Reducing lattice thermal conductivity by valence fluctuations: an experimental study on Ce(Pd$_{1-x}$Rh$_x$)$_3$

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Abstract

Intermetallic Ce(Pd$_{1-x}$Rh$_x$)$_3$ was studied by means of X-ray diffraction and transport measurements. The substitution of Pd/Rh causes a non-Vergard law like behaviour of the lattice constants which is attributed to a significant change of the system towards intermediate valence of the Ce ions. Simultaneously, the lattice softens. This substitution, however, is also responsible of a distinct decrease of the exceptionally large thermopower derived for CePd$_3$. The concomitant increase of the characteristic fluctuation temperature is able to reduce the lattice thermal conductivity and hence can be considered as novel mechanism with respect to an improvement of the thermoelectric performance of such valence fluctuating materials.

Introduction

Intermediate valent CePd$_3$ exhibits one of the highest Seebeck coefficients (about 100 to 120 μV/K at a broad maximum around 150 K) within Ce based intermetallics [1]. Such strongly enhanced $S(T)$ values are referred to an intense Kondo interaction responsible for a characteristic temperature T_K of about 220 K [2]. Enhanced values of T_K are a fingerprint of a strong $4f$-s,p,d hybridisation, which in turn promotes an intermediate electronic configuration of the Ce ion. Simultaneously, a high electron density of states at the Fermi level, associated with the Abrikosov Suhl resonance, provides the base requisite for a large Seebeck effect. Theoretically, within the scope of the single impurity Anderson model this relationship follows as $S_d = 2\,\pi/(|e|N)\gamma \cot(\eta(0))$, where γ is the Sommerfeld value, N the degeneracy of the $4f$ state and η is the phase shift [3]. This equation shows that the density of states at the Fermi energy, expressed by the Sommerfeld value, is the relevant parameter driving the Seebeck effect in Kondo type materials. Substitutions of Pd in CePd$_3$ by platinum metal elements such as Rh and Ru enlarge the Kondo temperature T_K via enhanced hybridisation and thus trigger significant valence fluctuations [4]. Since the maximum contribution in $S(T)$ occurs at a temperature roughly proportional to T_K the Pd/Rh substitution is expected to tune $S_{max}(T)$ in a continuous manner over a broad temperature range. Besides, phonons are strongly scattered on such valence fluctuations giving rise to a decrease of the lattice thermal conductivity [5]. Theoretically, this follows from the relaxation rate $1/\tau_c = E\omega$, where E is some material dependent constant and ω is the phonon frequency [6]. This type of scattering dominates at low temperatures and produces a T^2 behaviour of λ_{ph}. Increasing the strength of this interaction results in a suppression of the thermal conductivity maximum and eventually reveals a powerful decrease of λ_{ph} at high temperatures.

The aim of the present work is to verify in some detail the scenario outlined above by investigating the temperature dependent electrical resistivity, thermal conductivity and thermopower of various concentrations of the solid solution Ce(Pd$_{1-x}$Rh$_x$)$_3$ in a temperature range from 4.2 to about 300 K.

Experimental

Samples were prepared by high frequency melting using stoichiometric amounts of the constituents elements. After remelting for several times the ingots were sealed under vacuum in silica capsules and heat treated at 900°C for 1 week. Phase purity and lattice constants were tested by powder diffraction data obtained with a Huber-Guinier camera applying Cu Kα_1 radiation and employing the program package FULLPROF. Temperature dependent thermopower, electrical resistivity, and thermal conductivity data were collected using standard techniques. Details are described elsewhere Ref. [7].

Results and discussion

Ce(Pd$_{1-x}$Rh$_x$)$_3$ crystallizes in an ordered variant of the cubic AuCu$_3$ structure. Ce occupies the 1a site, while Pd and Rh are statistically distributed over the 3c sites of Pm-3m. The lattice parameter a of Ce(Pd$_{1-x}$Rh$_x$)$_3$ is shown in Fig. 1. Both border compounds, i.e., CePd$_3$ and CeRh$_3$ are in good agreement with the lattice constants reported in literature.

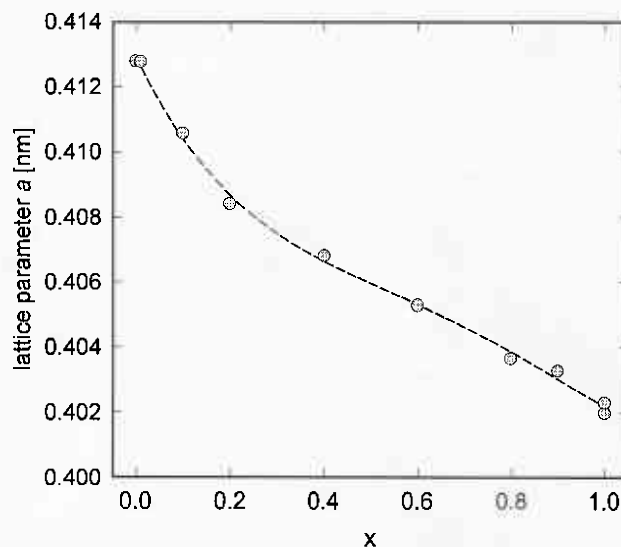Fig. 1: Concentration dependent lattice parameter a of Ce(Pd$_{1-x}$Rh$_x$)$_3$

The evolution of the lattice parameter a does not follow Vergard's rule. Rather, there is initially a much larger reduction of the unit cell volume initially when Pd is substituted by Rh. This observation may be due to either: i) Pd and Rh not being isoelectronic - the different electronic structure influences the unit cell volume in a non-monotonic manner, ii) the substitution of Pd by Rh driving the Ce ions towards the 4^+ state. As a result, the atomic radius of Ce decreases, and in combination with the influence of the Rh atomic radius, a non-linear variation of the lattice parameter may result. The valence change throughout the series, however, can be also a result of the alteration of the electronic structure caused by Rh as well as simply by chemical pressure exerted to the Ce ions by the shrinking unit cell volume throughout the series.

Temperature dependent resistivity measurements $\rho(T)$ of the entire series $Ce(Pd_{1-x}Rh_x)_3$ are summarized in Fig. 2.

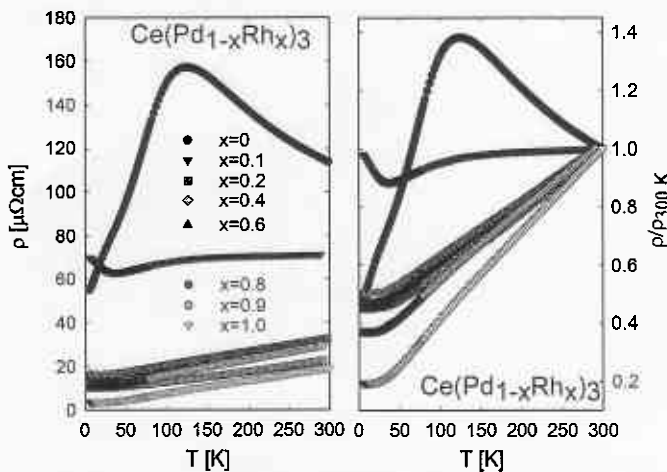Fig. 2: Temperature dependent electrical resistivity ρ of $Ce(Pd_{1-x}Rh_x)_3$ for various concentrations of x.(left panel). Right panel: ρ vs. T in a normalized representation.

The left panel shows the absolute $\rho(T)$ values, while the right panel of Fig. 2 displays a normalized representation of the data. $CePd_3$ exhibits the largest room temperature resistivity of the series, about 115 $\mu\Omega cm$, well in agreement with literature [8] and is characterized by a slow increase of ρ when T is reduced from room temperature. A maximum is observed around 130 K, coinciding with the weak maximum derived from susceptibility data on that compound [8]. Below this maximum, ρ drops rapidly, reaching about 50 $\mu\Omega cm$ at 4.2 K, which is, however, above the values given in literature for ρ_0. Slight deviations in the Pd concentration might cause enormous changes in the residual resistivity, while the room temperature values should be less influenced [9]. A shoulder in $\rho(T)$ around 25 K again evidences good agreement with literature [8]. A Fermi liquid ground state of $CePd_3$ is obvious from a quadratic temperature dependence of the resistivity roughly below 10 K, i.e., $\rho = \rho_0 + AT^2$ with $\rho_0 = 53.8$ $\mu\Omega cm$ and $A = 0.06$ $\mu\Omega cm/K^2$. The enhanced value of A point to heavy quasi-particles (compare literature data [8]). The maximum around 130 K can be interpreted in terms of a spin fluctuation temperature and particularly resembles the Kondo

scale usually dominating ground state properties of Ce compounds. This type of interaction is also responsible for the significantly enhanced thermopower values (see below). As Pd is substituted by Rh, $\rho(T)$ is altered distinctly. Inspecting the data for x = 0.1 reveals a minimum in $\rho(T)$ around 35 K; below that temperature, $\rho(T)$ starts to logarithmically increase, but below about 10 K the data level off reaching a constant behaviour at very low temperatures. The qualitative curvature is quadratic and thus follows features of Kondo physics at low temperatures. Further increase of the Rh content causes a total suppression of structure in $\rho(T)$, the temperature dependences for x > 0.2 resemble those of simple metallic non-magnetic compounds. Trying to account for $\rho(T)$ of $CeRh_3$ by considering the Bloch Grüneisen law reveals an excellent fit with a reasonable Debye temperature $\Theta_D = 220$ K. A similar quantitative description of resistivity data is possible for $0.2 < x \leq 1$. It should be noted that the general variation of the resistivity in the latter concentration range is somewhat irregular, but both, the absolute values and their particular dependencies do not vary significantly. The residual resistivity is the smallest in the case of $CeRh_3$, pointing to a well developed structure with a reduced number of lattice imperfections. Adding Pd to $CeRh_3$ causes an initial increase of the residual resistivity due to the statistic disorder of Pd and Rh at the 3c sites of the unit cell.

The temperature dependent electrical resistivity of the samples has also been studied also at various externally applied magnetic fields. Results for the lower temperature range of $CePd_3$ are shown in Fig. 3.
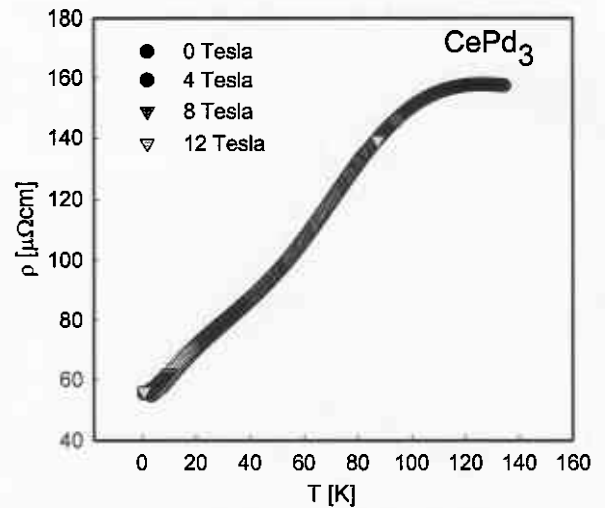

Fig. 3: Temperature dependent resistivity ρ of $CePd_3$ measured at various externally applied fields.

The overall change due to the application of a magnetic field is small and the largest change at 12 T and at lowest temperature does not exceed about 3%. This rather small field dependence can be associated with the large characteristic temperature of the system of about 220 K. An external field of 12 T, although large in absolute terms, is then still small in terms of energy (1 K ~ 1.5 T) and thus a significant influence on the spin fluctuation spectrum can not be expected.

The Seebeck coefficient S of $Ce(Pd_{1-x}Rh_x)_3$ was investigated for all samples of the series, results are summarized in Fig. 4. Within this series, $CePd_3$ exhibits exceptionally large S values throughout the temperature range studied and shows a maximum around 130 K, in excellent agreement with literature [10]. Below about 50 K a shoulder develops coinciding with the feature in $\rho(T)$. The giant thermopower derived cannot be associated with reduced carrier concentrations as it is the case for standard thermoelectric materials which are situated
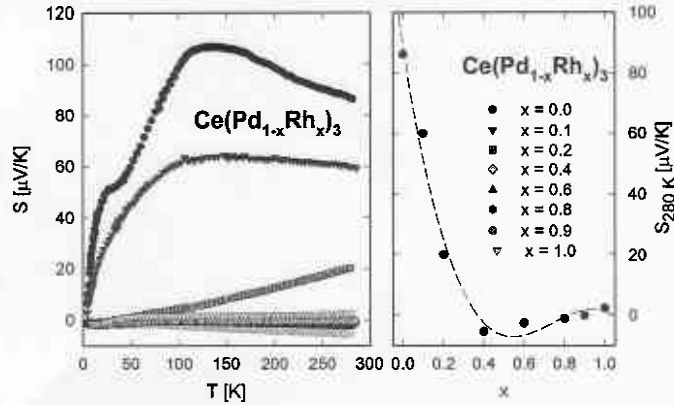

Fig. 4: Temperature dependent Seebeck coefficient S of $Ce(Pd_{1-x}Rh_x)_3$ for various concentrations of x (left panel). Right panel: Concentration dependent variation of S deduced at 280 K. The dashed line is a guide to the eye.

in the proximity of metallic and semiconducting regime. Rather, it is well known that Kondo type interactions cause a narrow density of states (DOS) near the Fermi energy thus giving rise to a huge energy derivative of this DOS [3]. Many of yet investigated Kondo compounds are characterized by either large positive or negative thermopower values. The substitution of Pd/Rh unfavourably alters the overall $S(T)$ values at least below room temperature (Fig. 4, left panel). Data collected at $T = 280$ K (Fig 4, right panel) corroborate this finding evidencing the thermopower of this series adopting negative values, before at the Rh rich end of the series small positive values arise. In terms of band structure this would refer to a change of sign with respect to the energy derivative of the DOS, while in the simplest carrier picture such an observation would be in line with a change of the carrier type from hole- to electron dominated transport. Finally, $CeRh_3$ seems to be governed again by holes. Since the crossover from $CePd_3$ to $CeRh_3$ is characterized by a significant change of the Kondo interaction strength from about 220 K for the former to about 1000 K for the latter, one can conclude that in a crude approximation an enhancement of the valence fluctuations does not improve overall thermopower. High temperature studies are in progress to corroborate this conclusion.

The thermal conductivity of $Ce(Pd_{1-x}Rh_x)_3$ was measured from 4 K up to room temperature and results are shown in Fig. 5. Largest and smallest overall thermal conductivity is found

for binary $CeRh_3$ and $CePd_3$, respectively, it is well above the theoretical thermal conductivity limit [11], which nearly realised in amorphous materials due to the well known rattling mechanism also suggested in the case of filled skutterudites. Thermoelectric application of these materials, however, require thermal conductivity values in the proximity of the theoretical limit.
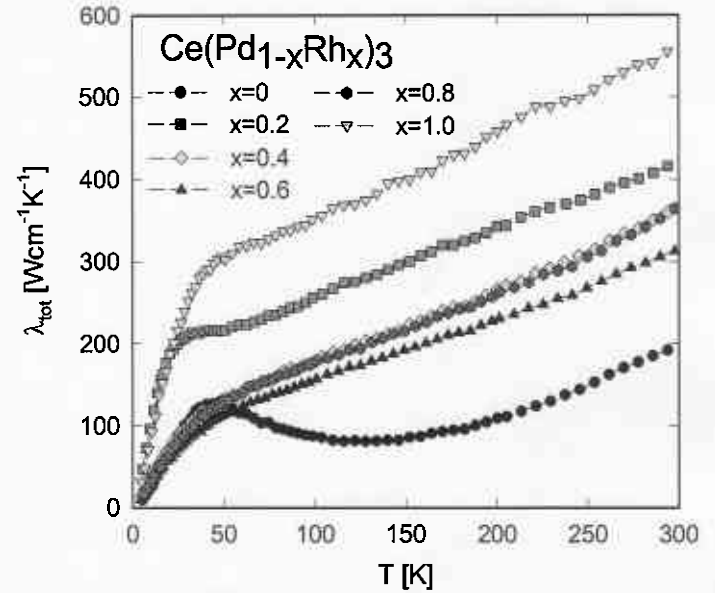

Fig. 5: Temperature dependent thermal conductivity $\lambda(T)$ of $Ce(Pd_{1-x}Rh_x)_3$ for various concentrations x.

The total thermal conductivity λ of metallic solids consists of an electronic contribution λ_e and a lattice contribution λ_{ph}; λ can thus be expressed as:

$$\lambda = \lambda_e + \lambda_{ph} \qquad (1)$$

Each individual channel is constrained by a variety of interaction- and scattering processes causing a finite thermal resistivity $W = 1/\lambda$. In order to split the total measured quantity into both parts, the Wiedemann Franz law can be taken into consideration. Although this model represents only a crude approximation, it is generally used to derive λ_e assuming that

$$\lambda_e = \frac{L_e T}{\rho} \approx \frac{L_0 T}{\rho} \qquad (2)$$

where L_e is the electronic Lorenz number which is usually replaced by the Lorenz number $L_0 = 2.45 \times 10^{-8}$ WΩ/K^2. Knowing the electrical resistivity (compare Fig. 2) allows to deduce λ_e, at least in a first approximation. Data for some concentrations of $Ce(Pd_{1-x}Rh_x)_3$ are summarized in Fig. 6 (left panel) and the lattice thermal conductivity associated with these concentrations is plotted in Fig. 6 (right panel). Comparison shows that the electronic contribution to the total thermal conductivity dominates in $Ce(Pd_{1-x}Rh_x)_3$ which appears to be typical for intermetallic compounds. Since this distinct contribution is always related to the electrical resistivity, an improvement of the thermoelectric performance may only be achieved by reduction of the lattice thermal conductivity λ_{ph}. Recently, it has been shown that the

interaction of the heat carrying phonons with Einstein-like modes ("rattling modes") can cause a dramatic suppression of λ_{ph} in filled skutterudites [12]. We have proposed that another mechanism, i.e., the interaction of phonons with the conduction electron system, can also be considered the reason of a significant decrease of λ_{ph}, if all other interaction processes remain unchanged. Kitagawa et al. [5] have demonstrated that for Kondo insulators an increase of T_K causes a distinct drop of λ_{ph} due do an enhanced electron phonon interaction. Adopting this model for $Ce(Pd_{1-x}Rh_x)_3$ yields a similar conclusion: Proceeding from $CePd_3$ with relatively low T_K to $CeRh_3$ with high T_K values infers a dramatic increase of the phonon electron interaction strength. This can be understood quantitavely by employing following analysis:
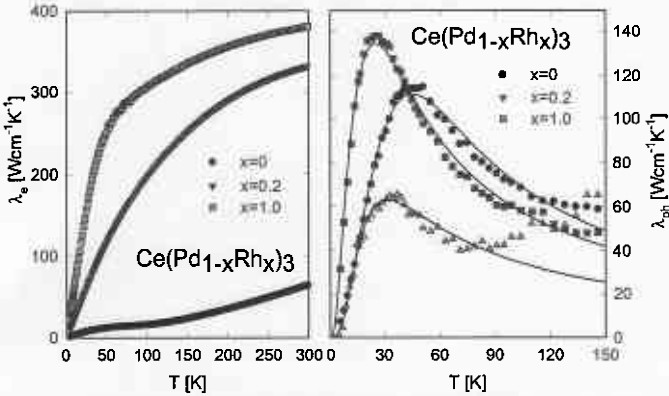

Fig. 6: Temperature dependent electronic contribution to the thermal conductivity λ_e for some concentrations x of $Ce(Pd_{1-x}Rh_x)_3$ (left panel). Right panel: Lattice thermal conductivity λ_{ph}. The solid line is a least squares fit according to Eqn. 3.

According to Ref. [13] the lattice thermal conductivity can be expressed as

$$\lambda_{ph} = CT^3 \int_0^{\theta_D/T} \frac{\tau_c x^4 \exp(x)}{[\exp(x)-1]^2} dx \qquad (3)$$

where C is a material dependent constant and τ_c is the overall relaxation time which defines the phonon mean free path. This model assumes each individual interaction process to be represented by a distinct relaxation time τ_i. If these processes are independent from each other, τ_c follows from

$$\tau_c^{-1} = \tau_B^{-1} + \tau_D^{-1} + \tau_U^{-1} + \tau_e^{-1} \qquad (4)$$

where the subscripts B, D, U and e refer to boundary scattering, interaction with point-like impurities, Umklapp processes and the electron-phonon interaction, respectively. These relaxation times are considered most important, relevant for phonon scattering in metallic compounds. According to Ref. [13], temperature and frequency dependencies for individual scattering processes obey the relations:

$$\tau_B^{-1} = B, \ \tau_D^{-1} = D\omega^4, \ \tau_U^{-1} = U\omega^2 T \exp(-\theta_D/3T), \ \tau_e^{-1} = E\omega \qquad (5)$$

Least squares fits of Eqn. 3 in the context of Eqns. 4 and 5 to the data shown in Fig. 6 (right panel) were performed, results of which are displayed as solid lines. Satisfying overall agreement between theory and experiment can be validated. The Debye temperatures obtained decrease continuously from $CePd_3$ to $CeRh_3$ indicating a softening of the lattice. This would be in nice coincidence with the fact that the system exhibits stronger signs of intermediate valence upon Pd/Rh substitution. In general a stable valence state is favored by a stable and stiff lattice, while valence fluctuations cause a decrease of lattice stability giving rise to a more soft crystal lattice. The most important observation, however, is the finding that the parameter E characterizing the phonon electron interaction (Eqn. 5) dramatically alters upon Pd/Rh substitution, thus evidencing the importance of the enhanced characteristic temperature attributed to $CeRh_3$. Corroborating this tentative conclusion on similar systems would give rise to a rather novel and promising mechanism for a reduction of the lattice thermal conductivity.

In conclusion, we have investigated the evolution of physical properties in the series $Ce(Pd_{1-x}Rh_x)_3$. The increase of the Ce valency towards the non-magnetic 4^+ state upon the increase of the Rh content is accompanied by a softening of the lattice and a dramatic decrease of the overall thermopower values. Concomitantly, however, the increase of T_K causes a substantial decrease of lattice thermal conductivity, primarily due to an enhancement of the phonon electron interaction parameter. This proves a novel possibility for a promising reduction of thermal conductivity with respect to thermoelectric applications.

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