Journal of Alloys and Compounds 509 (2011) 6518–6521

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Low-temperature magnetic and electrical transport properties of some ternary Ce–Rh–Si compounds

D. Kaczorowski[a,*], A. Lipatov[b], A. Gribanov[c], Yu. Seropegin[c]

[a] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland
[b] Department of Materials Science, Moscow State University, GSP-1, 119991 Moscow, Russia
[c] Department of Chemistry, Moscow State University,GSP-1, 119991 Moscow, Russia

ARTICLE INFO

Article history:
Received 1 March 2011
Accepted 23 March 2011
Available online 1 April 2011

Keywords:
Cerium intermetallics
Magnetic behavior
Electrical resistivity

ABSTRACT

Five novel cerium-based ternaries $Ce_2Rh_{3.1}Si_{0.9}$, $Ce_4Rh_{12}Si$, $Ce_8Rh_{21.9}Si_{3.1}$, $CeRh_{1.82}Si_{0.18}$ and $CeRh_3Si_{0.125}$ were studied by means of magnetic susceptibility and electrical resistivity measurements. All these phases were found to be Pauli paramagnets with metallic type of electrical conductivity.

1. Introduction

The Ce–Rh–Si system is known to be exceptionally rich in ternary phases. Recently, as many as 14 novel compounds have been identified, in addition to 13 previously reported ternaries [1]. Phase equilibria in this system are characterized by significant mutual solubilities between cerium silicides and cerium–rhodium compounds, as well as by extended homogeneity regions of some of the ternaries. These two effects seem most clearly observed at 33 at.% of cerium. It has been shown in Ref. [1] that up to 6.5 at.% of Si can substitute Rh in the binary compound $CeRh_2$, hence forming $Ce(Rh_{1-x}Si_x)_2$ phases. With further substitution along the line one obtains ternary compounds $Ce_{33.3}Rh_{58.2-55.2}Si_{8.5-11.5}$ (unknown structure type), $Ce_2Rh_{3+x}Si_{1-x}$ ($0.08 \le x \le 0.17$; Y_2Rh_3Ge-type) and $Ce_2Rh_{1-x}Si_{3+x}$ ($0 \le x \le 0.24$; Er_2RhSi_3–type), each with its specific homogeneity region. Finally, the formation of pseudobinary phases $Ce(Rh_xSi_{1-x})_2$ is observed with up to 10 at.% of Rh substituted for Si in the binary compound $CeSi_2$. Also the region with ~25 at.% of Ce atoms exhibits similar phase formation phenomena. Here, adding Si to the binary compound $CeRh_3$ results in two new compounds: $Ce_4(Rh_{1-x}Si_x)_{12}Si$ ($0.00 \le x \le 0.03$; self-type) and $Ce_8(Rh_{1-x}Si_x)_{24}Si$ ($0.07 \le x \le 0.10$; $Ce_8Pd_{24}Sb$-type). Moreover, one observes three other ternaries $CeRh_{2-x}Si_{1+x}$ ($0.0 \le x \le 0.1$; $CeIr_2Si$-type), $CeRh_{1.88}Si_{1.12}$ (inversed $CeNiSi_2$-type) and $Ce_2Rh_{3-x}Si_{3+x}$ ($0.05 \le x \le 0.36$; $Ce_2Rh_{1.35}Ge_{4.65}$-type), and eventually the phase $CeRh_{1-x}Si_{2+x}$ ($0 \le x \le 0.32$; $CeNiSi_2$-type).

Several ternary Ce–Rh–Si compounds have been investigated for their physical properties, and recently such studies have additionally been motivated the spectacular findings of heavy-fermion superconductivity in antiferromagnetic $CeRh_2Si_2$ [2] and $CeRhSi_3$ [3]. Though no other superconductors have been discovered in the system until now, a few ternaries have been found to exhibit intriguing physical phenomena, like complex long-range magnetic orderings and dense Kondo behaviors in $Ce_3Rh_3Si_2$ [4], $CeRh_3Si_2$ [5], Ce_2RhSi_3 [6] and $CeRh_2Si$ [7]. In turn, the compounds $CeRhSi_2$ and $Ce_2Rh_3Si_5$ have been characterized as intermediate valence systems [8].

In this paper we report for the first time the results of our investigations on the low-temperature physical properties of five ternary compounds that form with ~25 and 33 at.% of cerium, namely $CeRh_{1.82}Si_{0.18}$ (at the edge of the homogeneity range of $Ce(Rh_{1-x}Si_x)_2$; $MgCu_2$-type), $Ce_2Rh_{3.1}Si_{0.9}$ (Y_2Rh_3Ge-type), $CeRh_3Si_{0.125}$ ($CeRh_3$ doped with Si; Cu_3Au-type), $Ce_4Rh_{12}Si$ (self-type) and $Ce_8Rh_{21.9}Si_{3.1}$ ($Ce_8Pd_{24}Sb$-type).

2. Experimental details

Polycrystalline samples of $CeRh_{1.82}Si_{0.18}$, $Ce_2Rh_{3.1}Si_{0.9}$, $CeRh_3Si_{0.125}$, $Ce_4Rh_{12}Si$ and $Ce_8Rh_{21.9}Si_{3.1}$ were prepared by arc-melting high-purity elements (99.9 mass % Ce, 99.999% mass Si and 99.99 mass % Rh) on a water-cooled copper hearth under argon atmosphere. To promote homogeneity, the melting was repeated several times with the button turned over between each melting. The weight losses were always less than 0.2 mass%. Subsequently, the alloys were vacuum-sealed in a quartz tube and annealed at 950 °C for two weeks. This heat treatment was finished with quenching in cold water.

* Corresponding author. Tel.: +48 71 34 350 21; fax: +48 71 34 410 19.
E-mail address: D.Kaczorowski@int.pan.wroc.pl (D. Kaczorowski).

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doi:10.1016/j.jallcom.2011.03.144

Table 1
Crystallographic and EDX data of the Ce–Rh–Si samples.

Phase and homogeneity range Sample composition	Space group	Prototype	Lattice parameters (nm)	EDX (at.%)		
				CCe	RRh	SSi
$Ce(Rh_{1-x}Si_x)_2$ $0 \le x \le 0.1$ $CeRh_{1.82}Si_{0.18}$ ($x = 0.09$)	$Fd\bar{3}m$	$MgCu_2$	$a = 0.75265(1)$	33.3	60.7	6.0
$Ce_2Rh_{3+x}Si_{1-x}$ $0.08 \le x \le 0.17$ $Ce_2Rh_{3.1}Si_{0.9}$ ($x = 0.1$)	$R\bar{3}m$	Y_2Rh_3Ge	$a = 0.55427(1)$ $c = 1.18479(2)$	33.1	52.2	14.7
$Ce_8(Rh_{1-x}Si_x)_{24}Si$ $0.07 \le x \le 0.10$ $Ce_8Rh_{21.9}Si_{3.1}$ ($x = 0.0875$)	$Pm\bar{3}m$	$Ce_8Pd_{24}Sb$	$a = 0.82676(2)$	23.5	67.1	9.4
$Ce_4(Rh_{1-x}Si_x)_{12}Si$ $0.00 \le x \le 0.03$ $Ce_4Rh_{12}Si$ ($x = 0.0$)	$Im\bar{3}m$	$Ce_4Rh_{12}Si$	$a = 0.82072(3)$	24.2	70.3	5.5
$CeRh_3Si_{1-x}$ $0.81 \le x \le 1.00$ $CeRh_3Si_{0.125}$ ($x = 0.875$)	$Pm\bar{3}m$	Cu_3Au	$a = 0.40655(2)$	24.8	72.1	3.1

The products were examined by X-ray powder diffraction (XRD) and energy-dispersive X-ray analysis (EDX). The XRD data were collected at room temperature employing a STOE STADI P transmission diffractometer, equipped with a linear PSD (monochromatic $CuK\alpha_1$ radiation with $\lambda = 1.54056$ Å; $10^\circ \le 2\theta \le 90^\circ$). Quantitative Rietveld refinements of the XRD patterns were performed employing the FULLPROF program [9]. The EDX studies were made using a Carl Zeiss LEO EVO 50XVP scanning electron microscope equipped with a Link EDX INCA Energy 450 system (Q-BSD detector).

Magnetic measurements were carried out over the temperature interval 1.71–400 K in magnetic fields up to 5 T employing a Quantum Design MPMS-5 SQUID magnetometer. The electrical resistivity was measured from 4.2 K to room temperature by a conventional four-probe dc technique implemented in a home-made setup. Electrical leads (copper wires) were attached to the bar-shaped specimens using silver-epoxy paste.

3. Results and discussion

3.1. Sample characterisation

The XRD and EDX analyses indicated single-phase character of the $CeRh_{1.82}Si_{0.18}$, $Ce_8Rh_{21.9}Si_{3.1}$ and $CeRh_3Si_{0.125}$ samples with no impurities. In turn, $Ce_4Rh_{12}Si$ was present as a major phase in the relevant sample with a small amount (less than 0.5%) of cubic compound $Ce_2Rh_{15}Si_7$ as an impurity. In the case of $Ce_2Rh_{3.1}Si_{0.9}$, the electron probe microanalysis (EPMA) revealed significant inhomogeneity of the specimen: while bottom part of the sample had the proper composition, rather large amounts of $CeRh_2$ and $CeRh_2Si$ impurity phases were detected on its upper part. For this very sample a slab of 1 mm thickness was prepared from the bottom part of the ingot for the physical property measurements. The lattice parameters and the phase compositions of all the samples investigated are summarized in Table 1. In general, they are in good agreement with the data reported in Ref. [1].

3.2. Physical properties

The magnetic behavior of the Ce–Rh–Si ternaries studied in this work is presented in the five panels of Fig. 1. For each compound the magnetic susceptibility is positive in the entire temperature range covered. Moreover, it is hardly temperature dependent over an extended temperature interval, and only at very low temperatures the $\chi_m(T)$ curves show some upturns. This behavior is characteristic of weak Pauli paramagnets, which contain impurities having a Curie–Weiss (CW) paramagnetic character. In the present case it implies that all the cerium ions in the studied compounds would be nominally tetravalent with nonmagnetic $4f^0$ configuration. In turn, the impurity might essentially contain Ce^{3+} ions (e.g., in form of cerium oxides located on grain boundaries), each of them characterized by the effective magnetic moment $\mu_{eff}^{Ce3+} = 2.54\,\mu_B$. For such a system the experimental data can be analyzed in terms of the function $\chi_m(T) = \chi_{int} + C_{imp}/(T - \theta_{imp})$, where a Curie–Weiss-like term was added to the intrinsic temperature-independent susceptibility χ_{int} to account for the impurity contribution. The solid lines in Fig. 1 represent least-squares fits of this formula to the experimental data of $CeRh_{1.82}Si_{0.18}$, $Ce_2Rh_{3.1}Si_{0.9}$, $CeRh_3Si_{0.125}$, $Ce_4Rh_{12}Si$ and $Ce_8Rh_{21.9}Si_{3.1}$, and the so-derived values of χ_{int}, C_{imp} and θ_{imp} are collected in Table 2. Attributing the spurious term to Ce^{3+} ions only, one may estimate their amount, n, from the obtained value of $C_{imp} = n\,(\mu_{eff}^{Ce3+})^2/8$. These estimates are also given in Table 2. Clearly, the impurity content is very low in $Ce_4Rh_{12}Si$ and $Ce_8Rh_{21.9}Si_{3.1}$, a bit larger in $CeRh_{1.82}Si_{0.18}$ and $CeRh_3Si_{0.125}$, while it is relatively high in $Ce_2Rh_{3.1}Si_{0.9}$. This result well agrees with the EDX data collected for the samples studied. In line with this finding is also the magnitude of the magnetization reached at $T = 1.71$ K in a field of 5 T (see the insets to Fig. 1) that is much larger in $Ce_2Rh_{3.1}Si_{0.9}$ in respect to that measured for the other specimens. Regardless this difference, for all the compounds $\sigma(H)$ has a similar shape, characteristic of paramagnetic systems. As apparent from Table 2, the intrinsic behavior of these samples is characterized by the Pauli susceptibility of the order of 10^{-4} emu/(mol Ce-atom), typical for nonmagnetic metals. Somewhat enhanced χ_{int} values were found for $CeRh_{1.82}Si_{0.18}$ and $Ce_2Rh_{3.1}Si_{0.9}$, which seem indicate moderately strong electronic correlations (yet for the latter compound, any strong statement is hampered by the impurity contamination).

Fig. 2 presents the temperature variations of the electrical resistivity of the Ce–Rh–Si ternaries. These data reveal metallic nature of all these materials and corroborate their weakly magnetic character. In particular, the $\rho(T)$ curves measured for $CeRh_3Si_{0.125}$, $Ce_4Rh_{12}Si$ and $Ce_8Rh_{21.9}Si_{3.1}$ exhibit a behavior characteristic of nonmagnetic metals that can be described by the Bloch–Grüneissen–Mott (BGM) formula [10].

$$\rho(T) = \rho_0 + 4RT\left(\frac{T}{\Theta_R}\right)^4 \int_0^{\Theta_R/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} - KT^3$$

where ρ_0 stands for the residual resistivity due to static defects in the crystal lattice, the second term describes the phonon contribution to the total resistivity (the parameter Θ_R is considered as a measure of the Debye temperature Θ_D), and the third one represents s–d interband scattering processes. As can be inferred from Fig. 2, the BGM expression provides very good approximations of the experimental $\rho(T)$ data of these three compounds, and the so-derived values of the transport parameters are collected in Table 2. Also the resistivity of $CeRh_{1.82}Si_{0.18}$ can be represented by the BGM function, yet quality the least-squares fit is less good, especially close to room temperature, where $\rho(T)$ is markedly curved. Analysing the obtained parameters, it is worth noting that the ratio of the resistivity measured at room temperature to the residual resistivity is close to 1 (the only exception is $Ce_4Rh_{12}Si$), which can

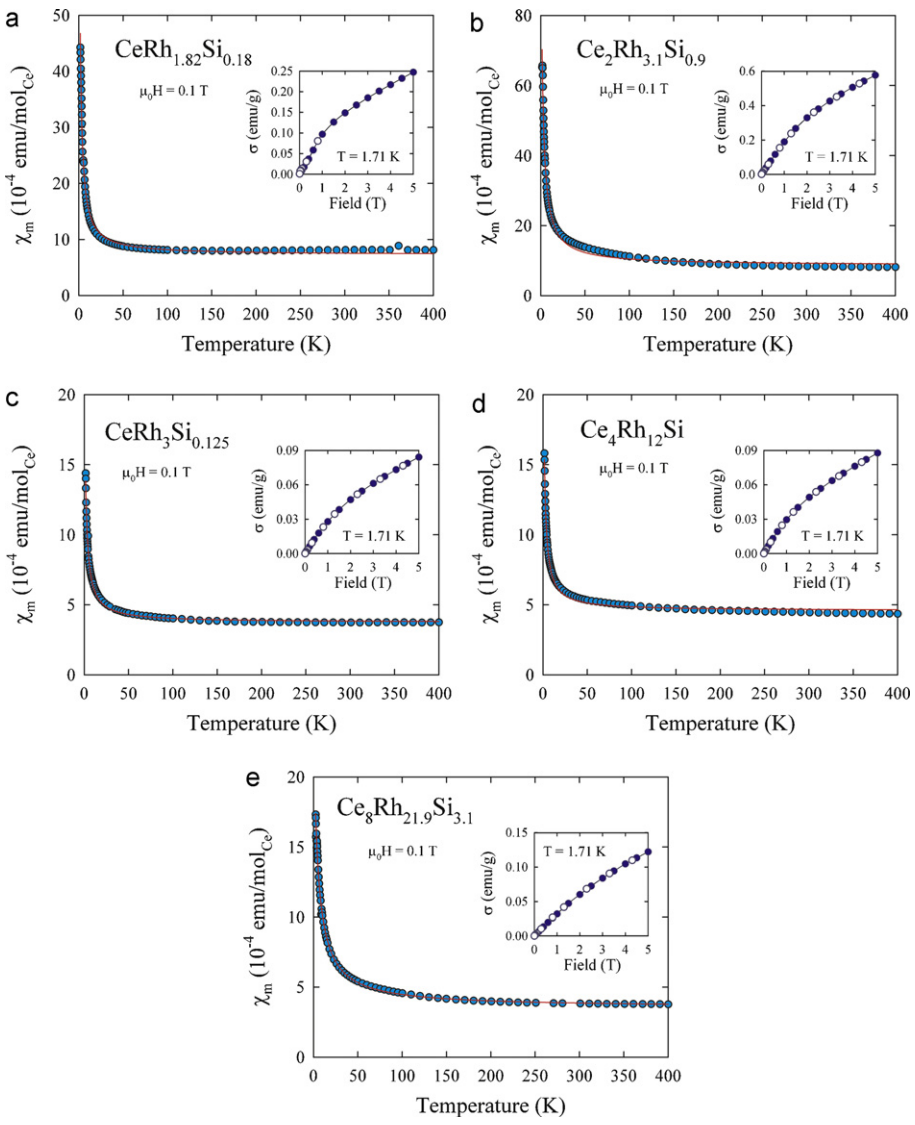

Fig. 1. Temperature dependencies of the molar magnetic susceptibility of (a) $CeRh_{1.82}Si_{0.18}$, (b) $Ce_2Rh_{3.1}Si_{0.9}$, (c) $CeRh_3Si_{0.125}$, (d) $Ce_4Rh_{12}Si$, and (e) $Ce_8Rh_{21.9}Si_{3.1}$, taken in a field of 0.1 T. The solid lines are the fits discussed in the text. The insets display the field variations of the magnetization measured at 1.71 K with increasing (full circles) and decreasing (open circles) the magnetic field strength.

be attributed to large degree of structural disorder inherent in all these ternaries [1] (here note that $Ce_4Rh_{12}Si$ exhibits full atomic order [1]). The scattering of conduction electrons on phonons, characterized by the values of Θ_R and R, appears similar in these compounds (an exception seems $Ce_4Rh_{12}Si$) and comparable to that in cerium-based intermetallics. In turn, the Mott contribution to the electrical conductivity is rather small (again except for the case of $Ce_4Rh_{12}Si$), while opposite signs of the parameter K derived for these systems likely signal different curvatures of their electronic bands near the Fermi level.

As seen in Fig. 2, the temperature dependence of the electrical resistivity of $Ce_2Rh_{3.1}Si_{0.9}$ is entirely dissimilar to those found for the other Ce–Rh–Si silicides. Below about 50 K, ρ(T) rapidly bends down and no saturation is observed down to the lowest temperatures measured. Such a behavior of the resistivity is typical for Ce-based systems with strong electronic correlations, and

Table 2
Magnetic and electrical characteristics of the Ce–Rh–Si samples.

Compound	$CeRh_{1.82}Si_{0.18}$	$Ce_2Rh_{3.1}Si_{0.9}$	$Ce_8Rh_{21.9}Si_{3.1}$	$Ce_4Rh_{12}Si$	$CeRh_3Si_{0.125}$
χ_{int} (10^{-4} emu/mol$_{Ce}$)	7.2	8.6	3.5	4.6	3.7
C_{imp} (10^{-3} emu/K mol$_{Ce}$)	9.5	18.8	9.7	2.8	2.9
n_{imp} (% per mol$_{Ce}$)	1.2	2.3	1.2	0.3	0.4
θ_{imp} (K)	−0.7	−1.3	−4.6	−0.9	−1.2
ρ_{290K} (μΩ cm)	116.3	114.4	57.4	64.8	104.1
ρ_0 (μΩ cm)	106.8	–	42.0	20.8	90.3
RRR = ρ_{290K}/ρ_0	1.1	–	1.4	3.1	1.2
Θ_R (K)	213.3	–	212.5	147.6	183.2
R (μΩ cm/K)	0.039	–	0.053	0.164	0.046
K (10^{-8} μΩ cm/K^3)	−5.1	–	2.2	−11.3	3.3

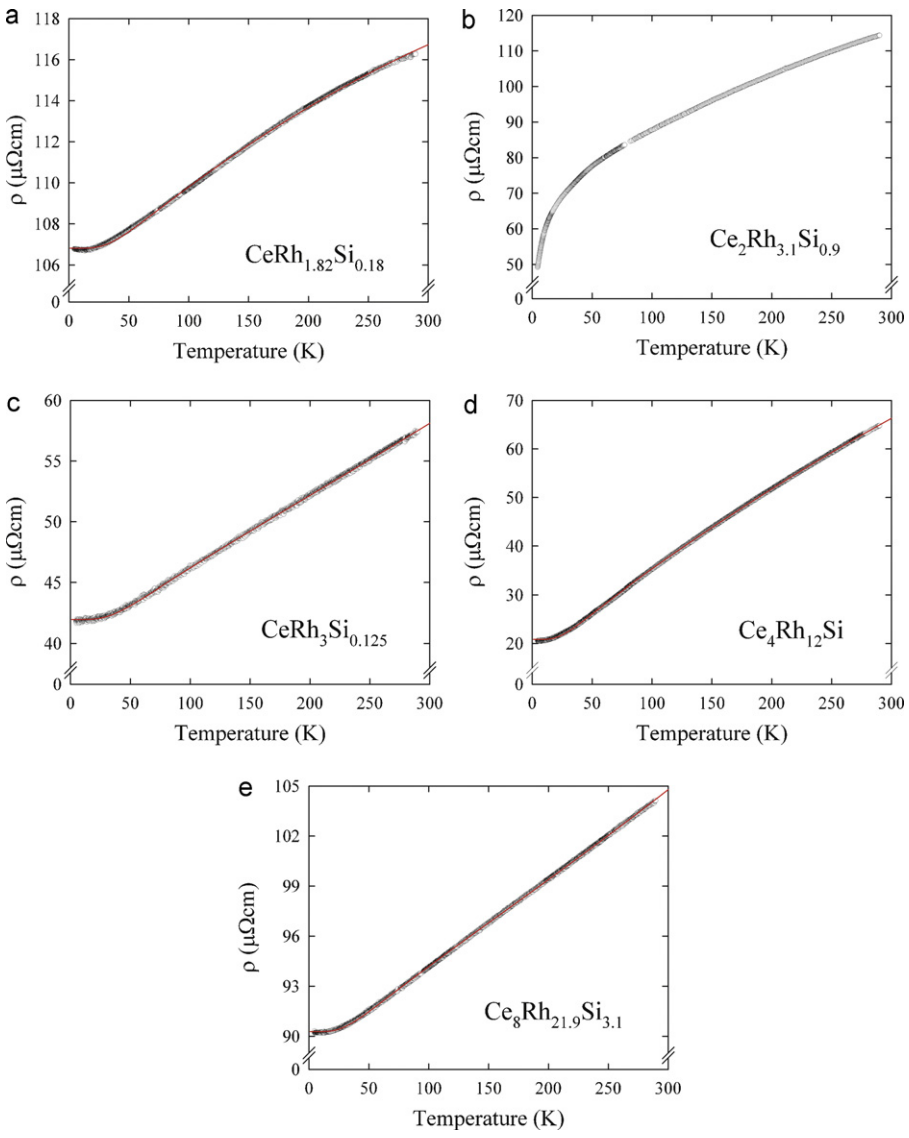

Fig. 2. Temperature dependencies of the electrical resistivity of (a) $CeRh_{1.82}Si_{0.18}$, (b) $Ce_2Rh_{3.1}Si_{0.9}$, (c) $CeRh_3Si_{0.125}$, (d) $Ce_4Rh_{12}Si$, and (e) $Ce_8Rh_{21.9}Si_{3.1}$. The solid lines represent the BGM fits discussed in the text.

seems compatible with the magnetic data of $Ce_2Rh_{3.1}Si_{0.9}$. Though the studied specimen contained some magnetic impurities (see above), it is very unlikely that the derived ρ(T) variation was significantly affected by their presence, as the electronic transport in metals is known to be hardly sensitive to small amount of foreign phases. Therefore, the obtained results may be attributed to intrinsic behavior in $Ce_2Rh_{3.1}Si_{0.9}$ and hence hint at some instability in the valence state for the Ce ions. To further explore this conjecture, more detailed investigations of the transport and thermodynamic properties of the compound are required, performed at much lower temperatures and possibly on higher quality samples.

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