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Metallurgic, structural and magnetic properties of $Ce(Pd_{1-r}Rh_r)_2Si_2$

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Abstract

We report on investigations of the metallurgic, crystallographic and magnetic properties of the $Ce(Pd_{1-r}Rh_r)_2Si_2$ system. While the as-cast samples show a miscibility gap for $0.3<r<0.7$, complete miscibility with a monotonous evolution of the lattice parameters is found in samples annealed at 1200°C. Although both pure compounds order antiferromagnetically at 10 K ($r=0$) and 36 K ($r=1$) respectively, our magnetic susceptibility (χ) results indicate a magnetically non-ordered state at intermediate concentrations. The ordering temperature decreases smoothly and continuously on the Pd-rich side, vanishing between $r=0.2$ and $r=0.3$. On the Rh-rich side, this decrease is faster and at $r=0.8$ the long-range magnetic order is replaced by enhanced magnetic fluctuations as evidenced by a broad maximum in $\chi(T)$ around 25 K. The orientation-dependent χ of the strongly textured samples indicates an evolution towards an easy-axis system with increasing Rh content. The results are discussed and compared to the related systems $Ce(Pd_{1-x}T_x)_2Si_2$ (T=Ru and Cu). © 1998 Elsevier Science S.A.

Keywords: Heavy-fermion systems; Metallurgy; Magnetic properties

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1. Introduction

The compounds $CePd_2Si_2$ and $CeRh_2Si_2$ as well as $CeCu_2Ge_2$ ($ThCr_2Si_2$-type structure) have recently attracted considerable interest since the application of hydrostatic pressure leads to the suppression of the antiferromagnetic (AF) state and to the onset of superconductivity [1–4]. They show a more or less rapid decrease of the Néel temperature T_N with applied pressure, and near the critical value at which T_N extrapolates to zero the superconducting ground state appears.

At ambient pressure $CePd_2Si_2$ orders AF at $T_N=10$ K [5] with a relatively low value of magnetic moments ($\mu_{ord}=0.66\ \mu_B$) ordered along the basal plane of the structure [6]. From the value of the Kondo temperature, $T_K \approx T_N$, this compound is classified as a local-moment Kondo lattice [5]. On the other hand, $CeRh_2Si_2$ orders at $T_N=36$ K, which is the highest AF transition temperature among all known Ce-based intermetallic compounds [7]. In the magnetically ordered state the magnetic moments ($\mu_{ord}=1.5\ \mu_B$) order along the *c*-axis direction of the structure [6,8]. Quasi-elastic neutron scattering results show that also in this compound $T_K \approx T_N$ [9], but the relatively high value of its Kondo temperature indicates that the AF order develops from a strongly hybridized paramagnetic state.

Previous studies of alloying effects on $Ce(Pd_{1-x}T_x)_2Si_2$ show that for T=Cu [10] and T=Ru [11,12] long-range magnetic order is suppressed for concentrations $x \approx 0.2$–0.3. A similar situation occurs for $Ce(T_{0.1}Rh_{0.9})_2Si_2$ (T=Co, Ni, Cu, Os, Ru, Pd, and Au) [13], where alloying leads to a decrease of T_N, and in some cases to the suppression of the AF-state of $CeRh_2Si_2$. In particular, $Ce(Pd_{0.1}Rh_{0.9})_2Si_2$ was observed to order at 28 K [13], suggesting the possibility of a non-magnetic state for intermediate Pd–Rh concentrations.

In order to study in more detail the effect of alloying on the magnetic to non-magnetic transformations in $Ce(Pd_{1-r}Rh_r)_2Si_2$ we have started the investigation of the metallurgic, crystallographic and magnetic properties of this system. A first account of our results are presented in this paper.

2. Experimental and results

Two groups of $Ce(Pd_{1-r}Rh_r)_2Si_2$ samples were pre-

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pared by arc-melting stoichiometric amounts of pure elements on a water-cooled Cu hearth in a Zr-gettered Ar atmosphere. The buttons were remelted several times inside the furnace in order to ensure homogeneity of the sample composition. The crystallographic properties of both groups were studied in the 'as cast' state as well as after different annealing procedures. The samples of the first group, with concentrations $r=0$, 0.2, 0.4, 0.6, 0.8, and 1, were annealed at 1000°C for 120 h and those of the second group, with $r=0.1$, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 0.95, were annealed at 1200°C for 80 h. The samples were characterized by powder X-ray diffractometry using Si as an internal standard. In all cases only reflections belonging to the tetragonal $ThCr_2Si_2$-type structure were observed within the experimental resolution (1.5% of the strongest (112) reflection).

The 'as cast' samples of both groups as well as the samples annealed at 1000°C show evidences of a miscibility gap for $0.3 \leq r \leq 0.7$, resulting in a phase separation into a Rh-rich and a Pd-rich phases. Since exchange of Pd by Rh leads to a decrease of the a-lattice parameter and an increase of the c parameter, the phase separation is best seen in the broadening and the splitting of the (200) reflections, whereas (hkl) reflections with both $h>0$ and $l>0$ are much less sensitive, as shown in Fig. 1 for $r=0.5$. The broadening of the (200) line is almost negligible for $r=0.3$ and $r=0.7$, it increases for $r=0.4$ and $r=0.6$, and for $r=0.5$ one observes a clear splitting into two peaks of similar intensities. Outside this concentration range, i.e., for $r \leq 0.2$ and $r \geq 0.8$, none of the studied samples show any evidence of inhomogeneity and have a single crystalline phase.

In Fig. 1b the result after the annealing process at 1200°C is shown. The double-peak structure completely vanishes and a single (200) peak, with a line-width comparable to those of the strongest reflections of the spectrum, i.e., the (112) and (103) lines, remains. This indicates that the miscibility gap closes when the samples are annealed at 1200°C and a complete homogeneity in composition is obtained in the whole concentration range at this temperature. We suspect that at 1000°C the homogeneous solution is also the thermodynamically stable state, but the diffusion rate at this temperature is too low to allow for a complete homogenization.

The composition dependence of the a and c lattice parameters, the ratio c/a and the unit-cell volume V of the $Ce(Pd_{1-r}Rh_r)_2Si_2$ system is shown in Fig. 2. Only the lattice parameters of those samples showing complete homogeneity after annealing are shown. Whereas the a-axis decreases with concentration, the c-axis increases, both showing a departure from linearity for $r>0.7$ (see Fig. 2a). The opposite behavior of $a(r)$ and $c(r)$ leads to a strong change of the c/a ratio of the order of 7%, whereas the V dependence decreases only by ~4% between $r=0$ and $r=1$ (see Fig. 2b), suggesting that the properties of the system should be governed by the c/a relationship instead of the $V(r)$ dependence.

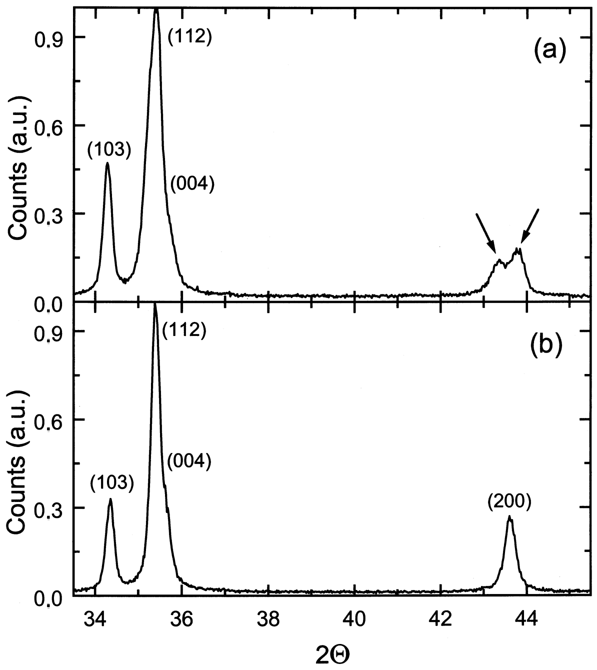

Fig. 1. Part of the X-ray diffraction spectrum of $Ce(Pd_{0.5}Rh_{0.5})_2Si_2$ showing the difference between the (a) 'as cast' and (b) annealed (1200°C) states. The arrows indicate the splitting of the (200) peak. After annealing (b) the width of the (200) line becomes comparable to (112) and (103).

In order to study the magnetic properties, small slices were cut form the buttons. It was observed that the slices present a clear texture. In this sense, the samples can no longer be treated as 'isotropic' polycrystals. For this reason the magnetic susceptibility was measured applying the

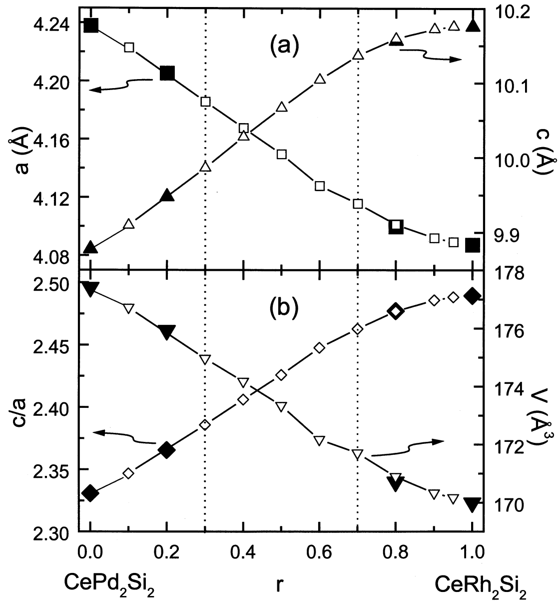

Fig. 2. (a) Lattice parameters a and c, (b) ratio c/a and unit cell volume of $Ce(Pd_{1-r}Rh_r)_2Si_2$ as a function of r. Full (open) symbols correspond to samples of the first (second) group. The lines are a guide.

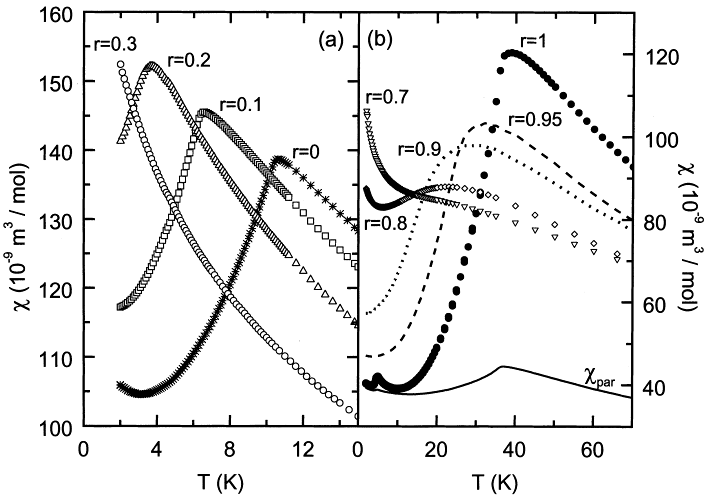

Fig. 3. Evolution of the AF transitions: (a) $\chi_{par}(T)$ for $r \leq 0.3$ and (b) $\chi_{per}(T)$ for $r \geq 0.7$. The $\chi_{par}(T)$ values of $CeRh_2Si_2$ are included as a full line for comparison.

magnetic field along the face of square slices in directions parallel χ_{par} and perpendicular χ_{per} to the direction of the textures.

In the Pd-rich region the difference between χ_{par} and χ_{per} is weak. In Fig. 3a the composition dependence of $\chi_{par}(T)$ below 15 K is shown for $r \leq 0.3$. The cusp related to the AF-ordering clearly shifts to lower temperatures with increasing r and disappears for $r=0.3$. In contrast, a strong anisotropy is observed in the Rh-rich samples. In Fig. 3b $\chi_{per}(T)$ of the samples with $r \geq 0.7$ are compared with $\chi_{par}(T)$ of $CeRh_2Si_2$. For this sample ($r=1$) the value of $\chi_{per}(T)$ above T_N is approximately three times $\chi_{par}(T)$. The pronounced anomaly related to the onset of AF-order at $T_N=36$ K in pure $CeRh_2Si_2$ shifts to lower temperatures and broadens with decreasing r. At $r=0.8$ the anomaly changes into a broad maximum, suggesting an evolution from long-range magnetic order to short-range correlations.

In the intermediate concentration range $0.3 \leq r \leq 0.8$ we found no evidence of magnetic order, as can be seen, e.g., in $\chi_{par}(T)$ in Fig. 4. Instead one observes for all the samples a continuous increase of the susceptibility with decreasing temperature, and the value of χ at $T=2$ K increasing continuously with decreasing r. In Fig. 5 we compare χ_{par} and χ_{per} at $T=40$ K and at $T=2$ K, respectively. As already pointed out, a pronounced anisotropy is only observed in the Rh-rich side above T_N. At

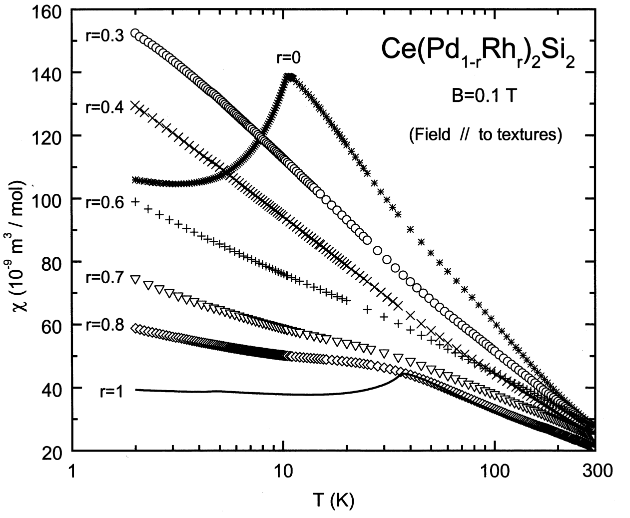

Fig. 4. Evolution of the magnetic susceptibility of $Ce(Pd_{1-r}Rh_r)_2Si_2$ samples with r for a field applied parallel to the direction of the textures.

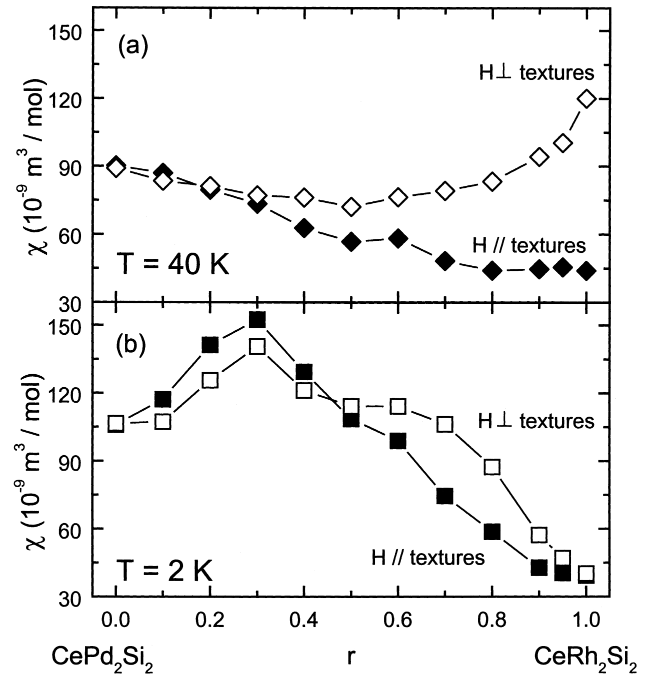

Fig. 5. Comparison of χ_{par} (full symbols) and χ_{per} (open symbols) as a function of concentration at $T=40$ K (a) and at $T=2$ K (b).

$T=2$ K, we observe only minor differences between χ_{par} and χ_{per} in the whole concentration range. The maximum of $\chi(T=2\text{ K})$ at $r=0.3$ reflects the disappearance of the magnetic ordered state.

3. Discussion

Our structural investigations reveals an intriguing behavior of the $\mathrm{Ce(Pd_{1-r}Rh_r)_2Si_2}$ system. The results indicate the presence of a miscibility gap at high temperatures in the concentration region $0.3<r<0.7$, a rather unusual behavior. Interestingly, a similar situation seems to be present in the $\mathrm{Ce(Pd_{1-x}Ru_x)_2Si_2}$ alloy: whereas one group of authors found a miscibility gap in the 'as cast' samples in the region $0.3<r<0.7$ [11], another could prepare homogeneous samples by a special heat treatment [12]. The occurrence of this high temperature miscibility gap can be related to another anomalous behavior: the non-monotonous dependence of the c/a-ratio within the $\mathrm{CeRu_2Si_2}$–$\mathrm{CeRh_2Si_2}$–$\mathrm{CePd_2Si_2}$ series [7]. Although the atomic volume of Ru, Rh and Pd are quite similar, which results in a weak and smooth evolution of V across the whole series, the c/a ratio presents a pronounced maximum for $\mathrm{CeRh_2Si_2}$, increasing from ~2.33 for $\mathrm{CeRu_2Si_2}$ and $\mathrm{CePd_2Si_2}$, to ~2.49 for $\mathrm{CeRh_2Si_2}$ [7]. Since this maximum is also clearly seen in the $\mathrm{Ce(Pd_{1-x}Ru_x)_2Si_2}$ system [12] it is obviously related to the filling of the d-shell and not due to steric effects. We suggest that the observed immiscibility gap at high temperatures and the anomalous dependence of the c/a ratio in this series have a common origin. Further structural and metallographic studies as well as calculations of the electronic states are under way in order to elucidate this intriguing behavior.

For the discussion of the susceptibility results one should take into account that in $\mathrm{Ce(Pd_{1-r}Rh_r)_2Si_2}$ we are dealing with structural as well as intrinsic magnetic anisotropies that strongly influence the magnetic response. The easy magnetization axis of the system should gradually change as a function of r from the basal plane for $\mathrm{CePd_2Si_2}$ to the c-axis direction for $\mathrm{CeRh_2Si_2}$. This situation is confirmed by the $\chi(T)$ results if we suppose that in the crystallization process (when the 'textures' are formed) the crystals grow with the c-axis perpendicular to the temperature gradient, i.e., with the c-axis direction parallel to the top and bottom surface of the sample, as already observed in single crystal growth of related compounds. This is also to be expected from the crystalline structure, since it corresponds to a faster growing along the basal plane, which is the closed-packed layer. Within this picture the $\chi_{\mathrm{par}}(T)$ values are expected to be enhanced for Pd-rich samples because the magnetic field is applied mainly along the basal plane, whereas $\chi_{\mathrm{per}}(T)$ values are expected to be enhanced for Rh-rich samples because then a component along the c-axis direction is measured (see Fig. 5). This configuration explains the different behavior of $\chi_{\mathrm{par}}(T)$ and $\chi_{\mathrm{per}}(T)$, in particular the strong difference observed for $\mathrm{CeRh_2Si_2}$ (see Fig. 3b and Fig. 5a).

Regarding the evolution of the ground-states properties of $\mathrm{Ce(Pd_{1-r}Rh_r)_2Si_2}$, our $\chi(T)$ data show that the effect of alloying clearly affects the AF states in a different way. At the Pd-rich side, the effect of Rh substitution continuously shifts the sharp maximum of $\chi(T)$ to lower temperatures, as shown in Fig. 3a. In contrast, the magnetic long-range order of $\mathrm{CeRh_2Si_2}$ is rapidly destabilized with alloying leading to a paramagnetic state with strong magnetic fluctuations mainly along the c-axis direction (see Fig. 3b). Preliminary electrical resistivity results (not shown) indicate a continuous and monotonous evolution to a highly-hybridized state as the concentration reaches $r=0.8$. This in agreement with the relative values of T_{K} of the pure compounds, where the larger value of T_{K} of $\mathrm{CeRh_2Si_2}$ indicates that the long-range AF order develops from a highly-hybridized state compared to $\mathrm{CePd_2Si_2}$.

Both the suppression of the magnetically ordered state of $\mathrm{CePd_2Si_2}$ and the increase of the characteristic energy of the f-electrons as a function of r resemble the behavior of $\mathrm{Ce(Pd_{1-x}Cu_x)_2Si_2}$ for $x<0.6$ [10,14], which also shows a gradually suppression of the AF order up to $x\approx0.3$. A notorious difference in both systems is that in $\mathrm{Ce(Pd_{1-x}Cu_x)_2Si_2}$ there is a non-monotonous concentration dependence of T_{K} [10,14], while for $\mathrm{Ce(Pd_{1-r}Rh_r)_2Si_2}$ our present results indicate a monotonous increment of T_{K} with alloying.

4. Conclusions

The present metallurgic studies on $\mathrm{Ce(Pd_{1-r}Rh_r)_2Si_2}$ alloys reveal that the as-cast samples show a miscibility gap for $0.3<r<0.7$. A complete miscibility with a monotonous evolution of the lattice parameters is found in samples annealed at 1200°C. Although both pure compounds order AF, our $\chi(T)$ results show a magnetically non-ordered state for intermediate r. The ordering temperature decreases smoothly and continuously at the Pd-rich side, vanishing between $r=0.2$ and $r=0.3$. On the Rh-rich side, this decrease is faster and already at $r=0.8$ the long-range magnetic order is replaced by enhanced magnetic fluctuations as evidenced by a broad maximum in $\chi(T)$ around 25 K. The orientation-dependent χ of the strongly textured samples indicates an evolution towards an easy-axis system with increasing Rh content. These preliminary results indicate a continuous increase of the Kondo temperature with r, in contrast to the behavior of $\mathrm{Ce(Pd_{1-x}Cu_x)_2Si_2}$ [10,14].

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