chi_0(T)$ was then estimated by plotting $M_{\text{meas}} - \chi_0 H$ versus H/T , using $\chi_0(T = 2 \text{ K})$ as an initial guess, and then adjusting $\chi_0(T)$ for each $M_{\text{meas}} - \chi_0 H$ isotherm such that all of the data collapse onto the lowest temperature curve.

The curves of $M_{\text{meas}} - \chi_0 H$ versus H/T for $\text{CeFe}_4\text{Sb}_{12}$ are plotted in figure 5, and three representative M versus H isotherms along with $\chi_0(T = 2 \text{ K})$ are plotted in the inset of figure 5. The values of $\chi_0(T)$ that were obtained using this procedure are plotted along with M/H ($H = 55 \text{ kOe}$) as a function of temperature for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$ and $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ in figure 6. For $\text{CeFe}_4\text{Sb}_{12}$, M/H diverges at low temperature due to the contribution from local moments, while $\chi_0(T)$ appears to saturate to a value of approximately $0.008 \text{ cm}^3 (\text{mol formula})^{-1}$. This temperature dependence and relatively large value of $\chi_0(T)$ is typical of the Pauli paramagnetism of the conduction electrons in cerium- and uranium-based heavy fermion systems. In the sample of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, we find that $\chi_0(T)$ continues to increase with decreasing temperature down to the lowest measured temperatures, but seems to approach a relatively large, constant value of $\sim 0.018 \text{ cm}^3 (\text{mol formula})^{-1}$ ($0.019 \text{ cm}^3 (\text{mol cerium})^{-1}$), rather than to diverge as $T \rightarrow 0$. Estimates of the Kondo temperature for these compounds using the formula $T_K = N_A \mu_{\text{eff}}^2 / (3k_B \chi_0(T = 2 \text{ K}))$ (assuming the free ion value for Ce^{3+} , $\mu_{\text{eff}} = 2.54 \mu_B$) yields $T_K \sim 101 \text{ K}$ for

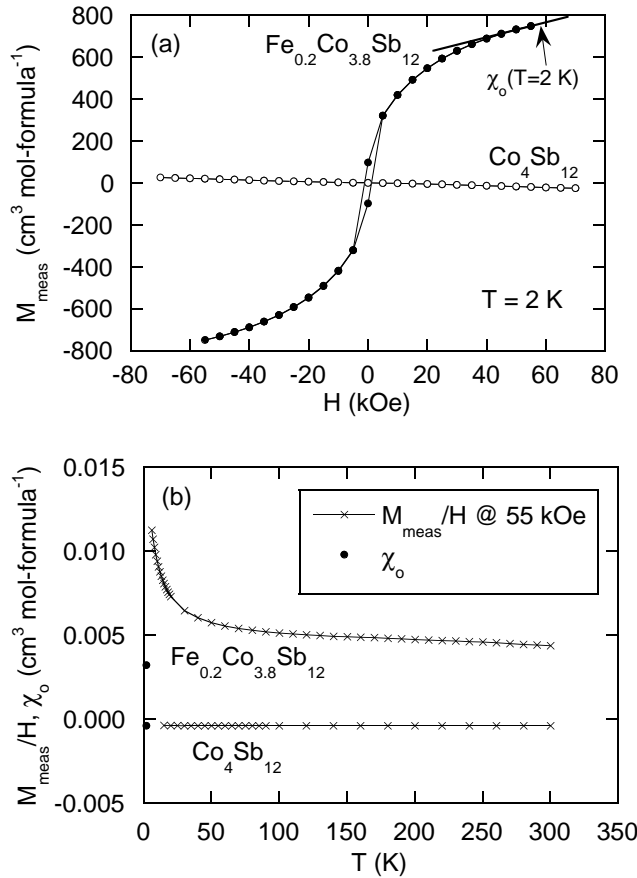


Figure 7. (a) Measured magnetization M_{meas} versus H for $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12}$ at $T = 2 \text{ K}$. (b) Linear high-field susceptibility χ_0 and magnetization M divided by magnetic field H versus temperature T .

$\text{CeFe}_4\text{Sb}_{12}$ and $T_K \sim 43 \text{ K}$ for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, which indicates that the conduction-4f electron hybridization is stronger in $\text{CeFe}_4\text{Sb}_{12}$ than in $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$. Since the magnetic fields that were used in this experiment were less than 70 kOe, $\mu_B H \ll k_B T_K$, and the assumption that χ_0 is field independent is valid. These values of χ_0 for the cerium-filled skutterudites are larger than that of $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$, where $\chi_0(T)$ of the latter appears to saturate to a value of approximately $0.0025 \text{ cm}^3 (\text{mol formula})^{-1}$ as shown in figure 6. They are also much larger than those of the unfilled skutterudites: $\text{Co}_4\text{Sb}_{12}$ has a diamagnetic susceptibility $\chi_0 \sim -0.0004 \text{ cm}^3 (\text{mol formula})^{-1}$ that is nearly temperature independent, as shown in figure 7(b). The doped compound $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{12}$ has some local moment magnetism as evident in the M_{meas} versus H curve in figure 7(a); $\chi_0(T)$ appears to saturate to a value of $\sim 0.0032 \text{ cm}^3 (\text{mol formula})^{-1}$ as $T \rightarrow 0$, as shown in figure 7(b).

In order to check that the estimates of χ_0 and γ correspond to the properties of itinerant electrons, the Wilson–Sommerfeld ratio R was calculated, where $R = (\chi_0/\gamma)(\pi^2 k_B^2/\mu_{eff}^2)$ is generally of the order of unity for heavy fermion systems ($R = 2$ for a spin-1/2 Kondo system [19]). The value of γ that was used to calculate the Wilson ratio was chosen simply by evaluating C_p/T at $T = 2 \text{ K}$, since an unambiguous determination of γ at $T = 0$ is

difficult due to the unusual temperature dependence of C_p/T at low temperature, and since the magnetic susceptibility was only measured down to 2 K. Using these values of γ along with the χ_0 values described earlier yields a value of the Wilson ratio of the order of unity for $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$, as shown in table 2; this provides evidence that these quantities correspond to a moderately large enhancement of the effective mass of itinerant electrons at low temperature.

Table 2. Values of the effective moment μ_{eff} and Curie–Weiss temperature θ obtained from high temperature Curie–Weiss susceptibility; specific heat coefficient γ and Pauli susceptibility χ_0 at $T = 2$ K that were used in the calculation of the Wilson ratio R and Kondo temperature T_K . See text for details.

	μ_{eff} (μ_B)	θ (K)	γ ($\text{mJ (mol formula)}^{-1} \text{K}^{-2}$)	χ_0 ($\text{cm}^3 \text{(mol formula)}^{-1}$)	R	T_K (K)
$\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$	2.6	−46	350	0.017	1.6	43
$\text{CeFe}_4\text{Sb}_{12}$	3.8	−124	180	0.008	1.5	101

4. Summary

In summary, the electrical resistivity of $\text{CeFe}_4\text{Sb}_{12}$ displays a relatively abrupt drop-off with decreasing temperature that shifts to higher temperature with increasing applied pressure, indicating 4f–conduction electron hybridization, which is interpreted as the onset of Kondo coherence; the resistivity of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ shows single ion Kondo-like behaviour down to 1.3 K. Specific heat and magnetic susceptibility measurements reveal that $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ exhibit relatively large values of the electronic specific heat coefficient γ and Pauli susceptibility χ_0 at low temperature that yield a value of the Wilson ratio of order unity. These properties are reminiscent of those of cerium- and uranium-based heavy fermion materials such as CeAl_3 and UPt_3 , and are unlike those of the lanthanum-filled or unfilled skutterudites which exhibit ordinary metallic or semiconducting behaviour. These properties are therefore interpreted as a reflection of a moderately heavy fermion ground state in $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$.

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