Transport and magnetic properties of Ce$_z$La$_{1-z}$Fe$_4$Sb$_{12}$

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Abstract
Transport and magnetic properties of $Ce_zLa_{1-z}Fe_4Sb_{12}$ have been investigated
in the whole range of substitution $0 < z < 1$. The cerium contribution ρ_{Ce} to
the resistivity goes through a maximum at temperature $\simeq 140$ K, close to the
spin fluctuation temperature T_{sf} for $CeFe_4Sb_{12}$. T_{sf} is the single magnetic energy
scale which accounts for the magnetic properties of the Ce Kondo lattice. At low
temperature, the resistivity shows a T^2-deviation from saturation. At $z \leqslant 0.7$
this is the behaviour expected for Ce impurities in metals in the Kondo limit. At
$z = 1$, however, Hall effect measurements show that this behaviour is due to a
decrease of the free carrier concentration which we can attribute to the formation
of a hybridization pseudogap $E_g \simeq 25$ meV. Upon dilution of the cerium, E_g
decreases and this pseudogap is smeared out, replaced by the Kondo resonance
at the Fermi level characteristic of Kondo impurities in the small z limit.

1. Introduction

During recent years, filled skutterudites have attracted considerable attention for their potential
application as thermoelements and their outstanding properties (for a review, see [1]). Their
generic formula is RM_4X_{12}, with M a transition element, R a rare earth, and X = P, As,
or Sb. The case M = Fe is of particular interest because the Fe-based skutterudites are
strongly correlated fermion systems, and show a very broad variety of outstanding behaviours.
Depending on X, some of them show all kinds of magnetic ordering, others show no magnetic
order at all; some are heavy fermion systems, others are not. A non-exhaustive list of such
Fe-based skutterudites exemplifying these different behaviours can be found in [2]. In this
earlier work, we reported the transport, magnetic and thermodynamic properties of $LaFe_4Sb_{12}$.
Since La is non-magnetic, this is the key material to which one has to refer to determine the

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properties of Fe in other Fe-based skutterudites when R is trivalent [3]. We have determined that $LaFe_4Sb_{12}$ is a non-Fermi liquid system close to a ferromagnetic quantum critical point, with a spin fluctuation temperature $T_{sf} = 50 \pm 15$ K.

Strong efficiency as thermoelectric generator requires small thermal conductivity κ. A value of κ as small as a few mW cm^{-1} K^{-1} has been recorded for $CeFe_4Sb_{12}$, close to the theoretical smallest thermal conductivity reached when the mean free path of the phonons is equal to their wavelength [4, 5]. This feature focused attention on this compound, which is a Kondo lattice system that does not order magnetically [7, 6]. In a prior work, we have investigated magnetic properties of the cerium in this compound [8]. This study allowed us to make a quantitative analysis of the Kondo lattice behaviour issued from the array of the magnetic cerium ions that are trivalent in this compound. As discussed in this work, the spin fluctuation temperature in such Kondo systems strongly depends on its definition. We have defined T_{sf} from the scaling relation $T_{sf} \simeq T_\chi^{max} \simeq \theta \simeq C/2\chi_{Ce}(0)$ where T_χ^{max} is the temperature at which the magnetic susceptibility $\chi_{Ce}(T)$ of the Ce^{3+} spin array goes through a maximum, θ the paramagnetic Curie temperature and C the Curie constant deduced from the Curie–Weiss law for $\chi_{Ce}(T)$ at high temperature. This scaling relation, first evidenced for other trivalent or nearly trivalent cerium intermetallic materials [9], is well verified in $CeFe_4Sb_{12}$ too, from which it is possible to define a temperature T_{sf} corresponding to a single magnetic energy scale. For $CeFe_4Sb_{12}$, this temperature is $T_{sf} = 120$ K [8]. However, we also pointed out in this prior work that some other physical properties such as transport properties might be sensitive to another energy scale, namely the crystal-field splitting energy Δ, that, in a cubic field environment, splits the ground multiplet $j = 5/2$ of the Ce^{3+} electron states into a doublet Γ_7 and a quartet Γ_8. The first aim of this paper is thus to complete the investigation of the transport properties of $CeFe_4Sb_{12}$ initiated in [6, 10, 11].

$Ce_zLa_{1-z}Fe_4Sb_{12}$ has been prepared in the whole range of composition $0 < z < 1$. Since La is also trivalent and non-magnetic, we can expect that the only significant effect of the substitution of Ce by La is the dilution of the magnetic lattice. Therefore, the physical properties of Ce-diluted samples ($z \ll 1$) will match those of isolated magnetic impurities in a metallic host, while the Ce-rich samples will realize a Kondo lattice system. The investigation of the physical properties of the solid solution as a function of z is thus desirable to study the transition from the Kondo lattice behaviour to the single Kondo impurity behaviour. This is the second purpose of this work.

The physics of a magnetic impurity in a metal has been known for many years. In particular, the nature of the ground state is understood through the renormalization group [12] and the Fermi liquid theory of the Kondo fixed point [13, 14]. Nevertheless, the resistivity of different metals embedding trivalent Ce impurities does not follow the temperature dependence expected for a Fermi liquid at low temperature [15]. Therefore, the investigation of transport properties of $Ce_zLa_{1-z}Fe_4Sb_{12}$ may be of interest even in the dilute limit to clarify this situation. At contrast with the Kondo impurity limit case, the theoretical situation regarding the ground state of dense Kondo lattices is as yet unclear. In strongly correlated Kondo systems where localized 4f electrons hybridize with conduction bands, a hybridization gap should form at low temperature. However, some materials like $Ce_3Pt_3Bi_4$ show up a true gap formation below the coherence temperature (in which case they are called Kondo insulators or Kondo semiconductors) [16, 17], while others show a coherent Kondo-lattice behaviour as in $CeAl_3$, with an electric resistivity [18, 19], magnetic susceptibility [18], and specific heat [19] characteristics of a Fermi liquid. In between these extreme cases, the formation of pseudogaps rather than true gaps is also met in rare-earth compounds [20].

An intensive study of filled skutterudites is currently under progress aiming at the understanding of the gap formation, since it has been recognized that some of them, like

Table 1. Initial composition z of the Ce$_z$La$_{1-z}$Fe$_4$Sb$_{12}$ samples investigated. The last column is the hole concentration p, deduced from the Hall coefficient at room temperature. Note that in the case $z \geqslant 0.9$ the amount of La in the sample is too small to allow for a quantitative estimate of its concentration in the final composition.

Initial composition z	Final composition	Lattice parameter (Å)	Hole concentration (formula unit)
1	Ce$_{0.96}$Fe$_4$Sb$_{12}$	9.132(3)	1.64
0.95	Ce$_{0.92}$La$_?$Fe$_4$Sb$_{12.27}$	9.134(2)	1.44
0.9	Ce$_{0.8}$La$_?$Fe$_4$Sb$_{12}$	9.137(3)	1.45
0.8	Ce$_{0.72}$La$_{0.16}$Fe$_4$Sb$_{11.8}$	9.140(2)	
0.7	Ce$_{0.62}$La$_{0.22}$Fe$_4$Sb$_{12.06}$	9.142(3)	1.65
0.5	Ce$_{0.43}$La$_{0.32}$Fe$_4$Sb$_{12.06}$	9.142(2)	1.8
0.25	Ce$_{0.17}$La$_{0.6}$Fe$_4$Sb$_{12.06}$	9.142(2)	1.9
0	La$_{0.95}$Fe$_4$Sb$_{12.14}$	9.142(2)	

CeOs$_4$Sb$_{12}$ [21], can be considered as Kondo semiconductors, while others, like CeRu$_4$Sb$_{12}$, show a pseudogap behaviour [22, 23]. The present study of Ce$_z$La$_{1-z}$Fe$_4$Sb$_{12}$ is part of this effort. The transport properties have been investigated as a function of the temperature in the range $1 < T < 300$ K, and as a function of the magnetic field H up to $H = 6$ T. In CeFe$_4$Sb$_{12}$, the variation of the Hall effect reveals the existence of a hybridization of a pseudogap. The resulting diminution of the free carrier concentration dominates the behaviour of the resistivity at low temperature. The coherent state and the corresponding pseudogap are destroyed upon dilution of the Ce lattice, so that at $z \leqslant 0.7$ this dilution process gives rise to a Kondo impurity behaviour and the onset of a Kondo resonance at the Fermi energy. The disruption of the Ce lattice coherence by alloying eliminating the pseudogap has also been observed in other Ce compounds (CeRhSb, CeNiSn and their alloys) [24], although Ce is in a mixed valence state in this case, while it is trivalent in Ce$_z$La$_{1-z}$Fe$_4$Sb$_{12}$.

2. Experimental details

The samples have been prepared by direct reaction between the elements in carbon-coated silica tubes under vacuum at 1050 °C during 48 h. After water quenching, the samples have been annealed at 700 °C for four days [25].

The structural analysis has been achieved by scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), and x-ray powder diffraction (XRD) experiments. The samples contain inclusions of Ce$_x$La$_{1-x}$Sb$_2$ and FeSb$_2$ revealed by SEM and EDX, but below the threshold of detection of XRD. The total amount of these secondary phases is of the order of 0.1% for the ternary compounds ($z = 0$, 1) and for the compounds $z > 0.8$. However, it is of the order of 1% for the compounds $0.25 < z < 0.8$, which illustrates the difficulty we met in preparing samples of good quality in this range of compositions.

All the samples are crystallized in the LaFe$_4$P$_{12}$ cubic structure of the filled skutterudites. The lattice parameter of the $z = 0$ sample (9.142 ± 0.002 Å) is consistent with the value reported by different authors [26–28] but significantly smaller than the value 9.1486 Å reported by Bauer *et al* [29]. The lattice parameter decreases only very slowly with z, ranging from 9.136 Å at $z = 1$ to 9.142 Å for $z = 0$ (see table 1). This is only a 0.07% variation that can be neglected, and this is consistent with the idea mentioned in the introduction that the only sizable effect of the substitution of Ce by La is the dilution of the Ce magnetic lattice. We can attribute this effect to the property that, among binary skutterudites of generic formula MX$_3$, those with

X = Sb have the large empty space at the 2(a) rare earth sites, so that the cage which embeds the rare earth ion (either Ce or La) in our samples is oversized. Therefore, the substitution of Ce by La does not affect the Fe_4Sb_{12} skeleton of the cage. This feature is known to be responsible for a rattling motion of the rare earth ions inside their cages at the origin of the small thermal conductivity and the potential use of these materials for thermoelectric applications recalled in the introduction. In the context of the present work, this feature is important because it implies that the La–Ce substitution does not alter the hybridization of s, p, and d electron states of Fe and Sb. This is a prerequisite to make sure that any change in the physical properties with z is solely attributable to the dilution of the Kondo cerium lattice.

As usual in filled skutterudites [30, 31], the rare earth site of the lattice is not entirely filled. One consequence is that the formula $Ce_zLa_{1-z}Fe_4Sb_{12}$ refers to the nominal composition, as expected from the relative amount of the different elements placed in the silica tube before the synthesis of the samples. The filling factor being lower than unity, the actual final composition determined by the structural analysis is different and it is reported in table 1. For simplicity in the notations, the samples are identified in the text and the figures as well by the value of z referring to the initial composition, but the reader should keep in mind that the actual composition is the corresponding one given in table 1. As a function of z, the filling factor goes through a minimum of about 0.75–0.8 for $0.25 < z < 0.8$. This is again evidence of the difficulty of growing samples of good quality in this range of compositions, already mentioned earlier in the text. As we shall see, this feature prevents us from any quantitative analysis of the magnetic properties.

The electronic transport properties under an applied magnetic field ranging from 0 to 7 T have been measured by the four probe Van der Pauw method, using dc current to measure the resistivity, and ac current at frequency 15 Hz to measure the Hall voltage. Ohmic contacts have been obtained with silver paste. The magnetic susceptibility measurements have been performed in field $H = 0.5$ T from 2 to 300 K, after cooling in zero field.

3. Magnetic properties

Both Fe and Ce contribute to the magnetic properties of these materials. An overall understanding of the magnetic properties of the cerium contribution to the magnetic susceptibility χ_{Ce} has been achieved in $CeFe_4Sb_{12}$ [8]. In this earlier work, χ_{Ce} has been estimated by the difference between the magnetic susceptibility of the material under investigation and the magnetic susceptibility of $LaFe_4Sb_{12}$. The extension to the present study can be written with obvious notations:

$$\chi_{Ce} = \chi(Ce_zLa_{1-z}Fe_4Sb_{12}) - \chi(LaFe_4Sb_{12}). \tag{1}$$

In magnetic measurements attention must be paid to avoid the contribution of extrinsic effects. An extreme case is met when ferromagnetic clusters give a significant contribution to the magnetization. This contribution saturates easily in the applied magnetic field, with the consequence that the magnetization is not linear in H in low magnetic fields. Such a situation has been met in a recent past in other skutterudite samples, where the presence of such ferromagnetic clusters has been detected even at room temperature [32]. It requires, however, the presence of ferromagnetic clusters with Curie temperature T_c exceeding the room temperature, which suggests either the formation of Fe-clusters, or more probably a pollution by oxygen to generate clusters of ferrite or maghemite. We have ourselves met this situation in other Fe-based compounds [33]. Fortunately, we do not have such inclusions here, either in the samples currently studied, or in the skutterudite samples we have studied in prior works [2, 8], and the magnetization is linear in H up to 4 T at $T > 50$ K. This is illustrated as an example
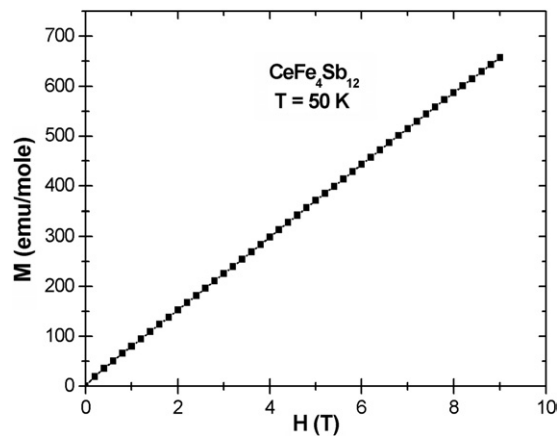
Figure 1. Magnetization as a function of the magnetic field measured at temperature $T = 50$ K in $CeFe_4Sb_{12}$. Symbols are experimental data; the full line is the linear fit.
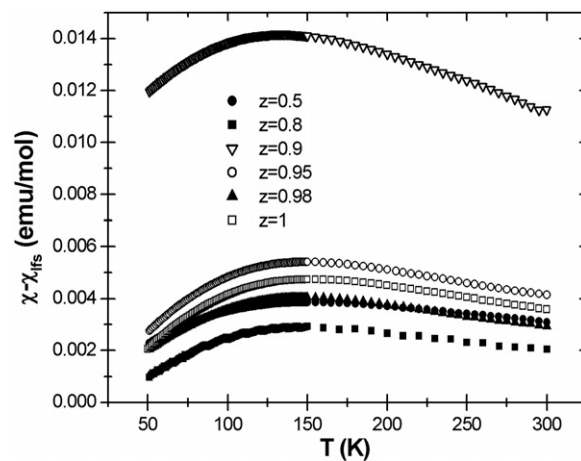
Figure 2. Temperature dependence of the Ce contribution to the magnetic susceptibility defined as the magnetic susceptibility of $Ce_zLa_{1-z}Fe_4Sb_{12}$ minus that of $LaFe_4Sb_{12}$.

in figure 1 at $T = 50$ K for the case $z = 1$. This result is not surprising when we consider the nature of the inclusions in our samples, since the formation of ferromagnetic clusters in our samples is only expected from $CeSb_2$ inclusions for which $T_c = 15$ K only [34]. We have already mentioned in a former work that such inclusions have a non-negligible effect on the magnetic susceptibility up to $T = 25$ K [11]. Above this temperature, the main extrinsic effect on the magnetic properties in our samples comes from isolated paramagnetic impurities. The way they affect the magnetization of the samples is more subtle: they do not alter the linearity of $M(H)$. However, their contribution to the magnetic susceptibility satisfies a Curie law and thus increases upon cooling. In practice, the contribution to these impurities becomes non-negligible below 50 K in our samples. For this reason, the results are reported in figure 2 at $T > 50$ K where such impurity effects are negligible, so that the second member in equation (1) reduces to χ_{Ce}.

The quantitative analysis of the magnetic susceptibility in figure 2 is difficult if not impossible as a consequence of the trend towards structural defects for compositions $0.25 < z < 0.8$ mentioned earlier, including the degradation of the filling factor for the rare earth site. Since the rare earth is in a trivalent state, and thus carries an important electronic charge, the variation of the filling factor will affect the free carrier concentration and the Fermi energy. Since Fe is close to a ferromagnetic instability, the Fe contribution in these materials is a Pauli contribution enhanced by a Stoner factor which strongly depends on the free carrier density at the Fermi energy, and thus on the Fermi energy itself. Therefore, equation (1) is not justified since the $z \neq 0$ samples do not have the same filling factor as the $LaFe_4Sb_{12}$. In addition, since the filling factor is not the same for samples with different z, the error on χ_{Ce} may be not only significant, but also different for different z, so that it becomes difficult to investigate the dependence of χ_{Ce} defined in equation (1) as a function of z. This difficulty might be the reason for a rather erratic variation of χ_{Ce} at a given temperature as a function of z evidenced in figure 2.

For these reasons, we shall focus attention on the features in figure 2 which actually do not depend on z, and are thus characteristics of the material, irrespective of z, of the filling factor, and structural defects. One trivial result is that the materials do not order magnetically. This is not a surprise since both $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ are known to remain paramagnetic down to the lowest temperature $T = 1$ K investigated. A much less trivial result is that χ_{Ce} goes through a maximum at a temperature T_χ^{max} which is of the order of 140 K for all the samples, at least for $z > 0.25$. The results for $z = 0.25$ (not shown in figure 2) suggest that the maximum in χ_{Ce} is smeared out, but the accuracy with which χ_{Ce} is determined from equation (1) is poor because the difference between the two quantities in the second member of equation (1) is too small at such small concentrations of Ce, so that no definitive conclusion can be drawn for $z \leqslant 0.25$. However, the existence of T_χ^{max} at $z > 0.25$ can be considered as reliable. For $CeFe_4Sb_{12}$, this result is not new [8], and has been attributed to the spin fluctuation temperature $T_{sf} \simeq T_\chi^{max}$. We can understand the relative independence of T_χ^{max} within the model of [8]. The spin fluctuation temperature T_{sf} separates two regimes. At $T \gg T_{sf}$ the Ce spin is free to fluctuate, as it is driven by the thermal fluctuations, while at $T \ll T_{sf}$ the Ce spin is locked by the antiferromagnetic coupling with the free electrons into a singlet non-magnetic state. This is true for a Kondo lattice such as $CeFe_4Sb_{12}$ when the magnetic interactions between Ce ions are small, so that the Kondo effect, which favours the formation of a singlet ground state, prevents any magnetic ordering. This is also true for the Kondo effect on a single Ce 'impurity'. In both cases T_{sf} separates the ranges of high temperatures where the Ce^{3+} ions act as localized spins $j = 5/2$, from the low temperature regime where the singlet state is formed. The nature of the singlet ground state is not the same, and we shall see that it has consequences on the transport properties, but no significant variation of T_χ^{max} is expected with z when switching from a periodic Ce lattice ($z = 1$) to the case of Ce impurity ($z \ll 1$), if the strength of the antiferromagnetic interaction between the Ce spins and the free carriers does not depend on z, a reasonable hypothesis since the lattice parameter does not depend significantly on z. The dilution of Ce in the lattice has then little effect on the magnetic properties. The investigation of transport properties will turn out to be a much more sensitive tool to distinguish between coherent state and impurity Kondo behaviours in these materials.

4. Transport properties

The temperature dependence of the resistivity $\rho(T)$ for the different samples is reported in figure 3. For the particular case $z = 1$, the resistivity curve just corroborates former results [6]. None of the samples shows the large drop of resistivity upon cooling below 15 K sometimes
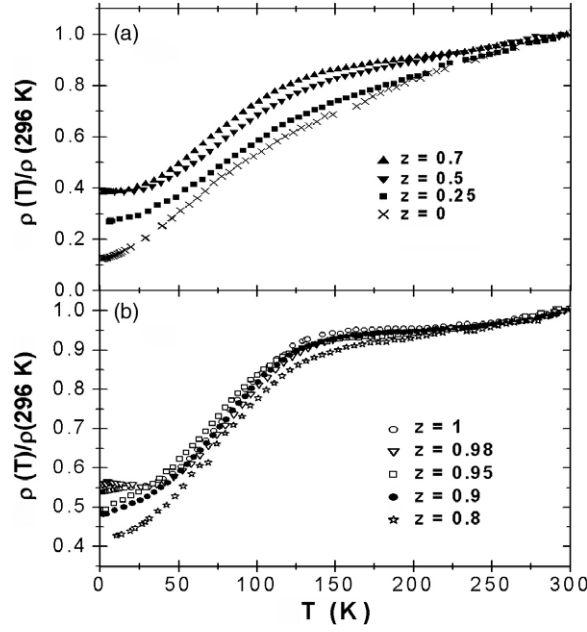
Figure 3. Temperature dependence of the electric resistivity of $Ce_zLa_{1-z}Fe_4Sb_{12}$.

observed in $CeFe_4Sb_{12}$ [30, 35]. The attribution of such a drop, when it exists, to the presence of secondary phases [6] is sustained by the strong drop of the resistivity of $CeSb_{12}$ upon cooling below 15 K [36]. The absence of this drop, together with the fact that the residual resistivity in our $z = 1$ sample is about three times smaller than in these prior works, give evidence of the good quality of our material.

To go further in the analysis, we extract the Ce contribution to the resistivity, ρ_{Ce}, by subtracting the resistivity of the $LaFe_4Sb_{12}$ from the data in figure 3. This is a very common procedure used in trivalent cerium compounds in general, including the case $CeFe_4Sb_{12}$ [4]. Usually, the validity of such a procedure is taken for granted. It may be of interest, however, to discuss this procedure for the $z \neq 1$, since the equivalent procedure for the magnetic experiments turned out to be questionable. Let us start from the Matthiessen rule, according to which the resistivity is the addition of several contributions:

$$\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_{Fe}(T) + \rho_{Ce}(T). \tag{2}$$

The first term is the residual resistivity, the second term is the contribution from the scattering of the free carriers by phonons, the third term is the contribution from the diffusion of the free carriers by the spin fluctuations associated with iron, which we have investigated in [2], and the last term is the contribution from the diffusion of the free carriers by the cerium spin fluctuations. First, we can question the Matthiessen rule itself. The reason is that the resistivity is a substantial fraction of the maximum value obtained when the mean free path of the free carriers is of the order of the lattice parameter (roughly the Ioffe–Regel limit). In this limit, the Matthiessen rule breaks down [37]. Note, however, that even if the addition of the three first terms is not justified if the Matthiessen rule is broken, these terms can still be concatenated to build the resistivity $\rho_{z=0}(T)$ of the $z = 0$ sample.

Yet the addition rule of the last term in equation (2) requires independence between magnetic fluctuations of Ce and Fe. With iron, one has to deal with itinerant magnetism, which
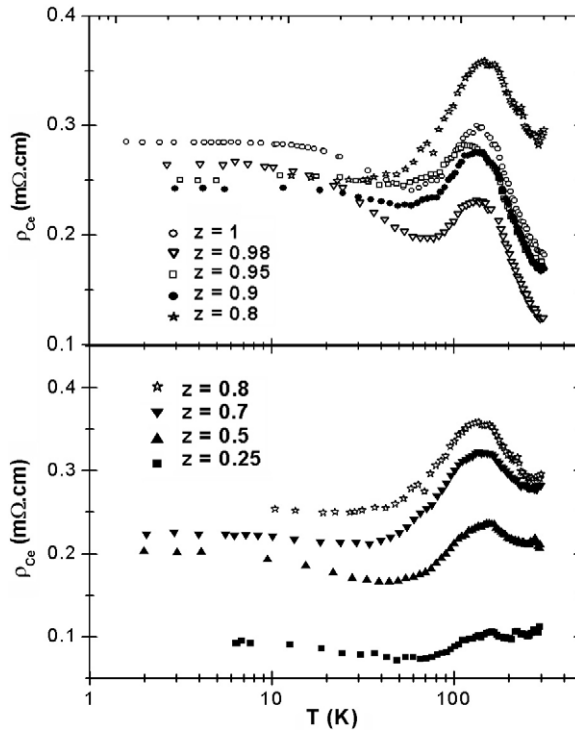
Figure 4. Temperature dependence of the Ce contribution to the electric resistivity, defined as the resistivity of $Ce_zLa_{1-z}Fe_4Sb_{12}$ minus that of $LaFe_4Sb_{12}$.

means that $\rho_{Fe}(T)$ is an interaction between the spins carried by the free carriers themselves. On the other hand, $\rho_{Ce}(T)$ results from an interaction between the spins carried by the free carriers and the quasi-localized spins carried by Ce^{3+} ions. Since the material is non-magnetic, the strong Kondo interaction screens the localized Ce spins to the point that the material cannot order at any temperature, which also means that we have a negligible indirect interaction between the Ce spins mediated via the free carriers (such as an RKKY type of interaction for instance). We can then assume that the simple addition of the last term to the other ones in equation (2) is also justified.

The problem with equation (2) does not come from the addition rule, but from a hidden dependence of the three first terms of equation (2) with z, while their addition is supposed to form the resistivity of $LaFe_4Sb_{12}$. ρ_{ph} should not be sensitive to the substitution La–Ce, especially as the lattice parameter does not depend on z. However, a change in the filling factor on the rare earth site means a change in the free carrier concentration and the filling of the Fe d band. Since the filling factor depends on z, so will ρ_{Fe} and ρ_0. The change $\delta\rho_0$ in ρ_0 is of no importance since it is just a constant, and it can be taken into account by writing equation (2) in the form

$$\rho_{Ce}(T) = \delta\rho_0 + \rho(T) - \rho_{z=0}(T). \tag{3}$$

However, any change in $\rho_{Fe}(T)$ will affect the temperature dependence of the resistivity, resulting in a violation of equation (3). This difficulty will prevent any quantitative analysis and reliable fit of $\rho_{Ce}(T)$.

Nevertheless, the plot of $\rho_{Ce}(T)$ as defined in equation (3) and reported in figure 4 is still quite instructive, because it shows some outstanding properties which are common to all the

samples (i.e. for different values of z irrespective of the filling factor), so that they are robust. In particular, ρ_{Ce} goes through a maximum at a temperature $T_\rho^{max} \simeq 120$ K. There are two possible interpretations for this maximum, depending on the magnitude of the Kondo temperature T_K with respect to the splitting energy Δ of the Ce 4f level under the effect of the crystalline electric field (CEF) Δ. If $\Delta \ll T_K$, such as in CePd$_3$, T_ρ^{max} ($\simeq 100$ K in CePd$_3$) corresponds to roughly the same temperature T_{sf} [38] at which the magnetic susceptibility also goes through a maximum. Since we find $T_\rho^{max} \simeq T_\chi^{max}$, this is indeed one possible interpretation in our case. For larger Δ, then the maximum in $\rho_{Ce}(T)$ results from the influence of the crystal field on the Kondo effect of alloys and compounds with cerium, modelled in [39]. This model accounts quantitatively for $\rho_{Ce}(T)$ in different compounds where cerium is trivalent, including CeAl$_3$, which is the archetype of a Kondo lattice system that, like the present material, does not order magnetically at low temperature [40]. In the framework of the model in [39] applied to this case, the resistivity goes through a maximum at a temperature which is smaller than Δ (in k_B units). A first estimation $\Delta = 130$ K had been proposed from the position of the inelastic peak in the spectrum of the neutron scattering intensity against energy transfer in CeFe$_4$Sb$_{12}$ [41]. This hypothesis, however, has been ruled out by more accurate neutron experiments [42]. Moreover, we have argued that the magnetic properties are not very sensitive to this parameter, so that the value of Δ cannot be inferred from their investigation [8]. This parameter is thus unknown. Transport properties are expected to be more sensitive than magnetic properties to the crystalline field splitting, since it is responsible for an inflection point in the resistivity curve $\rho_{Ce}(T)$ that has been well observed in some cerium compounds where the Kondo effects are negligible, such as CeTe and CeSb [43, 44]. Indeed, there is an inflection point in the resistivity curve $\rho_{Ce}(T)$ at $T_{inf} \sim 100$ K, in agreement with prior data [10]. According to the relation $k_B T_{inf} = 0.312\Delta$ [44], we find $\Delta = 320$ K. On the other hand, in Kondo systems, the existence of T_{inf} is usually not directly related to crystalline field effects as it may be due to the formation of the singlet ground state. Therefore, the estimation of $\Delta = 320$ K is doubtful. Moreover, even if this value was reliable, we would not take for granted the assumption that the maximum in $\rho_{Ce}(T)$ is an illustration of the model [39]. The reason is that T_ρ^{max} depends not only on Δ, but also on other parameters (position of the f levels with respect to the Fermi energy, cut-off temperature), which induces a dispersion of the ratio Δ / T_ρ^{max} in the range 1.5–3 according to this model [45]. Then, the value $\Delta = 320$ K would simply be compatible with the expectation value of T_ρ^{max}. We shall leave open the question of whether the maximum in $\rho_{Ce}(T)$ is associated with the spin fluctuation temperature or the effect of the crystalline field splitting; however, the fact that $T_\rho^{max} \simeq T_\chi^{max} \simeq T_{sf}$ strongly pleads in favour of the spin fluctuation effect.

Irrespective of the origin of the maximum in the resistivity curve, $\rho_{Ce}(T)$ is expected to have a logarithmic behaviour at $T > T_\rho^{max}$. This is well observed in figure 5 where the temperature has been reported in a log-scale to illustrate this purpose on the $z = 1$ sample.

If we compare the resistivity curves of CeAl$_3$ and CeFe$_4$Sb$_{12}$, we find that, in both cases, the resistivity saturates at low temperature. This is, however, the only similitude. The electrical resistivity decreases upon cooling at low temperatures in CeAl$_3$ according to a law $\rho_{Ce}(T) - \rho_{Ce}(0) \propto \alpha T^2$ with α a positive constant, which corresponds to the Fermi liquid behaviour in a non-magnetic ground state [40, 18, 19]. On the other hand, the resistivity increases upon cooling at low temperature in CeFe$_4$Sb$_{12}$. The resistivity at low temperature can still be described by a T^2 power law, according to

$$\rho_{Ce}(T)/\rho_{Ce}(0) = 1 - \beta T^2, \qquad (z = 1) \tag{4}$$

but with a minus sign if we want β to be positive. This law illustrated in figure 5 is expected in the Kondo impurity limit ($z \ll 1$) [15], but not in the coherent state of a Kondo lattice system.
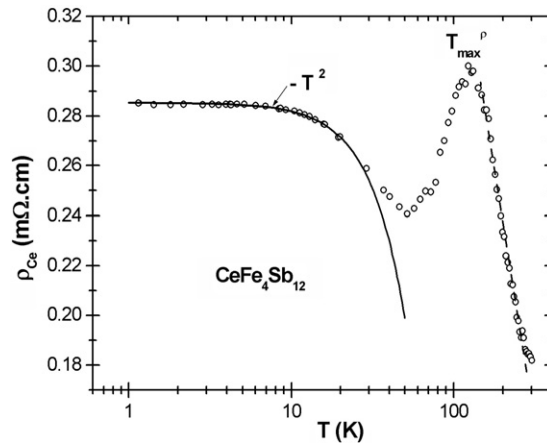
Figure 5. Ce contribution to the electric resistivity defined as in figure 3 for $CeFe_4Sb_{12}$ as a function of temperature in logarithmic scale. The broken lines represent logarithmic behaviour characteristic of the Kondo behaviour at high temperature $T > T_\rho^{max}$. The full line represents the T^2-law according to equation (4) at low temperature.
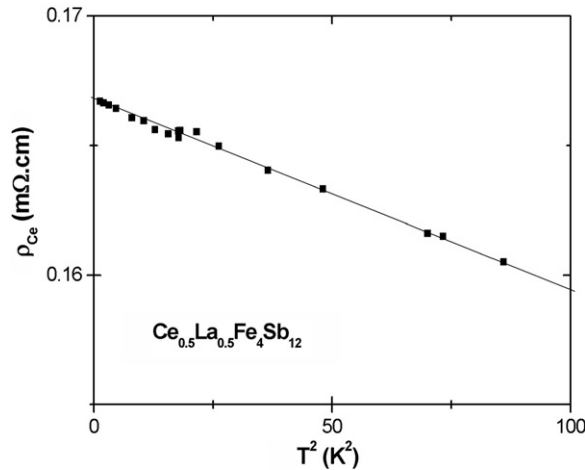
Figure 6. Ce contribution to the electric resistivity of the $z = 0.5$ sample (composition defined in table 1) as a function of T^2 to illustrate the T^2-increase of $\rho_{Ce}(T) - \rho_{Ce}(0)$ upon cooling below 10 K.

The consequence is that equation (4) stands for any z (with a β parameter which, however, depends on z). This is illustrated in figure 6 for $z = 0.5$. In addition, T_ρ^{max} does not depend on z either, which, however, leaves open the two possible interpretations of this temperature. If T_ρ^{max} is associated with the crystalline field splitting energy Δ, this lack of dependence on z results from the fact that the lattice parameter does not depends significantly on z. If T_ρ^{max} has the same meaning as T_χ^{max}, independence on z is also expected and has already been discussed in the section on magnetic properties. This is in essence why the dilution of the Ce^{3+} ions reduces ρ_{Ce} without changing the shape of the $T_\rho^{max}(T)$ curves. The enlightenment of this unexpected result will come from the magneto-transport experiments.
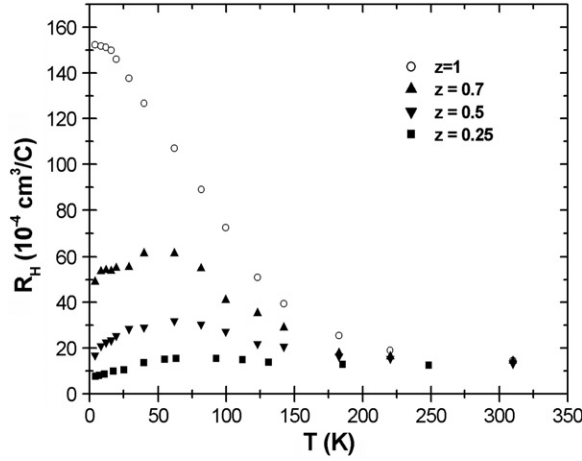
Figure 7. Temperature dependence of the Hall coefficient for $Ce_zLa_{1-z}Fe_4Sb_{12}$ samples with different z.

5. Magneto-transport properties

We found that the Hall resistivity is linear in H for all the compounds with $z \leqslant 0.25$ up to the highest field (7 T) available in the experiments. On one hand, this linearity allows us to define the Hall constant R_H. On the other hand, it implies that there is no significant anomalous contribution to the Hall effect, because the magnetization is far from linear in H in this range of magnetic fields at low temperature, so that any contribution proportional to the magnetization would result in a non linear H-dependence of R_H, at least at low temperature, which is not observed.
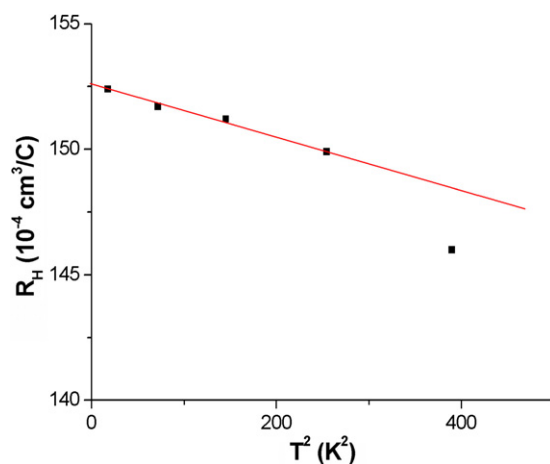
The temperature dependence of R_H for the different samples is reported in figure 7. In contrast with the magnetic properties and the resistivity curves discussed in the previous section, the curves are qualitatively different for the $z = 1$ sample and for $z \leqslant 0.7$ samples. Let us first discuss the case $z = 1$. For this sample, R_H increases by one order of magnitude upon cooling from $T = 300$ K down to 4 K. The free carrier concentration deduced for R_H at 300 K is $p = 1.6$ per formula unit (and this is the unit we use hereafter in this work). Note in a stoichiometric $CeFe_4Sb_{12}$, one would expect $p = 1$. However, the free carrier is always found to be larger in this material, because of a filling factor smaller than one on the rare earth site. The lower value of p with respect to other samples investigated in the past ($p = 4.2$ [46], $p = 2.1$ [30]) is thus an indication that the amount of defects on the cerium lattice (including vacancies) is small. Therefore, we cannot imagine that the defects can destroy the formation of a coherent Kondo state at low temperature to generate a Kondo impurity behaviour of the resistivity according to equation (4) [10]. On the other hand, the increase of R_H upon cooling means a drop of the free carrier concentration, so that $p \sim 0.15$ at $T = 4$ K, which suggests that the material is a semi-metal at low temperature as a result of a hybridization pseudogap. This pseudogap can be estimated from the activation energy E_g evidenced in figure 8 at $T > 100$ K: $E_g = 25$ meV. Since $R_H(T)$ for $z = 1$ saturates at low temperature, its temperature dependence is approximately of the form

$$R_H(T)/R_H(0) = 1 - \gamma T^2 \tag{5}$$

at $T < 10$ K as can be seen in figure 9. The resistivity can be written $\rho_{Ce} = R_H/\mu$, with μ a mobility associated with the scattering of the free carriers by spin fluctuations. In the
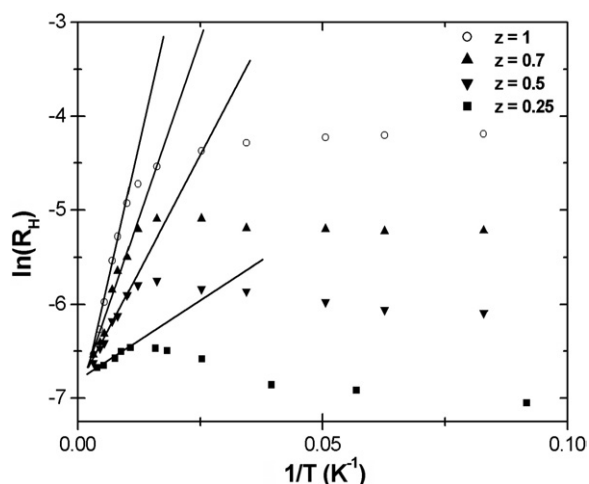
Figure 8. Illustration of the activated regime of the Hall effect above 100 K for $Ce_zLa_{1-z}Fe_4Sb_{12}$ samples with different z.

Figure 9. Illustration of the T^2-dependence of the Hall coefficient for $CeFe_4Sb_{12}$ below 10 K.

(This figure is in colour only in the electronic version)

present case, the variation of ρ_{Ce} with T is dominated by the temperature dependence of $R_H(T)$ according to equation (5), responsible for the overall behaviour of $\rho_{Ce}(T)$ below 10 K according to equation (4). As we shall see below, the situation will be opposite for $z \leqslant 0.7$, since we shall find that the same law in equation (4) is due to the temperature dependence of the mobility in the Ce-diluted samples.

To go further in the discussion for $z = 1$ would require a quantitative analysis of μ which is not possible, due to the accumulation of uncertainties at the different steps of the measurements required to get access to this parameter: measurements of $\rho(T)$ for a $z \neq 0$ sample, measurements of $\rho(T)$ for a $z = 0$ sample, measurements of R_H. In addition there is an unknown error coming from the difference in the filling factor on the rare earth site, as discussed in the previous section. It is then not possible to characterize a power-law in T^n for the increase of μ with T. This is not possible either for the Ce-diluted samples. The frustration,
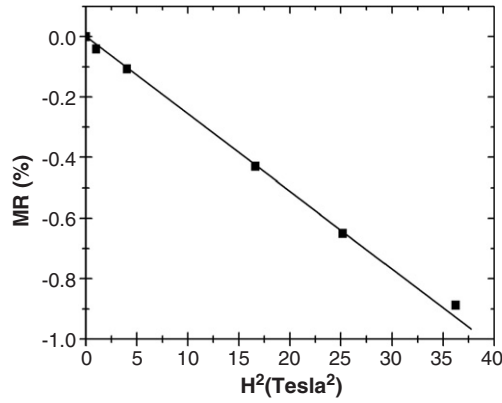
Figure 10. Magnetoresistance at the temperature $T = 4.2$ K as a function of the square of the magnetic field for the $z = 0.5$ sample.

however, is softened by the fact that the result would probably be sample specific, rather than an universal exponent such as $n = 2$ in the Fermi liquid theory when the carrier concentration is a constant. The reason comes from the fact that the formation of the pseudogap should lead not only to a variation of the free carrier concentration, but also of their effective mass [47]. The theories available on the Kondo problem do not allow us to estimate this effect. Moreover, it may depend on the details of the band structure of the material under investigation, hence a loss of universal behaviour.

Let us now turn on the dilute samples. At room temperature, the samples are also metallic, with hole concentrations 1.65, 1.8, and 1.9 for $z = 0.7, 0.5, 0.25$, respectively. Above 100 K, R_H still follows an activated regime, but E_g decreases with z: $E_g = 14, 9.6$, and 3 meV for $z = 0.7, 0.5$, and 0.25, respectively. It means a roughly linear decrease of E_g with z, so that we can extrapolate that E_g should vanish at $z = 0.15$. Therefore, the disorder generated by the substitution of Ce by La on the Kondo lattice fills the pseudogap. The effect is even more dramatic at low temperature, since in all these $z \neq 1$ samples, R_H goes through a maximum at a temperature $\simeq 70$ K, and decreases upon cooling at lower temperature. This decrease can be attributed to the onset of a Kondo resonance in the density of states at the Fermi energy, characteristic of a Kondo impurity behaviour. This variation of R_H should generate a decrease of ρ_{Ce} upon cooling, the opposite to equation (4). However, let us recall that the scattering probability of the free carriers at the Kondo resonance attains its maximum possible value in this case, which in turn explains the saturation of the resistivity as $T \to 0$ for the singlet ground state. This is consistent with the saturation observed in figure 4 for $z \neq 0$. This effect overcomes the increase in the hole concentration upon cooling revealed by the temperature dependence of R_H, so that the behaviour of ρ_{Ce} is now dominated by $\mu(T)$. This is in essence the reason for which equation (4) illustrated in figure 6 for the $z = 0.5$ sample is satisfied, in agreement with theoretical predictions [15]. Although unusual, such an inconsistent temperature dependence between ρ and R_H due to a temperature dependence of the mobility is not unique; it has been observed in CeNiSn [48].

This analysis of ρ_{Ce} for $z \leqslant 0.7$ is also consistent with the study of the magnetoresistance (MR). The MR of the samples has been investigated earlier in the case $z = 1$ [6], and $z = 0$ [2]. In both cases, the MR shows a small and complex temperature dependence with the magnetic field H. In the dilute samples, however, we find that the MR is negative, and varies in H^2 in the whole range of magnetic fields investigated. This behaviour, illustrated for $z = 0.5$ in figure 10,

is the behaviour expected for Kondo impurities [15], so that both the T^2-law for the resistivity illustrated in figure 6, and the H^2 law of the magnetoresistance illustrated in figure 10 is the Kondo impurity behaviour.

6. Concluding remarks

One major difficulty we have met in the study of the magnetic and transport properties of these skutterudites is related to the use of equations (1)–(3) to extract χ_{Ce} and ρ_{Ce}. In Ce compounds where Ce is trivalent, it is commonly accepted that it is sufficient to subtract from the resistivity or magnetic susceptibility of the material the signal measured for the same compound with the rare earth replaced by La to get the so-called magnetic part or χ or ρ. In Fe-based skutterudites, however, the free carriers mainly come from the d band of Fe. Although Fe is non-magnetic in the Hartree–Fock sense, the Fe electrons that are responsible for the transport also carry a spin that contributes significantly to the magnetism, owing to the strong Coulomb e–e correlations. If the filling factor on the rare earth site was simply the same in Ce and the La-substituted samples, and if the structural properties were the same, then equations (1)–(3) should not be more questionable than usual. Unfortunately, two specific features of our materials make this approach more hazardous. First, the filling factor and thus structural properties are not the same for samples with different z. Second, the Fe contribution to the physical properties can depend critically on such structural aspects, because Fe is responsible for a non-Fermi-liquid behaviour in $LaFe_4Sb_{12}$, which realizes a quantum critical point (QCP) system, showing that Fe is on the verge of a ferromagnetic instability [2]. In our opinion, this is the reason for the strong dependence of the transport and magnetic properties on the structural properties in this material. This feature is illustrated by one former attempt to determine $\rho_{Ce}(T)$ in $CeFe_4Sb_{12}$ [4]. Actually, a monotonic increase in $\rho(T)_{Ce}$ upon cooling had been reported (figure 10 in this former work), so that the maximum in the resistivity curve was overlooked by the strong temperature dependence of the background. This artifact takes its origin in the fact that the $LaFe_4Sb_{12}$ sample used in [4] had a residual resistivity about three times larger than in our sample, presumably due to a larger number of defects. Even if we could prepare $LaFe_4Sb_{12}$ with a reduced number of defects, we still may meet similar difficulties for the quaternary samples, although at a smaller scale, since the maximum in ρ_{Ce} could be detected at any z in the range $z > 0.25$. In particular, the QCP is taken as responsible for a huge non-linear dependence of the Hall resistivity on the magnetic field H in $LaFe_4Sb_{12}$. Nevertheless, we have pointed out that the Hall resistivity is linear in H in the $z \neq 0$ samples, which means that the antiferromagnetic coupling between the free carriers and the Ce^{3+} ions might destroy the ferromagnetic instability. On one hand, this linear dependence of the Hall resistivity is good news since it allowed us to determine unambiguously the free carrier concentration. On the other hand, the destruction of the QCP behaviour might affect both the magnetic and transport properties of the free carriers, so that equations (1)–(3) are not fully justified.

For these reasons, we have restricted the analysis of the resistivity and magnetic susceptibility curves to basic features which do not depend significantly on z, and thus do not depend on such details. Yet these basic features are remarkable. χ_{Ce} goes through a maximum at a temperature $T_\chi^{max} \simeq 140$ K, which can be identified as the Ce spin fluctuation temperature T_{sf} and the single characteristic magnetic energy, in reasonable agreement with the result $T_\chi^{max} \simeq 120$ K deduced in the particular case $z = 1$ in [8] from the analysis of $\chi_{Ce}(T)$ curve. It should also be noticed that the scaling law $T_{sf} \simeq T_\chi^{max} \simeq \theta \simeq C/2\chi_{Ce}(0)$ relates low temperature magnetic properties ($\chi_{Ce}(0)$) to magnetic properties measured at room temperature (Curie–Weiss parameters C, θ). If the crystal field excitation Δ was not significantly larger than room temperature, a reduction in the magnetic moment would be observed for $T \ll \Delta$,

altering the relationship between low and high temperature behaviours, i.e. the relationship $\theta \simeq C/2\chi_{Ce}(0)$ should have been violated. This is the reason for the violation of this relationship in $CeAl_3$ [9]. The fact that this relation holds true in $CeFe_4Sb_{12}$ is an additional proof that Δ has been underestimated in the past. It also suggests that the nature of the maximum in the resistivity $\rho_{Ce}(T)$ is not the same as in $CeAl_3$, and takes its origin in the spin fluctuation process rather than in crystal-field effects, although we cannot totally rule out that this crystal field also plays a role. An additional argument which suggests that the crystal field effects are marginal is provided by specific heat measurements. The specific heat in $CeFe_4Sb_{12}$ goes through a maximum at ~ 125 K [11]. This situation is the same as in YbCuAl, where the specific heat goes through a maximum at the same temperature as the susceptibility maximum [49]. This material is also a Kondo system, in which the rare earth is also trivalent [50], just like the cerium in our compounds. The maximum in entropy under the peak of susceptibility in YbCuAl is close to $R \ln 8$ expected for the angular momentum $j = 7/2$ relevant to the Yb^{3+}. Hence the total spin entropy is generated on a scale comparable to T_{sf}, which gives proof that this peak of susceptibility is a measurement of T_{sf}, just like the susceptibility maximum. Nevertheless, the link between the specific heat maximum and T_{sf} had not been made so far in $CeFe_4Sb_{12}$, and indeed such a peak is usually not observed in cerium intermetallics. The reason is that, in Kondo systems where Ce is trivalent, such as $CePd_3$, $CeBe_{13}$, etc, the subtraction of the lattice contribution cannot be performed for two reasons. In these Ce compounds, the maximum in the specific heat occurs at a temperature of the order of the Debye temperature, at which the lattice contribution is large. Moreover, the lattices of these Ce compounds are usually softer than their non-magnetic counterparts, so that the lattice contributions are different. The Ce-based skutterudites are thus one exception where such an effect on the specific heat can be observed, because the oversized cage in which the rare earth is embedded allows for a substitution of Ce by La without changing the lattice properties. As a result the electric resistivity, the magnetic susceptibility, and the specific heat curves go through a maximum at the same temperature T_{sf}, so that the whole set of physical properties is consistently dominated by the spin fluctuation phenomena.

The temperature dependence of the Hall constant is reliable, because its determination does not require its extraction from the comparison between $z = 0$ and $z \neq 0$ samples so that it does not suffer the same criticism as χ_{Ce} or ρ_{Ce}. The saturation of the Hall effect at low temperature suggests that the ground state of our $CeFe_4Sb_{12}$ sample is semi-metallic, with a hole concentration of the order of 0.1 per formula unit. This is one order of magnitude smaller than the hole concentration at room temperature, owing to the formation of the hybridization pseudogap. However, this is also of the order of magnitude of the hole concentration in excess with respect to pure and stoichiometric samples, due to structural defects including a filling factor on the rare earth site smaller than unity, and grain boundaries. It is then possible that the semi-metallic character of our $CeFe_4Sb_{12}$ sample in the low temperature limit is actually an extrinsic property due to these structural defects, which would mask the semiconducting nature of the ground state for the pure and stoichiometric material. These holes in excess might be the 'Kondo holes' mentioned in [6] to explain the low temperature behaviour of the resistivity. The investigation of the Hall effect in the present work shows that the increase of the resistivity upon cooling is the result of the variation of the carrier concentration and not the effect of an increase in the scattering efficiency associated with the Kondo impurity effect suggested in [10], but this does not invalidate the hypothesis of this earlier work that the low transport properties may be dominated by extrinsic effects responsible for the metallic ground state. On the other hand, Sugawara et al [51] have recently suggested that E_g roughly scales with the lattice parameter a in Ce-based skutterudites, those of them with $a < 8.4$ Å having an insulating ground state (mostly phosphorus compounds $CeFe_4P_{12}$, $CeRu_4P_{12}$, $CeOs_4P_{12}$), those

with $a > 8.4$ Å being metallic (antimonide compounds $CeFe_4Sb_{12}$, $CeRu_4Sb_{12}$, $CeOs_4Sb_{12}$). The ground state of $CeOs_4Sb_{12}$ is probably a semiconducting state [51], despite its very large lattice parameter (9.3 Å). The ground state of $CeRu_4Sb_{12}$ is reported to be metallic with a non-Fermi liquid behaviour [21, 52], for a lattice parameter slightly smaller than that of $CeRu_4P_{12}$. $CeFe_4Sb_{12}$ has a smaller lattice parameter $a = 9.14$ Å, which, however, is still larger than 8.4 Å, so that a metallic ground state is still expected. This consideration supports the idea that the metallic behaviour of $CeFe_4Sb_{12}$ should be an intrinsic rather than an extrinsic property. From an experimental point of view, however, the present work does not allow us to decide between these two hypotheses on the nature of the ground state.

On the other hand, the temperature dependence of the Hall effect in the present work shows the formation of a hybridization gap $E_g = 25$ meV in $CeFe_4Sb_{12}$. Irrespective of the nature of the ground state we have just discussed, such a gap has also been revealed by transport properties in $CeOs_4Sb_{12}$ ($E_g \simeq 10$ meV [21]), and in $CeRu_4Sb_{12}$, where a charge gap $E_g = 47.1$ meV [47] has been deduced from the optical conductivity. Therefore, we can conclude that all of the six skutterudite compounds CeM_4X_{12} with M = Fe, Ru, Os and X = P, Sb show the formation of hybridization pseudogaps. We also note that E_g increases in the series CeM_4Sb_{12} in the sequence M = Os, Ru, Fe, while the lattice parameter a decreases, which supports the correlation between E_g and a mentioned above [51].

Incidentally, our results reveal the remarkable similitude between physical properties of $CeFe_4Sb_{12}$ and the other skutterudite $CeRu_4Sb_{12}$. Both compounds form a coherent Kondo lattice state below a spin fluctuation which is about the same ($T_{sf} \sim 100$ K in the latter compound [10], against 120–140 K in the former one). In $CeRu_4Sb_{12}$, a maximum of the Ce contribution to the magnetic susceptibility curve $\chi_{Ce}(T)$, and a maximum of the electric resistivity $\rho_{Ce}(T)$, is observed at roughly the same temperature T_{sf} [52], just as in $CeFe_4Sb_{12}$. In addition, $CeRu_4Sb_{12}$ shows the same activated regime for the Hall coefficient associated with a reduction in the carrier density at low temperature [22], and the same logarithmic temperature dependence of $\rho_{Ce}(T)$ above 100 K [22] as $CeFe_4Sb_{12}$. Even the specific heat has the same basic features, characteristics of a non-Fermi liquid behaviour at low temperature [11, 21]. We would then expect that the cerium would have the same valence in $CeRu_4Sb_{12}$ and in $CeFe_4Sb_{12}$. Surprisingly, however, the former is considered in the literature as a mixed valence system (see for instance [23]), while the cerium is definitely trivalent in $CeFe_4Sb_{12}$ [8], just as in $CeOs_4Sb_{12}$. We were thus led to look in the literature for where this labelling of $CeRu_4Sb_{12}$ as a mixed valence system comes from. Actually, to our knowledge, no XAS experiments have ever been performed on this material. The idea that this system is a mixed valence compound only comes from the fact that the existence of a maximum in the resistivity curve (and thus the fact that the resistivity decreases at low temperature) has been tentatively attributed to a mixed valence effect [52]. It seems that, as time goes on, there has been a semantic shift from what was at the origin a simple hypothesis to what is today a classification of the material among mixed valence compounds, despite the fact that the investigation of the electronic structure did not confirm this hypothesis [53], and despite the fact, extensively discussed in the present work, that this behaviour of the resistivity has a quite different origin. Actually, our results suggest that the cerium in $CeRu_4Sb_{12}$ might be trivalent just as in $CeFe_4Sb_{12}$, and EXAFS experiments on this material are clearly needed to clarify this point.

Finally, the Hall effect measurements show an increase of the free carrier concentration at low temperature in $Ce_zLa_{1-z}Fe_4Sb_{12}$ when $z \leqslant 0.7$. This result suggests the possible formation of a Kondo resonance upon dilution of the Kondo cerium lattice when Ce is substituted by La. The formation of a Kondo resonance has also been suggested recently in another skutterudite: $PrFe_4Sb_{12}$ [54]. In this latter case, this assumption relies on an increase of the high resolution Pr $3d \rightarrow 4f$ resonance photoemission intensity at low temperature. We are eager to see

similar bulk-sensitive photoemission experiments performed on $Ce_zLa_{1-z}Fe_4Sb_{12}$, where such an effect is also expected. Actually, such measurements are also needed as a function of z to investigate both the formation hybridization pseudogap when $z = 1$ and the possible formation of a Kondo resonance upon dilution at smaller z, as a result of the hybridization between the Ce 4f states and the free carrier (hole) electronic states. Indeed, this hybridization is expected to be strong in these Fe-based skutterudites, since the proximity of the quantum critical point in $LaFe_4Sb_{12}$ [2] suggests an important partial density of 3d-Fe states at the Fermi energy.

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