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Evolution from the antiferromagnetic to the intermediate valence state in the $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ system

B Chevalier†, J Etourneau†, J Rossat-Mignod‡, R Calemczuk§ and E Bonjour§

† Laboratoire de Chimie du Solide du CNRS, 351 cours de la Libération, 33405 Talence Cedex, France

‡ Centre d'Etudes Nucléaires de Grenoble, DRF/SPh-MDN, 85X, 38041 Grenoble, France

§ Centre d'Etudes Nucléaires de Grenoble, DRF/SBT-LCP, 85X, 38041 Grenoble, France

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Abstract. The effects of substituting rhodium by cobalt in the tetragonal antiferromagnetic compound CeRh_2Si_2 are studied by *x*-ray investigation and magnetic, electrical and specific heat measurements. In the $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ solid solution, a transition from a magnetically ordered state to an intermediate valence state appears when *x* is nearly equal to 0.135. An increase of the linear coefficient of the specific heat γ is observed at this transition. For $x \leq 0.125$, the Néel temperature decreases rapidly when *x* increases.

1. Introduction

CeRh_2Si_2 crystallizes with the tetragonal ThCr_2Si_2 -type structure. This ternary silicide is magnetically ordered with an anomalously large Néel temperature of 36 K [1]. Below T_N it develops a magnetic ordering described by a wave vector $k = (\frac{1}{2}, \frac{1}{2}, 0)$ corresponding to an antiferromagnetic ordering within the (001) planes. This magnetic structure is unique among the RERh_2Si_2 (RE = rare earth) ternary silicides. Thompson *et al* [2] have found that a hydrostatic pressure strongly depresses this Néel temperature. This result may indicate that there is strong competition between the Kondo effect and magnetic interactions in CeRh_2Si_2 .

In order to understand further the origin of this rapid depression of T_N in CeRh_2Si_2 , we have investigated the effect of the substitution of rhodium by smaller cobalt atoms. According to a previous *x*-ray absorption study, the cerium is purely trivalent in CeRh_2Si_2 and in an intermediate valence state in CeCo_2Si_2 [3]. In this paper, we report the results of structural, magnetic, electrical and specific heat studies on the system $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$. These results are compared with those obtained recently for $\text{Ce}(\text{Rh}_{1-x}\text{Ru}_x)_2\text{Si}_2$ solid solution [4, 5].

2. Experiment

The $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ samples were prepared in two steps. First, CeSi_2 was synthesized by melting blocks of high purity cerium and silicon using an induction levitation furnace

Table 1. Lattice parameters (a , c) and unit-cell volume (V) for $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ solid solution: effective paramagnetic moment (μ_{eff}) and paramagnetic Curie (θ_p), Néel (T_N) and Kondo fluctuation (T_K , T_K^*) temperatures for these compounds.

x	a (Å)	c (Å)	V (Å) ³	μ_{eff} (μ_B)	θ_p (K)	T_N (K)	T_K (K)	T_K^* (K)
0	4.087	10.17	169.88	2.56	-61	36		
0.04	4.085	10.16	169.54	2.60	-63	32		
0.08	4.086	10.16	169.63	2.58	-82	26		
0.10	4.086	10.16	169.63	2.69	-84	24		
0.125	4.081	10.14	168.88	2.64	-82	6		
0.135	4.079	10.14	168.71				90	80
0.15	4.077	10.14	168.55				90	75
0.175	4.076	10.13	168.30				91	90
0.25	4.068	10.11	167.31				115	107
0.30	4.067	10.10	167.06				159	130
0.38	4.059	10.07	165.91				160	138
0.50	4.047	10.01	163.95				203	190
0.70	4.008	9.93	159.52				252	271
0.90	3.980	9.85	156.03				261	300
1.0	3.958	9.81	153.68					>300

in a purified argon atmosphere. Then, pressed pellets of stoichiometric amounts of powdered CeSi_2 , Rh and Co were melted in an arc furnace. Samples were annealed at 900 °C for one week in evacuated quartz tubes.

Crystal structure and lattice parameters have been determined by x-ray powder diffraction using CuK_α radiation. The electrical properties were investigated above 4.2 K by resistivity measurements using a four-probe DC technique. Magnetic susceptibility measurements were performed in the temperature range 4.2–300 K using a Faraday microbalance and for lower temperatures down to 2 K with a SQUID magnetometer. Specific heat was measured using an adiabatic dynamic method.

3. Results

3.1. Lattice parameters

X-ray diffraction studies have shown that for $0 \leq x \leq 1$ the solid solutions are single-phase materials crystallizing with the tetragonal ThCr_2Si_2 -type structure. The lattice parameters a and c , evaluated by a least-square refinement from room temperature Guinier photographs using Si as an internal standard, are given in table 1. The a and c parameters decrease when x increases. So the substitution of rhodium by cobalt atoms introduces a 'chemical-pressure' effect on cerium. In CeCo_2Si_2 and CeRh_2Si_2 , cerium atoms are surrounded by eight nearest-neighbouring silicon atoms and the cerium-silicon distances are slightly larger in CeRh_2Si_2 (3.157 Å) than in CeCo_2Si_2 (3.055 Å).

The variation of the lattice parameters as a function of the cobalt substitution shows a positive deviation from the Vegard law (figure 1). This behaviour results from an increase of the hybridization strength of 4f electrons with conduction electrons. Among RECo_2Si_2 silicides, CeCo_2Si_2 exhibits a volume anomaly [6] which suggests an intermediate valence state for cerium in CeCo_2Si_2 ; this was confirmed by x-ray absorption

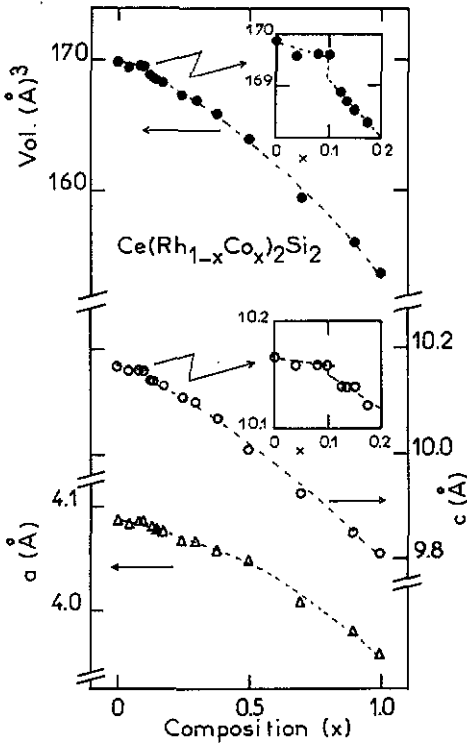


Figure 1. Composition dependence of the lattice parameters (a , c) and unit-cell volume (V) for $Ce(Rh_{1-x}Co_x)_2Si_2$.

[3]. From figure 1 it is clear that both the c parameter and unit-cell volume show an abrupt decrease in the range $x = 0.10$ to 0.125 . This volume collapse of $\Delta V/V = 0.5\%$ reflects a change in the bonding of cerium atoms with neighbouring silicon and transition elements for $x > 0.125$. For example the Ce–Si distances decrease from 3.156 \AA for $x = 0.10$ to 3.152 \AA for $x = 0.125$.

3.2. Magnetic susceptibility

Magnetic susceptibilities of $Ce(Rh_{1-x}Co_x)_2Si_2$ are reported in figure 2. For $CeCo_2Si_2$, these data are in good agreement with those previously reported in the literature [7].

For $0.15 \leq x \leq 1.0$, the magnetic susceptibility exhibits a broad maximum which is shifted to higher temperatures when the cobalt concentration increases (figure 2(b)). This behaviour is commonly observed in intermediate valence systems [8]. The sharp increase of χ at low temperatures is attributed to small amounts of impurity phase. The observed thermal dependence of the magnetic susceptibility $\chi(T)$ can be discussed in terms of a characteristic temperature T_K related to Kondo-type fluctuations [8]. In this scheme, T_K is defined as:

$$T_K \approx C/2\chi(0) \quad (1)$$

where C is the Curie constant for Ce^{3+} ions ($C = 0.807 \text{ emu K/mole}$), and $\chi(0)$ is the

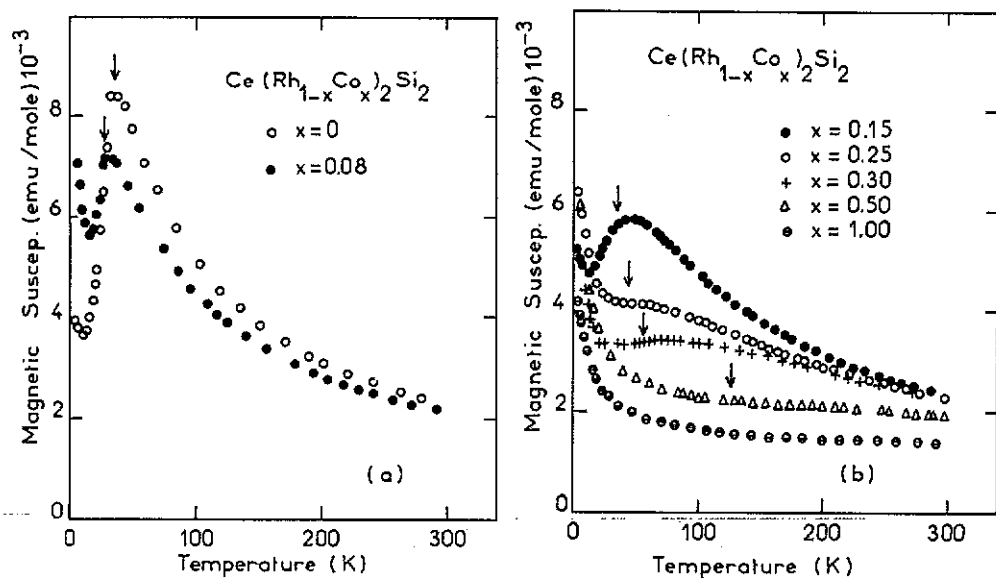


Figure 2. Magnetic susceptibility of $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ measured in a field of 0.76 T for: (a) $x = 0$ and 0.08 (the arrow indicates the Néel temperature) and (b) $0.15 \leq x \leq 1$ (the arrow indicates the Kondo fluctuation temperature).

magnetic susceptibility at $T = 0$ K. Above the broad maximum, $\chi(T)$ can be fitted by the expression:

$$\chi(T) = C/(T + T_K^*). \quad (2)$$

The resulting values for T_K and T_K^* are given in table 1. Let us note that the T_K and T_K^* values are in agreement. The hybridization characterized by the Kondo temperature increases practically linearly with the composition.

Above 120 K, the magnetic susceptibility of the solid solutions with $0 \leq x \leq 0.125$ follows a Curie-Weiss law. In this temperature range, the effective moment value μ_{eff} is very close to that calculated for a Ce^{3+} free ion ($2.54 \mu_B$). The slight increase of μ_{eff} with x , and the large negative value of the Curie paramagnetic temperature can be attributed to crystal field and Kondo effects (table 1). For these silicides, $\chi(T)$ curves show a sharp maximum similar to that observed for CeRh_2Si_2 , a behaviour typical for an antiferromagnet (figure 2(a)) [1]. For the two selected compositions $x = 0.125$ and $x = 0.15$, χ was measured in a magnetic field of 0.1 T down to 2 K. The results, reported in figure 3, give evidence for a magnetic transition near 6 K for $x = 0.125$ but no anomaly is detected for $x = 0.15$. By substituting 12.5% of rhodium by cobalt atoms, strong depression of the ordering temperature occurs as shown in figure 4. The variation of T_N with the cobalt composition is quite different from that observed for $\text{Ce}(\text{Rh}_{1-x}\text{Ru}_x)_2\text{Si}_2$ solid solution [4]. In the latter case, T_N falls off rapidly for $0 \leq x \leq 0.15$ and then keeps a nearly constant value of about 11 K up to $x = 0.40$ where a heavy fermion transition appears.

3.3. Specific heat

Figure 5 shows specific heat results for different x values in the temperature range 0.35 K–50 K. For the compositions $x = 0$ and $x = 0.10$, an anomaly corresponding to the

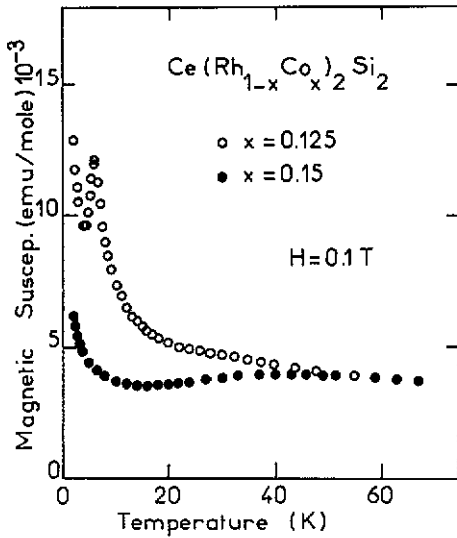


Figure 3. Magnetic susceptibility of $Ce(Rh_{1-x}Co_x)_2Si_2$ measured in a field of 0.1 T for $x = 0.125$ and 0.15.

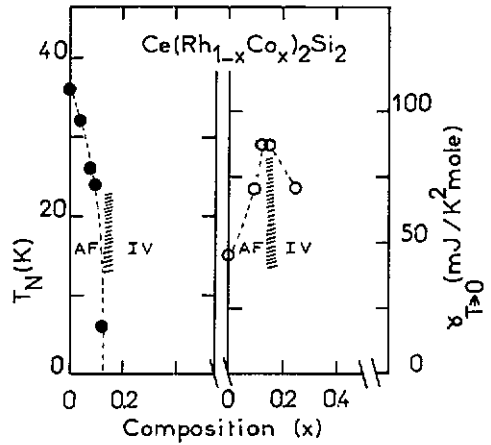


Figure 4. Néel temperature T_N and low temperature value of C/T as a function of the Co content for the $Ce(Rh_{1-x}Co_x)_2Si_2$ system.

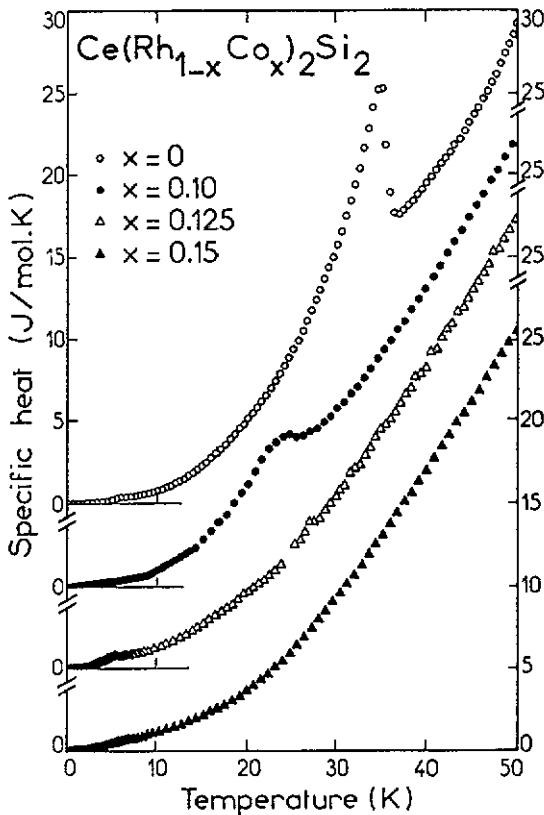


Figure 5. Temperature dependence of specific heat C/T for some $Ce(Rh_{1-x}Co_x)_2Si_2$ solid solutions.

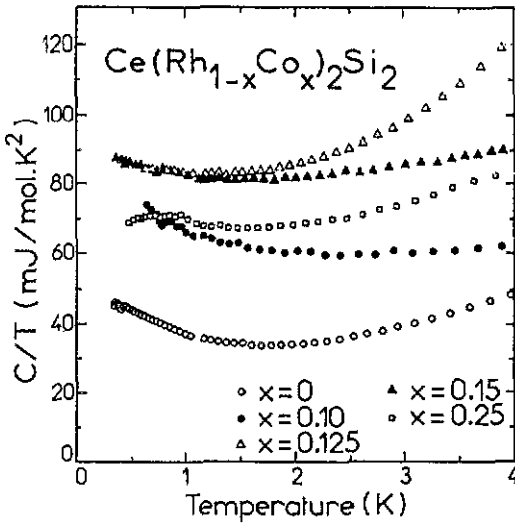


Figure 6. Temperature dependence below 4 K of specific heat C/T for some $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ solid solutions.

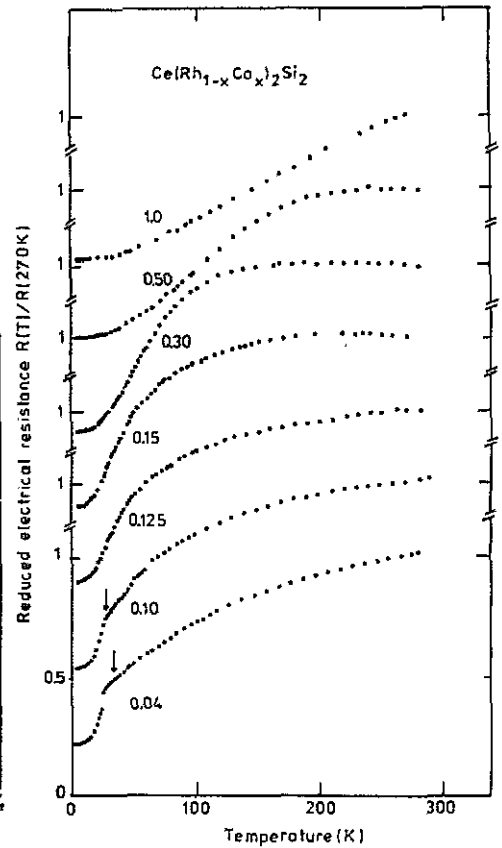


Figure 7. Reduced electrical resistance plotted against temperature for some $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ solid solutions (for clarity the curves are shifted vertically).

magnetic transition is observed at 35 K and 24.5 K, respectively: values close to those determined from magnetic susceptibility measurements. For $x = 0.125$ the specific heat exhibits a broad maximum around 5.8 K. We also note that a shoulder appears around 5–6 K in all samples. This very weak peak is presumably due to some magnetic impurities as observed earlier in other cerium compounds [9]. However, this anomaly is more pronounced for $x = 0.125$ confirming the antiferromagnetic ordering of this compound.

Specific heat data plotted as C/T against T in figure 6 show a small upturn below about 1–2 K for $0 \leq x \leq 0.15$. The more relevant feature is the noticeable enhancement of C/T as x approaches 0.125, where it reaches a maximum value of $87 \text{ mJ K}^{-2}/\text{mole}$. Above this x value it decreases with further cobalt substitution. Figure 4 shows that the maximum in γ which occurs at $x \approx 0.125$ –0.15 corresponding to the border between the antiferromagnetic and the intermediate valence states. The low value reached by γ indicates that in the $\text{Ce}(\text{Rh}_{1-x}\text{Co}_x)_2\text{Si}_2$ system the Kondo volume collapse inhibits the heavy fermion transition; the cerium state changes abruptly from a magnetic to an

intermediate valence state ($T_K \approx 90$ K). This behaviour is similar to that observed for the $Ce(Rh_{1-x}Ni_x)_2Si_2$ system [10].

3.4. Electrical resistivity

Electrical resistivity measurements performed between 4.2 K and 270 K are reported in figure 7. The behaviour of the resistivity shows a continuous transition from magnetically ordered compounds to intermediate valence compounds when rhodium is replaced by cobalt in $CeRh_2Si_2$. For $x < 0.125$, a sharp cusp in the reduced resistivity curve plotted against T corresponds to the onset of the magnetic order. The temperature of this abrupt decrease is in good agreement with the Néel temperature determined from magnetic susceptibility measurements.

Above 50 K, the resistivity of $CeCo_2Si_2$ is practically linear with respect to temperature, like in a normal metal. For $0.125 \leq x \leq 0.50$ the resistivity exhibits a T^2 behaviour at low temperatures, followed at higher temperatures by a flat maximum which can be attributed to an incipient Kondo effect on the crystal field split ground-state multiplet of cerium [10].

4. Discussion and conclusion

In $CeRh_2Si_2$, the magnetic properties result from a competition between the Kondo effect and magnetic interactions [11]. The Kondo temperature T_K depends exponentially on the strength hybridization between 4f and conduction electrons, whereas the intersite magnetic interactions increase quadratically. For this compound, T_N is greater than T_K [2]. Then, any increase of the hybridization, for example by a chemical or applied pressure, is sufficient to suppress the magnetic order.

When the rhodium atoms are replaced by cobalt in $CeRh_2Si_2$, the number of conduction electrons does not change significantly because Rh and Co are isoelectronic. However the unit cell volume is reduced, yielding an increase of the hybridization of 4f and conduction electrons. Therefore the main effect of substitution of Rh by Co in these silicide solid solutions is in a strong increase of the Kondo temperature inducing a drastic effect on the magnetic ordering. This study shows that the antiferromagnetic–non-magnetic transition occurs around $x = 0.135$, which is associated with a reduction of the unit cell volume $\Delta V/V \approx 0.5\%$. This result is quite similar to that observed for $CeRh_2Si_2$ under pressure that strongly reduces the ordering temperature [2]. The chemical pressure effect appears to be similar to an external pressure.

The behaviour of the $Ce(Rh_{1-x}Co_x)_2Si_2$ system is quite different from that found in $Ce(Rh_{1-x}Ru_x)_2Si_2$ for which we observed a continuous change from a magnetic to a heavy fermion regime [4, 5]. In the $Ce(Rh_{1-x}Ru_x)_2Si_2$ system the substitution of Rh by Ru has two effects: (i) a decrease of the conduction electron concentration; (ii) an increase of the unit cell volume. While these two effects have opposite tendency, the main result is an increase of T_K , as for the $Ce(Rh_{1-x}Co_x)_2Si_2$ solid solution. Therefore, there is not a straightforward explanation of why the Ru substitution leads to a heavy fermion whereas the Co substitution gives rise to a Kondo volume collapse.

However, in both systems a sharp decrease of T_N is observed which more probably results from a great density of states at the Fermi level in $CeRh_2Si_2$, which also accounts for its large T_N value.

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