Thermopower of Ce$_{1-x}$La$_x$TiGe with highly degenerate orbital ground state

N. Oeschler, M. Deppe, S. Hartmann, N. Caroca-Canales, C. Geibel, F. Steglich
Max Planck Institute for Chemical Physics of Solids, Noethnitzer Str. 40, 01187 Dresden, Germany
E-mail: oeschler@cpfs.mpg.de

Abstract. Large thermopower values at low temperatures are commonly observed for heavy fermion systems. Their thermopower is similarly enhanced compared to ordinary metals as the Sommerfeld coefficient of the electronic specific heat. Here, we present low-$T$ resistivity $\rho(T)$ and thermopower $S(T)$ results of CeTiGe and Ce$_{1-x}$La$_x$TiGe which show enhanced absolute thermopower values of 60-70 $\mu$V/K around 15 K. CeTiGe has been identified to exhibit the full Ce $J = 5/2$ multiplet ground state. The strongly enhanced thermopowers at low temperatures is, thus, attributed to the highly degenerate ground state. Upon substituting La on the Ce site, we study the effect of negative chemical pressure on the Kondo scale of CeTiGe. Combined with the metallic resistivity $\rho$, the power factor $PF = S^2/\rho$, which is of interest for thermoelectric applications, is in the same order as common thermoelectric materials.

1. Introduction
The search for appropriate materials for effective thermoelectric cooling at cryogenic temperatures is an active field of current research in solid state physics. The thermoelectric efficiency is given by the figure of merit $ZT = (S^2/\rho\kappa)T$ with $S$ the thermopower, $\rho$ the electrical resistivity and $\kappa$ the thermal conductivity. For metallic systems, the thermopower has to be larger than 156 $\mu$V/K with minimized the lattice thermal conductivity in order to achieve sufficient thermoelectric efficiency.

Heavy fermion systems exhibit a strongly enhanced density of states below the characteristic Kondo temperature at which the local $f$ moments get screened by the hybridization with the conduction electrons. The high density of states entails a large Sommerfeld coefficient of the specific heat and a high Pauli susceptibility. Likewise, the thermopower is observed to be enhanced. Values around 30 $\mu$V/K are commonly found around the Kondo temperature at which the thermopower peaks.

Below room temperature only few materials have considerable thermoelectric efficiencies. Besides the BiSb alloy with a $ZT$ of 0.7 at 150 K, the strongly correlated electron systems and, in particular, intermediate valence systems were found to have the highest thermopower in the temperature range between 100 K and 300 K. Typically, the thermopower exceeds values of 80 $\mu$V/K of either sign above 100 K [1]. However, except some work on CeB$_6$ potential thermoelectrics in the low temperature part below 50 K are hardly investigated. Recently, very promising results were obtained on the correlated semiconductor FeSb$_2$ which exhibits thermopower values as high as -45000 $\mu$V/K [2]. Subsequent studies reveal the importance...
Figure 1. Resistivity ratio $\rho(T)/\rho(300 \text{ K})$ of Ce$_{1-x}$La$_x$TiGe vs. $T$. Inset: Power factor $PF$ of Ce$_{1-x}$La$_x$TiGe vs. $T$.

of strong correlation as origin of the enhanced thermopower values [3]. Furthermore, the huge carrier mobility combined with a rather low resistivity yields a record power factor $PF = S^2\sigma = 2300 \mu\text{W/K}^2\text{cm}$ [2].

Here, we report on the resistivity and the thermopower of the metallic heavy fermion system CeTiGe and the substitution series Ce$_{1-x}$La$_x$TiGe. Previously, the specific heat as well as the magnetic susceptibility of CeTiGe have been shown to be well described by the Coqblin-Schrieffer model with involvement of the full $J = 5/2$ multiplet and a Kondo temperature of 55 K [4]. An enhanced Sommerfeld coefficient of 290 mJ/K$^2$mol indicates the high effective mass. No magnetic ordering was found in this system. The resistivity exhibits rather high values of more than 100 $\mu\Omega\text{cm}$ below room temperature until it drops below the coherence temperature at 20 K (shown in Fig. 1) [4]. The thermopower of CeTiGe has been reported in Ref. [4] to almost reach 60 $\mu\text{V/K}$ at 17 K close to the temperature at which the specific heat and the magnetic susceptibility exhibits a maximum [4].

We present the thermopower of CeTiGe and Ce$_{1-x}$La$_x$TiGe and compare their power factor and emphasize that higher thermopower values can be achieved in systems with highly degenerate orbital ground state. Furthermore, several aspects with respect to the thermoelectric properties are dealt with when substituting the compound with the non-magnetic La on the Ce site. Firstly, the Kondo temperature is expected to shift to lower temperatures due to the lattice expansion. Secondly, the induced disorder leads to a reduced lattice thermal conductivity. Thirdly, the absolute values of the thermopower are not reduced by dilution of the magnetic moments.
2. Results
Polycrystalline samples of CeTiGe and Ce$_{1-x}$La$_x$TiGe were prepared by arc melting and subsequently annealed as described in Ref. [4]. X-ray powder diffraction confirm the tetragonal CeFeSi-type structure and a linear increase of the unit cell volume for La substitution [4, 5]. The resistivity was measured by a standard 4-point method and the thermopower by a one heater-two thermometer technique with a relaxation-time method in a commercial cryostat (PPMS by Quantum Design) in the temperature range between 2 K and 300 K.

The resistivity ratio $\rho/\rho(300 \text{ K})$ of Ce$_{1-x}$La$_x$TiGe is shown in Fig. 1. Coherence effects in pure CeTiGe yield a sharp drop of the resistivity below 20 K from high absolute values of 148 $\mu\Omega$cm at room temperature as reported [4]. The resistivity values increase further to around 180 $\mu\Omega$cm upon substituting La for Ce due to the increased spin disorder. Whereas the coherence is suppressed, the small increase below 30 K indicate single-ion Kondo behavior of diluted $f$ moments.

The thermopower of CeTiGe (Fig. 2) exhibits large positive values below 100 K and peaks at a value of 60 $\mu$V/K at 17 K which is close to the maximum temperature in the specific heat [4]. $S(T)$ becomes linear in $T$ at lowest temperatures indicative of Landau-Fermi liquid behavior in agreement with specific heat results [4] (Inset of Fig. 2).

The thermopower of Ce$_{0.8}$La$_{0.2}$TiGe even increases in absolute values with a peak value of 67 $\mu$V/K at 12 K. For Ce$_{0.6}$La$_{0.4}$TiGe lower thermopower values are observed with a similar maximum temperature of 11 K. For temperatures down to 2 K no saturation is found for $S/T$ as depicted in the inset of Fig. 2.
3. Discussion
In the investigated substitution range of Ce$_{1-x}$La$_x$TiGe very large thermopower values are observed around their Kondo temperature. The thermopower maximum shifts slightly from 17 K to 12 K upon La substitution. Due to the larger ionic radius of the La compared to the Ce ion the lattice is expanded for increasing $x$. Such expansion weakens the hybridization of the $f$ moments with the conduction electrons and thus lowers the Kondo temperature. Interestingly, the thermopower value at the maximum is even higher for Ce$_{0.8}$La$_{0.2}$TiGe than for pure CeTiGe. Also the low-$T$ values are considerably larger which implies a higher effective mass in agreement with a more enhanced Sommerfeld coefficient $\gamma = 380$ mJ/molK$^2$ for $x = 0.2$ and $\gamma = 480$ mJ/molK$^2$ for $x = 0.4$ [5]. Since no constant $S/T$ can be resolved in the investigated temperature range the Fermi liquid regime seems suppressed. The dilution of the $f$ moments has little impact on the thermopower values at the peak position. By contrast, the resistivity increases by one order of magnitude at 2 K from $\rho = 11.8$ $\mu$Ωcm to 132.5 $\mu$Ωcm for $x = 0.2$ as the coherence is disturbed upon substitution.

Theoretical investigations of strongly correlated electron systems based on the single-ion Anderson model reveal an enhancement of the thermopower close to the Kondo temperature in the existence of a degenerate ground state [6]. Similar results were obtained by Bickers et al. [7]. The high entropy $R \ln N$ involved with a degenerate state entails a large thermopower. The maximum value in $S(T)$ is $N/2$-fold enhanced compared to a doublet ground state [6]. The results on Ce$_{1-x}$La$_x$TiGe support these conclusions. Indeed, the maximum value of 70 $\mu$V/K is approximately 3 times larger than those of heavy fermion systems with a doublet ground state. CeTiGe represents a rare case with high thermopower at rather low temperatures.

The power factor $PF = S^2/\rho$ of CeTiGe and Ce$_{1-x}$La$_x$TiGe as shown in Fig. 1 is of sizable order comparable to commercial thermoelectric materials. One of the unique properties of heavy fermion systems is the combination of high thermopower and metallic resistivity. In consequence, the power factor is often found to be by orders of magnitude larger than for ordinary metals.

4. Conclusion
Enhanced thermopower values are reported to be observed in heavy fermion systems with highly degenerate orbital ground state. The maximum in the thermopower is related to the Kondo scale and can be tuned by chemical substitution without degrading the thermoelectric properties. The thermopower of CeTiGe and Ce$_{1-x}$La$_x$TiGe reveal enhanced thermopower values of 60 $\mu$V/K to 70 $\mu$V/K due to the full $J = 5/2$ Ce momentum as ground state configuration. A sample with gradually varying Ce:La ratio might yield an optimized thermopower peak along the thermal gradient in a Peltier cooler. In order to further improve the thermoelectric figure of merit, the lattice thermal conductivity has to be minimized.

References
[1] Jaccard D and Sierrro J, 1982 Valence Instabilities, eds: P. Wachter and H. Boppart (North Holland, Amsterdam)
[2] Bentien A, Johnson S, Madsen GHK, Iversen BB and Steglich F 2007 Europhys. Lett. 80 17008
[3] Sun P, Oeschler N, Johnsen S, Iversen BB and Steglich F 2009 Phys. Rev. B 79 155308
[4] Deppe M, Caroca-Canales N, Hartmann S, Oeschler N and Geibel C 2009 J. Phys.: Cond. Matt. 21 206001
[5] Sereni J, et al, 2009 submitted to Physica Status Solidi
[6] Zlatić V, Monnier R and Freericks J.K. 2008 Phys. Rev. B 78 045113
[7] Bickers NE, Cox DL and Wilkins JW 1987 Phys. Rev. B 36 2036