Physical properties of the new cage compound
\(\text{Ce}_4\text{Pt}_{12}\text{Sn}_{25}\)

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Abstract. A promising route to highly efficient thermoelectric materials is to introduce the effect of strong electronic correlations into cage compounds which contain weakly bound ions in oversized cages of the framework structure. By this approach the low thermal conductivity of cage compounds shall be combined with giant thermopower values of strongly correlated systems, thus doubly optimizing the thermoelectric figure-of-merit. We present here results on a new candidate material, \(\text{Ce}_4\text{Pt}_{12}\text{Sn}_{25}\). There is a unique Ce site in the center of a polyhedron cage made up of 6 Pt and 12 Sn atoms. Synthesis, structure and various physical properties measured between room temperature and 2 K are presented.

1. Introduction
The potential of a material for thermoelectric applications is determined by it’s dimensionless thermoelectric figure-of-merit \(ZT = TS^2\sigma/\kappa\), where \(S\) is the thermopower, \(\sigma\) the electrical conductivity, \(\kappa\) the total thermal conductivity (which contains an electronic and a lattice contribution, \(\kappa_e\) and \(\kappa_l\)), and \(T\) the absolute temperature. Traditional thermoelectric materials currently in use have room temperature \(ZT\) values of approximately unity. A promising route to enhance \(\sigma/\kappa\) is the use of guest atoms in oversized cages as in intermetallic clathrates [1,2] or filled skutterudites [3]. In these systems, the “rattling” (localised oscillations) of guest atoms is believed to strongly scatter the heat carrying acoustic phonons leading to glass-like thermal conductivities. Since the charge carriers are confined to the framework, the rattling does not significantly affect the electronic properties (phonon glass – electron crystal concept) [4]. In order to optimize \(S\) in addition to \(\sigma/\kappa\) we are trying to introduce suitable rare earth elements with an unstable 4\(f\) shell (e.g, Ce, Yb, Sm, Tm) as guest atoms into cage compounds. Hybridisation between localised \(f\)-electron states and conduction electrons leads to a fluctuating valence or Kondo spin compensated state characterised by a narrow \(f\)-band or resonance near the Fermi level. This sharp feature in the density of states near the Fermi level can lead to a substantial enhancement of the thermopower [5,6]. Since \(S\) enters quadratically in \(ZT\) this contribution is particularly important.

\(\text{Ce}_4\text{Pt}_{12}\text{Sn}_{25}\) is a cubic compound with a large unit cell parameter \(a = 12.281\,\text{Å}\) and a unique Ce position. Ce atoms are encapsulated in cages of Pt and Sn with coordination number 18 (Fig. 1). X-ray diffraction revealed no exchange disorder between the Ce, Pt, and Sn sublattices but an anomalously large atomic displacement parameter of Sn at the 24\(g\) site, which can alternatively be described in terms of a split position [7].
2. Experimental details

Polycrystalline samples of Ce$_4$Pt$_{12}$Sn$_{25}$ were produced by repeated melting of the elemental Ce (99.95%), Pt (99.95%), and Sn (99.9999%) in a cold copper boat under argon atmosphere. The samples were annealed at 750°C for 5 days. The X-ray diffraction patterns of annealed samples showed that they were single phased. SEM/EDX investigations confirmed the absence of foreign phases and the correct elemental composition. Electrical resistivity, magnetic susceptibility, and magnetisation were measured in a Physical Property Measurement System (PPMS) in the temperature range 2-300 K and in magnetic fields up to 9 T. Electrical transport measurements were done using a standard four-point ac technique. Thermal transport was measured with a standard steady state four-point method.

![Figure 1. Three-dimensional arrangement of Ce-centered Pt/Sn polyhedra in the unit cell of Ce$_4$Pt$_{12}$Sn$_{25}$.](image1.png)

![Figure 2. Temperature dependence of the electrical resistivity, ρ(T), of Ce$_4$Pt$_{12}$Sn$_{25}$. The inset shows ρ vs $T^2$ below 6.3 K, together with a linear fit to the data (see text).](image2.png)

3. Experimental results and discussion

Figure 2 shows the temperature dependence of the electrical resistivity ρ(T) of Ce$_4$Pt$_{12}$Sn$_{25}$. The overall temperature dependence is metallic, with a linear decrease from 300 K to approximately 200 K, a steeper decrease down to 20 K, and the trend to saturation to a constant value at the lowest temperatures. The residual resistance ratio RRR = ρ(300K)/ρ(2K) is 2.5. A possible reason for the small RRR value is the “rattling” motion/split position of the Sn atoms at the 24g site [7]. Since Sn is a framework and not a guest atom it is likely to act not only as scatterer for phonons but also for electrons.

In the inset of Fig. 2 ρ(T) is plotted vs $T^2$ below 6.3 K. A linear fit ρ = $\rho_0 + AT^2$ to the data up to 5.5 K yields $\rho_0 = 82.5 \, \mu$Ωcm and $A = 0.021 \, \mu$Ωcm/K$^2$. For many Ce-based heavy fermion compounds it has been shown that the ratio $A/\gamma^2$, where $\gamma$ is the Sommerfeld coefficient of the specific heat, takes the universal value of $1 \times 10^{-5} \, \mu$Ωcm(molK/mJ)$^2$ [8]. From the above $A$ value $\gamma$ is calculated to be approximately 45 mJ/molK$^2$, indicating a moderate mass enhancement.

Figure 3 presents the temperature dependence of the Seebeck coefficient of Ce$_4$Pt$_{12}$Sn$_{25}$. S is positive in the entire temperature range. Above 50 K, S increases linearly with temperature. The relatively small values of S are in agreement with the metallic behaviour evidenced by ρ(T). For a wide range of heavy fermion compounds there is a correlation between S/T and $\gamma$ [9]. The low-temperature value of $S/T$ of Ce$_4$Pt$_{12}$Sn$_{25}$ is approximately 0.07 $\mu$V/K which corresponds,
in this scheme, to a $\gamma$ value of approximately 7 mJ/molK$^2$, much below the value estimated from $\rho(T)$. This small value might be caused by cancellation effects due to two types of charge carriers in Ce$_4$Pt$_{12}$Sn$_{25}$. Clearly, measurements of the specific heat and of the electrical resistivity and thermopower at lower temperatures are needed to conclude on the strength of the correlations present in Ce$_4$Pt$_{12}$Sn$_{25}$.

The thermal conductivity $\kappa$ of Ce$_4$Pt$_{12}$Sn$_{25}$ is shown between room temperature and 2 K in Fig. 4. To estimate the lattice contribution $\kappa_l$ we determined the electronic contribution $\kappa_e$ assuming the validity of the Wiedemann Franz law $\kappa/\sigma = LT$ where $L$ is the Lorenz number $2.44 \times 10^{-8}$ WΩK$^{-2}$. $\kappa_l = \kappa - \kappa_e$ is almost constant at temperatures above 50 K. At temperatures below 25 K, $\kappa_l$ decreases rapidly with decreasing temperature. The absence of a pronounced peak in $\kappa_l$, characteristic of crystalline materials, might be attributed to the rattling modes in this compound [7].

In Fig. 5 we present the dc magnetic susceptibility $\chi$ of Ce$_4$Pt$_{12}$Sn$_{25}$ in the form $1/\chi$ vs $T$ in an applied field of 0.1 T. At temperatures above 150 K, $\chi(T)$ can be described by a Curie-Weiss law $\chi(T) = C/(T - \Theta_p)$. A fit to these data yields $\Theta_p = -50$ K for the paramagnetic Weiss temperature and $\mu_{\text{eff}} = 2.3 \mu_B$/Ce for the effective magnetic moment. $\mu_{\text{eff}}$ is slightly lower than the full moment $2.54 \mu_B$ expected for a free Ce$^{3+}$ ion. We have also measured magnetization vs magnetic field curves at several temperatures (Fig. 6). It is seen that the moment reached at 2 K and 7 T is only about 70% of the saturation moment of free Ce$^{3+}$.

In summary, we synthesized single phased polycrystalline Ce$_4$Pt$_{12}$Sn$_{25}$ samples and investigated, for the first time, various physical properties of this new cage compound. While our data corroborate the presence of rattling modes related to the previously observed large atomic displacement parameters of framework Sn atoms clear evidence for strong correlations will have to await experiments at lower temperatures. Due to the metallic character, the dimensionless thermoelectric figure-of-merit is low ($ZT=0.014$ at room temperature). Thus, to enhance the thermoelectric performance, substitutions will be needed to reduce the charge carrier concentration.
Figure 5. Temperature dependence of the inverse magnetic susceptibility, $1/\chi(T)$, of Ce$_4$Pt$_{12}$Sn$_{25}$. The solid line represents a Curie-Weiss fit to the experimental data (see text).

Figure 6. Isothermal magnetization vs magnetic field curves, $M(\mu_0 H)$, of Ce$_4$Pt$_{12}$Sn$_{25}$.

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References
[1] P. Rogl, Formation and crystal chemistry of clathrates, in Thermoelectrics Handbook (ed. D. M. Rowe, CRC Press, Taylor and Francis Group, Boca Raton, 2006), Chap. 32.
[2] G. S. Nolas, Structure, transport, and thermoelectric properties of clathrate compounds, in Thermoelectrics Handbook (ed. D. M. Rowe, CRC Press, Taylor and Francis Group, Boca Raton, 2006), Chap. 33.
[3] C. Uher, Skutterudite-based thermoelectrics, in Thermoelectrics Handbook (ed. D. M. Rowe, CRC Press, Taylor and Francis Group, Boca Raton, 2006), Chap. 34.
[4] J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf, and G. A. Slack, Phys. Rev. Lett. 82 (1999) 779.
[5] G. Aeppli and Z. Fisk, Comments Condens. Matter Phys. 16 (1992) 155.
[6] S. Paschen, Thermoelectric aspects of strongly correlated electron system, in Thermoelectric Handbook (ed. D. M. Rowe, CRC Press, Taylor and Francis Group, Boca Raton, 2006), Chap. 15, and Refs. herein.
[7] B. Chaïk, G. Venturini, and B. Malaman, Mat. Res. Bull. 25 (1990) 807.
[8] N. Tsuji, H. Kontani, and K. Yoshimura, Phys. Rev. Lett. 94 (2005) 057201.
[9] K. Behnia, D. Jaccard, and J. Flouquet, J. Phys. Condens. Matter 16 (2004) 5187.