

# Magnetic structures of $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$ ( $x = 0.0, 0.2, 0.4, 0.6$ ) compounds

E. Wawrzyńska<sup>a</sup>, L. Keller<sup>b</sup>, E.V. Sampathkumaran<sup>c</sup>, A. Szytuła<sup>a,\*</sup>

<sup>a</sup> *M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland*

<sup>b</sup> *Laboratory for Neutron Scattering, ETHZ & PSI, CH-5232 Villigen, Switzerland*

<sup>c</sup> *Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India*

Received 3 November 2003; accepted 11 November 2003

## Abstract

Polycrystalline samples of  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  for  $x$  equal to 0.0, 0.2, 0.4 and 0.6 have been studied by neutron diffraction. All these compounds exhibit a hexagonal crystal structure of the  $\text{AlB}_2$ -type. In  $\text{Ce}_2\text{PdSi}_3$  below 3.5 K, features attributable to short-range magnetic order are observed. The neutron diffraction patterns for the other compositions are typical of simple magnetic structures described by an orthorhombic unit cell ( $a, \sqrt{3}a, c$ ). The magnetic moment at low temperatures equals  $0.37(14)\mu_B$  at 1.6 K for  $x = 0.2$ ,  $1.27(5)\mu_B$  at 1.6 K for  $x = 0.4$  and  $0.55(8)\mu_B$  at 1.85 K for  $x = 0.6$ . The moments are parallel to the  $b$ -axis of the orthorhombic magnetic unit cell.

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**Keywords:** Rare earth compounds; Transition metal compounds; Magnetically ordered materials; Neutron diffraction; Magnetic measurements; Magnetic structures

## 1. Introduction

There has been a considerable interest in understanding the interplay between the crystalline-electric-field (CEF) effect, the indirect exchange (Ruderman–Kittel–Kasuya–Yosida (RKKY)) interaction among the 4f magnetic moments and the Kondo effect in Ce compounds, since these are the decisive factors of the physical properties in these compounds. It is therefore worthwhile to carry out careful investigations in different Ce compounds. We report here the results of neutron diffraction measurements carried out on the solid solution compounds  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  for  $x = 0, 0.2, 0.4$  and  $0.6$ . On the basis of these data the parameters of the magnetic structures are determined. The  $\text{Ce}_2\text{PdSi}_3$  compound has been reported to form an  $\text{AlB}_2$ -derived hexagonal crystal structure and to exhibit a Kondo effect [1–3]. Magnetization, heat capacity, electrical resistivity, thermoelectric power and the Hall effect investigation on a single crystal indicate antiferromagnetic ordering below the Néel temperature of about 3 K [4].

The X-ray diffraction data indicate the existence of the solid  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  solution in the whole concentration range [5]. The reciprocal magnetic susceptibilities obey the Curie–Weiss law with negative values of the paramagnetic Curie temperatures and effective magnetic moments close to the free  $\text{Ce}^{3+}$  ion value ( $2.54\mu_B$ ), which do not change with the Co content [5].  $\text{Ce}_2\text{CoSi}_3$  is a nonmagnetic Kondo lattice [6]. Though the magnetization, specific heat and electrical resistivity measurements indicate the existence of magnetic ordering at low temperatures [7], the nature of the magnetic ordering apparently varies with  $x$ . The ac susceptibility behaviour for the compositions  $x = 0.0, 0.2$  and  $0.4$  is spin-glass-like, while the compound with  $x = 0.6$  exhibits features attributable only to long-range magnetic ordering [8].

In order to obtain a better picture of the magnetism of these alloys, we have performed neutron diffraction measurements on this solid solution.

## 2. Experimental details and results

The experiments were performed on freshly prepared samples, as in a previous study [7]. Neutron diffraction

\* Corresponding author. Tel.: +48-12-632-4888;

fax: +48-12-633-7086.

E-mail address: szytuła@if.uj.edu.pl (A. Szytuła).

experiments were carried out on the DMC powder diffractometer at the Paul Scherrer Institut, Villigen, Switzerland. The incident wavelength was  $2.5676(2) \text{ \AA}$  and the temperature was varied between 1.5 and 10 K. The obtained data were processed with a Rietveld-type programme: FULLPROF [9].

### 2.1. Crystal structure

Neutron diffraction patterns of the  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  compounds in paramagnetic state (at 10 K) were analysed in two models of the hexagonal crystal structure described by the same space group  $P6/mmm$  (No. 191), in which the atomic ordering is different due to structure type:

1. In the  $\text{AlB}_2$ -type with lattice parameters ( $a$ ,  $a$ ,  $c$ ) the atoms occupy following positions:

- the Ce atoms are at the 1a: (0, 0, 0) positions;
- the Pd, Co and Si atoms are statistically distributed over the 2b: (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2) positions.

2. In the  $\text{Ce}_2\text{CoSi}_3$ -type with lattice parameters ( $2a$ ,  $2a$ ,  $c$ ), where  $a$  and  $c$  are the lattice parameters for the  $\text{AlB}_2$ -type structure, the atoms occupy the following positions:

- the Ce(1) atoms are at the 1a: (0, 0, 0) positions;
- the Ce(2) atoms are at the 3f: (1/2, 0, 0), (0, 1/2, 0) and (1/2, 1/2, 0) positions;
- the Pd and Co atoms are at the 2b: (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2) positions;
- the Si atoms are at the 6m: ( $x$ ,  $2x$ , 1/2), ( $2\bar{x}$ ,  $\bar{x}$ , 1/2), ( $x$ ,  $\bar{x}$ , 1/2), ( $\bar{x}$ ,  $2\bar{x}$ , 1/2), ( $2x$ ,  $x$ , 1/2) and ( $\bar{x}$ ,  $x$ , 1/2) positions.

The model of the  $\text{Ce}_2\text{CoSi}_3$ -type structure gives additional (100) and (110) superlattice peaks [5]. In our experiment these peaks in the  $2\theta$  angular regions near  $21^\circ$  and  $36.5^\circ$  were not observed. One of the reasons of the absence of these peaks is the small difference between the neutron scattering lengths of Pd ( $0.591 \times 10^{-14} \text{ m}$ ) and Si ( $0.415 \times 10^{-14} \text{ m}$ ). However, the comparison of the reliability factors for both models (see Table 1) suggests that the  $\text{AlB}_2$ -type structure with atomic disorder is adequate to describe the crystal struc-

Table 1

The values of the reliability factors for the two structure models of the  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  ( $x = 0, 0.2, 0.4$  and  $0.6$ ) compounds

Compound	Reliability factor (%)	$\text{AlB}_2$ model	$\text{Ce}_2\text{CoSi}_3$ model
$\text{Ce}_2\text{PdSi}_3$ at 10 K	$R_{\text{Bragg}}$	1.62	2.88
	$R_{\text{F}}$	1.42	4.94
$\text{Ce}_2\text{Pd}_{0.8}\text{Co}_{0.2}\text{Si}_3$ at 8 K	$R_{\text{Bragg}}$	18.91	20.28
	$R_{\text{F}}$	11.53	17.89
$\text{Ce}_2\text{Pd}_{0.6}\text{Co}_{0.4}\text{Si}_3$ at 10 K	$R_{\text{Bragg}}$	9.08	10.09
	$R_{\text{F}}$	10.82	14.92
$\text{Ce}_2\text{Pd}_{0.4}\text{Co}_{0.6}\text{Si}_3$ at 10 K	$R_{\text{Bragg}}$	10.55	9.59
	$R_{\text{F}}$	8.24	14.61

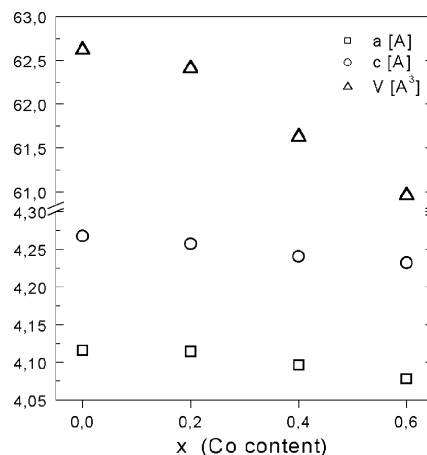


Fig. 1. The values of the  $a$  and  $c$  lattice parameters and the unit cell volume  $V$  for the  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  ( $x = 0.0, 0.2, 0.4, 0.6$ ) compounds.

ture of the investigated  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  ( $x = 0, 0.2, 0.4$  and  $0.6$ ) compounds. A similar model of the crystal structure of  $\text{Ce}_2\text{PdSi}_3$  was proposed in previous neutron diffraction experiments [2,3].

The values of the  $a$  and  $c$  lattice parameters and the unit cell volume  $V$  are presented in Fig. 1. All these parameters decrease with increase of the Co content because the atomic radius of the Co atom ( $1.25 \text{ \AA}$ ) is smaller than of the Pd atom ( $1.38 \text{ \AA}$ ).

### 2.2. $\text{Ce}_2\text{PdSi}_3$

Comparison of the neutron diffraction pattern of  $\text{Ce}_2\text{PdSi}_3$  recorded in the paramagnetic state (for example at 10 K) with that obtained at 1.5 K reveals the presence of an additional broad peak at  $2\theta \approx 7^\circ$ , similar to those observed in previous experiments [2,3]. The angular positions of these peaks are in agreement with the data in Ref. [2]. The temperature dependence of the intensity of this peak, which we did divide into two peaks (one of them at about  $6.5^\circ$  and the other one at  $7^\circ$ ) indicates that this order disappears at 3.5 K (both above mentioned peaks disappear at this temperature; see insets in Fig. 2). The determined value of the temperature of disappearance of these peaks is in good relation with the maximum in the thermal dependence of the magnetic susceptibility and the specific heat, which is interpreted as the Néel temperature in Ref. [4]. It indicates that short-range order exists in this compound. The newly collected neutron diffraction data of higher intensity does not show the presence of additional low intensity peaks as observed in Ref. [2], which suggests that the model of the magnetic structure proposed in Ref. [2] is not correct.

### 2.3. $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$ ( $x = 0.2, 0.4, 0.6$ )

Comparison of the neutron diffraction patterns recorded below 1.9 K and above 8 K for all three compounds (see Fig. 3) indicates the presence of additional peaks of magnetic

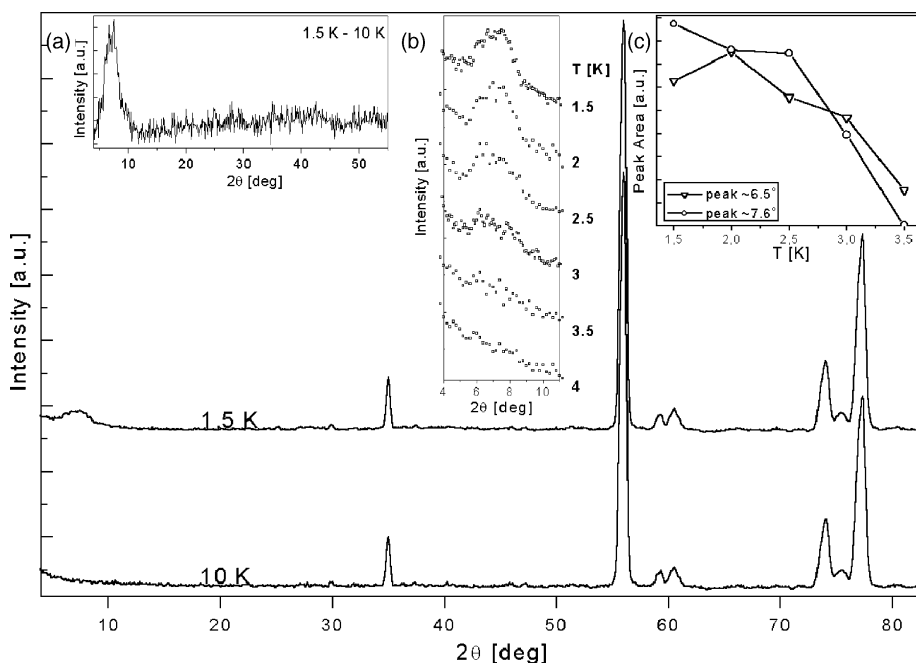


Fig. 2. Neutron diffraction patterns of  $\text{Ce}_2\text{PdSi}_3$  recorded at 1.5 and 10 K. The insets show the difference pattern (a), the narrow  $2\theta$  range ( $4^\circ$ – $11^\circ$ ) at several temperatures (b) and the temperature dependence of the area of the peaks visible in the middle inset (c).

origin at low temperatures. In contradiction to  $\text{Ce}_2\text{PdSi}_3$  the peak at  $2\theta \approx 7^\circ$  is not observed for  $x = 0.2, 0.4$  and  $0.6$ . The peaks of magnetic origin are indexed in an orthorhombic magnetic unit cell with the lattice parameters derived from the hexagonal cell:  $a_m = a$ ,  $b_m = \sqrt{3}a$  and  $c_m = c$ , where  $a$  and  $c$  are the lattice parameters of the hexagonal crystal unit cell. The magnetic unit cell defined above contains two cerium atoms located at the following positions: Ce1 at  $(0, 0, 0)$  and Ce2 at  $(1/2, 1/2, 0)$ . Only one type of antiferromagnetic ordering is possible, in which the magnetic moments of the Ce atoms align mutually antiparallely.

The obtained results are summarized in Table 2. The values of the magnetic moments change due to the  $x$  value and are equal to  $0.37(4)\mu_B$  for  $x = 0.2$ ,  $1.27(5)\mu_B$  for  $x = 0.4$  and  $0.55(8)\mu_B$  for  $x = 0.6$ . The values of FWHM (full width of the peak at half height) are similar for the magnetic and nuclear peaks. These results suggest that in these compounds

long-range magnetic ordering does exist, in contradiction to  $\text{Ce}_2\text{PdSi}_3$ .

### 3. Discussion

The neutron diffraction experiment suggests that the  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  ( $x = 0.0, 0.2, 0.4, 0.6$ ) compounds have a hexagonal structure of the  $\text{AlB}_2$ -type and the data indicate different magnetic ordering schemes at low temperatures. Pure  $\text{Ce}_2\text{PdSi}_3$  crystallizes in the simple  $\text{AlB}_2$ -type structure, which changes with thermal treatment [5]. This result is in contradiction to the result of X-ray data, which suggests the atomically ordered structure of  $\text{Ce}_2\text{CoSi}_3$  type for  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  ( $x = 0.2, 0.4, 0.6$ ). In these measurements the superlattice  $(100)$  and  $(110)$  peaks of small intensities are observed. In our neutron diffraction experiment the additional peaks (for example  $(100)$  at  $2\theta = 20.75^\circ$  and  $(110)$  at  $2\theta = 36.35^\circ$  for  $x = 0.2$ ) are not observed.

For  $\text{Ce}_2\text{PdSi}_3$  our data confirm the existence of short-range magnetic order below 3.5 K. For the remaining three compounds, features attributable to the existence of long-range magnetic order of the Ce moments at low temperatures were observed (in the latter compounds, the peak at  $2\theta \approx 7^\circ$ , connected with the short-range order is not observed).

The determined magnetic structures for  $x > 0.0$  are similar to those observed in the isostructural compounds  $\text{Ce}_2\text{RhSi}_3$  [10] and  $\text{Ce}_2\text{Au}_{0.4}\text{Co}_{0.6}\text{Si}_3$  [11] and the values of the magnetic moments are reduced when compared with the free  $\text{Ce}^{3+}$  ion value ( $2.14\mu_B$ ). The same tendency has been observed in a large number of other cerium intermetallic

Table 2

The refined parameters for the neutron diffraction patterns for the  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  ( $x = 0.2, 0.4, 0.6$ ) compounds

	$x$		
	0.2	0.4	0.6
$T$ (K)	1.6	1.6	1.85
$a$ (Å)	4.1141(4)	4.0959(3)	4.0784(4)
$c$ (Å)	4.2571(6)	4.2409(5)	4.2329(7)
$\mu$ ( $\mu_B$ )	0.37(14)	1.28(5)	0.55(8)
FWHM <sub>mag</sub>	0.33(3)	0.35(1)	0.35(2)
FWHM <sub>nucl</sub>	0.47(4)	0.35(1)	0.36(1)
$R_{\text{Bragg}}$ (%)	18.0	10.3	11.0
$R_F$ (%)	11.6	11.7	7.27

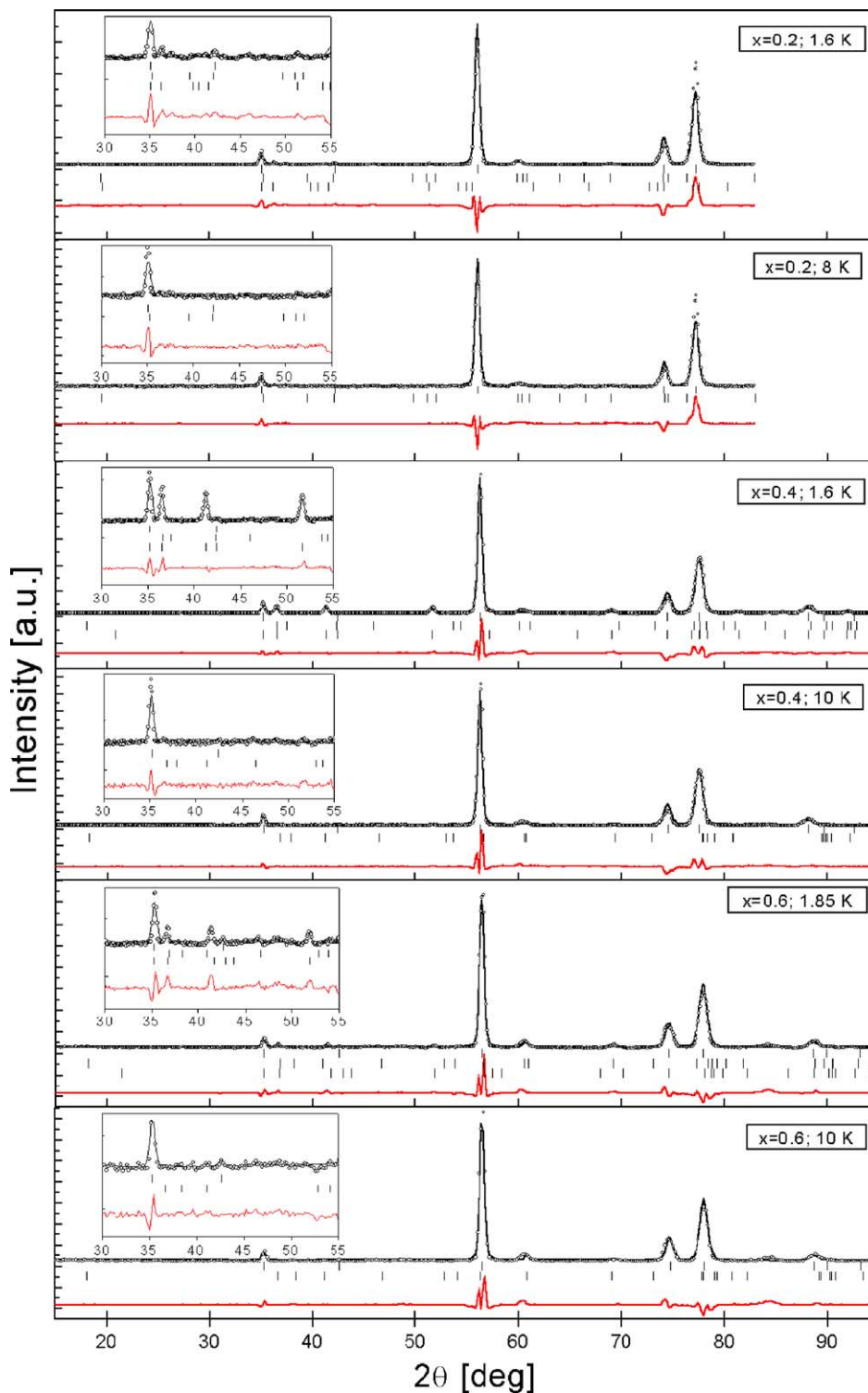


Fig. 3. Neutron diffraction patterns of the  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  ( $x = 0.2, 0.4, 0.6$ ) compounds recorded at different temperatures between 1.6 and 10 K. The insets show the magnified  $30^\circ$ – $55^\circ$   $2\theta$  range in each case.

compounds (see for example Ref. [12]) and is commonly attributed either to valence fluctuations or to interplay between the crystalline-electric-field and Kondo effects [13].

The magnetic moments lie in the basal plane, which indicates, according to the data in Ref. [14], that the sign of the  $B_2^0$  parameter of the crystal electric field is positive.

The interatomic Ce–Ce distances are large, above 4.05 Å. According to the systematics of the magnetic behaviour of the Ce compounds based on the Ce–Ce interatomic distances, in this region the RKKY-type of antiferromagnetism is preferred [15]. This is in a good agreement with the observed magnetic structure.

The investigated  $\text{Ce}_2\text{Pd}_{1-x}\text{Co}_x\text{Si}_3$  compounds are Kondo lattices with the Kondo temperature  $T_K$  of 8 K for  $\text{Ce}_2\text{PdSi}_3$  [4] and increasing values for the increasing Co concentration [7]. The values of the Néel temperatures determined from the specific heat and magnetic measurements are equal to 3.0, 3.3, 3.3, 3.1 and 2.3 K for  $x = 0.0, 0.2, 0.4, 0.6$  and  $0.7$ , respectively. These results indicate that it is possible to describe the evolution of the magnetic properties of these compounds with Doniach's model [16].

### Acknowledgements

The work was performed at the spallation neutron source SINQ, Paul Scherrer Institut, Villigen, Switzerland. The expert technical assistance of L.K. is gratefully acknowledged. One of us (E.V.S.) would like to thank K.K. Iyer for his assistance in sample preparation.

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