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Complex magnetic behavior in $\text{Ce}_{5}\text{Rh}_{4}\text{Sn}_{10}$ doped with La

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RESEARCH ARTICLE

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Ce₅Rh₄Sn₁₀ is known as an heavy-fermion antiferromagnet with temperature of magnetic ordering $T_{N2} = 4.3$ K. We report a new antiferromagnetic phase transition at $T_{N1} = 1.4$ K. In the series of Ce_{1-x}La_xRh₄Sn₁₀ compounds both magnetic phase transitions at T_{N1} and T_{N2} shift towards lower temperatures. For Ce₃La₂Rh₄Sn₁₀ and Ce_{3.5}La_{1.5}Rh₄Sn₁₀ we found the only one transition. In the temperature region $T_{N1} < T < T_{N2}$, magnetization M measured as a function of magnetic field H exhibits a large jump at very low fields of ~ 0.03 T with very little hysteresis loop. This abnormal behaviour could be due to spin-flip transition. Thermodynamical properties of the series of Ce_{1-x}La_xRh₄Sn₁₀ compounds are discussed in terms of antiferromagnetic Kondo-lattice.

Keywords: rare earth compounds; strongly correlated electron systems; Kondo effect;

1. Introduction

The RE₅M₄X₁₀ compounds, where RE=rare-earth, M=Co, Rh, Ir, Os, and X=Si, Ge, Sn mostly crystallize with the tetragonal structure of Sc₅Co₄Si₁₀-type (space group $P4/mbm$) [1–4]. These phases show a variety of magnetic properties that are predominantly related to the interaction between the 4*f*-electrons of the lanthanide element and the conduction electrons. Some of them undergo superconducting transition at low temperatures and charge density wave (CDW)-type ordering at ~ 80 K [4, 5], others like RE₅Rh₄Sn₁₀ (RE=Ce, Pr, Nd) order antiferromagnetically with some metamagnetic features [2]. Moreover, magnetic measurements revealed that the magnetic ordering can be related to the crystallographic properties of the RE₅M₄X₁₀ series, namely, RE atoms occupy three inequivalent sites, which usually leads to complex ground state properties.

The Ce-based phase Ce₅Rh₄Sn₁₀ has attracted particular attention due to its intriguing magnetic and electrical transport properties. In the literature report it was characterized as a moderate heavy fermion (HF) antiferromagnet (AF) with the Néel temperature $T_N \approx 4.3$ K [2, 6]. The x-ray photoemission XPS spectra indicated that Ce atoms are in a trivalent state, consistent with magnetic susceptibility data.

The magnetic behavior of a dense Kondo system is largely controlled by the strength of the on-site $f-s$ hybridization V_{fs} among conduction and f -electron states. The strength of the $f-s$ exchange interaction can be tuned by either the composition or pressure and results in a competition between the intrasite Kondo and the intersite Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. The first such model of the HF metals was proposed by Doniach [7], who obtained a simple phase diagram which displays the magnetic ordering temperature T_{RKKY} as a function of $J_{fs}N(\epsilon_F)$, where the exchange-coupling $J_{fs} \sim V_{fs}^2$ and $N(\epsilon_F)$ is the

density of states (DOS) at the Fermi level. The J_{fs} can be varied by chemical substitution. A good deal of theoretical work (e.g., [8]) on Kondo three dimensional lattices has been carried out since Doniach's work. The essence of physics in the low-temperature region is grasped by periodic Anderson model. It has been shown [8], that the stability of the magnetic ground state in the Kondo-lattice limit is strongly dependent on V_{fs} , the number of valence electrons and finally on the intrasite $f-f$ interaction U . In $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ Ce atoms occupy three nonequivalent crystallographic positions, which strongly complicates the magnetic ground state properties due to the different local $f-f$ and $f-s$ interactions [6]. We therefore, investigate $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ doped by La to find the influence of alloying on the change of local parameters V_{fs} and U and the ground state properties of the $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ system of compounds. Our XPS studies confirm the localized f -states of Ce in the series of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ compounds and the small hybridization effect between the f and conduction electron states ($V_{fs} \approx 40$ meV), which determine the ground state properties of the Kondo lattice. In this work we reinvestigated the magnetic and electrical transport properties of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$. These experimental results obtained for $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ substituted by La are new. Moreover, we measured the specific heat in the wide temperature range 0.35 – 300 K and at different magnetic fields. The experimental data are discussed in the context of the recently calculated electronic structure of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$. The most important result is an observation of a new low-temperature antiferromagnetic phase in $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ and the doped $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ compounds below the temperature T_{N1} . We also observed a large jump in the magnetization at very low magnetic fields with very small hysteresis, which could be due to a spin-flip transition.

2. Experimental Details

Polycrystalline samples of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ and $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ with $x \leq 2$ have been prepared by arc melting the constituent elements on a water cooled copper hearth in a high-purity argon atmosphere with a Al getter. The sample was remelted several times to promote homogeneity and annealed at 800 °C for 2 weeks.

The powder diffraction pattern was measured on Rigaku-Denki D/MAX RAPID II-R diffractometer (Rigaku Corporation, Tokyo, Japan) with a rotating anode Ag K_α tube ($\lambda = 0.5608$ Å), an incident beam (002) graphite monochromator and an image plate in the Debye Scherrer geometry.

Thermodynamic properties were measured with Quantum Design Physical Properties Measurement System (QD-PPMS); resistivity with ACT, susceptibility with ACMS, and magnetization with VSM option. Magnetization M vs magnetic field H was measured for the $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ sample in magnetic fields up to 2 T with the step ΔH of 20 Oe, using a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer.

The XPS spectra were obtained with monochromatized Al K_α radiation at room temperature using a PHI 5700 ESCA spectrometer. The polycrystalline sample was scraped with a diamond file under high vacuum of 6×10^{-10} Torr immediately before taking a measurement. The spectra were calibrated according to [9]. Binding energies were referenced to the Fermi level ($\epsilon_F = 0$).

Figure 1. Lattice parameters a , c of the series of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ compounds vs x .

3. Results and discussion

3.1. Crystal structure

Crystal structure refinement confirmed that the series $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ crystallize in tetragonal symmetry, within the space group $P4/mbm$. The x-ray powder-diffraction pattern of the samples did not show the presence of any impurity phases. The lattice parameters listed in table 1 are also plotted in figure 1. We clearly see the lanthanide contraction which confirms that the samples were of good quality. The linear $a(x)$ and $c(x)$ behaviour also suggests, that the La atoms occupy the Ce-sites in the series of the $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ compounds. Stoichiometry and homogeneity of the $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ samples was checked by the XPS and microprobe (scanning microscope JSM-5410) technique, and the deviations from the nominal composition were small. To find the exact La distribution over three Ce sites, we compared the observed and calculated diffraction pattern for all the investigated samples. The Rietveld analysis of the diffraction patterns was done with FULLPROF program, the Bragg factor R_B was between 4 – 6%. Pseudo-Voigt line shape and six polynomial background coefficients were used. Ce/La concentration was assumed to be constant in 2a and 4h Wyckoff positions, and fixed to the stoichiometric value.

Table 1. Lattice parameters of the series of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ of compounds.

compound	a (Å)	c (Å)
$\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$	14.0685(96)	4.6281(36)
$\text{Ce}_{4.5}\text{La}_{0.5}\text{Rh}_4\text{Sn}_{10}$	14.0806(90)	4.6339(34)
$\text{Ce}_4\text{LaRh}_4\text{Sn}_{10}$	14.0858(61)	4.6364(22)
$\text{Ce}_{3.5}\text{La}_{1.5}\text{Rh}_4\text{Sn}_{10}$	14.0863(70)	4.6371(25)
$\text{Ce}_3\text{La}_2\text{Rh}_4\text{Sn}_{10}$	14.1011(64)	4.6433(23)

3.2. Specific heat

Figure 2 displays the low-temperature behavior of the specific heat of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ measured in several magnetic fields up to 2 T. Pronounced λ -shaped anomaly in zero-field heat capacity $C(T, H = 0)$ clearly manifests two magnetic phase transitions that occur at $T_{N1} = 1.4$ K and at $T_{N2} = 4.1$ K, which are typical for either ferromagnetic or antiferromagnetic second-order phase transition. The first magnetic phase transition at T_{N1} has not been known yet in the literature, while the second one was recently considered as paramagnetic-antiferromagnetic transition [2]. In figure 2 the low-temperature feature shifts to lower temperatures with rising magnetic field which characterizes the antiferromagnetic (AF) low-temperature phase, while the second one shifts to higher temperatures when the field increases, which can be attributed to ferromagnetic (F) ordering of Ce-moments in $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ between 1.4 K and 4.1 K. The low-field magnetization data, to be discussed later, show that at $H = 0$, $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ is ferrimagnet above T_{N2} . Since the corresponding isomorphous $\text{La}_5\text{Rh}_4\text{Sn}_{10}$ does not exist we are unable to analyze the heat-capacity data by subtracting off the C of the La-reference compound to give the magnetic contribution ΔC of the $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$. Nevertheless, well above T_{N2} the $C(T)/T$ vs T^2 curve behave linearly, which allowed us to fit the C/T data by using $C = \gamma T + \beta T^3$ equation to obtain the electronic and lattice contributions to the heat capacity. In the T -region 10 – 17 K a least-squares fit yields $\gamma = 410$ mJ/molK² and $\beta = 5.57$

mJ/molK⁴. The value of the Debye temperature derived from β is 184 K (i.e., it is consistent with that of many other Ce-ternary compounds). The enhanced value of the electronic specific heat coefficient γ suggests that Ce₅Rh₄Sn₁₀ compound is a heavy fermion system. The C/T vs T^2 analysis for the La-doped Ce₅Rh₄Sn₁₀ compounds gives a very similar values of β coefficients, however, γ decreases with doping; $\gamma = 0.33$ J/(mole K² Ce) for the sample Ce_{4.5}La_{0.5}Rh₄Sn₁₀ and 0.24 J/(mole K² Ce) for Ce₄LaRh₄Sn₁₀. The magnetic heat-capacity behaviours at T_{N2} imply that Ce₅Rh₄Sn₁₀ and Ce_{5-x}La_xRh₄Sn₁₀ can not be classified as a normal antiferromagnetic systems, which are basically characterized by the specific heat jump being suppressed in the external magnetic fields. The observed behaviours shown in figure 2 are much more similar to that of a ferromagnet. Thus, from the heat-capacity data one can conclude that Ce₅Rh₄Sn₁₀ is a ferromagnet, but as will be shown (the ac and dc susceptibility data obtained at different magnetic fields) this is not the case at $H = 0$.

In the series of Ce_{5-x}La_xRh₄Sn₁₀ compounds both peaks at T_{N1} and T_{N2} shift toward lower temperatures (see figure 3) as the exchange interaction between Ce atoms is reduced due to alloying, and finally melt to one peak for the sample $x = 2$. For the samples $x \leq 1$ the low-temperature tail of the specific heat peak at T_{N1} can be well described by the expression $C(T) = \gamma T + \beta T^3 + AT^n \exp(-\delta/T)$ for an anisotropic antiferromagnetic system with a small gap δ of about 0.5 K in the magnon dispersion, $\gamma = 0.41$ J/moleK², $\beta = 0.00557$ J/molK⁴, $A = 2.5$ J/molK⁻ⁿ, and $n = 2.5$ (very closed to $n = 3$). The second peak at T_{N2} due to small temperature separation of two transitions, cannot be well approximated by $C(T) = \gamma T + \beta T^3 + AT^n \exp(-\delta/T)$ with exponent n characteristic of antiferromagnetic ($n = 3$) or ferromagnetic ($n = 3/2$) phase. Considering, that the lattice contribution to the specific heat of Ce₅Rh₄Sn₁₀ is negligible in the low temperature region (i.e., for the temperature region $T < 4$ K), we note that the magnetic contribution $\Delta C = C(T) - C_{lattice}$ per Ce atom is much smaller at T_{N1} and T_{N2} instead of $\Delta C = 12.48$ J/(mol K) for a magnetic conventional $S = 1/2$ two-level system, and this reduction most likely arises due to the Kondo effect. At the same time, the entropy at the both magnetic phase transitions is also strongly reduced in comparison to the entropy of the ground state doublet. The magnetic entropy, defined as a $S(T) = \int_0^T \frac{C(T)}{T} dT$ is plotted as dotted line in figure 2. As seen, the entropy releases $S/R \ln 2$ amount to 0.2 for Ce₅Rh₄Sn₁₀ at T_{N1} and is $\sim 0.5 R \ln 2$ at the second phase transition at T_{N2} . The value of $R \ln 2$ is achieved at a temperature as high as $T \approx 15$ K. This feature is in concert with the reduced value of the jump ΔC at the temperature of the both phase transitions, and supports the Kondo effect behavior. A correlation between specific heat ΔC and the ratio T_K/T_N was studied recently in different Kondo-lattices [10]. It has been shown, that for the large ratio of $T_K/T_N \geq \sim 2.5$, the zero-field specific-heat jump ΔC at T_N amounts only ~ 2.5 J/(mol K Ce) instead of 12.48 J/(mol K Ce), this is the case of Ce₅Rh₄Sn₁₀ (c.f., figure 4). When Ce atoms in Ce₅Rh₄Sn₁₀ are replaced by La, the entropy per Ce atom does not change at T_{N1} and T_{N2} , which suggests the strong electronic correlations also in the system of Ce_{5-x}La_xRh₄Sn₁₀ samples. According to Schotte *at al.* [11], in paramagnetic Kondo systems the characteristic Kondo temperature T_K can be estimated as the temperature, at which the magnetic entropy is $0.68 R \ln 2$. Such estimation roughly predicts $T_K \approx 9.5$ K, in fairly good agreement with the value estimated from the magnetic susceptibility data (will be discussed).

Within a simple two level model with an energy splitting of $k_B T_K$ the magnetic entropy of a magnetic Kondo system is related to the ratio T_K/T_N in the following manner [12], $S(T_K/T_N) = R \left[\ln(1 + e^{-T_K/T_N}) + \frac{T_K}{T_N} \frac{e^{-T_K/T_N}}{1 + e^{-T_K/T_N}} \right]$. The Kondo tem-

Figure 2. Temperature dependencies of the specific heat divided by temperature, $C(T)/T$, measured in different magnetic fields and entropy $S(T)$ per one Ce-atom (dotted line) for $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$.

Figure 3. Temperature dependence of the specific heat of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ (a), $\text{Ce}_{4.5}\text{La}_{0.5}\text{Rh}_4\text{Sn}_{10}$ (b), $\text{Ce}_4\text{LaRh}_4\text{Sn}_{10}$ (c), $\text{Ce}_{3.5}\text{La}_{1.5}\text{Rh}_4\text{Sn}_{10}$ (d), and $\text{Ce}_3\text{La}_2\text{Rh}_4\text{Sn}_{10}$ (e) in the C/T versus T representation. The low- T data ($T < T_{N1}$) in (a), (b), and (c) plots are fitted by expression $C(T) = \gamma T + \beta T^3 + AT^n \exp(-\delta/T)$ (dotted line), where $n = 3$ and the remaining coefficients are described in the text.

Figure 4. Specific heat $C(T)$ data (points) for $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$, the magnetic contribution to the specific heat calculated for Kondo model $S=1/2$ (continuous line) and the electronic contribution γT (dotted line) obtained for $\gamma = 0.41 \text{ J}/(\text{mol K}^2)$.

perature T_K estimated from this relation is $\sim 6 \text{ K}$; i.e., very close to the value of T_K obtained on the base of Schotte *et al.* model, and nearly same as that derived from the magnetic susceptibility data. The small contribution of the lattice specific heat in the temperature region $T < 10 \text{ K}$ does not change the obtained value of T_K significantly. In figure 4 the specific heat of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ exhibits a curvature at the narrow T -range $\sim 2 \text{ K}$ above T_{N2} , that signals some other than electronic and phonon contribution to $C(T)$, probably of Kondo-like origin. If the Kondo maximum is located at about $4 - 5 \text{ K}$ and is characteristic of the $S = 1/2$ Kondo model, than the rough estimate gives $T_K = T_{max}/0.45 \approx 9 - 11 \text{ K}$ [13]. In figure 4 C -anomaly is roughly compared to the theoretical curve (line) of $S = 1/2$ Kondo model with Kondo temperature $T_K = 9 \text{ K}$. In our crude analysis we do not considered the phonon contribution, which is at the low temperatures rather low. The reason is the following, we tried to synthesize the reference compound $\text{La}_5\text{Rh}_4\text{Sn}_{10}$ for the investigated series, however, we did not succeed.

3.3. Resistivity

In figure 3 we present the low-temperature resistivity $\rho(T)$ data for $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$. Here, the complex magnetic behavior manifests itself as the kinks on the $\rho(T)$ curves, that occurs at T_{N1} and T_{N2} . The residual resistivity ρ_0 is about $\sim 20 - 40 \mu\Omega\text{cm}$ for the series of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ alloys, except abnormally large value of $\rho_0 \sim 200 \mu\Omega\text{cm}$ for the sample $\text{Ce}_{3.5}\text{La}_{1.5}\text{Rh}_4\text{Sn}_{10}$, which is addressed to unphysical effect. Figure 5 displays the temperature dependence of resistivity, $\rho(T)$, for $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$. A similar $\rho(T)$ dependences were also observed for the remaining $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ compounds. As seen, in the paramagnetic region the $\rho(T)$ curves exhibit metallic conductivity, however, the residual resistivity ρ_0 is rather large, that is characteristic of electron scattering on structural disorder. Usually, the similar $\rho(T)$ curves can be well approximated at the paramagnetic region by the Bloch-Grüneisen-Mott formula $\rho(T) = \rho_0 + \rho_{ph} + \rho_M$, where $\rho_{ph} = 4RT(\frac{T}{\Theta_D})^4 \int_0^{\frac{\Theta_D}{T}} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}$, $\rho_M = -KT^3$, ρ_0 is the residual resistivity, Θ_D stands for the Debye temperature and R is a constant, whereas the cubic term KT^3 describes interband scattering processes [14]. However, one can rather poorly fit this expression to the experimental data in the limited temperature region $75 - 300 \text{ K}$ (the dotted line in figure 5), with $\rho_0 \approx 280 \mu\Omega\text{cm}$ that is three times larger than the residual resistivity obtained from $\rho(T)$ measurements. Within the same range of T the $\rho(T)$ of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ samples is much better fitted by the parallel resistor model (PRM, solid curve in figure 5) [2, 15]. In this model

$$\frac{1}{\rho(T)} = \frac{1}{\rho_{max}} + \frac{1}{\rho_0 + \rho_{ph}(T)}$$

Figure 5. Parallel Resistor Model (PRM) and Bloch-Grüneisen-Mott (BGM) fits above $T = 75$ K to the resistivity $\rho(T)$ data for Ce₅Rh₄Sn₁₀.

Figure 6. Low-temperature dependences of the electrical resistivity of Ce₅Rh₄Sn₁₀ measured in several different magnetic fields. The zero-field $\rho(T)$ data display a $T^{3/2}$ temperature below the ordering temperature T_{N1} . In the temperature region between T_{N1} and T_{N2} $\rho(T) \sim T^{2.5}$.

where ρ_{max} is the saturation resistivity which is temperature independent. The parameters obtained from the best fit to the ρ -data are enlisted in table 2. As is shown in figure 5 the calculated $\rho(T)$ curve on the base of PRM model is much below the experimental data in the temperatures $T < 70$ K. Therefore, the interband scattering, which gives a positive contribution to the calculated ρ vs T behaviour, should also be considered as an important contribution. Basing on our recent electronic structure calculations [6] the $f-d$ interband scattering is the most probable.

As displayed in figure 6, the low-temperature resistivity of Ce₅Rh₄Sn₁₀ exhibits a distinct feature that is related to the onset of magnetically ordered states observed below $T_{N2} = 4.3$ K and $T_{N1} = 1.4$, respectively. In zero field, resistivity has a power law $\rho(T) \sim T^{3/2}$ at $T < T_{N1}$, corresponding to antiferromagnetic spin fluctuations [16, 17], while in the temperature region between $T > T_{N1}$ and $T < T_{N2}$ the resistivity varies as $\rho(T) \sim T^{2.5}$. The higher power exponent in the temperature dependence of ρ suggests different magnetic scattering at $T_{N1} < T < T_{N2}$. Upon applying magnetic field, the resistivity hardly changes above T_{N1} . The kink due to the magnetic phase transition at T_{N2} is smeared out and shifted to higher temperatures in a manner known for ferromagnetic compounds.

The magnetoresistance defined as $MR = [\rho(H) - \rho(0)]/\rho(0)$ is negative except for the region of the ordered magnetic state at $T < T_{N1}$; e.g., for the samples $x = 0$ and $x = 0.5$, $MR \approx 30\%$ in the magnetic field of 9 T at $T = 4.3$ K, whereas for the sample $x = 1$, $MR \approx 54\%$ at the same temperature and magnetic field. The negative MR is characteristic of Kondo diluted magnetic alloys. In several theoretical works (e.g., [18]) it has been shown, that in an external magnetic field, the anomalous resistivity of dilute magnetic alloy decreases, giving rise to a negative magnetoresistance. The negative MR effect is also characteristic of Kondo-lattice compounds; e.g., [19], but it is also compatible with the behavior predicted for ferromagnets above their ordering temperature [20]. In case of Ce_{5-x}La_xRh₄Sn₁₀ probably the both effects are dominant.

The kink in $\rho(T)$ associated with the onset of the ordered state at $T < T_{N1}$ shifts towards lower temperatures, as usually observed for antiferromagnets. The field dependences of the resistivity $\rho(T)$ for Ce₅Rh₄Sn₁₀ and the series of Ce_{5-x}La_xRh₄Sn₁₀ compounds are at T_{N1} and T_{N2} related to the heat capacity results discussed above.

Table 2. PRM fit to the $\rho(T)$ data in the temperature range 75 K - 300 K.

compound	ρ_{max} ($\mu\Omega\text{cm}$)	Θ_D (K)
Ce ₅ Rh ₄ Sn ₁₀	478	267
Ce _{4.5} La _{0.5} Rh ₄ Sn ₁₀	180	127
Ce ₄ LaRh ₄ Sn ₁₀	869	102

4. Magnetic properties

Shown in figure 7 are magnetic susceptibility χ data above 2 K, measured in the magnetic field of 0.1 T using VSM magnetometer. As can be seen, the inverse

Figure 7. $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$; the magnetic susceptibility plotted as χ^{-1} vs T and the Curie-Weiss fit for sample $x = 2$ (a) and $x = 0$ (b).

Figure 8. Magnetization M vs magnetic field; $M(H)$, in the range -9 T to 9 T. Lower inset shows $M(H)$ in the small magnetic fields between -0.07 T and 0.07 T for the system $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ of compounds. In the inset, the sample $\text{Ce}_4\text{LaRh}_4\text{Sn}_{10}$ shows metamagnetic M vs H behaviour. Upper inset displays saturated and effective magnetic moments versus Ce atoms count. The effective magnetic moment is obtained from the fit of Curie-Weiss law.

Figure 9. Isothermal magnetization of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ as a function of magnetic field, measured for different temperatures, below and above the temperature T_{N2} . The inset displays the hysteresis loop in very weak magnetic fields at the temperatures $T < T_{N2}$.

susceptibility χ^{-1} follows the Curie-Weiss (CW) law above 60 K: $\chi(T) = \frac{1}{8} \frac{\mu_{eff}^2}{T - \theta_{CW}}$, where μ_{eff} is the effective magnetic moment and θ_{CW} is the paramagnetic Curie-Weiss temperature. Note also, that $1/\chi$ vs T curves are almost not x -dependent, when the susceptibility is given per Ce atom. We therefore, present $1/\chi$ vs T plots only for two selected samples which exhibit the most divergent $1/\chi$ T -dependencies in the series.

Least-square fitting procedure yields $\mu_{eff} \sim 2.64 - 2.75 \mu_B/\text{Ce}$ and $\theta_{CW} \sim -45$ K (see table 3). The obtained value of μ_{eff} is within an experimental error close to a value expected for a free Ce^{3+} ion ($2.56 \mu_B$) and allows us to assume that magnetism is due only to the cerium sublattices. Negative paramagnetic CW temperature, much larger than T_N , points an antiferromagnetic character of interactions between the moments and its enlarged absolute value suggests presence of Kondo-type interactions with the characteristic temperature $T_K = |\theta_{CW}|/4 \approx 13$ K [21]. In figure 7 the susceptibility presented as $1/\chi$ vs T behaves as a Curie-Weiss law at high temperatures, while at the low- T region ($T_{N2} < T < \sim 60$ K) a distinct deviation is observed. The data in figure 7 suggest the ferrimagnetic (FR) ordering below T_{N2} for $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$, if the magnetic moments of Ce atoms are not identical. This scenario basis on the crystallographic symmetry of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ with three inequivalent Ce sites. Our recent LSDA+ U (local spin density approximation; $U \neq 0$) band structure calculations [6] showed that the magnetic spin moments for Ce atoms in nonequivalent positions are slightly different; namely, the magnetic moment of Ce(1) at $2a$ site is $1.01 \mu_B$, while the calculated magnetic moments of Ce(2) and Ce(3) atoms occupying $4f$ sites are $0.93 \mu_B$ and $1.01 \mu_B$, respectively.

Figure 8 shows magnetization M of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ measured at $T = 2$ K as a function of magnetic field. M exhibits a large jump at very low fields of ~ 0.03 T with very little hysteresis of ~ 28 Oe in the forward and reverse direction of the field sweep (figure 9). If $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ is the Kondo system with Kondo temperature $T_K \approx 10$ K, the magnetic moment should be saturated at the field $H_K = k_B T_K / \mu_B \sim 15$ T, not four orders of magnitude below. This abnormal behaviour could be due to a spin-flip transition at extremally small magnetic fields in the temperature region $T_{N1} < T < T_{N2}$.

The complex magnetic behavior in this T -range manifests itself in the magnetic susceptibility measured in different magnetic fields and at different frequencies (figure 10). In the low-field limit ($H = 10$ Oe) the real component of magnetic ac susceptibility χ_{ac} shows a sharp rise across the paramagnetic to ferrimagnetic transition at T_{N2} . When $\chi_{ac}(T)$ is measured at different frequencies: 11 Hz, 160 Hz, 1 kHz, and 10 kHz, it shows strong frequency dependence; however, the peak at the transition does not shift, which excludes spin-glass-like behavior. When the dc susceptibility $\chi(T)$ is measured at the field of 0.1 T (this field is 3 times larger than the critical field of the spin-flip transition) then χ saturates at the lowest temperatures.

In figure 8, magnetization M of $\text{Ce}_4\text{LaRh}_4\text{Sn}_{10}$ measured as a function of the

Figure 10. $\chi_{dc}(T)$ measured for $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ series at $B = 0.1$ T. $\chi_{ac}(T)$, shown in the inset as χ'_{ac} vs T plot, are measured at the field with amplitude $H = 0.001$ T and at various frequencies (1 Hz, 160 Hz, 1 kHz, and 10 kHz) for $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$.

magnetic field shows in the low fields at $T = 2$ K a metamagnetic spin-flip-like transition. A possible interpretation is presented below. One can suspect that the doping of $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$ with La does not spread La atoms homogeneously among Ce 2a and 4h sites. It seems to be very probable that in particular case of $\text{Ce}_4\text{LaRh}_4\text{Sn}_{10}$, La has a preference to occupy only the 2a site. Then, the remaining Ce atoms can form an AF ground state, with a spin-flip transition induced by the magnetic field. The saturation magnetic moment of the series of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ compounds was obtained at $T = 2$ K by extrapolation of M vs $1/H$ to $1/H \rightarrow 0$. The magnetization exhibits a rapid jump from 0 to almost saturated value of $\sim 0.9 \mu_B/\text{Ce}$. We note that the experimental value of μ_{sat} is in agreement with LSDA + U calculations [6]. We believe that either M vs H behavior in the $T_{N1} < T < T_{N2}$ region, or the χ_{ac} anomaly at T_{N2} characteristic of antiferromagnetic-like splitting presumably manifests some spin metamagnetic-like transition at very low magnetic fields, which seems to be characteristic for the family of $\text{RE}_5\text{Rh}_4\text{Sn}_{10}$ compounds. Recently [3], a very similar M vs H behaviour was reported for $\text{Pr}_5\text{Rh}_4\text{Sn}_{10}$ and $\text{Nd}_5\text{Rh}_4\text{Sn}_{10}$ at similar very weak magnetic fields.

Table 3. Magnetic moments across the $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ series, saturation moment per formula unit extrapolated from $1/H \rightarrow 0$ $M(H)$ dependence and the effective moment per one Ce atom obtained from the Curie-Weiss fit to the $\chi(T)$ data in the temperature region $T > 60$ K.

compound	$\mu_{sat}/f.u. (\mu_B)$	$\mu_{eff}/atCe (\mu_B)$	$\Theta_{CW}(\text{K})$
$\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$	4.6	2.75	-45.3
$\text{Ce}_{4.5}\text{La}_{0.5}\text{Rh}_4\text{Sn}_{10}$	4.32	2.67	-39.0
$\text{Ce}_4\text{LaRh}_4\text{Sn}_{10}$	3.88	2.67	-40.24
$\text{Ce}_{3.5}\text{La}_{1.5}\text{Rh}_4\text{Sn}_{10}$	3.36	2.66	-42.43
$\text{Ce}_3\text{La}_2\text{Rh}_4\text{Sn}_{10}$	2.65	2.64	-48.78

5. Concluding remarks

From the evolution of the x dependence of specific heat, susceptibility and resistivity of $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$, the following physical picture emerges and can be summarized.

Substitution of Ce with La decreases exchange interactions and lowers ordering temperature. For $\text{Ce}_3\text{La}_2\text{Rh}_4\text{Sn}_{10}$ the antiferromagnetic peak at T_{N1} gradually disappears in the specific heat $C(T)$ plot. In the case of $\text{Ce}_4\text{LaRh}_4\text{Sn}_{10}$, when exactly one Ce atom is replaced by La, metamagnetic features are observed in $M(H)$ curve. It is a strong indicator that La is not homogeneously spread across 3 inequivalent Ce sites. Comparison of $\chi(T)$, $M(H)$ and C/T data suggest that the transition at T_{N2} cannot be described as simple ferro or antiferromagnetic. We would lean toward thesis that there rather exist ferrimagnetic ordering at $H = 0$, while a very small magnetic field induces a spin-flip transition. We suggest that neutron diffraction experiment or full relativistic non-collinear band structure calculations would be helpful to explain the character of magnetic phase transition at T_{N2} .

The Ce 3d XPS spectra (discussed in details in recent work [6]) show the stable valence of Ce ions in $\text{Ce}_5\text{Rh}_4\text{Sn}_{10}$. The Gunnarson-Schönhammer (GS) analysis [23] of the XPS 3d core level spectra gives the hybridization energy Δ of about 50 meV. A very similar value of Δ we obtained from the Ce 3d XPS spectra for the doped by La $\text{Ce}_{5-x}\text{La}_x\text{Rh}_4\text{Sn}_{10}$ samples (the XPS results are not presented in this

work). In the GS model the hybridization energy Δ describes the hybridization strength between the Ce $4f$ shell and conduction electron states. Energy Δ is defined as $\pi V_{fs}^2 \rho_{max}$, where ρ_{max} is the maximum value of the DOS and V_{fs} is the hybridization matrix element in the Anderson impurity Hamiltonian. The XPS data confirm well the localized f states in the Ce_{5-x}La_xRh₄Sn₁₀ AF Kondo lattice, they also exclude the mixed valence character of Ce atoms. For the microscopic parameters: $V_{fs} \approx 40$ meV and occupation number of the f -shell, $n_f = 1$, the ground state phase diagram for periodic Anderson model [8] predicts AF Kondo lattice, in agreement to our experimental results.

The AF exchange coupling J_{fs} of the local f moments and the conduction electron states gives rise to two competing processes in the system Ce_{5-x}La_xRh₄Sn₁₀, which determine the ground state properties of Kondo lattice: the on-site Kondo screening of the localized Ce $4f$ moments by the band states and the long range RKKY interaction between the local f moments [7]. Ce_{5-x}La_xRh₄Sn₁₀ show the complex magnetic behavior in the Kondo lattice. Our investigations of the Ce_{5-x}La_xRh₄Sn₁₀ series allowed to conclude, that the Ce atoms occupying the $4h$ sites mostly decide about formation of the metamagnetic phase at T_{N2} . Especially interesting is a sample with one La atom in $2a$ position which displays metamagnetic properties in the M vs H plot.

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