Neutron Diffraction Studies of $PrNi_5Sn$

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Powder neutron diffraction measurements of $PrNi_5Sn$ performed in the temperature range 1.5–76 K indicate that the compound crystallizes in a hexagonal $CeNi_5Sn$-type crystal structure (space group $P6_3/mmc$). The a lattice parameter and the unit cell volume V increase while the c lattice parameter does not change with increasing temperature. No long range magnetic ordering was detected down to 1.5 K, in contradiction to bulk magnetometric results.

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1. Introduction

RNi_5Sn rare-earth compounds crystallize in a hexagonal $CeNi_5Sn$-type crystal structure (space group $P6_3/mmc$). They have been a subject of investigations for many years [1–3], as potential hydrogen storage materials, too [4, 5]. Magnetic measurements of $PrNi_5Sn$ performed in the temperature range 80–400 K indicated paramagnetic properties [6]. New dc and ac magnetic data reported a maximum in the temperature dependence of magnetic susceptibility $\chi(T)$ at 25 K and an increase in the χ_{dc} and χ_{ac} values at low temperatures [7], suggesting possibility of magnetic ordering at low temperatures. Electronic structure and thermodynamic properties of $PrNi_5Sn$ and other RNi_5Sn compounds (R = La, Ce, Nd) were recently calculated [8] and the determined Debye temperature values are typical for intermetallics.

Powder neutron diffraction measurements have been carried out to clarify the problem of magnetic ordering in $PrNi_5Sn$ and determine crystal structure parameters in the temperature range between 1.5 and 76 K.

2. Experimental details

The sample was obtained by standard procedure: arc-melting of high purity elements (99.9 wt% for Pr; 99.99 wt% for Ni and Sn) and then annealing the obtained ingot at 650 °C for one month. Powder X-ray diffraction pattern collected at room temperature confirmed the hexagonal crystal structure of the $CeNi_5Sn$-type (space group $P6_3/mmc$), reported in Ref. [7].

Neutron diffraction experiments were performed on powder sample (5 g) using the E6 diffractometer (position sensitive detector, resolution $\Delta d/d \approx 0.01$, incident neutron wavelength 2.447 Å) at BER II reactor (Helmholtz-Zentrum Berlin). Several neutron diffraction patterns ($2\Theta = 5° - 135°$) were collected in the temperature range 1.5–76 K. The data were analyzed using the Rietveld-type program FullProf [9].

3. Results and discussion

The neutron diffraction pattern of $PrNi_5Sn$ collected at 1.5 K together with the plot visualizing the difference between the patterns collected at 1.5 K and 76 K is shown in Fig. 1.Similar diffraction patterns were detected at the other temperatures in the investigated range. Analysis of the neutron diffraction data confirms that $PrNi_5Sn$ crystallizes in the hexagonal crystal structure (space group $P6_3/mmc$; No. 194) with the atoms distributed in two Pr sublattices with Pr1 at 2c site: $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and Pr2 at 2a site: (0,0 0), four Ni sublattices with Ni1 at 2b site: $(0, 0, \frac{1}{4})$, Ni2 at 2d site: $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$, Ni3 at 4f site: $(\frac{1}{3}, \frac{2}{3}, z_1)$ and Ni4 at 12k site: (x, y, z_2) and one Sn sublattice with the atoms at 4f site: $(\frac{1}{3}, \frac{2}{3}, z_3)$. This crystal structure could be considered as a stacking of alternating $PrNi_5$ and $PrNi_5Sn_2$ layers, along the [001] direction in a hexagonal lattice, as shown in Fig. 2a.

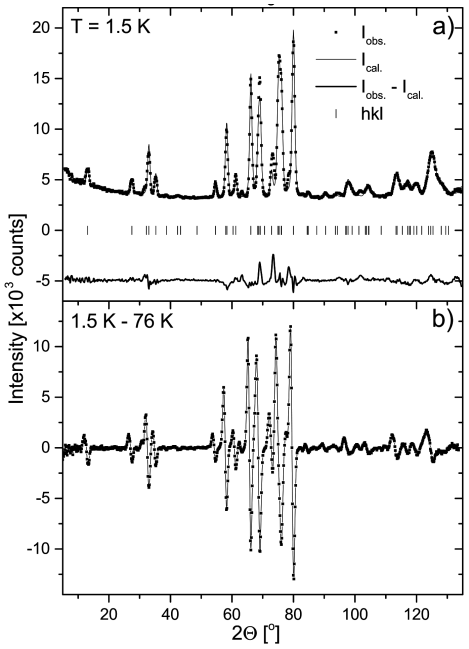

Fig. 1. (a) Neutron diffraction pattern of $PrNi_5Sn$ at 1.5 K. The solid squares are for the experimental data and the solid line shows the profile calculated by the Rietveld method, the vertical bars indicate the positions of the nuclear Bragg peaks and the difference between the observed and calculated intensities is plotted below. (b) Differential pattern visualizing the difference between the diffraction patterns collected at 1.5 K and 76 K.

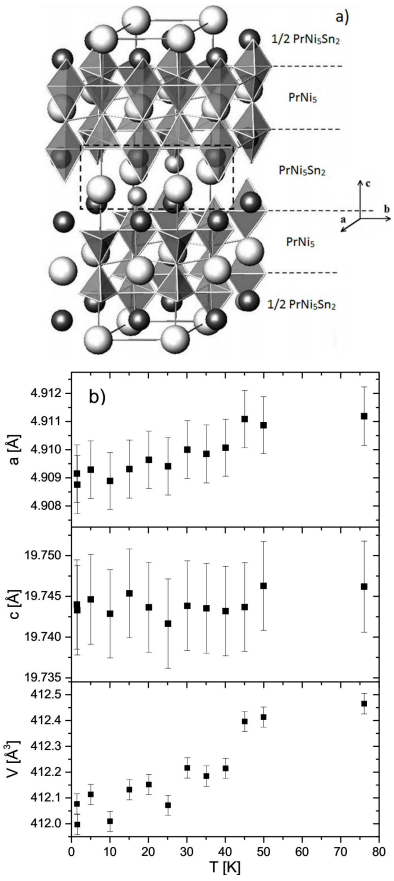

Fig. 2. (a) Crystal structure of $PrNi_5Sn$ visualized as formed by $PrNi_5$ and $PrNi_5Sn_2$ layers alternating along the [001] direction in a hexagonal lattice. The Ni4 tetrahedra are marked. Big bullets are for Pr, small dark bullets are for Ni and small light ones are for Sn. (b) Temperature dependence of the a and c lattice parameters and the unit cell volume V of $PrNi_5Sn$.

TABLE I

Crystal structure parameters of $PrNi_5Sn$ at 1.5 and 76 K determined by Rietveld-type refinements of neutron diffraction patterns.

parameter		1.5 K	76 K
a [Å]		4.909(1)	4.911(1)
c [Å]		19.743(5)	19.746(6)
V [Å^3]		412.00(17)	412.47(17)
Ni3	z_1	0.5433(4)	0.5436(4)
Ni4	x	0.8310(3)	0.8310(3)
	y	0.6703(18)	0.6699(18)
	z_2	0.1449(3)	0.1450(3)
Sn	z_3	0.0871(7)	0.0873(7)
R_{Bragg} [%]		8.4	8.5
$R_{profile}$ [%]		7.1	7.3

The crystal structure parameters determined by the Rietveld refinement are collected in Table I and Fig. 2b. The values are in good agreement with the previously published results [6, 7]. The a lattice parameter and the unit cell volume V increase with increasing temperature while the c lattice parameter is constant in the limit of experimental error (Fig. 2b). The maxima in the diffraction patterns could be indexed as nuclear Bragg peaks only (Fig. 1a) and comparison of the data collected at 1.5 K with those collected at 76 K does not give any evidence of additional intensities of magnetic origin (see the differential pattern in Fig. 1b). The observed differences result from the temperature dependence of the a lattice parameter. This, resulting from neutron diffraction data, absence of a long range magnetic order is in contradiction to the former magnetometric measurements [7]. The same behavior have been also observed for the isostructural $NdNi_5Sn$ [10].

4. Summary

The reported neutron diffraction experiments carried out on $PrNi_5Sn$ below 76 K show that the value of the c lattice parameter does not depend on temperature changes. This suggests small interactions between the alternating $PrNi_5$ and $PrNi_5Sn_2$ layers building up the structure along the [001] direction. On the other hand, the increase of the a lattice parameter means that the interatomic distances between the atoms in the Pr_3NiSn trigonal bipyramide increase with increasing temperature. Neutron powder diffraction data did not detect any long range magnetic order down to 1.5 K, which is in contradiction to the earlier published macroscopic magnetic data [7].

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