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## Pressure dependence of the electrical resistivity of the filled skutterudites $\text{LnFe}_4\text{Sb}_{12}$ ( $\text{Ln} = \text{Ce}, \text{Yb}$ )

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**Abstract.** We report the pressure dependence of the electrical resistivity of two filled skutterudite compounds  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CeFe}_4\text{Sb}_{12}$  from 1.2 K up to room temperature and under applied pressures up to 17 kbar. Both  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CeFe}_4\text{Sb}_{12}$  show a rapid decrease of  $\rho$  at  $\sim 50$  K and  $\sim 100$  K, respectively, which is caused by the onset of coherent scattering of electrons from the rare-earth sublattice. The resistivity curves can be collapsed onto the ambient pressure curve using a single scaling temperature  $T_0$ , indicating that a single characteristic energy dominates the transport properties. For  $\text{CeFe}_4\text{Sb}_{12}$ ,  $T_0$  is found to increase with pressure, while the opposite behaviour is observed for  $\text{YbFe}_4\text{Sb}_{12}$ . The pressure dependence of  $\rho$  as well as the change of  $T_0$  are similar to the findings for a number of other intermediate-valence and heavy-fermion systems.

### 1. Introduction

Intermediate-valence and heavy-fermion materials are intermetallic compounds containing rare-earth (e.g., Ce, Yb) or actinide (e.g., U) elements that exhibit valence instabilities and whose low-temperature properties are characterized by a small energy scale  $\sim 10$ – $100$  K associated with interactions between the localized 4f or 5f electrons and the conduction electrons (see reviews [1–3]). This small energy scale gives rise to an enhanced conduction-electron effective mass as indicated by the large values of the electronic specific heat coefficient  $\gamma = C_P/T$  and dc magnetic susceptibility  $\chi$  at low temperatures. Pressure measurements have been useful in probing intermediate-valence/heavy-fermion materials [4] for two main reasons: (1) modest amounts of pressure are able to produce significant changes in the physical properties due to the small energy scales and (2) the application of pressure results in changes in volume without introducing disorder caused by chemical substitution.

The family of ‘filled’ skutterudite compounds with the formula  $\text{MT}_4\text{X}_{12}$  ( $M =$  alkaline earth, rare earth, or actinide;  $T = \text{Fe}, \text{Ru}, \text{or Os}$ ;  $X = \text{P}, \text{As}, \text{or Sb}$ ), crystallize [5, 6] in a BCC structure (space group  $Im\bar{3}$ ). These materials display a number of different ground states such as superconductivity [7] and ferromagnetism [8], and can be metals or hybridization gap semiconductors [9]. Two of the filled skutterudites,  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CeFe}_4\text{Sb}_{12}$ , have been shown [10–12] to behave as moderately heavy Fermi liquids with  $\gamma(0) \sim 140 \text{ mJ mol}^{-1} \text{ K}^{-2}/\text{f.u.}$  [11] and  $\sim 180 \text{ mJ mol}^{-1} \text{ K}^{-2}/\text{f.u.}$  [12], respectively.

Measurements [14] of the unit-cell dimensions of the whole family of filled skutterudites show anomalies in the lattice parameters of compounds with Ce, Eu, and Yb; i.e., rare-earth ions with an unstable valence. As the lighter transition metal or pnictogen atoms are replaced with heavier ones, the unit-cell volume increases and lanthanide valences decrease; Ce progresses

from tetravalency to trivalency, while Eu and Yb progress from trivalency to divalency. The compound  $\text{YbFe}_4\text{Sb}_{12}$  was recently found to exhibit intermediate-valence behaviour [12, 13].

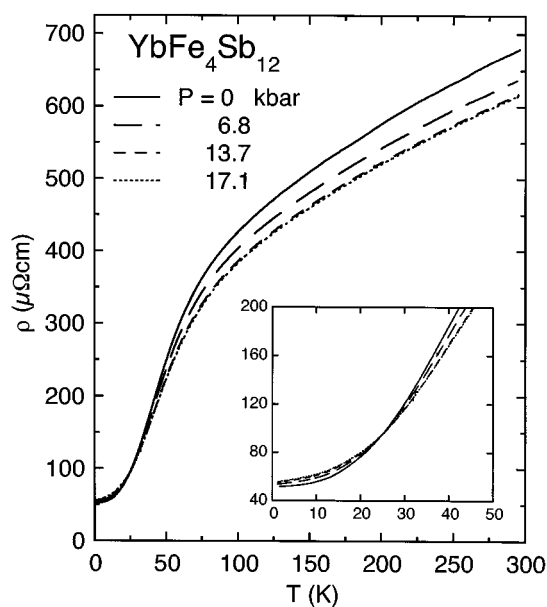
## 2. Experimental details

Polycrystalline samples of  $\text{CeFe}_4\text{Sb}_{12}$  were prepared at Oak Ridge National Laboratory by a hot isostatic pressing technique yielding a solid with >95% of the theoretical x-ray density [15]. Polycrystalline samples of  $\text{YbFe}_4\text{Sb}_{12}$  were made by placing the constituents (in a ratio of  $\text{Yb}_{1.05}\text{Fe}_4\text{Sb}_{12}$ ) in a graphite crucible sealed in a quartz tube with 150 Torr of ultrahigh-purity argon. The sample was then melted in an induction furnace at  $\sim 950^\circ\text{C}$  and annealed under argon at  $600^\circ\text{C}$  for 20 h. Further details can be found in [12].

Measurements of the electrical resistivity,  $\rho$ , were performed under hydrostatic pressure in a beryllium–copper piston–cylinder clamp device up to 17 kbar using Fluorinert FC75 as a pressure-transmitting medium. The resistivity was measured from 1.2 to 295 K using an ac-resistance bridge operating at a frequency of 16 Hz and a current of 1–10 mA. The pressure was inferred inductively from the superconducting transition of a Pb manometer [16].

## 3. Results and discussion

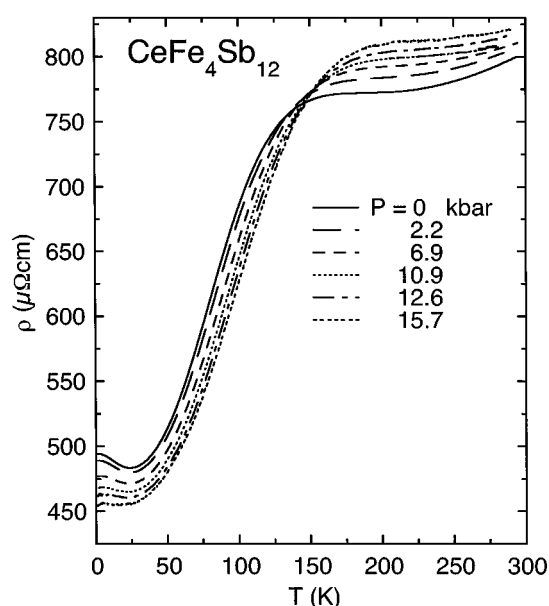
Figure 1 shows the resistivity of  $\text{YbFe}_4\text{Sb}_{12}$  as a function of temperature  $T$  at a number of applied pressures up to 17.1 kbar. At ambient pressure, the resistivity decreases with decreasing temperature above 100 K and decreases more rapidly below  $\sim 50$ –70 K. This type of behaviour has been observed in other intermediate-valence/heavy-fermion systems and is believed to be caused by a sharp decrease in the magnetic scattering due to the onset of coherent scattering of charge carriers by the Yb-ion sublattice. Below  $\sim 25$  K, the resistivity decreases with a weaker



**Figure 1.** Resistivity  $\rho$  versus temperature  $T$  for  $\text{YbFe}_4\text{Sb}_{12}$  at various applied pressures. Inset:  $\rho$  versus  $T$  at low temperatures showing the increase of  $\rho$  with applied pressure.

$T$ -dependence and becomes nearly linear below  $\sim 5$  K. The application of pressure causes a decrease of  $\rho$  at higher temperatures and an increase of  $\rho$  below 25 K as shown in the inset of figure 1. This kind of pressure dependence of  $\rho$  has been observed in other intermediate-valence/heavy-fermion systems, most notably  $\text{YbAgCu}_4$  [17],  $\text{YbCu}_2\text{Si}_2$  [17],  $\text{YbRh}_2\text{Si}_2$  [17], and  $\text{Yb}_2\text{Cu}_9$  [18].

The resistivity of  $\text{CeFe}_4\text{Sb}_{12}$  versus  $T$  is shown in figure 2 at various applied pressures up to 15.7 kbar. Above 150 K,  $\rho$  has a small temperature dependence. The coherence temperature for this compound is around  $\sim 80$ – $100$  K as indicated by the rapid drop of  $\rho$  in that region. A minimum appears at  $\sim 30$  K at all pressures and may be due to a Kondo effect caused by magnetic impurities such as uncompensated Ce ions in a different crystalline environment (e.g., grain boundaries, vacancies, surface layers, etc). The effect of pressure is to increase  $\rho$  at higher temperatures above 150 K, increase the coherence temperature, and decrease  $\rho$  at low temperatures. This behaviour is opposite to what is observed in  $\text{YbFe}_4\text{Sb}_{12}$  and will be discussed below. Pressure dependences of  $\rho$  similar to that of  $\text{CeFe}_4\text{Sb}_{12}$  have been observed in other systems such as  $\text{CeAgCu}_4$  [17],  $\text{CeSi}_2\text{Cu}_2$  [17],  $\text{CeCu}_6$  [19],  $\text{Ce}_3\text{M}$  ( $\text{M} = \text{Sn}, \text{In}$ ) [20], and  $\text{CePd}_3$  [21].

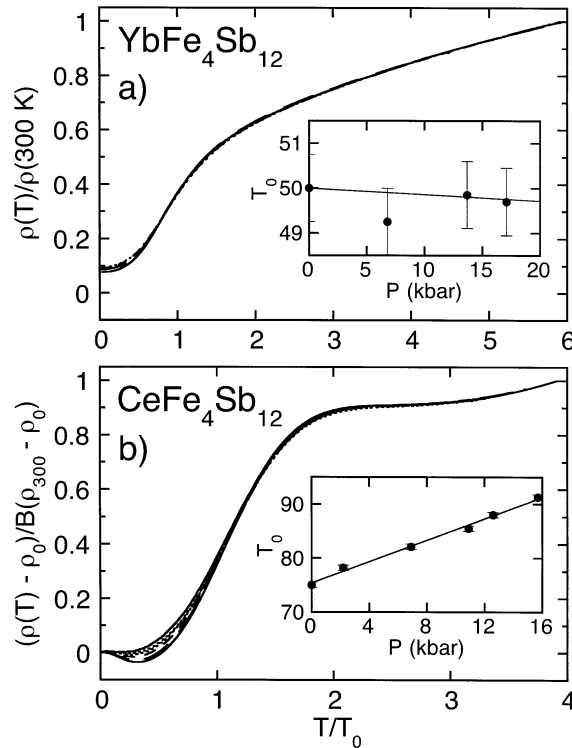


**Figure 2.** Resistivity  $\rho$  versus temperature  $T$  for  $\text{CeFe}_4\text{Sb}_{12}$  at various applied pressures.

The presence of crystalline-electric-field effects in  $\text{CeFe}_4\text{Sb}_{12}$  may provide an alternative explanation of the features in the resistivity. For cubic systems, the sixfold-degenerate  $J = 5/2$  Hund's rule multiplet of cerium will usually split into a lower-lying  $\Gamma_7$  doublet and a higher-lying  $\Gamma_8$  quartet. If the overall splitting  $\Delta$  is of the order of 100 K, then at high temperatures  $T \simeq \Delta$  all of the states will contribute to the magnetic scattering. Below  $\sim 100$  K, the quartet becomes less populated and the magnetic scattering is reduced. At lower temperatures the Kondo-like behaviour manifested in the minimum in  $\rho$  could be associated with the magnetic scattering of electrons from the  $\Gamma_7$  ground state.

In a number of intermediate-valence/heavy-fermion compounds containing U, Ce, and Yb [17, 19, 22], the resistivity scales with a characteristic temperature  $T_0$  which is defined as

the temperature of the maximum in  $\rho$ ; or, if a well-defined maximum in  $\rho$  does not exist, the temperature of the inflection point. Such scaling is regarded as evidence that the low-temperature electronic properties are governed by one characteristic energy. In figure 3(a) we show scaled resistivity curves for  $\text{YbFe}_4\text{Sb}_{12}$ , plotted as  $\rho(T)/\rho(300\text{ K})$  versus  $T/T_0$ , where  $T_0$  is the scaling temperature. The scaled resistivity curves for  $\text{CeFe}_4\text{Sb}_{12}$  are shown in figure 3(b), plotted as  $(\rho(T) - \rho_0)/B(\rho_{300} - \rho_0)$  versus  $T/T_0$ , where  $\rho_0$  is the resistivity at the lowest measured temperature,  $\rho_{300}$  is the room temperature value of the resistivity, and  $B$  is a constant slightly greater than 1. As there is no clear maximum in  $\rho$  for either compound, we have chosen initial scaling temperatures  $T_0$  (near the inflection point) of 50 K and 75 K for  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CeFe}_4\text{Sb}_{12}$ , respectively.



**Figure 3.** (a) Scaled resistivity  $\rho(T)/\rho(300\text{ K})$  versus  $T/T_0$  for  $\text{YbFe}_4\text{Sb}_{12}$ , where  $T_0$  is the scaling temperature. Inset: the pressure dependence of  $T_0$  showing a slight decrease of  $T_0$  with pressure. The line is a guide to the eye. (b) Scaled resistivity of  $\text{CeFe}_4\text{Sb}_{12}$   $(\rho(T) - \rho_0)/B(\rho_{300} - \rho_0)$  versus  $T/T_0$ , where  $\rho_0$  is the resistivity at the lowest measured temperature,  $\rho_{300}$  is the room temperature value of the resistivity, and  $B$  is a constant. Inset: the pressure dependence of  $T_0$  showing an increase of  $T_0$  with pressure. The line is a fit to the data.

Figure 3(a) shows the scaling of the  $\rho(T)$  curves at various pressures for  $\text{YbFe}_4\text{Sb}_{12}$ , and the inset of figure 3(a) shows the pressure dependence of the scaling temperature  $T_0$ . The scaling temperature  $T_0$  appears to decrease slightly with pressure. The solid line is a guide to the eye and the error of  $\pm 0.5\text{ K}$  was estimated from the value of  $T_0$  at which the higher-pressure curves no longer scale with the ambient pressure data. The  $\rho(T)$  curves at various pressures for  $\text{CeFe}_4\text{Sb}_{12}$  also scale with a single  $T_0$ , at least at temperatures above  $\sim 75\text{ K}$ . The pressure dependence of  $T_0$  for this compound is shown in the inset of figure 3(b) along with a fit to the data showing that  $T_0$  increases linearly at a rate of  $1.0\text{ K kbar}^{-1}$ .

We can understand these results for  $\text{CeFe}_4\text{Sb}_{12}$  if we assume that the scaling temperature  $T_0$  is proportional to the Kondo temperature  $T_K$  associated with the f-electron/conduction-electron interaction. Cerium is nominally trivalent in  $\text{CeFe}_4\text{Sb}_{12}$  at ambient pressure as indicated by lattice parameter and magnetic susceptibility measurements [14, 15]. Since a higher valence state  $f^0$  ( $\text{Ce}^{4+}$ ) is preferred under the application of pressure, the  $f^1$  state ( $\text{Ce}^{3+}$ ) moves towards the Fermi level. In addition, the f level widens under pressure due to the increased hybridization between the f-electron and the conduction-electron states. Herbst and Wilkins [23] have shown that the  $f^1$  level is stable under applied pressure so it seems likely that an increase in hybridization is the dominant change in the electronic structure under applied pressure. We emphasize that a change in the occupation of the f level and an increase in hybridization with pressure are possible but our resistivity measurements are unable to determine the dominant mechanism. In any case, both of these effects increase the magnitude of the conduction-electron/f-electron exchange interaction parameter  $\mathcal{J}$  and hence  $T_K$ , which is given by the formula

$$k_B T_K \sim E_F e^{-1/N(E_F)\mathcal{J}}$$

where  $N(E_F)$  is the density of states at the Fermi level  $E_F$ . The exchange interaction parameter is given by

$$\mathcal{J} = -\langle V_{kf}^2 \rangle / |E_F - E_f|$$

where  $V_{kf}$  is the matrix element that admixes f-electron and conduction-electron states and  $E_f$  is the energy of the f level. As  $\text{YbFe}_4\text{Sb}_{12}$  is in the mixed-valence regime, a somewhat different approach is in order. The Yb  $f^{13}$  ( $\text{Yb}^{3+}$ ) configuration is preferred under applied pressure causing the system to become more magnetic. If we view the scaling temperature  $T_0$  as a crossover temperature from non-magnetic (below  $T_0$ ) to magnetic behaviour (above  $T_0$ ), then  $T_0$  should decrease with applied pressure. The small pressure dependence of  $T_0$  in  $\text{YbFe}_4\text{Sb}_{12}$  may indicate that there is only a small change in the occupation of the f level with pressure. The increase of  $\rho$  with pressure at room temperature in  $\text{CeFe}_4\text{Sb}_{12}$  is probably caused by an increase in Kondo scattering as a result of  $T_K$  increasing with pressure. The opposite behaviour observed for  $\text{YbFe}_4\text{Sb}_{12}$  can be explained using a similar argument. Although we cannot rule out the possibility of sample and/or contact deformation contributing to changes in  $\rho$  with pressure, the changes in the electronic structure are expected to be the dominant effect.

As seen in figures 1 and 2, the residual resistivity  $\rho_0$  decreases in  $\text{CeFe}_4\text{Sb}_{12}$  and increases in  $\text{YbFe}_4\text{Sb}_{12}$  with pressure. A possible explanation in the case of  $\text{CeFe}_4\text{Sb}_{12}$ , in which pressure causes large changes in  $\rho_0$ , might be the existence of ‘Kondo holes’; i.e., lattice distortions, vacancies, or otherwise uncompensated Ce ions which disorder the Ce sublattice and lead to a large residual and pressure-dependent resistivity at  $T = 0$ . This argument was used to explain the resulting Kondo-like resistivity when  $\rho$  for  $\text{La}_{0.03}\text{Ce}_{0.97}\text{Pd}_3$  was subtracted from that for pure  $\text{CePd}_3$  [21] (although this matter is still under debate [24]) and also that of  $\text{U}_{1-x}\text{Th}_x\text{Ru}_2\text{Si}_2$  [25]. The Kondo hole model is appealing for  $\text{CeFe}_4\text{Sb}_{12}$  because  $\rho_0$  is large ( $\sim 450 \mu\Omega \text{ cm}$ ) and there also appears to be a resistivity minimum at  $\sim 30 \text{ K}$ . An alternative explanation for the change of  $\rho_0$  with pressure, mainly based on empirical evidence for compounds such as  $\text{CeAl}_2$  and  $\text{CeCu}_6$  [4, 26], is that  $\rho_0$  is inversely proportional to  $T_0$ . This result agrees reasonably well both in sign and magnitude with those for the two Ce and Yb filled skutterudites discussed here.

The magnetic contribution to the resistivity in Kondo lattice systems has many similar characteristics to that for dilute Kondo systems; in particular,  $d\rho/dT$  is negative in both cases which is caused by an antiferromagnetic coupling of the conduction-electron and impurity spins [27]. However, a distinction between the two systems appears in the resistivity at the

lowest temperatures:  $\rho$  decreases from the unitarity scattering limit at  $T = 0$  as

$$\rho = \rho_0[1 - (T/T_K)^2]$$

but for Kondo lattice systems  $\rho$  increases with temperature as  $\rho = \rho_0 + AT^2$ . The transition from local moment behaviour at higher temperatures to a Fermi liquid ground state at low temperatures is associated with the formation of a resonance (Abrikosov–Suhl resonance) at or near  $E_F$  with a width of order  $T_K$ . Therefore, the Kondo temperature is the relevant energy scale of the system (although the RKKY interaction should not be overlooked [28]). For many systems involving Ce, Yb, and U, the square of the electronic specific heat coefficient  $\gamma$  is proportional to the  $T^2$ -coefficient of the resistivity  $A$  which implies that  $A \propto 1/T_K$  [29]. Further evidence for the relation comes from resistivity measurements under pressure in which the temperature of the maximum in the resistivity,  $T_{\max}$ , or the inflection point,  $T_{\inf}$ , vary as  $A^{-1/2}$ . All three quantities ( $T_{\max}$ ,  $T_{\inf}$ , or  $A$ ) may be used to scale the resistivity curves which implies that they are related to the same energy scale, which in the framework mentioned above is  $T_K$ . The best fits for  $\text{YbFe}_4\text{Sb}_{12}$  were obtained using a power law  $\rho - \rho_0 = AT^n$  from 2 K to 10 K. The ambient pressure resistivity follows a  $T^2$ -behaviour ( $n = 2$ ) from 1.6 K  $\leq T \leq$  6.5 K with  $A = 0.036 \mu\Omega \text{ cm K}^{-2}$ . For the higher-pressure data, a fit to a power law yields an exponent of  $n \simeq 1-1.5$ . Fits to the resistivity at low temperatures for  $\text{CeFe}_4\text{Sb}_{12}$  were not possible because of the minimum in  $\rho$  at  $T \sim 30$  K.

In summary, we have measured the electrical resistivity under applied pressure for two filled skutterudites,  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CeFe}_4\text{Sb}_{12}$ . Both  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CeFe}_4\text{Sb}_{12}$  show a rapid decrease of  $\rho$  at  $\sim 50$  K and  $\sim 100$  K, respectively, which signals the onset of coherence in the rare-earth sublattice. The resistivity curves for both compounds can be collapsed onto the ambient pressure curve with a single temperature  $T_0$ , indicating that a single energy scale is present. For  $\text{CeFe}_4\text{Sb}_{12}$ ,  $T_0$  is found to increase with pressure, while for  $\text{YbFe}_4\text{Sb}_{12}$ ,  $T_0$  appears to decrease with pressure. Our results presented here for  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{CeFe}_4\text{Sb}_{12}$  are consistent with the behaviour of a number of other intermediate-valence and heavy-fermion systems.

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