

Low Temperature Thermoelectric Power of $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$

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Abstract We present the thermoelectric power $S(T)$ of the $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$ alloy for temperatures $1.5 \text{ K} < T < 300 \text{ K}$. We observe three characteristic features across the $0 < x < 1$ substitution range: two positive maxima and a negative minimum, that are typical for Ce compounds that display, or lie close to, magnetism. Our analysis of the data shows that the high- T maximum is related to the Kondo effect on excited crystal-field levels, but that the low- T one cannot be simply associated with the Kondo scale, T_K . We speculate that disorder induced by alloying can be at the origin of this discrepancy and can also be responsible for the low $S(T)$ measured at low temperatures in the $0.2 < x < 0.8$ concentration range. We have extended electrical resistivity measurements on $\text{Ce}(\text{PdCu})\text{Si}_2$ ($x = 0.5$) down to $T \sim 40 \text{ mK}$ in applied fields as high as 16 T.

Keywords Heavy fermions · Antiferromagnetic transition · Thermopower · Electrical resistivity

1 Introduction

CePd_2Si_2 and CeCu_2Si_2 are two well-known Kondo lattice compounds that crystallize in the ThCr_2Si_2 -type tetragonal structure. The ground state (GS) of the Pd compound is antiferromagnetic, with $T_N = 10.3 \text{ K}$ and a reduced ordered moment $\mu = 0.66 \mu_B$ oriented perpendicular to (110) planes [1]. Applied pressure suppresses its magnetism

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around the critical pressure $p_c^{\text{Pd}} \approx 28$ kbar and induces superconductivity with $T_c \sim 0.5$ K in samples with low residual resistivity $\rho_0 \lesssim 2 \mu\Omega \text{ cm}$ [2]. On the other hand, CeCu_2Si_2 is already located at the critical pressure for superconductivity [3], $p_c^{\text{Cu}} \approx 0$. Actually, its GS can be tuned between magnetic phases A and X or superconducting S by small composition variations in $\text{Ce}_{1\pm x}\text{Cu}_{2\pm y}\text{Si}_2$ [4]. In this case, superconductivity with $T_c \sim 0.7$ K is observed even in samples with large residual $\rho_0 \gtrsim 50 \mu\Omega \text{ cm}$.

Considering now the alloy between the aforementioned compounds, one could naively expect that in $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$ $T_N(x)$ would evolve progressively down to $T_N \sim 0$ as $x \rightarrow 1$. It was shown [5–7] that this is not the case since antiferromagnetism is abruptly suppressed for $x \gtrsim 0.2$, giving place to a non-Fermi-liquid phase. This is concomitant with an increase of the Kondo temperature, from $T_K(x=0) \approx 10$ K up to $T_K \approx 50$ K for $x = 0.7$, while in the Cu-rich side $T_K(x)$ drops again down to $T_K(x=1) \approx 10$ K [7]. This nonmonotonous evolution of $T_K(x)$ points to a complex dependence of the hybridization strength Γ between the $4f$ and conduction-band states in this system: substitution of Pd by Cu results both in chemical positive pressure that enhances Γ (probably dominant on the Pd-rich side) and a change in chemical potential that reduces Γ on the Cu-rich samples.

The thermoelectric power, or Seebeck coefficient $S(T)$, is a powerful tool to investigate Ce intermetallics as Γ is changed by means of a control parameter. In these compounds, $S(T)$ is usually positive and displays one or two well-resolved maxima depending on Γ . Link et al. [8] described the different behaviors of $S(T)$ as Γ increases with applied pressure from magnetism intermediate-valence behavior. This description, based on $S(T)$ results from several Ce compounds and their pressure evolution, is used here to analyze the $S(T, x)$ dependence in $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$ [9]. We profit from the available thermal, transport, and magnetic data on this alloy [7] to reinterpret $S(T)$ results in the presence of large degree of disorder.

2 Experimental Details

We performed $S(T)$ measurements between 1.5 and 300 K on the same samples that were used to measure the physical properties reported in Ref. [7]. These samples were prepared as polycrystalline buttons by arc melting the stoichiometric amounts of the pure elements and annealed as already described. They were cut to a typical dimension of $1 \times 1 \times 10 \text{ mm}^3$ using a low-speed diamond saw. Surfaces were polished using small-grain sand paper prior to spot welding the thermocouple wires for the $S(T)$ and the gold wires for $\rho(T)$ measurements.

In the basic thermopower measurement, a thermal gradient ΔT is established across the sample and the voltage $\Delta V = (S_w - S)\Delta T$ is determined. If the thermoelectric power of the measuring wires S_w is known, one can determine S from a linear fit to the ΔV versus ΔT data. The method we use to determine the thermopower of the sample $S(T)$ is a variation usually described as “dynamic method”, see for example Ref. [10, 11]: two thermocouples, chromel-sample and $\underline{\text{Au}}\text{Fe}$ -sample, are measured simultaneously as the power on a resistive heater when the hot extreme of the sample is increased (the other extreme is held at a constant base temperature T during the measurement). The measured voltages $\Delta V_K = (S_K - S)\Delta T$ and $\Delta V_A = (S_A - S)\Delta T$

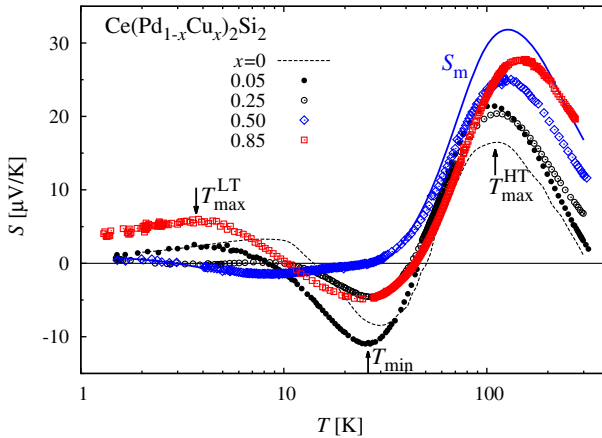


Fig. 1 Thermopower $S(T)$ of $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$ versus a logarithmic T -scale, compared to $x = 0$ data from Ref. [12] (dashed line). Arrows signal the three different $S(T)$ anomalies. The full line is an estimation of the magnetic contribution to S , see the text. The statistical error of the $S(T)$ data is smaller than the symbol size (Color figure online)

allow one to determine the temperature gradient $\Delta T = (\Delta V_K - \Delta V_A)/(S_K - S_A)$ and the thermopower $S = S(T + \frac{\Delta T}{2}) = S_A + (S_K - S_A)/(1 - \frac{\Delta V_K}{\Delta V_A})$. The ratio $\frac{\Delta V_K}{\Delta V_A}$ is the slope of ΔV_K versus ΔV_A data, while S_K and S_A are, in our case, the Seebeck coefficients of chromel (Ni90Cr10) and AuFe 0.07 at.% at $T + \frac{\Delta T}{2}$. The calibration of our thermocouple wires is described in Ref. [9].

The electrical resistivity of $\text{Ce}(\text{PdCu})\text{Si}_2$ ($x = 0.5$) was measured in extended temperature and field ranges using a new dilution fridge with 25 mK base temperature available at our laboratory, operating inside an 18 Tesla magnet¹. Four-probe resistivity measurements were performed using an ac technique with an LR700 resistance bridge.

3 Results and Discussion

In Fig. 1 we present the thermoelectric power $S(T)$ of $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$ (for complementary data at other concentrations see Ref. [9]), plotted along with the $S(T)$ data for CePd_2Si_2 (full line) taken from Ref. [12]. In a first approximation, the $S(T)$ curves show similar dependences. With decreasing temperature they typically display three anomalies: a high-temperature maximum, $T_{\text{max}}^{\text{HT}} \sim 130$ K, a negative minimum at $T_{\text{min}} \sim 20$ K, and a low- T maximum at $T_{\text{max}}^{\text{LT}} \lesssim 10$ K. In Fig. 2 we present the available data on $S(T, x)$ as a gray-scale contour plot. This representation helps to stress the complex dependence of the thermopower of this alloy when one looks in further detail.

The thermopower of the $x = 0.05$ sample resembles that of CePd_2Si_2 , although the exact position of the anomalies and the magnitude of $S(T)$ changes slightly. At low

¹ Dilution refrigerator MCK50-400 from Leiden Cryogenics B.V., inside a 18 Tesla superconducting magnet from Oxford Instruments.

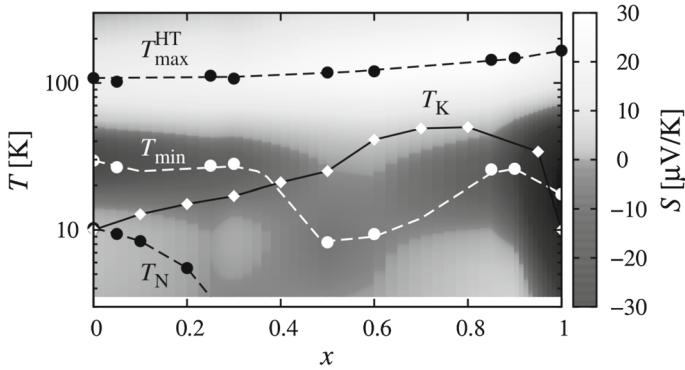


Fig. 2 Gray-scale contour plot of $S(T, x)$ of $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$. Points are the x -dependence of $T_{\text{max}}^{\text{HT}}$ and T_{min} along with T_{N} and T_{K} taken from Ref. [7]. Lines are guides to the eye

temperatures we do not observe in $S(T)$ an anomaly related to the antiferromagnetic transition at $T_{\text{N}} = 9.4\text{ K}$, although it appears as a clear drop in $\rho(T)$ [7]. In the intermediate Cu-content range, $0.2 < x < 0.8$, $|S(T)| < 1.5\ \mu\text{V/K}$ for temperatures $T \lesssim 15\text{ K}$. Despite these comparable low values, $S(T)$ still displays some structure that can be seen in the gray-scale coding of Fig. 2. As Cu content increases further, $x > 0.8$, $S(T)$ again reaches large negative values at low temperatures. The thermopower of CeCu_2Si_2 depends on the exact composition of the measured sample, but it can attain $S \sim -30\ \mu\text{V/K}$ at $T \sim 20\text{ K}$ [13]. Notice that in a very small concentration range between $x = 0.9$ and $x = 1$, the magnitude $|S(T_{\text{min}})|$ increases by a factor 3.

In Fig. 2 we present the evolution of $T_{\text{max}}^{\text{HT}}(x)$ and $T_{\text{min}}(x)$ along with $T_{\text{K}}(x)$ and $T_{\text{N}}(x)$ taken from Ref. [7]. In Ce compounds, the high- T maximum in $S(T)$ is usually associated with Kondo scattering on the thermally populated crystal electric field's (CEF) excited levels at a typical energy Δ above the GS [8, 14, 15]. Assuming $T_{\text{max}}^{\text{HT}} \sim 0.4\Delta/k_{\text{B}}$ for $k_{\text{B}}T_{\text{K}} \ll \Delta$, we can estimate an overall CEF splitting increasing from $\Delta/k_{\text{B}} \sim 270\text{ K}$ for CePd_2Si_2 up to $\Delta/k_{\text{B}} \sim 420\text{ K}$ for CeCu_2Si_2 . This increasing tendency of $\Delta(x)$ coincides with the expected behavior based on neutron-scattering data, that finds excited doublets at $\Delta_1/k_{\text{B}} = 200\text{ K}$ and $\Delta_2/k_{\text{B}} = 260\text{ K}$ for CePd_2Si_2 , [16] and $\Delta_1/k_{\text{B}} = 140\text{ K}$ and $\Delta_2/k_{\text{B}} = 360\text{ K}$ for CeCu_2Si_2 [17].

In many cerium systems the low- T maximum in $S(T)$ is linked to the Kondo effect on the GS, $T_{\text{max}}^{\text{LT}}(x) \sim T_{\text{K}}$. This seems not to be the case in $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$. In this alloy, neither $T_{\text{max}}^{\text{LT}}(x)$ nor $T_{\text{min}}(x)$ can be simply related to the Kondo scale as determined in Ref. [7]. However, the zero crossing of $S(T)$ between $T_{\text{min}}(x)$ and $T_{\text{max}}^{\text{HT}}(x)$, is roughly anticorrelated to $T_{\text{K}}(x)$. This is consistent with a numerical description of CeRu_2Ge_2 , but it is not an expected general feature in Ce compounds (compare Fig. 2 of Ref. [15] and Fig. 3 of Ref. [18], calculated on a doublet-quartet CEF scheme).

For simple metals and many strongly correlated systems [19] the simple relation $S(T)/T \equiv S_0 \propto \gamma$ holds in the $T \rightarrow 0$ limit, where $\gamma \equiv C/T \sim N(\epsilon_{\text{F}})$ is the Sommerfeld coefficient of the specific heat. This $S/T \sim C/T$ relationship seems to hold, at least qualitatively, even for non-Fermi liquids in which a divergence is observed in both properties [20, 21]. In Fig. 3, we plot $S(T)/T$ for different samples covering the

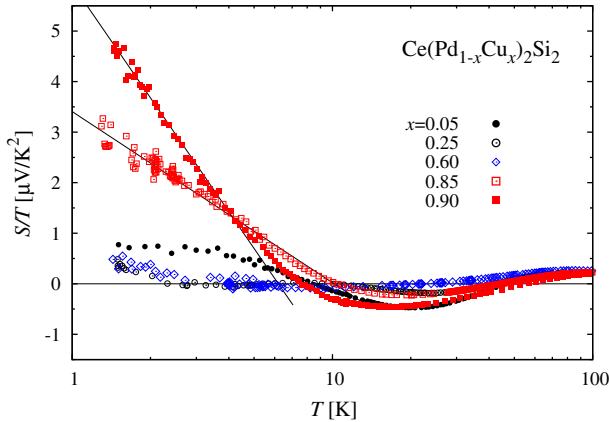


Fig. 3 $S(T)/T$ data of selected samples displaying a $S/T \sim \ln(T_0/T)$ dependence at low- T and $x \sim 1$. The full lines are fits to the data with $T_0(x = 0.85) \approx 10$ K and $T_0(x = 0.9) \approx 6$ K. Notice the low temperature S/T saturation for $x = 0.05$ (Color figure online)

whole x -range. For $x = 0.05$ we observe a saturation value of $S/T \approx 0.75 \mu\text{V}/\text{K}^2$ for $T \lesssim 3$ K. We take $T_{\text{ref}} = 1.5$ K (roughly the lowest temperature in our $S(T)$ measurements) as a reference and we calculate the quantity $q(T_{\text{ref}}) \equiv N_{\text{Av}} e \frac{S(T_{\text{ref}})}{C(T_{\text{ref}})}$, with the notation of Ref. [19]. For $x = 0.05$ we get $q(1.5 \text{ K}) \approx 0.5$, that is half the $q \approx 1$ observed in the $T \rightarrow 0$ limit in many Ce compounds [19]. On the Cu-rich side, where $S/T \sim \ln(T_0/T)$, we calculate $q(1.5 \text{ K}) \approx 1.2$ for the $x = 0.85$ and 0.90 samples, close to $q = 0.9$ for CeCu_2Si_2 under an applied magnetic field [19]. In the intermediate range, $0.2 < x < 0.8$, the values $q(1.5 \text{ K}) \sim 0.08\text{--}0.22$ are almost an order of magnitude smaller than expected. Despite $q(T_{\text{ref}})$ in a magnetic or a non-Fermi-liquid phase will depend on the chosen T_{ref} , the above estimation helps to stress the fact that in this intermediate substitution range the low- T $S(T)$ is abnormally small.

We believe that this reduced $S(T)$ and the absence of $T_{\text{K}} - T_{\text{max}}^{\text{LT}}$ correlation are not just trivial consequences of the Gorter–Nordheim rule, i.e., the weighting of each independent thermopower contribution S_i by the corresponding resistivity: $S = \sum_i S_i \rho_i / \rho$. To show this, we estimate the magnetic contribution to $S(T)$ for the sample $x = 0.5$ as $S_m = \rho_m^{-1}(\rho S - \rho_{\text{ref}} S_{\text{ref}})$. We use the total resistivity of $\text{La}(\text{Pd}_{0.4}\text{Cu}_{0.6})_2\text{Si}_2$ for ρ_{ref} ,² the thermopower of LaCu_2Si_2 taken from Ref. [22] for S_{ref} , and $\rho_m = \rho - \rho_{\text{ref}}$.³ The computed $S_m(T)$ for $\text{Ce}(\text{PdCu})_2\text{Si}_2$ is displayed as a full line in Fig. 1, with temperature dependence and values close to those of the total $S(T)$. Since $S(T) \sim S_m(T)$, substitutional disorder (which is present in both the Ce and La alloys) seems not to be the sole ingredient for a reduced $S(T)$. Notice that this large reduction of the low- T $S(T)$ seems to be absent in $\text{Ce}(\text{Pd}_{1-x}\text{Ni}_x)_2\text{Si}_2$, [12] that

² The $\rho(T)$ data for this La-alloy can be roughly described, in $\mu\Omega \text{ cm}$, by $\rho(T) = 126.2 + 3.4(T/60)^{2.4}$ below 60 K and $\rho(T) = 121.5 + 0.132T$ above.

³ Notice that $\rho_m = \rho - \rho_{\text{ref}}$ still has a very large contribution at low T of the order of $350 \mu\Omega \text{ cm}$. An overestimation of ρ_m , due e.g., microcracks in the sample, would lead to underestimate S_m .

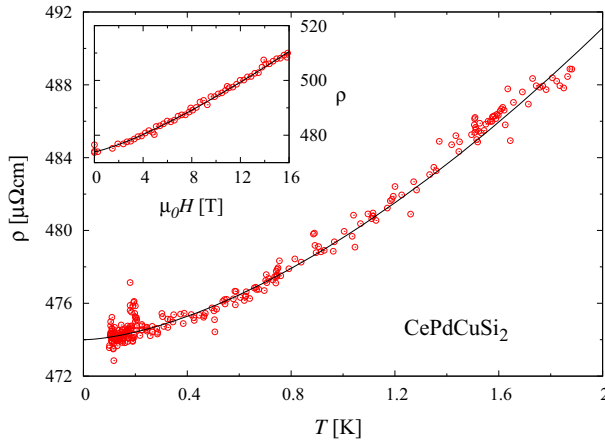


Fig. 4 Low-temperature resistivity of $\text{Ce}(\text{PdCu})\text{Si}_2$ ($x = 0.5$) for $T < 2$ K. *Inset* magnetoresistance measured at 45 mK. *Full lines* are fits to the data as explained in the text (Color figure online)

actually resembles CePd_2Si_2 under pressure [8], or $\text{Ce}(\text{Rh}_{1-x}\text{Ni}_x)_2\text{Si}_2$ [23]. Then, the random substitution of hole-like Pd by electron-like Cu could be relevant to explain our results. We speculate that in $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$ alloys, substitutional disorder could result in quite different local environments at neighboring sites resulting in a large distribution of (local) Kondo temperatures or even crystalline anisotropies [24]. This could lead to a “cancellation” effect in the thermopower, that has several sign changes at low temperatures according to x (Fig. 2).

To complement this $S(T)$ study, we have undertaken the extension of $\rho(T)$ measurements to check the reported T -dependences [7] to temperatures $T < 0.5$ K, see Fig. 4. For $\text{Ce}(\text{PdCu})\text{Si}_2$ ($x = 0.5$) in the range $T < 1.8$ K we obtain $\rho(T) = (474 + 5.6T^{1.61}) \mu\Omega\text{cm}$, consistent with the $T^{1.67}$ non-Fermi-liquid dependence determined at higher temperatures [7]. At 45 mK, this sample shows a positive magnetoresistance (see the inset of Fig. 4) with a field dependence $\rho(H) = (474 + 1.1H^{1.27}) \mu\Omega\text{cm}$ for $\mu_0H \leq 16$ T. A positive magnetoresistance is expected for a coherent Kondo state in the lattice at low temperatures [25].

In summary, our measurements show that in $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_2\text{Si}_2$, $S(T)$ retains several typical characteristics of Ce compounds close to a magnetic instability, despite the loss of long-range magnetism for $x > 0.2$ and the five times increase of $T_K(x)$ between $x = 0$ and $x = 0.8$. The comparison with $\text{Ce}(\text{Pd}_{1-x}\text{Ni}_x)_2\text{Si}_2$, [12] shows that equivalent volume changes in both alloys result in very different $S(T)$ dependences, pointing to the importance of the increasing electron count under Cu-doping. Additionally, we suggest that Cu-doping induces an enhanced effect of substitutional disorder, that could be at the origin of the low $S(T)$ values for $T \lesssim 15$ K observed in the $0.2 < x < 0.8$ substitution range. Further information on the transport problem could involve the careful combined measurement of $\rho(T)$ and $S(T)$ on oriented single crystals in order to study the crystalline anisotropy of the alloys and to get a better estimation of the different scattering contributions.

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