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# Kondo insulating behaviour in the filled skutterudite compound $\text{CeOs}_4\text{Sb}_{12}$

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## Abstract

The filled skutterudite  $\text{CeOs}_4\text{Sb}_{12}$  and its nonmagnetic analogue  $\text{LaOs}_4\text{Sb}_{12}$  have been synthesized in single-crystal form using the molten-metal-flux growth technique with Sb flux. Electrical resistivity measurements on  $\text{CeOs}_4\text{Sb}_{12}$  indicate that it is a Kondo insulator with an energy gap of  $\Delta E/k_B \sim 10$  K. Lattice parameter and magnetic susceptibility measurements suggest that the Ce ions are trivalent in  $\text{CeOs}_4\text{Sb}_{12}$ . Specific heat and magnetization measurements reveal an enhanced value of the electronic specific heat coefficient  $\gamma \sim 92$  mJ mol<sup>-1</sup> K<sup>-2</sup> and Pauli susceptibility, reminiscent of a moderately heavy-fermion material.

## 1. Introduction

Ternary transition metal pnictides with the chemical formula  $\text{RT}_4\text{X}_{12}$  (R = alkaline earth, rare earth, or actinide; T = Fe, Ru, or Os; X = P, As, or Sb) crystallize in the cubic skutterudite  $\text{LaFe}_4\text{P}_{12}$  structure (space group  $Im\bar{3}$ ) [1, 2]. The filled skutterudite compounds, derived by filling voids in the  $\text{CoAs}_3$  structure with R atoms, display a variety of strongly correlated electronic phenomena, mainly due to the behaviour of the R atoms. Superconducting [3–5], magnetic [6, 7], heavy-fermion [8–10], intermediate-valence [11–13], non-Fermi-liquid [14, 15], and semiconducting behaviour [16, 17] have been observed in these materials. The semiconducting behaviour of some of the filled skutterudites is probably caused by the formation of an energy gap due to hybridization between the localized f states and conduction electron states; as a result, these materials are often referred to as ‘hybridization gap semiconductors’ or ‘Kondo insulators’. Band-structure calculations [18], optical studies [19], and XANES measurements [20, 21] support this view. The Sm compound  $\text{SmS}$  in its collapsed ‘gold’ phase [22, 23] and  $\text{SmB}_6$  [24] were the first materials to be identified as hybridization gap semiconductors. The skutterudites  $\text{CeFe}_4\text{P}_{12}$  and  $\text{UFe}_4\text{P}_{12}$  were the first materials based on a rare-earth or actinide element other than Sm found to exhibit this type of behaviour. A number of other lanthanide and actinide Kondo insulators have been discovered since then (for

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a review, see [25, 26]). In this paper, we report on single-crystal synthesis and the physical properties of the filled skutterudites  $\text{ROs}_4\text{Sb}_{12}$  ( $\text{R} = \text{La}, \text{Ce}$ ) by means of x-ray diffraction, electrical resistivity, dc magnetization, and specific heat measurements. Our results indicate that  $\text{CeOs}_4\text{Sb}_{12}$  is a hybridization gap semiconductor with an energy gap  $\Delta E/k_B \sim 10$  K but with an enhanced electronic specific heat coefficient and Pauli susceptibility reminiscent of heavy-fermion behaviour.

## 2. Experimental details

The filled skutterudite antimonide compounds were prepared using a molten-metal-flux growth method with Sb flux. High-purity starting materials ( $\text{R}$ : AMES 4N;  $\text{Os}$ : Colonial Metals, 3N5;  $\text{Sb}$ : Alfa Aesar, 6N) were placed in the ratio  $\text{R}:\text{Os}:\text{Sb} = 1:4:20$  in evacuated carbon-coated quartz tubes, heated to  $950^\circ\text{C}$  for 24 hours, and then cooled slowly ( $\sim 3^\circ\text{C h}^{-1}$ ) to  $650^\circ\text{C}$ ; this was followed by a quench ( $\sim 200^\circ\text{C h}^{-1}$ ) to room temperature. The single-crystal specimens were removed from the excess antimony flux by etching in aqua regia ( $\text{HCl}:\text{HNO}_3 = 1:1$ ). The crystals were usually cubic or rectangular in shape and ranged from 0.1 to 2 mm in diameter.

X-ray powder diffraction measurements were made using a 9 kW Rigaku diffractometer to check the sample purity and crystal structure. A silicon standard was used for more accurate determination of the lattice parameter. The electrical resistivity was measured in a commercial Quantum Design PPMS cryostat at temperatures  $1.8\text{ K} \leq T \leq 300\text{ K}$  using a standard four-wire technique with excitation currents from 1 to 10 mA. Magnetization measurements were made in a Quantum Design MPMS magnetometer from 1.8 to 300 K in magnetic fields up to 5.5 T. Specific heat measurements were made in a semi-adiabatic  $^3\text{He}$  calorimeter using a standard heat-pulse technique.

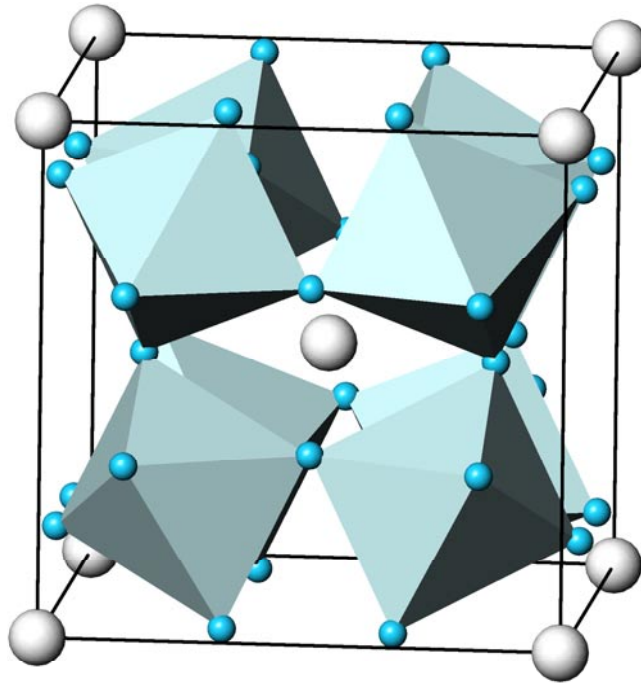
## 3. Results

### 3.1. Crystal structure

The filled skutterudites have the chemical formula  $\text{RT}_4\text{X}_{12}$  ( $\text{R} =$  alkaline earth, rare earth, or actinide;  $\text{T} = \text{Fe}, \text{Ru}, \text{or Os}$ ;  $\text{X} = \text{P}, \text{As}, \text{or Sb}$ ) and crystallize in the BCC ( $Im\bar{3}$ ) structure shown in figure 1. The R atoms are located at the body centre and corners of the cubic structure and are surrounded by a cage of corner-sharing  $\text{T}_4\text{X}_{12}$  octahedra. The lattice parameter measurements obtained for  $\text{ROs}_4\text{Sb}_{12}$  ( $\text{R} = \text{La}, \text{Ce}$ ) are in good agreement with previous measurements [2] and are listed in table 1. It has been found that the lattice parameters of other filled antimonide skutterudites containing osmium follow the trivalent rare-earth-ion lanthanide contraction. Therefore, a trivalent Ce configuration is expected (at least at room temperature).

### 3.2. Resistivity

The normalized resistivity  $\rho/\rho(300\text{ K})$  versus  $T$  of four different samples of  $\text{CeOs}_4\text{Sb}_{12}$  is displayed in figure 2 for typical values of  $\rho(300\text{ K}) \sim 500\ \mu\Omega\text{ cm}$ . The resistivity is weakly temperature dependent above 100 K and a knee appears at  $\sim 100$  K, similar to that observed in  $\text{CeFe}_4\text{Sb}_{12}$  [8, 9] and  $\text{CeRu}_4\text{Sb}_{12}$  [14]. For  $T < 50$  K, the resistivity increases rapidly with decreasing temperature, indicating semiconducting behaviour. This type of behaviour has been observed in phosphide skutterudite compounds, such as  $\text{CeFe}_4\text{P}_{12}$  [16],  $\text{UF}_4\text{P}_{12}$  [16],  $\text{CeRu}_4\text{P}_{12}$  [17], and  $\text{CeOs}_4\text{P}_{12}$  [17], and recently some skutterudites containing Yb [13]. The  $\rho(T)$  curves of the four  $\text{CeOs}_4\text{Sb}_{12}$  samples are slightly different but exhibit the same qualitative



**Figure 1.** Crystal structure of the filled skutterudites  $RT_4X_{12}$ . R atoms: large circles; X atoms: small circles; T atoms: located in the centre of the  $T_4X_{12}$  octahedra.

(This figure is in colour only in the electronic version, see [www.iop.org](http://www.iop.org))

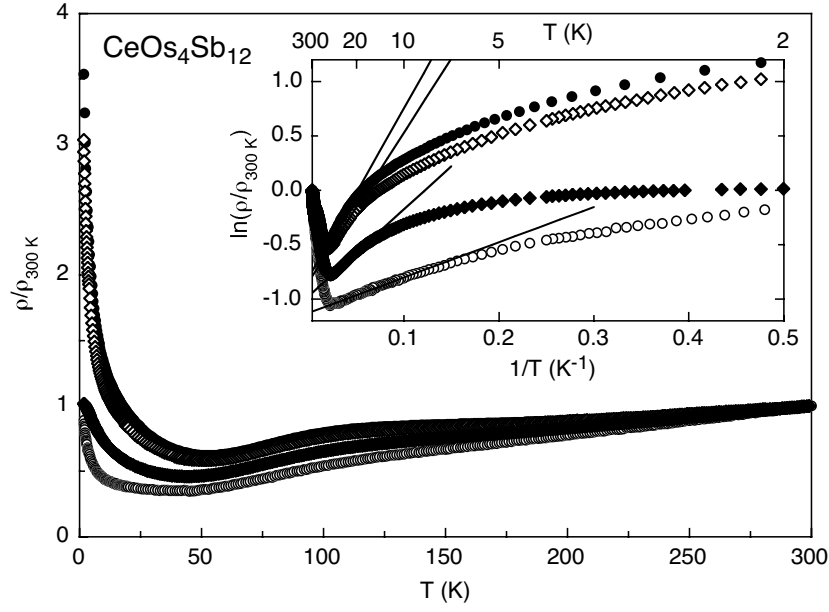
**Table 1.** Physical properties of  $ROs_4Sb_{12}$  (R = La, Ce).  $a$ : cubic lattice parameter;  $V$ : unit-cell volume;  $\mu_{eff}$ : effective moment;  $\theta_{CW}$ : Curie–Weiss temperature;  $\gamma$ : electronic specific heat coefficient;  $\theta_D$ : Debye temperature;  $T_K$ : Kondo temperature;  $R_W$ : Wilson ratio. The values of the effective moment  $\mu_{eff}^{HT}$  and Curie–Weiss temperature  $\theta_{CW}$  were obtained from fits of the high-temperature magnetic susceptibility data. The values of the effective moment  $\mu_{eff}$  and CEF temperature  $\Delta$  were obtained from fits of the magnetic susceptibility data to a CEF model as discussed in the text. The electronic specific heat coefficient  $\gamma$  and Debye temperature  $\theta_D$  were determined from fits to low-temperature specific heat data. Errors in the last digit are given in parentheses.

	$a$ (Å)	$V$ (Å <sup>3</sup> )	$\mu_{eff}^{HT}$ ( $\mu_B$ )	$\theta_{CW}$ (K)	$\mu_{eff}$ ( $\mu_B$ )	$\Delta$ (K)	$\gamma$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	$\theta_D$ (K)	$T_K$ (K)	$R_W$
CeOs <sub>4</sub> Sb <sub>12</sub>	9.302(1)	804.6(2)	1.88	6	2.0	327	92	304	90	3.2
LaOs <sub>4</sub> Sb <sub>12</sub>	9.307(1)	806.3(2)	—	—	—	—	36	304	—	—

behaviour, i.e., they show a decrease at 100 K and display semiconducting behaviour. Least-squares fits in the range  $25 \text{ K} < T < 50 \text{ K}$  to an activated conduction law

$$\rho = \rho_0 \exp(\Delta E/k_B T) \quad (1)$$

where  $\rho_0$  is a scaling resistivity,  $\Delta E$  is an energy gap, and  $k_B$  is the Boltzmann constant, yield  $\Delta E/k_B \sim 5\text{--}15 \text{ K}$  as shown in a plot of  $\ln(\rho/\rho_{300\text{K}})$  versus  $T^{-1}$  (inset of figure 2). At temperatures below 25 K, the resistivity deviates from activated behaviour, presumably due to the presence of impurity states in the gap.



**Figure 2.** Normalized electrical resistivity  $\rho/\rho_{300\text{K}}$  versus temperature  $T$  for four different samples of  $\text{CeOs}_4\text{Sb}_{12}$ . Inset:  $\ln(\rho/\rho_{300\text{K}})$  versus  $T^{-1}$ . The lines are fits of the data to an activated conduction law  $\rho = \rho_0 \exp(\Delta E/k_B(T))$ .

### 3.3. Magnetic susceptibility

The magnetic susceptibility  $\chi \equiv M/H$  versus  $T$  for  $\text{CeOs}_4\text{Sb}_{12}$  is shown in figure 3 along with the inverse magnetic susceptibility  $\chi^{-1}$  (lower inset) and a temperature-dependent effective moment (upper inset),  $\mu'_{eff}(T)$ , defined as

$$\mu'_{eff}(T) \equiv \sqrt{\frac{3k_B\chi T}{N_A}}. \quad (2)$$

The shape of the  $\chi(T)$  curve is very similar to that for  $\text{CeFe}_4\text{Sb}_{12}$  [8, 9] and  $\text{CeRu}_4\text{Sb}_{12}$  [14], although the broad hump which is observed for these compounds at 100 K is less pronounced. A least-squares fit to a Curie–Weiss law

$$\chi = C/(T - \theta_{CW}) \quad (3)$$

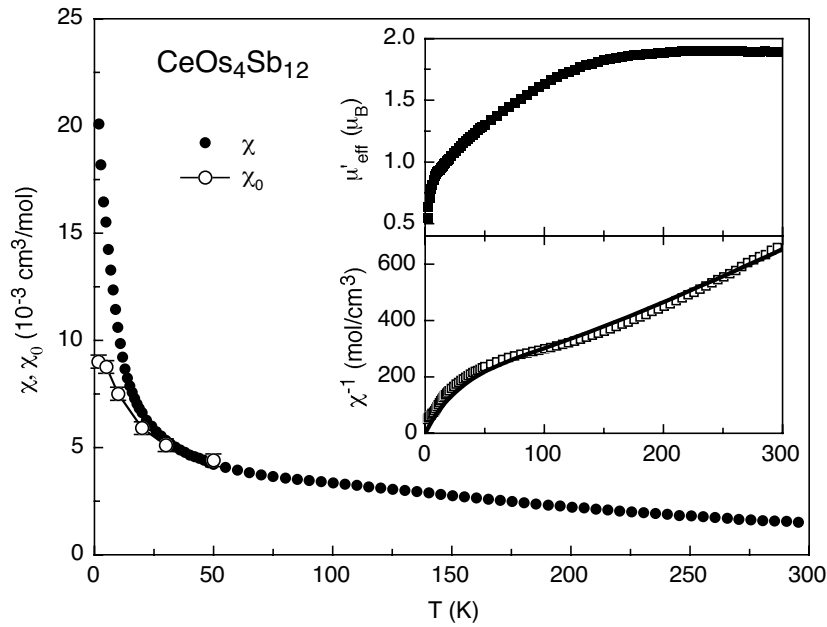
where  $C = N_A\mu_{eff}^2/3k_B$ ,  $\theta_{CW}$  is the Curie–Weiss temperature, and  $\mu_{eff}$  is the usual constant effective moment, from 220 K to 300 K yields  $\mu_{eff} = 1.88 \mu_B$  and  $\theta_{CW} = 6$  K. The effective moment  $\mu'_{eff}(T)$  appears to saturate to a value of  $\sim 1.9 \mu_B$  at high temperatures and extrapolates to a smaller value of  $\sim 1 \mu_B$  as  $T \rightarrow 0$ , if one ignores the data below 10 K. The curvature in  $\chi^{-1}(T)$  and  $\mu'_{eff}(T)$  at low temperatures suggests the presence of crystalline-electric-field (CEF) effects. In a cubic environment, the CEF will split the sixfold-degenerate Ce Hund's rule  $J = 5/2$  multiplet into a  $\Gamma_7$  doublet and a  $\Gamma_8$  quartet [27]. The magnetic susceptibility of a  $\text{Ce}^{3+}$  free-ion contribution in a cubic CEF is given by

$$\chi = F\left(\frac{\Delta}{T}\right) \frac{C}{T} \quad (4)$$

where  $\Delta$  is the temperature (corresponding to the energy  $=k_B \Delta$ ) between the doublet and the quartet energy levels, and

$$F(x) = \frac{[5/21 + (26/21)e^{-x} + (32/21x)(1 - e^{-x})]}{1 + 2e^{-x}} \quad (5)$$

with  $x = \Delta/T$ . A least-squares fit of equation (5) to the  $\chi^{-1}(T)$  data shown as the solid line in the lower inset of figure 3 (results collected in table 1) yields  $\mu_{eff} = 2.0 \mu_B$  and  $\Delta = 327$  K for the splitting between the  $\Gamma_7$  doublet ground state and the  $\Gamma_8$  quartet excited state. For temperatures below 25 K, the susceptibility follows a Curie law with an effective moment of  $\sim 1.2 \mu_B$  which is close to the value of the moment expected for the doublet ground state ( $\mu_{eff} = 1.4 \mu_B$ ). The successful description of the  $\chi(T)$  data by equation (4) indicates that the Ce ions are trivalent (or nearly so) in this compound. Sales *et al* [28] found that the behaviour of another filled skutterudite, Ce<sub>0.9</sub>Fe<sub>3</sub>CoSb<sub>12</sub>, can also be described using this type of CEF model with similar parameters  $\mu_{eff} = 2.9 \mu_B$  and  $\Delta = 350$  K.



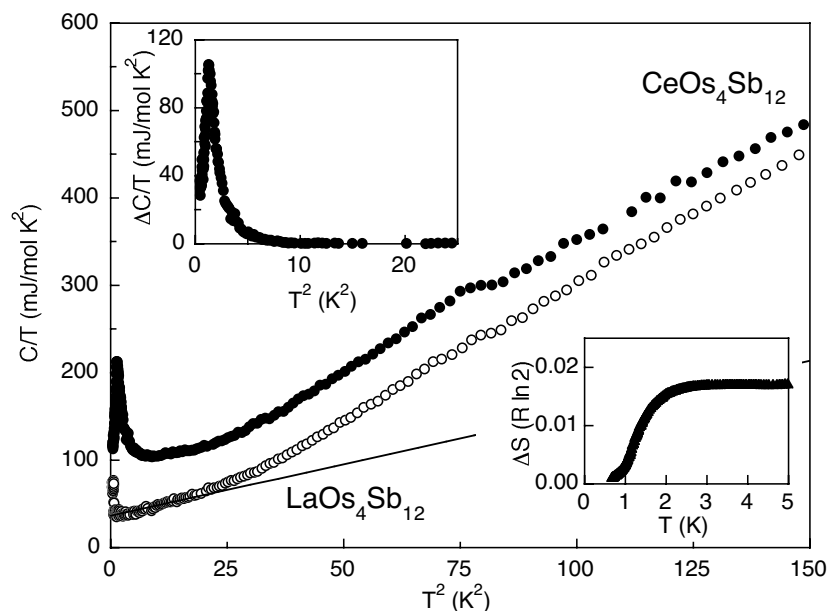
**Figure 3.** Magnetic susceptibility  $\chi$  versus temperature  $T$  in a magnetic field of  $H = 5$  kOe for CeOs<sub>4</sub>Sb<sub>12</sub>. Upper inset: temperature-dependent effective moment  $\mu'_{eff}$  versus  $T$ . Lower inset: inverse magnetic susceptibility  $\chi^{-1}$  versus  $T$ . The line is a fit of the data using a CEF model. See the text for details.

In order to estimate the Pauli susceptibility of the conduction electrons in CeOs<sub>4</sub>Sb<sub>12</sub>, magnetization  $M$  versus magnetic field  $H$  measurements were made and analysed using the following procedure: the measured magnetization was assumed to be composed of a saturable contribution arising from a small amount of magnetic impurities and a Pauli paramagnetic contribution such that  $M_{meas} = \chi_0 H + M_{imp}(H/T)$  where  $\chi_0$  is the Pauli susceptibility (assumed to be independent of  $H$ ) and  $M_{imp}$  is the impurity magnetization. The assumption that  $\chi_0$  is independent of  $H$  is valid only when  $\mu_B H \ll k_B T_K$ , which is the case for CeOs<sub>4</sub>Sb<sub>12</sub> as will be discussed below. At the lowest temperature of 1.8 K,  $\chi_0$  was estimated by extrapolation of  $M/H$  versus  $H^{-1}$  to the limit of  $H^{-1} \rightarrow 0$ .  $\chi_0(T)$  was estimated by scaling (not shown)  $M_{meas}$  versus  $H/T$  by the appropriate  $\chi_0(T)$  such that the  $M_{imp}(H/T) = M_{meas} - \chi_0 H$

curves collapsed onto the lowest-temperature curve using  $\chi_0(1.8 \text{ K})$  as an initial guess. The  $\chi_0(T)$  values are shown as open circles in figure 3 where  $\chi_0(T)$  appears to saturate to a value of  $0.009 \text{ cm}^3 \text{ mol}^{-1}$ . The impurity contribution at  $T = 1.8 \text{ K}$  amounts to  $M_{imp} \sim 220 \text{ emu mol}^{-1}$  which corresponds to a reasonable value of  $0.04 \mu_B/\text{Ce atom}$ .

### 3.4. Specific heat

Specific heat divided by temperature  $C/T$  versus  $T^2$  data for  $\text{CeOs}_4\text{Sb}_{12}$  and the nonmagnetic analogue  $\text{LaOs}_4\text{Sb}_{12}$  are displayed in figure 4. The similar slopes of the curves indicate that the phonon contributions for  $\text{LaOs}_4\text{Sb}_{12}$  and  $\text{CeOs}_4\text{Sb}_{12}$  are similar. We therefore assume that the two compounds have the same Debye temperatures and any differences in the electronic structure are taken into account by the different values of the electronic specific heat coefficient  $\gamma \equiv C/T$ . Least-squares fits to the data from  $0.6 \text{ K} \leq T \leq 3.5 \text{ K}$  of  $C/T = \gamma + \beta T^2$ , where  $\beta = 12\pi^4 r R / (5\theta_D^3)$  is the Debye phonon coefficient,  $r (=17)$  is the number of atoms per formula unit,  $R$  is the universal gas constant, and  $\theta_D$  is the Debye temperature, yield  $\theta_D = 304 \text{ K}$  and values of  $\gamma$  of  $36 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $92 \text{ mJ mol}^{-1} \text{ K}^{-2}$  for  $\text{LaOs}_4\text{Sb}_{12}$  and  $\text{CeOs}_4\text{Sb}_{12}$ , respectively. A peak is observed in  $C/T$  for  $\text{CeOs}_4\text{Sb}_{12}$  at  $\sim 1.1 \text{ K}$  indicating a phase transition of some kind. A similar peak was observed in another closely related filled skutterudite,  $\text{CeFe}_4\text{Sb}_{12}$ , at  $\sim 1.5 \text{ K}$  [9]. The magnetic contribution to the specific heat  $\Delta C/T$  for  $\text{CeOs}_4\text{Sb}_{12}$  is obtained by subtracting the specific heat of  $\text{LaOs}_4\text{Sb}_{12}$  from that of  $\text{CeOs}_4\text{Sb}_{12}$  and is shown in the upper inset of figure 4. The entropy associated with this phase transition is shown in the lower inset of figure 4 and amounts to less than 2% of  $R \ln 2$ . This is too small to be a bulk transition involving all of the Ce moments or a spin-1/2 Kondo peak; therefore, we conclude that it is caused by a transition of an impurity phase containing Ce.



**Figure 4.** Specific heat divided by temperature  $C/T$  versus  $T^2$  for  $\text{LaOs}_4\text{Sb}_{12}$  (open circles) and  $\text{CeOs}_4\text{Sb}_{12}$  (filled circles). The line is a fit of the data to the expression  $C/T = \gamma + \beta T^2$ . Upper inset: magnetic specific heat divided by temperature  $\Delta C/T$  versus  $T^2$ . Lower inset: magnetic entropy  $\Delta S$  associated with peak at  $1.1 \text{ K}$  versus  $T$ .

#### 4. Discussion

A number of filled skutterudite compounds exhibit semiconducting behaviour at low temperatures with an energy gap  $\Delta E/k_B$  ranging from 400 K (CeOs<sub>4</sub>P<sub>12</sub> [17]) to 1500 K (CeFe<sub>4</sub>P<sub>12</sub> [16]). Band-structure calculations [18] on CeFe<sub>4</sub>P<sub>12</sub> show that the Ce 4f level is close to the Fermi level and is strongly hybridized with the Fe d and phosphorus p levels. This hybridization leads to the formation of a gap in the density of states at the Fermi level [25, 29], which leads to the observed activated behaviour of the electrical resistivity. The magnitude of the gap in CeOs<sub>4</sub>Sb<sub>12</sub> is closer to what is found in compounds such as the collapsed ‘gold’ phase of SmS (under pressure) [22, 23] and SmB<sub>6</sub> [24] in which  $\Delta E$  is of the order of a few meV. These two compounds also exhibit intermediate-valence behaviour, in which temporal fluctuations between the Sm 4f<sup>5</sup> (magnetic) and 4f<sup>6</sup> (nonmagnetic) configurations give rise to (among other properties) a magnetic susceptibility that is weakly temperature dependent below about 100 K [29] indicating a nonmagnetic ground state. However, the Ce ions appear to have a nearly integral valence in CeOs<sub>4</sub>Sb<sub>12</sub> given that the lattice parameter follows the trivalent rare-earth-ion lanthanide contraction and the magnetic susceptibility can be well described by a crystal-field-split Ce<sup>3+</sup> configuration. Recent XANES studies on CeFe<sub>4</sub>P<sub>12</sub> [20] and CeRu<sub>4</sub>P<sub>12</sub> [21] indicate that Ce is mainly trivalent in these two materials (at least at room temperature).

We estimated the Kondo temperature for CeOs<sub>4</sub>Sb<sub>12</sub> by assuming that the enhanced susceptibility at low temperatures is due to the Kondo effect. Using the values of the Pauli susceptibility  $\chi_0$  in the following formula (assuming a free-ion value of  $\mu_{eff} = 2.54 \mu_B$ ):

$$T_K = \frac{N_A \mu_{eff}}{3k_B \chi_0 (1.8 \text{ K})} \quad (6)$$

we obtain  $T_K \sim 90$  K for CeOs<sub>4</sub>Sb<sub>12</sub>. Therefore, our assumption that  $\chi_0$  is independent of  $H$  is justified, since  $\mu_B H \ll k_B T_K$ . The Kondo temperature for the isostructural compound CeFe<sub>4</sub>Sb<sub>12</sub>, estimated in this way, is  $T_K \sim 101$  K [9]. The estimates for  $T_K$  for these materials are supported by the observation of a rapid drop in the resistivity below  $\sim 100$  K in both of the compounds that is associated with the decrease in scattering caused by the onset of coherence in the Ce sublattice as the Ce ions become increasingly screened by the conduction electrons. In order to determine whether the enhanced magnetic susceptibility and specific heat at low temperatures are both due to itinerant electrons, we calculated the Wilson–Sommerfeld ratio  $R_W = (\pi^2 k_B^2 / 3 \mu_{eff}^2) (\chi_0 / \gamma)$ . As an unambiguous choice of  $\gamma$  for CeOs<sub>4</sub>Sb<sub>12</sub> was not possible, we chose the value  $\gamma = 122 \text{ mJ mol}^{-1} \text{ K}^{-2}$  at 1.8 K, which was the lowest temperature of the susceptibility measurements (the results are collected in table 1). We used the value  $\mu_{eff} = 2.54 \mu_B$  appropriate for the Hund’s rule  $J = 5/2$  Ce multiplet and  $\chi_0 = 0.009 \text{ cm}^3 \text{ mol}^{-1}$ , from which we determined  $R_W = 3.2$ . The Wilson–Sommerfeld ratio is of the order of unity for CeOs<sub>4</sub>Sb<sub>12</sub>, indicating that the thermodynamic and transport properties of this system are due to conduction electrons and an enhancement of the effective mass at low temperatures, typical of heavy-fermion systems.

Among the hybridization gap semiconductors, there are a number of compounds, such as Ce<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub> [30] and CeRhAs [31], which have very small values of the electronic specific heat coefficient  $\gamma \sim 3\text{--}10 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . However, some of these materials, for instance SmB<sub>6</sub> [32], CeNiSn [33], CeRhSb [34], have an enhanced  $\gamma$  of the order of  $\sim 30\text{--}100 \text{ mJ mol}^{-1} \text{ K}^{-2}$  yet still exhibit semiconducting behaviour in their transport properties. It appears that CeOs<sub>4</sub>Sb<sub>12</sub> falls into this latter class of Kondo insulating materials. In some cases, such as that of CeNiSn [35], the compound was proposed to be a semimetal in which the conduction and valence bands overlap slightly, in order to explain the finite density of states at the Fermi



level. We merely point out that  $\text{CeOs}_4\text{Sb}_{12}$  has an enhanced susceptibility and specific heat coefficient leading to a Wilson ratio of the order of unity which is consistent with heavy-fermion behaviour. Further investigation such as measurements of the Hall effect, optical reflectivity, and electrical resistivity under pressure would be helpful in determining the nature of the gap observed in  $\text{CeOs}_4\text{Sb}_{12}$ .

## 5. Conclusions

Electrical resistivity, magnetic susceptibility, specific heat, and x-ray diffraction measurements were performed on single crystals of  $\text{CeOs}_4\text{Sb}_{12}$ . The electrical resistivity measurements suggest that  $\text{CeOs}_4\text{Sb}_{12}$  is semiconducting with a small energy gap  $\Delta E/k_B \sim 10$  K. Lattice parameter and magnetic susceptibility measurements indicate that Ce is trivalent in this compound. The electronic specific heat coefficient  $\gamma$  is estimated to be  $\sim 92$  mJ mol<sup>-1</sup> K<sup>-2</sup>, suggesting an enhancement of the electron effective mass at low temperatures.

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