

Thermoelectric properties of Ce(La)Fe₄Sb₁₂ skutterudites under a magnetic fieldRomain Viennois,^{1,2,3,*} Luc Girard,² Didier Ravot,² Silke Paschen,^{3,4} Salam Charar,¹ A. Mauger,⁵ P. Haen,⁶ and J. C. Tedenac²¹GES, CC074, Université Montpellier II, Place Eugène Bataillon, F-34095 Montpellier, France²Institut Gerhardt, Université Montpellier II, Place Eugène Bataillon, F-34095 Montpellier, France³Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, D-01187 Dresden, Germany⁴Institut für Festkörperphysik, Technische Universität Wien, Wiedner Hauptstr. 8-10, A-1040 Wien, Austria⁵IMPMC, Université Paris 6, 140 rue de Lourmel, France, F-75105 Paris⁶Institut Néel, Depto. MCBT, CNRS and Université Joseph Fourier, 25 Avenue des Martyrs, BP 166, F-38042 Grenoble, France

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We show that LaFe₄Sb₁₂ is a ferromagnetic quantum critical point system and that CeFe₄Sb₁₂ is a moderate heavy fermion compound. This is supported by our thermoelectric and thermodynamic experiments under magnetic field on both compounds, and a comparison with other physical properties of these compounds. For LaFe₄Sb₁₂, the quenching of the ferromagnetic spin fluctuations explains both the negative magnetothermopower and the decrease in the electronic heat capacity under magnetic field. We propose that the negative magnetothermopower is a generic property of compounds with ferromagnetic spin fluctuations when the diffusion term by spin fluctuations dominates at low temperature. On the other hand these critical ferromagnetic fluctuations are smeared out in CeFe₄Sb₁₂ due to the antiferromagnetic coupling between the *d* electrons of Fe and the 4*f* electron of Ce. As a result, CeFe₄Sb₁₂ is a moderate heavy fermion compound with Kondo temperature T_K of about 80 K, which is consistent with the fact that cerium is almost trivalent in this material, and the partially screened magnetic moment of the cerium ions at $T \ll T_K$ is $0.3\mu_B$. Finally, in both compounds, the power laws observed at low temperature in the lattice thermal conductivity κ_l could be explained by electron-phonon scattering.

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I. INTRODUCTION

Since one decade, filled skutterudites RM_4X_{12} (where *R* is an actinide, a rare earth, an alkaline earth or an alkaline metal atom; *M*=Fe, Ru, or Os; *X*=P, As, or Sb) have attracted attention due to their promising thermoelectric properties similar to those of the state-of-the-art thermoelectric materials in the temperature range $600 < T < 900$ K. These properties are due to the low thermal conductivity of these compounds, owing to the interaction of heat-carrying phonons with low-energy vibration modes of *R* atoms that are intercalated in oversized Sb₁₂ nanocages.^{1–3} In addition, these materials have interesting ground-state properties.¹ In particular, CeFe₄Sb₁₂ is a moderate heavy fermion compound^{4,5} and a spin pseudogap,⁶ as in CeRu₄Sb₁₂.^{7,8}

The physical properties of CeFe₄Sb₁₂ have been understood taking into account not only the role played by the 4*f* electrons of the Ce³⁺ ions, but also the contribution of the correlated *d* electrons of the iron.⁹ In LaFe₄Sb₁₂, only the Fe *d*-electron contribution remains, which makes this material a heavy fermion system with non-Fermi-liquid (NFL) behavior close to a quantum critical point (QCP), with ferromagnetic spin fluctuations,^{10–12} although antiferromagnetic interactions have also been invoked to account for the *T* dependence of the relaxation time in NMR experiments.¹³

In these prior works, the thermal properties (heat capacity, thermal conductivity, thermopower) of CeFe₄Sb₁₂ and LaFe₄Sb₁₂ have been investigated in absence of magnetic fields (excepted for heat capacity for which also experimental data at 9 T were reported), and it is the purpose of the present work to investigate in details their magnetic field

dependence. To our knowledge, the investigation of the magnetic field dependence of the thermopower in “spin-fluctuation” 3*d* compounds has been limited to few cases only, in particular, Y(Al_xCo_{1-x})₂,¹⁴ Pd_{1-x}Ni_x,¹⁵ and Pt_{1-x}Co_x,¹⁶ and no detailed analysis of these experimental data was done. Note that all these systems have ferromagnetic spin fluctuations, as is the case for LaFe₄Sb₁₂. In LaFe₄Sb₁₂, only the magnetic field dependence of the heat capacity has been investigated by Schnelle *et al.*¹⁷ but their analysis was not complete. Also in the case of heavy fermion systems, the magnetic field dependence of the thermoelectric properties has been systematically investigated only in few compounds [CeCu_{6-x}Au_x,¹⁸ U₂Ru₂Sn,¹⁹ and CeNiSn (Ref. 20)]. The investigation of the spin-fluctuation compound LaFe₄Sb₁₂ and of the Kondo compound CeFe₄Sb₁₂ presented in this paper is then also intended to explore the basic thermoelectric properties and their magnetic field dependence in these two kinds of strongly correlated systems.

II. EXPERIMENTAL DETAILS

The synthesis of the samples is made by direct reaction of the elements inside a carbon-coated silica tube under vacuum. After heating to 1050 °C for 48 h, the sample is water quenched and then annealed at 700 °C for 4 days.^{21,22} Typical x-ray diffraction (XRD) pattern is shown in Fig. 1 demonstrating the good quality of our samples. From XRD and scanning electron microscopy and electron dispersive x-rays (EDX) experiments, we observe that the sample is nearly single-phase polycrystalline with some inclusions of RSb₂ (*R*=La or Ce). By EDX experiments, the filling of the

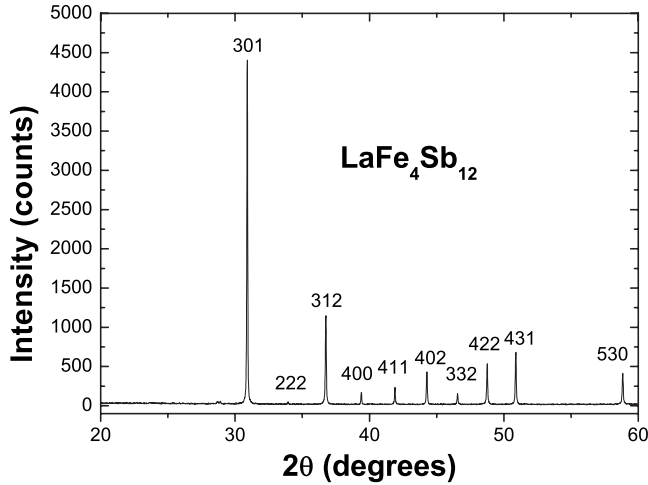


FIG. 1. XRD pattern of the skutterudite Compound $\text{LaFe}_4\text{Sb}_{12}$.

rare-earth site was found to be about 95% for both compounds $\text{LaFe}_4\text{Sb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$. For simplicity, we keep this notation, although the actual composition of the final product is $R_{0.95}\text{Fe}_4\text{Sb}_{12}$, like in our prior work.^{21–23} The thermoelectric measurements have been performed between 2 and 300 K with a relaxation method described elsewhere²⁴ in a PPMS apparatus from Quantum Design in magnetic fields up to 9 T. The magnetic field was applied in the same direction as the heat current so that we have studied the longitudinal magnetothermopower.

III. RESULTS

A. Thermal conductivity

The temperature dependence in zero field of the thermal conductivity κ of the skutterudites $\text{CeFe}_4\text{Sb}_{12}$ and $\text{LaFe}_4\text{Sb}_{12}$ is reported in Fig. 2. The thermal variations in $\kappa(T)$ measured in an applied field of 9 T are superposed to those in zero field (not shown for clarity). The independence of $\kappa(T)$

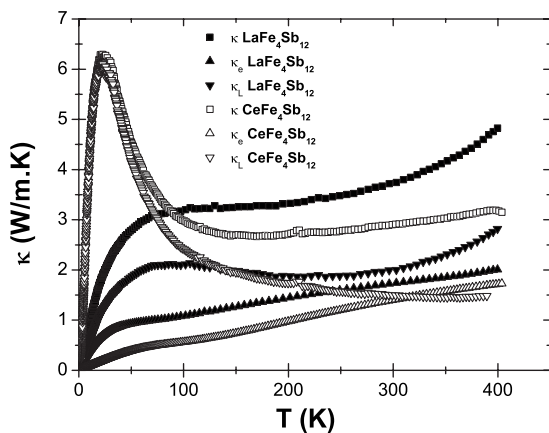


FIG. 2. Thermal variation in the thermal conductivity κ and its different contributions in zero field for $\text{CeFe}_4\text{Sb}_{12}$ and $\text{LaFe}_4\text{Sb}_{12}$. κ_e is the electronic contribution provided the Wiedemann-Franz law is valid (see discussion in the text), and $\kappa_l = \kappa - \kappa_e$.

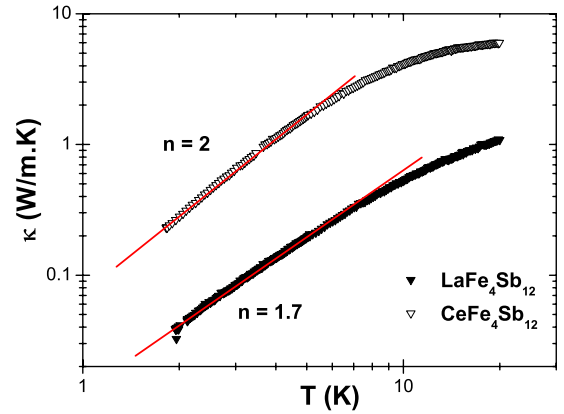


FIG. 3. (Color online) Double logarithmic plot of the thermal variation in the lattice thermal conductivity κ_l for $\text{CeFe}_4\text{Sb}_{12}$ and $\text{LaFe}_4\text{Sb}_{12}$.

on the magnetic field is a remarkable result giving evidence that the spin fluctuations have no effect on the thermal conductivity. Further analysis requires the separation between the electronic and the lattice contributions to the thermal conductivity, κ_e and κ_l , respectively. This is usually achieved by assuming that: (i) these contributions are independent (Matthiessen rule), so that $\kappa = \kappa_l + \kappa_e$, (ii) the Wiedemann-Franz law is valid so that $\kappa_e = L_0 T / \rho$, where L_0 the classical Lorentz number and is equal to $2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ and ρ is the electrical resistivity. The first hypothesis is doubtful when the electron-phonon interaction is non-negligible. Deviations to Matthiessen's rule are predicted even for a free electron model in polyvalent metals,²⁵ and are already observed in weakly doped metals such as copper²⁶ or aluminum.²⁷ In $\text{CeFe}_4\text{Sb}_{12}$ and $\text{LaFe}_4\text{Sb}_{12}$ where the electron-phonon interaction is large due to the rattling motion of the rare earth elements in the cages, the deviations are expected to be even stronger. Note that breakdown of this rule has also been reported in doped cerium heavy-fermion (HF) systems.²⁸ Nevertheless, the deviation from the Matthiessen rule should affect the determination of κ_l only quantitatively. More dramatic might be the breakdown of the Wiedemann-Franz law since this law is not expected to be a reasonable approximation in highly correlated systems²⁹ and is not valid at intermediate temperatures, so that it should not apply to our materials. Deviations should be more important in $\text{LaFe}_4\text{Sb}_{12}$ because this material is close to a quantum critical point, in which case this law is known to be strongly violated, due to the presence of low energy critical modes (see Ref. 30 for review). As a consequence, there is no proof that the classical procedure to deduce κ_e makes sense, despite the fact that its validity has not been questioned in skutterudites, to our knowledge. Nevertheless, let us assume for the moment that the classical procedure is valid, in which case κ_e as deduced from the Wiedemann-Franz law and $\kappa_l = \kappa - \kappa_e$ are reported in Fig. 2 as a function of temperature for both $\text{CeFe}_4\text{Sb}_{12}$ and $\text{LaFe}_4\text{Sb}_{12}$. The log-log plot of κ_l at low temperature reported in Fig. 3 shows that κ_l satisfies a T^2 law at low temperature ($T < 5$ K) in the case of $\text{CeFe}_4\text{Sb}_{12}$. In addition, κ_e is found to be negligible below 50 K in this compound, so that this variation

$$\kappa_l \propto T^n (T < 5 \text{ K}) \text{ with } n = 2$$

is valid, even if the Wiedemann-Franz law is not valid. Such a variation has also been observed in clathrates, another type of materials in which rattling atoms are intercalated in oversized nanocages, just like in the case of skutterudites, and it has been attributed to the electron-phonon scattering.^{31,32} The same should hold true in CeFe₄Sb₁₂. We can then conclude that the T^2 law observed in CeFe₄Sb₁₂ is the signature of the phonon-electron scattering that is the dominant mechanism responsible for the thermal conductivity in this material at low temperature. This is consistent with the fact that the thermal conductivity does not depend on the magnetic field.

In the case of LaFe₄Sb₁₂, the log-log plot of $\kappa_l = \kappa - \kappa_e$ with κ_e deduced from the Wiedemann-Franz law gives approximately a power law $\kappa_l \propto T^{1.7}$ ($T < 5$ K) also shown in Fig. 3. Within experimental uncertainty, this power law is the same as the $T^{5/3}$ law we have found for the electrical resistivity $\rho(T)$ (Ref. 10) and has been confirmed for the resistivity by some other groups.^{17,33} For $\rho(T)$ this exponent was attributed to spin fluctuations.¹⁰ However, the same interpretation for the lattice part of the thermal conductivity is unlikely because, just like in the case of CeFe₄Sb₁₂, κ_l does not depend on the magnetic field, which suggests that spin fluctuations do not govern the temperature dependence of κ_l . On the other hand, and contrary to the case of CeFe₄Sb₁₂, the electronic contribution κ_e deduced from the Wiedemann-Franz law is no longer negligible, even at low temperature. Therefore, the $T^{1.7}$ variation may also be an artifact due to the estimation of κ_e by the application of the Wiedemann-Franz law if this law is violated. Indeed, in correlated systems characterized by narrow conduction bands, this law is known to overestimate κ_e .³⁴ Nevertheless, the present result suggests that the lattice part of the thermal conductivity in LaFe₄Sb₁₂ is still due to phonon-electron scattering. In particular, it compares very well with the results found in clathrate compounds: in that case, the disorder due to the low-energy vibrational modes modifies the phonon-electron scattering, and shifts the exponent n to below 2.^{31,32}

The absence of the peak is linked to the lower filling of the rare earth site (90% in the La compound, against 95% in the Ce compound). A similar effect has been observed, for instance, in Eu_yFe_{4-x}Co_xSb₁₂.³⁵ In this particular case, the peak in $\kappa(T)$ is no longer observed when $y < 0.8$. This phenomena is linked to the fact that κ_e , which is negligible at low temperature, increases monotonously with temperature when $y < 0.8$, while $\kappa_l(T)$ goes through a maximum that is broadened by the dilution of the rare earth, so that $\kappa_e + \kappa_l$ does not go through a maximum anymore.³⁵ In LaFe₄Sb₁₂, this effect is already observed at $y = 0.9$, as it can be seen in Fig. 2.

B. Thermopower

The thermal variation in the thermopower S of LaFe₄Sb₁₂ and CeFe₄Sb₁₂ in zero magnetic field is reported in Fig. 4. The results are in agreement with data from other groups,³⁶⁻³⁹ but the maximum in the Ce compound is more pronounced. Above about 150 K S increases with tempera-

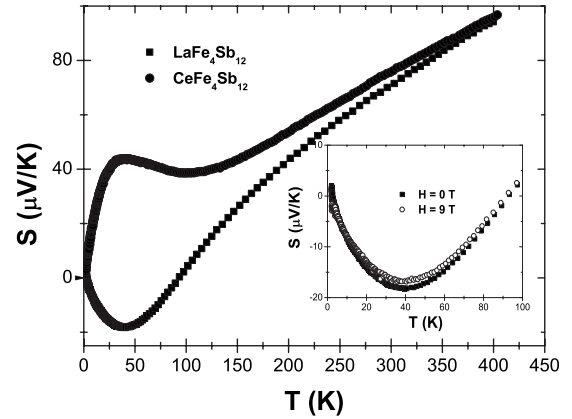


FIG. 4. Thermal variation in the thermopower S in zero field for CeFe₄Sb₁₂ and LaFe₄Sb₁₂. Also shown is the Ce contribution of the thermopower estimated as $\Delta S = S(\text{CeFe}_4\text{Sb}_{12}) - S(\text{LaFe}_4\text{Sb}_{12})$. Inset: thermal variation in the thermopower S at $H = 0$ and 9 T for LaFe₄Sb₁₂.

ture and becomes comparable in both compounds, and therefore it is difficult to estimate the different contributions to thermopower from the standard procedures for either different scattering processes in the same band (Nordheim-Gorter law) or scattering processes coming from different bands.⁴⁰ However, we believe that at high temperature, S is dominated by the contribution of Fe because the value of S at room temperature is in agreement with the value predicted from the calculation of the density of states at the Fermi level, and these states are essentially d states of Fe hybridized with the p states of Sb.¹² At low temperature, however, the behavior is different for the two materials.

The occurrence of a maximum of S near 40 K in CeFe₄Sb₁₂ recalls the standard behavior observed in HF systems that present generically a maximum in the thermopower near the temperature that marks the onset of coherent scattering from Kondo sites.^{41,42} In many cases, this temperature T_S^{max} is about twice smaller than T_ρ^{max} associated with the maximum of the resistivity in HF systems,⁴³ but in case of Ce compounds in which Ce is almost trivalent such as in CeFe₄Sb₁₂, $T_S^{\text{max}} \sim T_\rho^{\text{max}}/3$.⁴³ In any case, we recover the standard situation met in HF materials where the maximum of S or ΔS is in the range $[T_\rho^{\text{max}}/3, T_\rho^{\text{max}}/2]$ since $T_\rho^{\text{max}} = 120$ K.^{5,23} Therefore, the maximum in the thermopower in this compound is unambiguously due to the cerium. In addition, we observed that S is independent of the magnetic field up to the highest field available in our experiments ($H = 9$ T). This feature is consistent with the fact that S is positive at any temperature. The investigation of S on a variety of cerium compounds leads to the conclusion that this behavior is characteristic of HF compound with high Kondo temperature, typically $T_K > 100$ K, whereas S is negative at low temperature in compounds with $T_K < 100$ K.⁴⁴ In the latter case, a field dependence of S is usually observed, such as in CeAl₃,⁴¹ or CeRu₂Si₂,⁴⁵ for instance. In this context, the thermopower in CeFe₄Sb₁₂ would behave like in high- T_K compounds. However, the estimation $T_K = 80$ K (Ref. 46) is still too small to class this compound in the family of high- T_K (mixed-valence) systems. Moreover, we know that Ce is

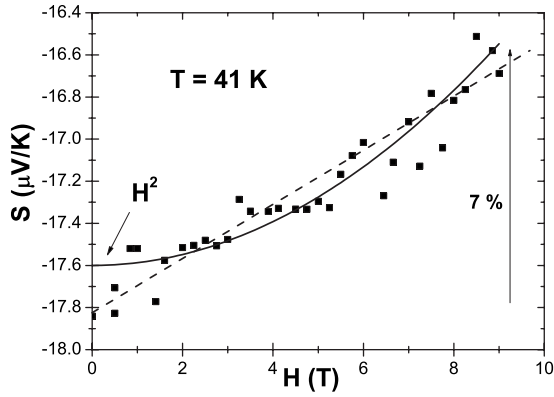


FIG. 5. Magnetic field variation in the thermopower at $T=40$ K for $\text{LaFe}_4\text{Sb}_{12}$.

nearly trivalent in this compound⁵ and the other physical properties unambiguously show that $\text{CeFe}_4\text{Sb}_{12}$ must be considered as a medium- T_K compound. It is thus a counterexample to the classification scheme suggested in Ref. 44 from the thermopower analysis only. There are other counterexamples, such as CeCoIn_5 (Ref. 47) in which $S(T)$ is positive, goes through a single maximum, and also depends on H , although T_K is even smaller than in $\text{CeFe}_4\text{Sb}_{12}$. These results show that it is not possible to detect a general behavior of the thermopower that might be used to classify the Ce compounds unambiguously, and the investigation of other physical properties is needed for this purpose.

In $\text{LaFe}_4\text{Sb}_{12}$, the thermopower is positive only for $T > 90$ K and becomes negative for lower temperatures with a minimum at about 40 K. This result is in good agreement with other studies,^{36,37} and was first attributed to the spin fluctuations at $H=0$,²¹ since this compound is close to a QCP.^{10–12,46} Indeed, this behavior is also observed in other systems with large spin fluctuations, such as Pd-Ni and $\text{Y}(\text{Al}_x\text{Co}_{1-x})_2$.^{14,15} We also note that the value of the low- T slope is very high and comparable to the values found for strongly correlated fermion systems.⁴⁸ This analysis is confirmed by the magnetic field dependence of S with H reported in the inset of Fig. 4. The H dependence is largest (in absolute value) in the vicinity of the minimum of $S(T)$, namely, at $T \sim 40$ K. At this temperature $|\Delta S(H)/S(0)|$, where $|\Delta S(H)| = S(H) - S(0)$, reaches -7% at $H=9$ T. In addition, we find $\Delta S(H)/S(0) \propto -H^n$ (see Fig. 5). However, it is difficult to determine the exponent n that is between 1 and 2.

Theoretically, the thermoelectric effects in $\text{LaFe}_4\text{Sb}_{12}$ at low temperature may arise from two contributions. The first one is the boson-drag thermopower resulting from charge carriers interacting with bosons (paramagnons and/or phonons) and being drag by them in a temperature gradient. The second one is the diffusion thermopower that depends on the density and mobility of the carriers. Both contributions can be affected by the application of a magnetic field. If the boson-drag effect is dominant, S and $\Delta S(H)/S(0)$ are positive,⁴⁹ contrary to the present case. Moreover, the expected magnitude of $\Delta S(H)/S(0)$ is much larger in the case of phonon drag (about 0.5–1) than in the present case (about 0.05–0.1). The diffusion thermopower is also ruled out by the diffusion by spin fluctuations near a ferromagnetic

transition,⁴⁹ in which case $\Delta S(H)/S(0) \propto \Delta\rho(H)/\rho(0) \propto M(H)^2$ and is negative. We know from our prior investigations that $M(H) \propto H$ at $T=40$ K.¹⁰ The magnetoresistance in presence of ferromagnetic spin fluctuations is $\Delta\rho(H)/\rho(0) \propto H^2$,⁵⁰ which is consistent with a possible H^2 law for $\Delta S(H)/S(0)$. However, this H^2 -law for the magnetoresistance has not been observed in $\text{LaFe}_4\text{Sb}_{12}$, because the diffusion of the spin carriers by spin fluctuations is not the only process that contributes to the magnetoresistance, as pointed out in Ref. 10, and presumably is not the dominant mechanism for the magnetoresistance, while it is the dominant mechanism for the thermopower. Also, we wish to mention that this mechanism works not only in $\text{LaFe}_4\text{Sb}_{12}$ but also in $\text{Y}(\text{Al}_x\text{Co}_{1-x})_2$ where the magnetoresistance is positive because the classical magnetoresistance is the main contribution,¹⁵ while the main contribution to the thermopower comes from the spin fluctuations and is very similar to that of $\text{LaFe}_4\text{Sb}_{12}$. Indeed, $\Delta S(H)/S(0)$ in $\text{Y}(\text{Al}_x\text{Co}_{1-x})_2$ has the same sign and same order of magnitude as in $\text{LaFe}_4\text{Sb}_{12}$, and should have the same origin, namely, the suppression of ferromagnetic spin fluctuations by the application of a magnetic field, because $\text{Y}(\text{Al}_x\text{Co}_{1-x})_2$ is a compound with ferromagnetic spin fluctuations.¹⁵ Thus, we believe that the present model used for understanding the magnetic field dependence of thermopower for ferromagnetic spin fluctuations can be applied in a general manner. Therefore, due to the field dependence of S in $\text{LaFe}_4\text{Sb}_{12}$ and because the magnitude of S is one order of magnitude larger than in normal metals, we believe that boson-drag effects are unimportant here, so that the thermopower is mainly due to the diffusion of the charge carriers by ferromagnetic spin fluctuations.

Finally, we note that in $\text{CaFe}_4\text{Sb}_{12}$, the magnetothermopower is negative such as in $\text{LaFe}_4\text{Sb}_{12}$, but much larger.⁵¹ Also, in this case, the magnetoresistance is positive and large.¹⁷ However, there are some essential differences for the magnetic properties of these compounds compared to $\text{LaFe}_4\text{Sb}_{12}$. In particular, $d\chi/dT$ is positive in the alkaline-earth samples when $S(H)$ is negative, whereas $d\chi/dT$ is always negative in $\text{LaFe}_4\text{Sb}_{12}$. In both cases, however, anomalies in the thermopower are due to the ferromagnetic spin fluctuations that are quenched by the effect of the magnetic field. Further theoretical studies are needed for understanding the origin of the magnetothermopower of the alkaline samples.

Finally, we wish to discuss the linear temperature dependence of the thermopower at low temperatures in $\text{LaFe}_4\text{Sb}_{12}$. A quasiuniversal ratio $q = (S/T) (e/\gamma)$, with e the electron or hole charge and γ the Sommerfeld coefficient of the specific heat, has been observed in many correlated metals,⁴⁸ with $q = \pm 1$ in the limit of low temperature depending of the charge carrier. In the case of free electrons (holes) with relaxation time independent of the energy, $q = -1$ (1), while $q > -1$ ($q < 1$) in case the relaxation time depends on energy. The case of non-Fermi liquids near a QCP has been investigated in Ref. 52. The result is that q remains essentially unchanged for a ferromagnetic QCP, but decreases considerably (in absolute value) for an antiferromagnetic QCP. For $\text{LaFe}_4\text{Sb}_{12}$, we find $S/T = -0.865 \mu\text{V}/\text{K}^2$ for $T < 8$ K. Taking into account that $\gamma = 195 \text{ mJ}/\text{mole K}^2$,¹⁰ we obtain

$q = -0.426$, which is a further indication for the ferromagnetic nature of the critical spin fluctuations since $|q|$ would have been much smaller in the antiferromagnetic case. This is consistent with the other physical properties at low temperature,¹⁰⁻¹² according to the non-Fermi-liquid behavior nearby a ferromagnetic QCP observed in this compound.

C. Specific heat

1. Case of LaFe₄Sb₁₂

The specific heat C_p of LaFe₄Sb₁₂ at low temperatures has been reported elsewhere.¹⁰ In this prior work, we have shown, in particular, that, in the temperature range $0.8 \leq T \leq 4$ K, C_p satisfies the well-known law

$$C_p = \gamma T + \beta T^3. \quad (1)$$

The first term is the electronic part that can be decomposed in⁵⁰

$$\gamma = \gamma_e + \gamma_s(H). \quad (2)$$

The term $\gamma_s(H)$ corresponds to the paramagnon enhancement factor due to the spin fluctuations below the spin-fluctuation temperature T_{sf} , and is suppressed by the application of sufficiently high magnetic field, generally $H > 5$ T.⁵³ In the same way, the second term in Eq. (1) can be written

$$\beta = \beta_l + \beta_s(H) \quad (3)$$

with β_l the normal lattice contribution; $\beta_s(H)$ is due to an induced moment on the magnetically active sites (iron in our case), which is zero at $H=0$, but increases with H and seems to saturate for several materials at $H=7-9$ T.⁵³

In addition, a contribution of the form $-\sigma T^3 \ln(T/T_{sf})$ is also predicted.⁵⁴ However, this term is important only at lower temperature $T < 0.8$ K, where it might be responsible for the up turn of the C_p/T versus T^2 curve, although the up turn may also have a nuclear origin¹⁰ (see Fig. 8 in Ref. 10). More recently, an attempt has been made to estimate this $T^3 \ln(T/T_{sf})$ contribution, in a fit that also included an additional term representing the contribution of an Einstein mode at temperature Θ_E .¹⁷ The addition of these two terms was found to reduce least-square deviation of the fit and was considered as an argument in favor of their existence. This, however, is questionable, since the simple fact to add two fitting parameters ($\Theta_E; \sigma$) to the two other ones (γ, β) is sufficient to technically improve the fit. Nevertheless the up turn of the C_p/T versus T^2 curve is consistent with the existence of the $T^3 \ln(T/T_{sf})$ and the fact that this compound is close to a QCP with ferromagnetic spin fluctuations. Note finally that the Einstein term itself has been found to give a negligible contribution to the heat capacity below 7 K, both in our previous work¹² and by Schnelle *et al.*¹⁷ In addition, it does not depend on the magnetic field.

The variations in γ and β (determined by fitting the heat capacity) with H are reported in Figs. 6 and 7. In the whole range of magnetic field investigated, $\gamma(H)$ can be fit by the quadratic law

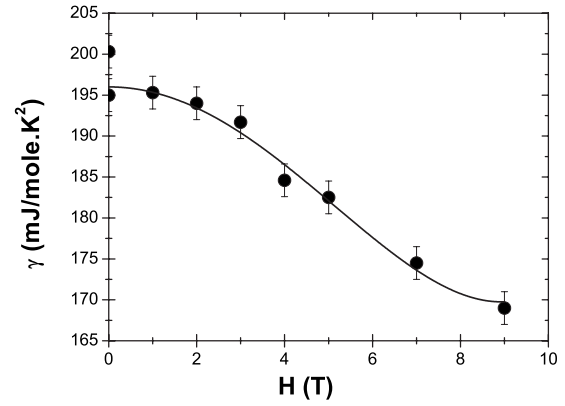


FIG. 6. Magnetic field dependence of the Sommerfeld coefficient in LaFe₄Sb₁₂. The full curve is the fit by a power series (see text).

$$\gamma(H) = \gamma(0) - aH^2 + bH^4 \quad (4)$$

with a and b the fitting parameters. Note that such a quadratic law has also been observed for the magnetic susceptibility $\chi(H) = M(H)/H$.¹² This is compatible with a scaling $\gamma(H) \propto \chi(H)$, as expected for such correlated fermion systems.⁵⁵ It is difficult, however, to determine if the parameters a and b are the same in the series development of $\chi(H)$ and $\gamma(H)$, because the nonlinear coefficients in the $\chi(H)$ law strongly depend on T .¹⁰ Nevertheless, our results suggest that the quadratic law in Eq. (4) should have the same origin as that of $\chi(H)$, namely, ferromagnetic spin fluctuations.¹⁰ Indeed, the term $-aH^2$ in Eq. (4) is the low-field behavior predicted for the Sommerfeld coefficient within the theory of paramagnons.^{56,57} With this regard, the H^4 term in Eq. (4) is the first term of a series development needed in the fit in Fig. 6 to mimic the saturation of $\gamma(H)$. Note that within the highest field used in our experiments this saturation is already detected but not complete. Complete saturation of $\gamma(H)$ should actually require higher fields, and the saturation predicted by Eq. (4) is overestimated by the truncation of the series development to the H^4 term. The field H_s required to smear out the effect of spin fluctuations on the Sommerfeld

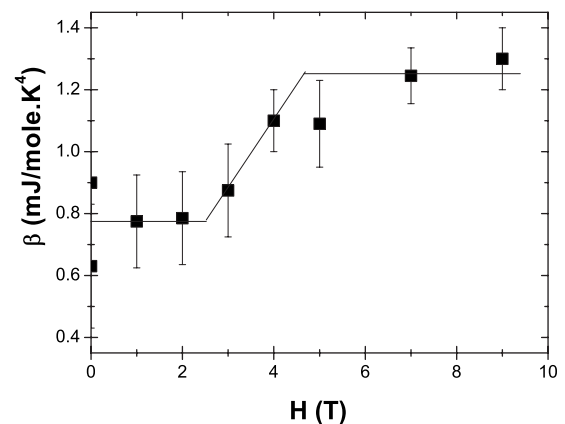


FIG. 7. Magnetic field dependence of the β parameter of the specific heat in LaFe₄Sb₁₂.

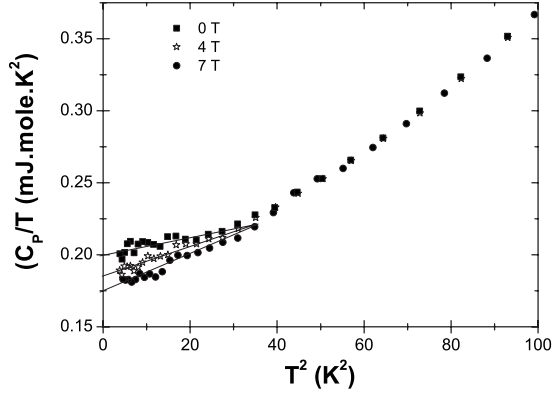


FIG. 8. Temperature dependence of the specific heat C_p in $\text{LaFe}_4\text{Sb}_{12}$ at different magnetic fields ($H=0, 4,$ and 7 T). The straight lines that fit the data at $T \leq 6$ K, in agreement with Eq. (1), merge at $T=6$ K, and C_p does not depend on H above 7 K, which also means that spin-fluctuations contribution is negligible above 7 K.

parameter can be estimated from the low-field behavior of $\gamma(H)$ when Eq. (4) reduces to $\gamma(H) = \gamma(0) - aH^2$. According to prior works,^{52,55,56}

$$\frac{a}{\gamma(0)} = \frac{0.1S_t}{\ln(S_t)} H_s^2, \quad (5)$$

where H_s is the effective field for quenching spin fluctuations, S_t is the Stoner enhancement factor of the magnetic susceptibility defined by the relation

$$\chi_i(T \rightarrow 0) = S_t \chi_{\text{pauli}}, \quad (6)$$

where $\chi_i(T \rightarrow 0)$ is the intrinsic part of the magnetic susceptibility at low temperature, and χ_{pauli} is the Pauli susceptibility

$$\chi_{\text{pauli}} = 2N(E_F) \mu_B^2. \quad (7)$$

The density of electron states at the Fermi energy $N(E_F)$ has been determined from band-structure calculations,^{12,58,59} and we have shown in the previous section that this estimation is reliable, as it accounts quantitatively for the value of the thermopower of this material at high temperature. Then, taking the value of $\chi_i(T \rightarrow 0)$ we have determined in our prior work,¹⁰ we find that S_t in $\text{LaFe}_4\text{Sb}_{12}$ in Eq. (6) is $S_t = 13.8$. Reporting this value in Eq. (5), we find, with the values of a and $\gamma(0)$ determined from the fit of $\gamma(T)$ in Fig. 7, $H_s = 16$ T. This is consistent with the fact that the bH^4 term is already non-negligible at 9 T, and also that $\gamma(H)$ is still decreasing in this system up to 14 T as reported by Schnelle *et al.*¹⁷

The critical ferromagnetic spin fluctuations associated with the paramagnons near $T=0$ are suppressed by the application of the magnetic field H_s , but they are also suppressed by the increase in the temperature. This is evidenced from Fig. 8 where we show $C_p(\text{LaFe}_4\text{Sb}_{12})$ as a function of temperature at different magnetic fields. We can see that C_p depends on the magnetic field only in the range $T < 7$ K, so that the temperature $T_\gamma = 7$ K is the temperature above which the spin fluctuations have a negligible effect on the heat ca-

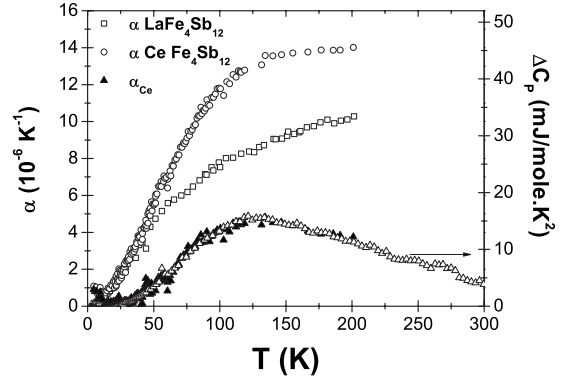


FIG. 9. Temperature dependence of the thermal dilatation α of $\text{CeFe}_4\text{Sb}_{12}$, $\text{LaFe}_4\text{Sb}_{12}$ and their difference α_{Ce} , together with the Ce part of the heat capacity, $C_p(\text{Ce})$ defined by Eq. (5), showing the scaling of $C_p(\text{Ce})$ with α_{Ce} .

capacity. Note that this temperature is expected to be related to H_s by the relation $T_\gamma = (\mu_B H_s) / k_B$. With $H_s = 16$ T determined from Eqs. (5)–(7), $T_\gamma = 10.8$ K, which is comparable to the temperature 7 K determined from Fig. 9, so that the analyses of the heat capacity as a function of T and as a function of H are consistent. These values also compare well with the scaling temperature $T_{\text{NFL}} \approx 20$ K below which non-Fermi-liquid behavior was found in transport and magnetic properties^{10,21} and with the scaling temperature deduced from the low-temperature power law behavior for the magnetic susceptibility ($\theta^* \approx 20$ K) and the resistivity ($T_0 \approx 15$ K).^{10,21}

In addition, we find that β increases by roughly 50% with H between 3 and 5 T, and saturates at higher field, as seen in Fig. 7. This is also the situation met in other materials with spin fluctuations, such as Ni-Pd alloys.⁶⁰

Spin fluctuators have been classified in to six categories based on the field dependence of the low-temperature heat capacity.⁵³ In this scheme, $\text{LaFe}_4\text{Sb}_{12}$ belongs to the so-called type-3 class (archetype CeSn_3) characterized by the presence of the $T^3 \ln(T/T_{sf})$ term at low temperature (at least at $H=0$), a decrease in γ and an increase in β with H .

2. Case of $\text{CeFe}_4\text{Sb}_{12}$

The specific heat of $\text{CeFe}_4\text{Sb}_{12}$ at $H=0$ and its Ce contribution

$$C_p(\text{Ce}) = C_p(\text{CeFe}_4\text{Sb}_{12}) - C_p(\text{LaFe}_4\text{Sb}_{12}) \quad (8)$$

have been investigated elsewhere.^{6,46} In addition, we report in Fig. 9 the temperature dependence of the thermal dilatation coefficient α . As usually done,^{61,62} we define the Ce contribution by

$$\alpha(\text{Ce}) = \alpha(\text{CeFe}_4\text{Sb}_{12}) - \alpha(\text{LaFe}_4\text{Sb}_{12}), \quad (9)$$

and we find that $C_p(\text{Ce}) \propto \alpha(\text{Ce})$ at all temperatures $T > 7$ K. Assuming that the difference between the heat capacity at constant volume and constant pressure is negligible, we can define the Grüneisen parameter Ω_{Ce} through the relation

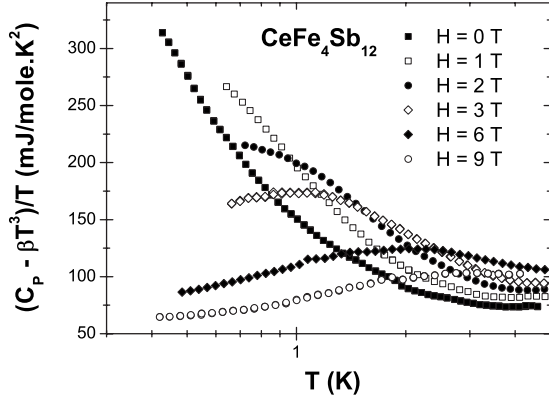


FIG. 10. Plot of $(C_p - \beta T^3)/T$, with a T and H independent value $\beta = 1.17 \times 10^{-3}$ J/mole K⁴, as a function of the temperature T in CeFe₄Sb₁₂. If Eq. (1) would still be valid, this quantity should have been reduced to the Sommerfeld constant of this compound. The temperature dependence is then attributable to the Schottky resonance Due to Zeeman splitting of the ground state.

$$\Omega_{\text{Ce}} = [3\alpha_{\text{Ce}}/C_p(\text{Ce})](B_t V_M), \quad (10)$$

where V_M is the molar volume and B_t the bulk modulus. $B_t = 88$ GPa is independent of temperature.⁶² Since $C_p(\text{Ce}) \propto \alpha(\text{Ce})$ (Fig. 10), this implies that $\Omega_{\text{Ce}} = 19$ is also independent of temperature. This value is much larger than values typically found in mixed valence systems,^{61,62} which is another evidence for CeFe₄Sb₁₂ is moderate HF compound with moderate T_K (see the discussion in the previous section on the thermopower). Note also that Ω_{Ce} is much larger than the value (0.66) in the free electron gas model which reflects the volume dependence of the Fermi temperature, but smaller than typical values found in HF systems.⁶² This is then also consistent with the claim that CeFe₄Sb₁₂ is only a moderately HF system.^{5,6,23,46}

The confirmation of the $C_p(\text{Ce}) \propto \alpha(\text{Ce})$ behavior in the present work also validates Eqs. (8) and (9) and the similar approach to the magnetic susceptibility that has been used in the interpretation of the Ce properties in prior work on CeFe₄Sb₁₂.^{5,6,23,44} The origin of the maximum in $C_p(\text{Ce})$ at about 120 K was discussed in Ref. 6 where it was attributed to a spin pseudogap, and the same arguments hold here for the thermal expansion. At low temperatures ($T < 7$ K), the use of Eq. (5) gives unphysical (negative) values of $C_p(\text{Ce})$. This feature can hardly be seen from Fig. 9 because the heat capacity of both compounds is very small, and so is the difference. However, this unphysical result means that Eq. (8) is no longer valid, i.e., the spin fluctuations on iron that dominate the heat capacity of LaFe₄Sb₁₂ at $T < 7$ K (see Fig. 9) are weaker in CeFe₄Sb₁₂. Indeed, CeFe₄Sb₁₂ is a moderately heavy fermion system, so that the d electrons of iron are coupled antiferromagnetically with the f electrons of Ce³⁺ ions to screen their magnetic moment, smearing out the ferromagnetic spin fluctuations observed in LaFe₄Sb₁₂. In the absence of spin fluctuations, β does not depend on temperature and magnetic field [Eq. (1)] and is related to the Debye temperature θ_D , $\beta = 12\pi^4 NR / (5\theta_D^3)$, where R is the universal gas constant and N the number of atoms per formula unit.

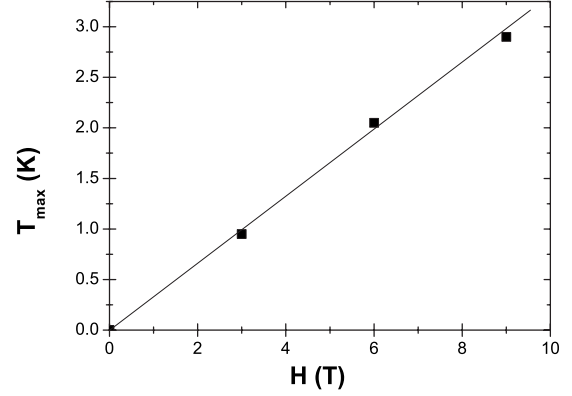


FIG. 11. Temperature T_{max} of the maximum of the Shottky anomaly shown in Fig. 10 as a function of the magnetic field H . Note that $T_{\text{max}} \propto H$ hints for the influence of the Zeeman effect.

$\theta_D = 250$ K was determined from ultrasonic experiments.^{63,64} The heat capacity is shown in Fig. 11 as a function of temperature in the range $T < 5$ K for different magnetic fields in the form $(C_p - \beta T^3)/T$. According to Eq. (1), this quantity should reduce to the Sommerfeld coefficient γ . At low fields, the heat capacity increases upon cooling, down to the lowest temperature (0.4 K). At higher fields, the heat capacity goes through a maximum at temperature T_{max} that is proportional to H (see Fig. 11). This behavior is characteristic of a Schottky anomaly due to Zeeman splitting of the crystalline electric field ground-state Γ_7 doublet.⁶⁵ The same behavior has been recently observed in CePt₄In.⁶⁶ From the slope of $T_{\text{max}}(H)$, one can estimate the partially screened magnetic moment of the cerium ions in CeFe₄Sb₁₂ to be $0.3\mu_B$, just like in CePt₄In.⁶⁶ Actually, we find that CeFe₄Sb₁₂ and CePt₄In are closely related materials. Both compounds have $4f$ electrons that have well-localized character at high temperatures, contradicting the previous hypothesis that both of them might be intermediate valence compounds. At low temperatures, both give rise to moderately heavy fermion behavior. Indeed, CePt₄In has a positive peak in $S(T)$,⁶⁶ a large Curie-Weiss temperature at high temperature and a broad magnetic signal in inelastic neutron scattering experiments at low temperature,⁶⁷ just like for CeFe₄Sb₁₂.⁶ The magnetic moment deduced from the present thermodynamic experiments is in reasonable agreement with the value $0.17\mu_B$ deduced for the magnetization at 9 T and 2 K.²³

IV. NATURE OF SPIN FLUCTUATIONS IN LaFe₄Sb₁₂

Since the nature (ferromagnetic or antiferromagnetic) of the quantum critical spin fluctuations has been subject to debate, it may be of interest to discuss this result in this context. The temperature dependence of the electrical resistivity at low temperature is $\rho(T) \propto T^{5/3}$ at zero magnetic field. This experimental result¹² has been confirmed by Schnelle *et al.*¹⁷ and Tanaka *et al.*³³ also found a deviation from the T^2 behavior that they attribute to spin fluctuations according to our previous work.¹² However, in contrast to Schnelle *et al.*,¹⁷ we attribute the exponent $5/3$ to ferromagnetic interactions.⁶⁸ The $T^{1.35}$ and $T^{-2/3}$ laws for the magnetic sus-

ceptibility and the Grüneisen parameters are also characteristic of ferromagnetic fluctuations¹² just as the low-temperature magnetic field and temperature dependence of thermopower and heat capacity shown in the present work. NQR experiments on Sb used to determine the relaxation time T_1 at $H=0$ also lead to the conclusion that the spin fluctuations are ferromagnetic below 40 K,¹³ a result that has been confirmed in Ref. 69. NMR experiments on La are then the only ones to suggest antiferromagnetic spin fluctuations.¹⁵ This result, however, has been deduced from the analysis of the NMR resonances in magnetic fields of 6 T, while all the other experiments that provided evidence for the existence of ferromagnetic fluctuations concern properties at zero magnetic field. The result from NMR experiments then suggests that critical ferromagnetic spin fluctuations are at least partly suppressed in fields of 6 T, as confirmed by the field dependence of the specific heat.

V. CONCLUSION

Our investigation of the magnetic field dependence of various properties of $\text{CeFe}_4\text{Sb}_{12}$ and $\text{LaFe}_4\text{Sb}_{12}$ confirms that these compounds are correlated fermion systems. The heat-capacity measurements show that $\text{LaFe}_4\text{Sb}_{12}$ belongs to the class 3 of correlated systems in the classification scheme of Ref. 50. The negative minimum observed at about 40 K in the thermopower S of $\text{LaFe}_4\text{Sb}_{12}$ is due to spin fluctuations. $S(T=40 \text{ K})$ increases with H as a consequence of the reduction in the spin fluctuations by the magnetic field, according to a quadratic law $S(H) - S(0) \propto -H^n$ that is evidence for this

compound being close to a ferromagnetic QCP, in agreement with the power laws that have been observed in the temperature dependence of different physical properties.⁸

The size of the critical spin-fluctuation contributions in $\text{LaFe}_4\text{Sb}_{12}$ very much depends of the physical property. We have shown in a prior work⁸ that they strongly affect the temperature dependence of the magnetic susceptibility and the Grüneisen parameter up to 40 K. We find in the present work that this is also the case for the thermopower. On the other hand, the heat capacity is affected by spin fluctuations only up to 7 K, and the thermal conductivity is not sensitive to them even at low temperature.

$\text{CeFe}_4\text{Sb}_{12}$ is a moderately heavy fermion system with moderate Kondo temperature ($T_K=80 \text{ K}$). The H dependence of the specific heat shows that the magnetic moment of the $4f$ electron of Ce^{3+} in the crystalline electric field ground-state Γ_7 doublet is reduced to $0.3\mu_B$ at low temperature. This antiferromagnetic coupling between the $4f$ electron and the delocalized d electrons of the La ions destroys the ferromagnetic spin fluctuations observed in $\text{LaFe}_4\text{Sb}_{12}$. As a consequence, the cerium effect on the physical properties cannot be investigated by simply subtracting the respective data of the reference compound $\text{LaFe}_4\text{Sb}_{12}$ at low temperatures where the spin fluctuations are important. This is a major difference with respect to other cerium compounds where such a procedure is commonly used. Only the thermal conductivity is not sensitive to the spin fluctuations at low temperature, since it is dominated by the diffusion by phonons.

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