TRANSPORT AND SPECIFIC HEAT STUDIES OF RFe_4Sb_{12} (WITH R = Ce, La)*

R. Viennois, F. Terki, A. Errebbahi, S. Charar, M. Averous

GES, Universite Montpellier II, Place Eugene Bataillon
34095 Montpellier, France

D. Ravot, J.C. Tedenac

LPMC, Universite Montpellier II, Place Eugene Bataillon
34095 Montpellier, France

P. Haen

CRTBT, CNRS, BP 166, 38042 Grenoble cedex 9, France

and C. Sekine

Departement of Electrical and Electronic Engineering
Muroran Institut of Technology
27-1 Mizumoto-cho, Muroran 050-8585, Japan

(Received July 10, 2002)

The T-dependence of the resistivity ρ of a start-of-the-art polycrystalline sample of $CeFe_4Sb_{12}$ was measured between 5 and 300 K. The cerium contribution to the resistivity, ρ(Ce) was obtained by substracting the resistivity of $LaFe_4Sb_{12}$. As a function of T, ρ(Ce) exhibits a maximum near 150 K. This maximum is attributed to a combination of a Crystal Electric Field (CEF) and the Kondo effect. This interpretation is consistent with Hall data in the same temperature range. Our heat capacity data confirm that the electronic specific heat coefficient γ for $LaFe_4Sb_{12}$ is larger than that for $CeFe_4Sb_{12}$. The Debye temperatures of both materials are near 250 K.

PACS numbers: 71.27.+a, 71.70.Ch, 72.15.Qm

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

1. Introduction

Compounds with "filled" skutterudite structure were discovered in 1977 [1]. The Bravais lattice of these ternary compounds is bcc, and the space group is $Im3$ ($T_h{}^5$). The unit-cell contains two unit-formula RM_4X_{12} (where R = actinid, rare earth or alkaline earth; M = Fe, Ru or Os; X = P, As or Sb). Among the filled skutterudites which show various very interesting properties, $CeFe_4Sb_{12}$ has attracted considerable attention because both itinerant and localized magnetism coexist in this compound [2], and because its thermoelectric properties are very promising [3–5]. Some studies have shown that $CeFe_4Sb_{12}$ has a moderate heavy fermion behaviour [6], and that the cerium is trivalent [2]. A drop of the resistivity $\rho(T)$ near 150 K has been previously attributed either to the onset of coherent scattering in the cerium sublattice [6, 7] or to a (CEF) effect combined with a decrease of scattering by phonons [2, 7]. Two earlier data for the temperature variations of the Hall constant $R_H(T)$ in $CeFe_4Sb_{12}$ differed from each other [3, 4]. For these reasons, we performed new resistivity and Hall measurements on $CeFe_4Sb_{12}$. To interpret the data we also performed $\rho(T)$ measurements on $LaFe_4Sb_{12}$. The electronic specific heat coefficient γ was previously measured in $CeFe_4Sb_{12}$ [6], and in $LaFe_4Sb_{12}$ [8]. The result that the La compound has the higher γ was surprising, which is why we also repeated the specific heat mesurements.

2. Experimental

The synthesis and characterization of $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ samples were very similar as for an earlier sample [9]. The polycrystalline samples studied were almost single phase (more than 95 percents), similar to other state-of-the-art polycrystalline samples [5, 6]. Hall and resistivity measurements were performed between 5 and 300 K using the Van Der Pauw method. The Hall data were taken with an ac electric current. The Hall voltage was linear with magnetic field, up to 8 T. Heat capacity measurements between 3.5 and 20 K were performed with the relaxation method using a commercial microcalorimeter from Oxford Instruments.

3. Results

Figure 1 shows $\rho(T)$ of both $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$. The results are in good agreement with previous works [6–8]. The cerium contribution to the resistivity of $CeFe_4Sb_{12}$, $\rho(\mathrm{Ce}) = \rho(CeFe_4Sb_{12}) - \rho(LaFe_4Sb_{12})$ is shown in the same figure as a solid curve. The maximum in the latter curve, near 150 K, is much more pronounced than in Ref. [5]. A similar maximum, but near 75 K, has been reported for a single-crystal of $CeRu_4Sb_{12}$ [10]. Above 150 K, $\rho(\mathrm{Ce})$ in Fig. 1 follows a negative logarithmic temperature dependence, which we attribute to the Kondo effect. The maximum of $\rho(\mathrm{Ce})$ may be attributed

either to the CEF effect, or to the coherent scattering. In the latter case, a maximum in $R_H(T)$ around the same temperature is expected. But the inset of the Fig. 1 indicates that this is not the case. On cooling, R_H shows a large increase below 100 K, and then seems to saturate around 10 K, in the same manner as for a single-crystal of $CeRu_4Sb_{12}$ [10]. This gives us confidence that our results better represent the intrinsic behaviour of R_H in $CeFe_4Sb_{12}$ than those previously reported [3, 4]. The T-dependence of R_H may be due to a change in the hole concentration, to the anomalous Hall effect, or to a combination of both. It seems likely that the anomalous Hall effect due to the Kondo effect plays a significant role.In our opinion, the peak for ρ(Ce) in both $CeFe_4Sb_{12}$ and $CeRu_4Sb_{12}$ is due to the CEF effect combined with the Kondo effect.

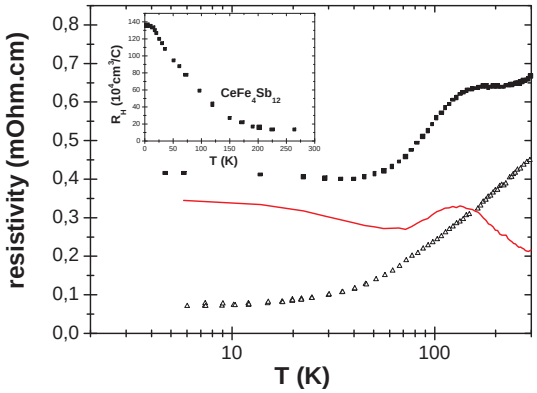

Fig. 1. T-dependence of the electrical resistivity ρ of $CeFe_4Sb_{12}$ (closed square)and $LaFe_4Sb_{12}$ (open triangle). The difference (solid curve) is the cerium contribution, ρ(Ce), to the resistivity of $CeFe_4Sb_{12}$. The insert shows the T-dependence of the Hall constant R_H of $CeFe_4Sb_{12}$.

In Fig. 2, the specific heat of $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ is plotted as C_P/T *versus* T^2. Surprisingly, below 9 K C_P/T for $LaFe_4Sb_{12}$ is higher. Thus, the electronic specific heat γ (from extrapolation of the data in Fig. 2 to 0 K) is larger for $LaFe_4Sb_{12}$ than for $CeFe_4Sb_{12}$. This should be due to a variation of the Fermi level (FL) between these two compounds. Indeed, the main contribution to the Density of States at the FL seems to be due to the iron related states. The value for $CeFe_4Sb_{12}$ (about 60 mJ/mole*K^2) agrees with the previous value [6] while the one for $LaFe_4Sb_{12}$ is smaller than in Ref. [8]. The Debye temperatures θ_D found for $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ are 249 and 260 K, respectively. The value for $CeFe_4Sb_{12}$ agrees with the previous value [6], but our θ_D for $LaFe_4Sb_{12}$ is well below the value 348 K found in Ref. [8].

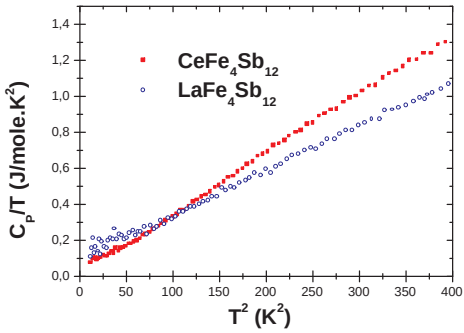

Fig. 2. Specific heat of $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$, plotted as C_P/T *versus* T^2.

In summary, based on our resistivity and Hall data, we attribute the maximum of ρ(Ce) in $CeFe_4Sb_{12}$, near 150 K, to a combination of the CEF and the Kondo effect. The total resistivity of $CeFe_4Sb_{12}$ also contains a significant contribution from phonon scattering. We also propose the same interpretation for the maximum in ρ(Ce) in $CeRu_4Sb_{12}$ observed previously by Abe et al [10]. Additional studies are needing for a better understanding of the transport properties. Our heat capacity data confirm that the electronic specific heat coefficient γ for $LaFe_4Sb_{12}$ is higher than that for $CeFe_4Sb_{12}$. The Debye temperatures θ_D of both materials are near 250 K.

REFERENCES

[1] W. Jeitschko, D.J. Braun, *Acta Crist.* , **B33**, 3401 (1977).

[2] L. Chapon, D. Ravot, J.C. Tedenac, *J. Alloys Compds*, **299**, 68 (2000).

[3] D.T. Morelli, G.P. Meisner, *J. Appl. Phys.* **77**, 3777 (1995).

[4] B. Chen, J.H. Xu, C. Uher, D.T. Morelli, G.P. Meisner, J.P. Fleurial, T. Caillat, A. Borschevski, *Phys. Rev.* **B55**, 1476 (1997)

[5] B.C. Sales, D. Mandrus, B.C. Chakoumakos, V. Keppens, J.R. Thompson, *Phys. Rev.* **B56**, 15081 (1997)

[6] D.A. Gajewski, N.R. Dilley, E.D. Bauer, E.J. Freeman, R. Chau, M.B. Maple, D. Mandrus, B.C. Sales, A.H. Lacerda, *J. Phys.: Cond. Mat.* **10**, 6973 (1998)

[7] E.D. Bauer, R. Chau, N.R. Dilley, M.B. Maple, D. Mandrus, B.C. Sales, *J. Phys.: Cond. Mat.* **12**, 1261 (2000)

[8] E. Bauer, S. Berger, A. Galatanu, M. Galli, H. Michor, G. Hilscher, C. Paul, B. Ni, M.M. Abd-Elmeguid, V.H. Tran, A. Grytsiv, P. Rogl, *Phys. Rev.* **B63**, 224414 (2001)

[9] L. Chapon, D. Ravot, J.C. Tedenac, *J. Alloys & Compds.* **282**, 58 (1999)

[10] K. Abe, T.D. Matsuda, H. Sugawara, T. Namiki, Y. Aoki, H. Sato, *Physica B* **312-313**, 256 (2002)