Ferromagnetism and transport properties of the Kondo system Ce₄Sb₁.₅Ge₁.₅

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1. Introduction

The ternary intermetallic cerium compounds form a great variety of systems with non-trivial physical properties, including Kondo lattices, intermediate valence, heavy-fermion compounds, etc. In particular, they can demonstrate anomalous magnetic ordering (including small magnetic moments), which is accompanied by anomalies of electronic characteristics [1,2]. Besides that, some systems have promising thermoelectric properties, i.e. high Seebeck coefficient and figure of merit ZT [3].

Here, we discuss transport characteristics of a number of Ce₄Sb₁₋ₓTx (T=Ge, Si, Sn, Pb, Al) alloys. As for thermoelectric properties, this system can be compared with β-Zn₄Sb₃ and rare-earth based anti-Th₃P₄ structure systems [4].

In more detail, we investigate magnetism and transport properties of the system with the composition Ce₄Sb₁₋ₓGeₓ which corresponds to optimal thermoelectric properties (highest Seebeck coefficient). This indicates high density of states at the Fermi level and anomalies of other electron properties.

Investigation of the related systems was performed in a number of works. The Kondo lattice Ce₄Sb₃ demonstrates moderately heavy-fermion behavior with γ=180 mJ/K² mol Ce and ferromagnetic ordering [5]. According to Ref. [5], a very sharp peak of specific heat at 3.9 K in zero magnetic field corresponds to the phase transition from paramagnetic to ferromagnetic order. Specific heat data indicate that antiferromagnetic components may exist in the ferromagnetic state, as well as in other R₄X₃ intermetallics [6]. The presence of such a complicated magnetism has been further confirmed by the neutron diffraction study that evidences commensurate antiferromagnetic ordering at 2 K in zero magnetic field. Saturation magnetization value of only 0.93 μB/Ce ion was observed at 1.8 K [7].

Magnetic properties of Ce–Co–Ge system were discussed in Refs. [8,9]. Some phases (including Ce₄Ge₃) which exhibit ferromagnetic-like ordering (or complex ordering including a ferromagnetic component) with low Curie temperature were also considered.

The magnetic structures of Ce₄Sb₃ [7] and Ce₄Ge₃ [6] turn out to be not compatible from the point of view of their magnetic symmetry: they demonstrate commensurate antiferromagnetic order with different orderings of Ce₄ cluster. Therefore, the solid solution Ce₄Sb₁₋ₓGeₓ demonstrates an interesting object for physical investigation. In the present paper, we find in Ce₄Sb₁₋ₓGeₓ ferromagnetism with strongly reduced moments, which is characteristic for the Kondo systems.

2. Experimental

The polycrystalline samples of Ce₄Sb₁₋ₓGeₓ were synthesized by melting the starting mixture followed by annealing. The preparation technique included an electric arc furnace under an argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper tray [10]. The purity of the component
Table 1
Physical properties at T=300 K of Ce₄Sb₃₋ₓTeₓ systems and related compounds: electric resistivity ρ (μΩ cm), Seebeck coefficient S, thermal conductivity κ and figure of merit parameter ZT = S²T/ρκ. The Wiedemann–Franz parameter is \(WF = \frac{\mu e T}{2 \pi k_B}\) being the free electron Lorentz number (\(k_B\) is the Boltzmann constant and \(e\) the electronic charge). The data on Zn₄Sb₃ are presented in comparison with Ref. [12]. The lattice parameter \(a\) was investigated not for all systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a), nm</th>
<th>(S), μV/K</th>
<th>(\rho), μΩ m</th>
<th>(\kappa), W/m K</th>
<th>(WF)</th>
<th>(ZT)</th>
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<td>Zn₄Sb₃ [12]</td>
<td>114.3</td>
<td>20.42</td>
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<td></td>
<td></td>
<td></td>
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<td>Zn₄Sb₃</td>
<td>128</td>
<td>29.0</td>
<td>5.9</td>
<td>23.3</td>
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<td>Ce₄Sb₃</td>
<td>0.95302(5)</td>
<td>8.7</td>
<td>1.69</td>
<td>8.96</td>
<td>2.06</td>
<td>0.0015</td>
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<td>Ce₄Sb₂₃Sb₀₈</td>
<td>0.94470(24)</td>
<td>13.0</td>
<td>3.2</td>
<td>8.2</td>
<td>3.58</td>
<td>0.0019</td>
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<tr>
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<td>13.7</td>
<td>2.1</td>
<td>8.0</td>
<td>2.29</td>
<td>0.0034</td>
</tr>
<tr>
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<td>0.93395(45)</td>
<td>11.4</td>
<td>13.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ce₄Sb₂₃Ge₁₅</td>
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<td>1.97</td>
<td>8.0</td>
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<td>2.29</td>
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<td>2.15</td>
<td>5.7</td>
<td>1.7</td>
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</tr>
<tr>
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<td>17.2</td>
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<td>11.93</td>
<td>0.0001</td>
</tr>
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<td>Ce₄Sb₂₃Sn₁₅Pb₀₄</td>
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<td>7.3</td>
<td>2.14</td>
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<td>7.5</td>
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<td>1.67</td>
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The transport properties of a number of Ce₄Sb₃₋ₓTeₓ systems measured at room temperature are present.

Fig. 1. Temperature dependence of inverse magnetic susceptibility from SQUID measurements. The inset shows low-temperature behavior.

3. Magnetic properties

We studied the field and temperature dependences of the magnetization for Ce₄Sb₃₋ₓTeₓ in the broad interval of magnetic fields (\(H < 5.0 \text{ kOe}\)) and temperatures (\(2 < T < 300 \text{ K}\)). The measurements demonstrated occurrence of a small ferromagnetic moment below at about 13 K.

Despite divergence of magnetic susceptibility near 13 K, the paramagnetic Curie temperature \(θ_c = – 9 \text{ K}\) is negative (Fig. 1), which is typical for the Kondo systems where on-site antiferromagnetic Kondo coupling dominates over intersite magnetic interactions [1]. The small value of saturation moment obtained (about 0.1 μB, Fig. 2) is also typical for the dense Kondo systems because of the Kondo screening. A similar situation takes place, e.g., in the compound CeRuSi₂ [2].

The \(T^{3/2}\)-interpolation characteristic for weak itinerant ferromagnetism with strong non-spin-wave fluctuations turns out to fit our data somewhat better than the \(T^{1/2}\)-interpolation (spin-wave theory for localized systems). This also confirms unusual nature of magnetic state.

4. Transport properties

The transport characteristics of a number of Ce₄Sb₃₋ₓTeₓ (\(T = \text{Ge, Si, Sn, Pb, Al}\)) systems measured at room temperature are present.
in Table 1. One can see that $\text{Ce}_4\text{Sb}_{1.5}\text{Ge}_{1.5}$ has largest value of the Seebeck coefficient. Therefore we present a detailed investigation of its properties in a wide temperature region.

The $\text{Ce}_4\text{Sb}_{1.5}\text{Si}_{1.5}$ sample has rather large residual resistivity about $1.4 \times 10^{-7}$ $\Omega \cdot \text{m}$. The temperature dependence of resistivity at low temperatures is shown in Fig. 3. A nearly linear behavior is observed below magnetic transition temperature (about 13 K) where inflection point of $\rho(T)$ occurs. This is connected with that the magnetic scattering becoming weakened in the ordered phase. Such a behavior is similar to that observed in ferromagnetic $\text{CeRuSi}_2$ [2,15].

From the data of Ref. [5] on $\beta T^3$-term in specific heat of $\text{Ce}_4\text{Sb}_3$, we can estimate the Debye temperature as $\theta_D = 200$ K. Then, by using the Bloch–Grüneisen formula we can extract the lattice (phonon) contribution to resistivity (Fig. 4). Thus magnetic resistivity demonstrates a high-temperature maximum near 150 K, which is characteristic for Kondo systems and can be approximately described by a logarithmic law in some temperature interval (cf. also the data on $\text{CeRuSi}_2$ [2]).

The temperature dependence of thermoelectric power is shown in Fig. 5. One can see that, as well as in resistivity, an inflection point seems to occur near the Curie temperature.

Data on thermal conductivity are present in Fig. 6 together with the temperature dependence of the modified Lorentz number.
$L = \kappa p / T$. A comparison with the Wiedemann–Franz demonstrates that electron and phonon contributions are comparable, and the latter contribution is not a dominating one at high temperature. Nevertheless, despite large value of the Seebeck coefficient, the figure of merit $ZT$ reaches at room temperatures about 0.8% only because of rather high thermal conductivity (see Table 1).

5. Discussion and conclusions

The results obtained demonstrate that Ce$_8$Sb$_{1.5}$Ge$_{1.5}$ is a ferromagnetic Kondo lattice. Although magnetic ordering is a rather usual phenomenon in Kondo systems, examples of ferromagnetic Kondo compounds are quite not numerous [1,2]. The presence of magnetic transition is confirmed by direct SQUID measurements and the presence of anomalies in transport properties (resistivity and thermoelectric power).

Our results on transport characteristics can be compared with typical dependences of resistivity and Seebeck coefficient including the Kondo features, which are presented in Ref. [9]. The magnetic phase transitions in intermetallic compounds usually manifest themselves in the thermoelectric power as inflection points in its temperature variation, and frequently are not discernible at all. In particular, the ferromagnetic orderings are hardly visible in thermoelectric properties of a number of Ce$_x$CoGe$_m$ systems. A similar situation takes place for the resistivity.

Acknowledgments

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References