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# Neutron diffraction and magnetization studies of pseudoternary $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$ solid solutions ( $0 \leq x < 2$ )

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## Abstract

Neutron powder diffraction and magnetometric studies of the  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  series of solid solutions ( $x = 0, 0.5, 0.75, 1.0, 1.5, 1.8$ ) are reported. The intermetallics investigated crystallize in the body-centred-tetragonal  $\text{ThCr}_2\text{Si}_2$ -type structure (space group  $I4/mmm$ ). All the samples order antiferromagnetically at low temperatures. For low values of the dilution parameter  $x$  a simple collinear antiferromagnetic structure of the AFI type is stable. Below  $T_N$  the magnetic moments are parallel to the  $c$ -axis and then, below  $T_i$ , deflect forming an angle  $\varphi$  with the  $c$ -axis. Further replacement of Rh by Pd results in the development of a sine-wave-modulated magnetic structure with one two-component propagation vector and magnetic moments in the basal plane. For  $x = 1.8$  a sine-wave-modulated structure similar to that reported for  $\text{HoPd}_2\text{Si}_2$  (i.e. with a two-component propagation vector and magnetic moments parallel to the  $b$ -axis) was found.

## 1. Introduction

The structure and magnetic properties of ternary rare-earth–transition metal silicides and germanides have been intensively studied for about three decades. There has been special interest in compounds of the general formula  $\text{RM}_2\text{X}_2$  crystallizing in the tetragonal  $\text{ThCr}_2\text{Si}_2$ -type structure (R stands for rare earth, M for 4d- or 5d-electron metal and X for silicon or germanium) because of the wide variety of physical properties along with the simplicity of the crystal structure.

The unit cell of the  $\text{ThCr}_2\text{Si}_2$ -type structure (space group  $I4/mmm$ ) consists of two formula units and can be described as a stacking of atomic layers (each layer contains atoms of a single type). The layers are perpendicular to the  $c$ -axis and stacked according to the sequence  $-\text{R}-\text{X}-\text{M}-\text{X}-\text{R}-$ . In the ideal  $\text{ThCr}_2\text{Si}_2$ -type structure the rare-earth ions (R) occupy the Wyckoff position 2(a): (0 0 0), the 4d- or 5d-electron metals (M) occupy the position 4(d): (0 1/2 1/4) and silicon/germanium is located at 4(e): (0 0  $z$ ) with  $z \approx 0.38$ . This layer crystal structure leads to highly anisotropic magnetic interactions and, in consequence, to a wide variety of magnetic properties and complex magnetic structures [1].

The  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  solid solutions exist over the whole range of the dilution parameter  $x$  and all have the body-centred-tetragonal crystal structure of the  $\text{ThCr}_2\text{Si}_2$  type [2]. The magnetic properties of the parent compounds are quite different:  $\text{HoRh}_2\text{Si}_2$  is a collinear antiferromagnet of the AFI type [3].  $\text{HoPd}_2\text{Si}_2$  was found to belong to the group of materials with mixed magnetic phases where a particular element localized at a unique crystallographic site has two distinct magnetic states: one nonmagnetic and the other with a well-defined magnetic moment. In the case of  $\text{HoPd}_2\text{Si}_2$  this leads to the onset of a short-range magnetic ordering in the temperature region 5–20 K followed by a complex magnetic structure of a sine-wave-modulated type with two propagation vectors at lower temperatures [4].

This paper reports the results of magnetization and neutron diffraction measurements carried out to determine the magnetic properties and structure of  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  ( $x = 0, 0.5, 0.75, 1.0, 1.5, 1.8$ ) solid solutions.

## 2. Experimental details

The samples were prepared by standard arc melting of stoichiometric amounts of high-purity elements in an argon atmosphere. Then they were annealed at 800 °C for one week. X-ray powder diffraction patterns (Siemens, Co  $K\alpha$ ) confirmed the  $\text{ThCr}_2\text{Si}_2$ -type crystal structure with Ho at 2(a): (0 0 0), Rh and Pd randomly distributed at 4(d): (0 1/2 1/4) and Si at 4(e): (0 0  $z$ ) positions with  $z \approx 0.385$  for all the samples studied.

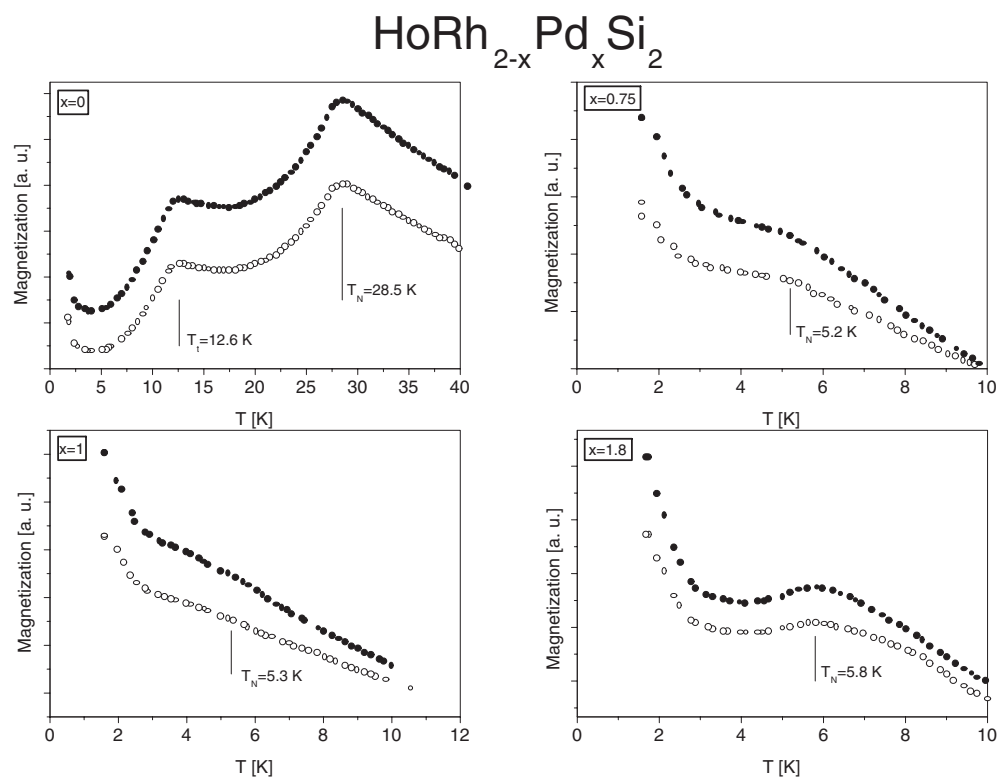
Magnetization measurements were carried out using a vibrating-sample magnetometer and a SQUID magnetometer. The temperature dependences of the magnetization over the temperature range 1.8–40 K were collected at 50 and 75 Oe.

Neutron powder diffraction data were collected at the E6 diffractometer ( $\lambda \sim 2.4 \text{ \AA}$ ) at the BERII reactor (Berlin Neutron Scattering Centre, Hahn-Meitner Institute, Germany) at several temperatures below 30 K. The analysis of the diffraction patterns obtained was performed by means of the Rietveld-type profile refinement program FULLPROF [5].

## 3. Results and discussion

Bulk magnetization measurements carried out at 50 and 100 Oe show that  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  intermetallics order antiferromagnetically at temperatures lower than 30 K:  $\text{HoRh}_2\text{Si}_2$  (figure 1) orders at  $T_N = 28.5 \text{ K}$  and then, at  $T_I = 12.6 \text{ K}$ , a further magnetic phase transition is visible in the temperature dependence of the magnetization. Substitution of Pd for Rh results in significant lowering of the ordering temperature: all the other intermetallics of the reported series order at about 5 K—that is close to the Néel temperature of  $\text{HoPd}_2\text{Si}_2$  ( $T_N = 5.8 \text{ K}$  [4]). Magnetic transition temperatures are listed in table 1, in which the crystal and magnetic structure parameters determined by the Rietveld refinements are also collected.

Powder neutron diffraction patterns collected in the paramagnetic region confirm the body-centred-tetragonal  $\text{ThCr}_2\text{Si}_2$ -type crystal structure of  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  intermetallics.



**Figure 1.** Temperature dependences of the magnetization in the  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  series of solid solutions measured at 50 Oe (○) and 100 Oe (●).

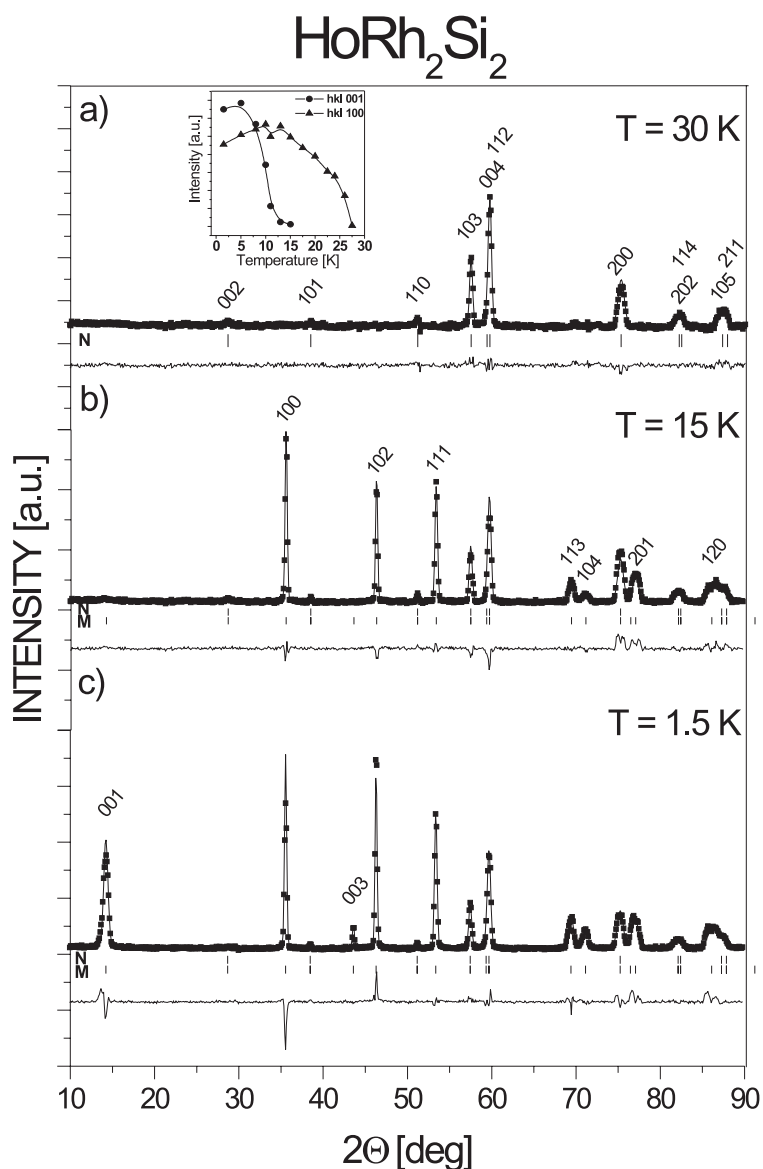
**Table 1.** Structural and magnetic parameters of  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  solid solutions as determined from the Rietveld refinements to neutron diffraction patterns collected at 1.5 K and from magnetization measurements ( $T_N$  and  $T_I$ ).

Dilution parameter ( $x$ )	$a$ (Å)	$c$ (Å)	$T_N$ (K)	$T_I$ (K)	$k_x$	$k_z$	$\mu$ ( $\mu_B$ )	$R_{mag}$ (%)	$R_f$ (%)
0	3.9986(6)	9.8624(20)	28.5	12.6	0	1	9.3(1)	11.6	10.9
0.5	4.0068(11)	9.9044(34)	19.5	10.5	0	1	6.8(1)	7.8	11.7
0.75	4.0552(9)	9.8652(28)	5.2		0.6119(12)	0.1027(23)	6.9(1)	8.6	4.9
1.0	4.0328(21)	9.9016(68)	5.3		0.6310(15)	0.0794(38)	— <sup>a</sup>		
1.5	4.0726(13)	9.9217(49)	6.7		0.6227(9)	0.0940(20)	7.58(10)	11.9	2.8
1.8	4.0729(9)	9.8297(26)	5.8		0.5866(3)	0.1628(8)	7.18(10)	9.8	5.7
2.0 <sup>b</sup>	4.0999(3)	9.8805(14)	5.8		0.5774(3)	0.1716(7)	4.9 (1)	8.6	3.4
					0.5787(3)	0.0054(13)	6.5(1)	8.8	

<sup>a</sup> The sample contaminated by  $\text{HoRh}_2\text{Si}_2$ , that enabled determination of the magnetic moment with sufficient accuracy.  $k_x, k_z$  are the components of the propagation vectors of the modulated magnetic structures (in all the cases  $k_y = 0$ ).

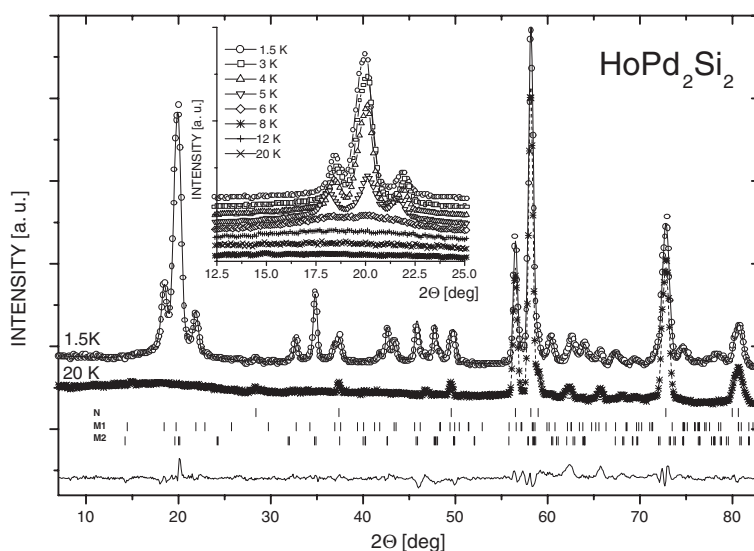
<sup>b</sup> As reported in [4].

To illustrate typical features of neutron diffraction patterns obtained in paramagnetic and magnetically ordered states in this series of solid solutions, some representative pictures are shown in figures 2–5.



**Figure 2.** Neutron diffraction patterns of HoRh<sub>2</sub>Si<sub>2</sub> at different temperatures (solid curves show results of the refinements). The inset shows the temperature variations of the two main magnetic reflections. The vertical bars mark the positions of nuclear (N) and magnetic (M) peaks. The curves below the bars show the difference between the experimentally observed and the refined patterns.

The neutron diffraction patterns of the parent compounds: HoRh<sub>2</sub>Si<sub>2</sub> (this work) and HoPd<sub>2</sub>Si<sub>2</sub> (after [4]) are shown in figures 2 and 3, respectively. HoRh<sub>2</sub>Si<sub>2</sub> is paramagnetic at 30 K and the scattering by the nucleus gives rise to nuclear Bragg peaks that could be indexed on the basis of the space group *I4/mmm* (figure 2(a)). Below the Néel temperature, HoRh<sub>2</sub>Si<sub>2</sub> is a collinear antiferromagnet of the AFI type. In the temperature region between  $T_N$  and  $T_I$ , holmium magnetic moments are parallel to the *c*-axis (figure 2(b)). Then, down to 1.5 K, the occurrence of the magnetic (001) and (003) reflections proves that the magnetic moments



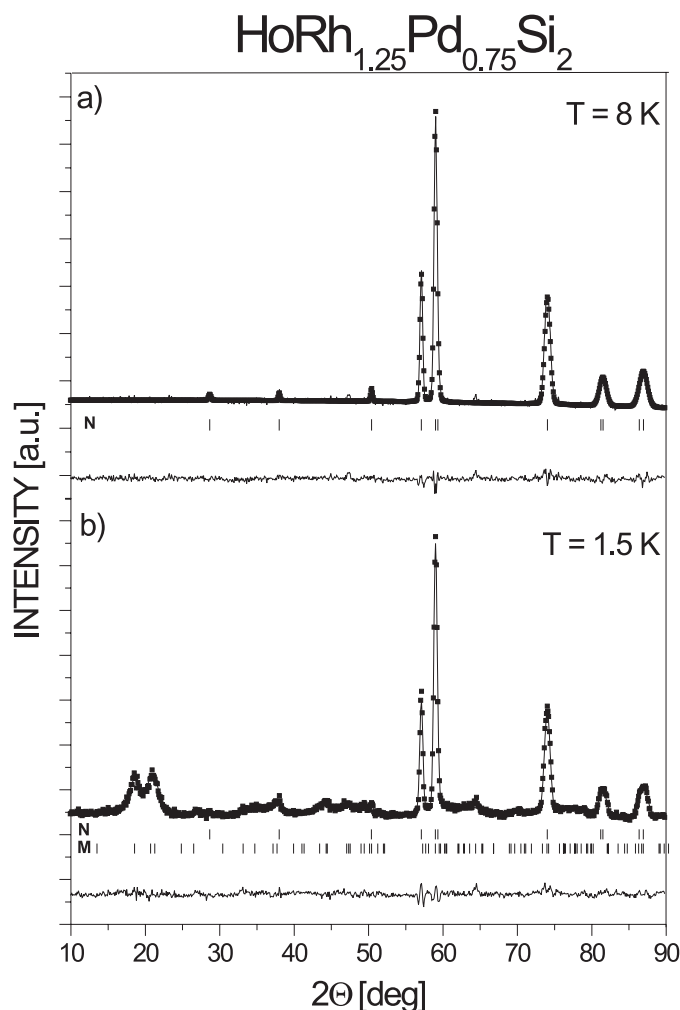
**Figure 3.** Neutron diffraction patterns of HoPd<sub>2</sub>Si<sub>2</sub> collected at 20 K (paramagnetic region) and at 1.5 K (ordered state). Solid curves show results of the refinements. The inset shows the temperature variation of the diffraction pattern about  $2\Theta = 20^\circ$ . The vertical bars mark the positions of nuclear (N) and magnetic (M1 and M2) peaks as refined for  $T = 1.5$  K. The curve at the bottom is the difference between the experimentally observed and the refined pattern at 1.5 K. The figure is taken from [4].

form an angle with the  $c$ -axis (figure 2(c)). The value of this angle increases with decreasing temperature and is equal to  $32.5(9)^\circ$  at 1.5 K. HoPd<sub>2</sub>Si<sub>2</sub>, the compound located at the other end of the composition range studied, was found to belong to the group of materials with mixed magnetic phases. This means that Ho has two distinct magnetic states: one nonmagnetic and the other with a well-defined magnetic moment. In the ordered state, HoPd<sub>2</sub>Si<sub>2</sub> is an antiferromagnet with the Néel temperature of 5.8 K and a complex magnetic structure of a sine-wave-modulated type described by two propagation vectors and Ho magnetic moments parallel to the  $b$ -axis. At higher temperatures, up to 20 K, a short-range magnetic order was reported [4].

In the case of HoRh<sub>1.5</sub>Pd<sub>0.5</sub>Si<sub>2</sub> the evolution of the magnetic structure with changing temperature is similar to the one observed in the HoRh<sub>2</sub>Si<sub>2</sub> parent compound: below  $T_N = 19.5$  K, antiferromagnetic ordering of the AFI type develops and down to  $T_t = 10.5$  K the magnetic moments are parallel to the  $c$ -axis. The magnetic peaks (001) and (003) present in the neutron diffraction patterns at temperatures lower than  $T_t$  are evidence that, in this temperature region, the magnetic moments form an angle with the  $c$ -axis ( $\varphi = 34.2^\circ$  at 1.5 K).

Quite different neutron diffraction patterns were obtained for HoRh<sub>1.25</sub>Pd<sub>0.75</sub>Si<sub>2</sub> (figure 4). The magnetic peaks, of relatively small intensities, could be indexed by the propagation vector  $\mathbf{k} = (0.612, 0, 0.103)$ . The Ho magnetic moments, equal to  $6.9(1) \mu_B$ , are parallel to the  $b$ -axis and form a sine-wave-modulated structure. This ordering is stable up to the Néel temperature of 5.2 K. Above  $T_N$  a broad diffuse maximum develops, that might represent a short-range magnetic order. The same type of sine-wave-modulated magnetic structure with Ho magnetic moments parallel to the  $b$ -axis was also found in HoRhPdSi<sub>2</sub> and HoRh<sub>0.5</sub>Pd<sub>1.5</sub>Si<sub>2</sub>.

The magnetic ordering of HoRh<sub>0.2</sub>Pd<sub>1.8</sub>Si<sub>2</sub> is similar to the one reported for HoPd<sub>2</sub>Si<sub>2</sub> [4]. The best refinement for the pattern collected at 1.5 K (figure 5(c)) was obtained assuming a sine-wave-modulated antiferromagnetic structure with two propagation vectors:  $\mathbf{k}_1 = (0.587, 0, 0.163)$  and  $\mathbf{k}_2 = (0.587, 0, 0.961)$ . The Ho magnetic moments  $\mu_1 = 4.5(1) \mu_B$



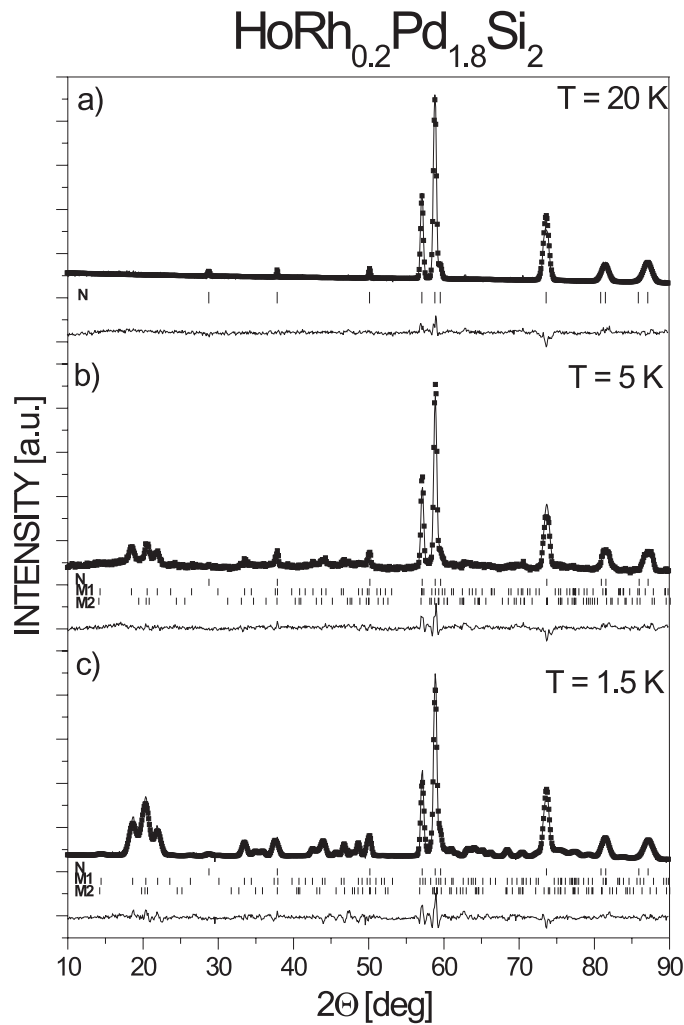
**Figure 4.** Neutron diffraction patterns of  $\text{HoRh}_{1.25}\text{Pd}_{0.75}\text{Si}_2$  collected at: (a) 8 K (paramagnetic region) and (b) 1.5 K (ordered state). Solid curves show results of the refinements. The vertical bars mark the positions of nuclear (N) and magnetic (M) peaks. The curves below the bars show the difference between the experimentally observed and the refined patterns.

and  $\mu_2 = 7.2(1) \mu_B$  are parallel to the  $b$ -axis. With increasing temperature the values of the magnetic moments  $\mu_1$  and  $\mu_2$  decrease but neither the directions of the magnetic moments nor the components of the propagation vectors change.

The reported results show clearly that on changing the dilution parameter  $x$  one affects exchange interactions as well as crystalline-electric-field (CEF) effects, which are the main factors which account for magnetic ordering in rare-earth intermetallics. The interaction of the CEF with the multiple moments of rare-earth electrons at a site of a crystal lattice of  $4/mmm$  point symmetry is given by the Hamiltonian

$$H_{CF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^4 \hat{O}_4^4 + B_6^0 \hat{O}_6^0 + B_6^4 \hat{O}_6^4,$$

where  $\hat{O}_n^m$  is the Stevens operator and  $B_n^m$  is a CEF parameter as defined by Hutchings [6]. It is well known that the  $B_2^0$ -parameter plays the dominant role in the CEF Hamiltonian. For



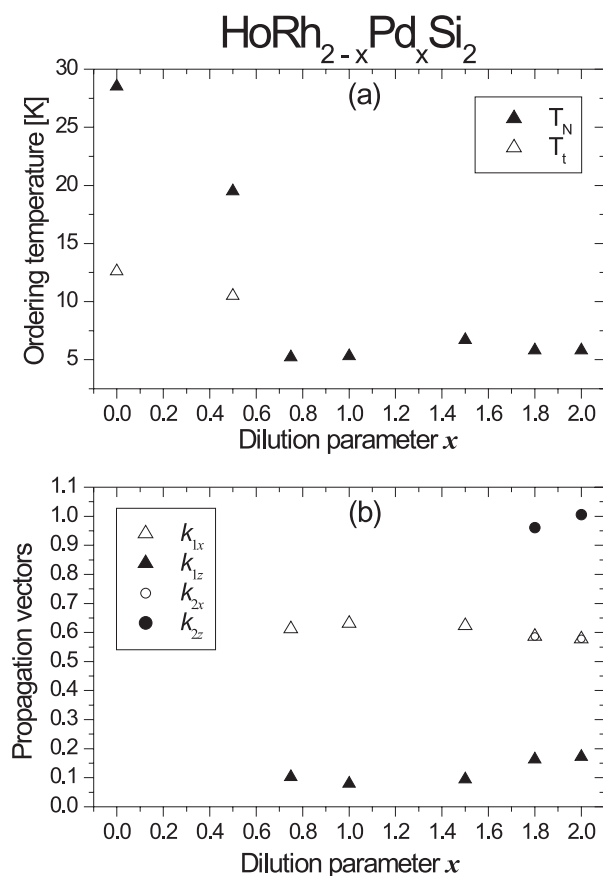
**Figure 5.** Neutron diffraction patterns of  $\text{HoRh}_{0.2}\text{Pd}_{1.8}\text{Si}_2$  at different temperatures. Solid curves show results of the refinements. The vertical bars mark the positions of nuclear (N) and magnetic (M1 and M2) peaks. The curves below the bars show the difference between the experimentally observed and the refined patterns.

$\text{HoRh}_2\text{Si}_2$  the  $B_2^0$ -value is negative [7, 8] while for  $\text{HoPd}_2\text{Si}_2$  it is positive [8], which agrees well with the orientation of Ho magnetic moments found in these compounds. The angle that magnetic moments form with the  $c$ -axis is a function of the  $B_2^0/B_4^0$  ratio and is given by the formula [9]

$$\cos \varphi = \frac{1}{J} \sqrt{\frac{3}{7} J(J+1) - \frac{3}{70} \frac{B_2^0}{B_4^0}}.$$

The value of  $\varphi$  calculated for  $\text{HoRh}_2\text{Si}_2$  on the basis of the above equation, using the magnitudes of  $B_2^0$  and  $B_4^0$  reported in [8], is equal to  $36^\circ$ , which is in good agreement with the experimentally determined value ( $32.5^\circ$  at 1.5 K).





**Figure 6.** Dependences of the ordering temperatures (a) and the propagation vectors of the modulated magnetic structures (b) on the dilution parameter  $x$  in the  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  series of solid solutions.

#### 4. Summary

All the  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  intermetallics studied crystallize in the body-centred-tetragonal crystal structure of the  $\text{ThCr}_2\text{Si}_2$ -type with rhodium and palladium randomly distributed at the 4(d) sites. Substituting Pd for Rh does not change the type of the crystal structure. Nevertheless, it changes the lattice parameters and, related to them, the distances between the magnetic moments. With increasing content of Pd, the number of conduction electrons also increases. These features account for the dependences of the magnetic properties on the dilution parameter  $x$  observed in this series of solid solutions.

The reported results show clearly that, even if diluting the rhodium sublattice with palladium does not change the crystal structure in the  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  series of solid solutions, it significantly influences the magnetic properties. Some general trends are visible in the diagrams presented in figure 6. For the lowest values of the dilution parameter  $x$  a collinear antiferromagnetic structure of the AFI type, described by the propagation vector  $\mathbf{k} = (0, 0, 1)$ , was observed and between  $T_N$  and  $T_t$  the magnetic moments are parallel to the  $c$ -axis. Then, below  $T_t$ , the magnetic moments form an angle with the  $c$ -axis. With increasing palladium content the magnetic structure changes into a sine-wave-modulated one, described by one two-

component propagation vector, with magnetic moments parallel to the  $b$ -axis. For  $x = 1.8$  a magnetic structure similar to the one reported for  $\text{HoPd}_2\text{Si}_2$  [4] was found: a sine-wave-modulated structure with magnetic moments parallel to the  $b$ -axis and two two-component propagation vectors.

The two factors that determine the type and stability of ordering of the magnetic moments in ternary rare-earth intermetallics are exchange interactions and the crystalline electric field CEF. Fairly large Ho–Ho interatomic distances (about 4–5 Å) suggest that the magnetic interactions in the series of solid solutions reported on should be discussed in terms of the RKKY model. The results obtained show that changing the Pd content ( $x$ ) affects both above-mentioned factors: the collinear antiferromagnetic ordering observed for Rh-rich samples changes into sine-wave-modulated structures with increasing Pd content. The change of the direction of the magnetic moment from parallel to the  $c$ -axis for Rh-rich intermetallics to parallel to the  $b$ -axis for Pd-rich intermetallics is an effect of the CEF.

The magnetic properties of  $\text{HoRh}_{2-x}\text{Pd}_x\text{Si}_2$  are similar to those observed in the isostructural system  $\text{HoRh}_{2-x}\text{Ru}_x\text{Si}_2$  [10]. The collinear order observed in Rh-rich solid solutions changes into a sine-wave-modulated one upon substituting Ru for Rh. The sign of the  $B_2^0$ -parameter for  $\text{HoRu}_2\text{Si}_2$  is negative (for  $\text{HoPd}_2\text{Si}_2$  it is positive), leading to different directions of magnetic moments in Ru- and Pd-rich solid solutions.

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