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Antiferromagnetic ordering in PrCuSn and NdCuSn

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Abstract. The magnetic properties of polycrystalline samples of PrCuSn and NdCuSn, including their magnetic structures, were determined by magnetic and neutron diffraction measurements. Both compounds show the hexagonal, CaIn₂-type crystal structure and are antiferromagnetic at low temperatures. Below $T_N = 3$ K, the sine modulated magnetic structure with the wave vector $\mathbf{k} = (0.349, 0, 0)$ is observed in PrCuSn, while in NdCuSn below $T_N = 9$ K the collinear antiferromagnetic ordering described by the wave vector $\mathbf{k} = (1/2, 0, 0)$ was detected. In both phases the magnetic moments are parallel to the hexagonal c -axis.

1. Introduction

This paper is a part of our systematic studies of the magnetic properties of ternary stannides RTSn where R is a lanthanide element, T is Cu, Ag, Au. The successively obtained results have been published in [1–7].

X-ray diffraction data for polycrystalline samples of RCuSn (R = La–Lu) give the CaIn₂-type structure, space group $P6_3/mcm$ with a random distribution of Cu and Sn atoms [8]. X-ray single-crystal data for GdCuSn [9] and DyCuSn [10] and neutron diffraction data for polycrystalline RCuSn (R = Tb–Er) compounds [6] indicate the LiGaGe-type structure (space group $P6_3mc$) with Cu and Sn atoms located at separate sites in the crystal lattice.

A survey of the literature related to the magnetic properties of RCuSn compounds has revealed that:

- CeCuSn is an antiferromagnet below 8.6 K [11–13].
- For NdCuSn the absence of any long-range magnetic order at 4.2 K has been claimed. Instead, spin glass behaviour was suspected below a freezing temperature close to 10 K [9].
- RCuSn (R = Sm, Gd–Er) order antiferromagnetically at low temperatures [4, 6, 9, 14]. Magnetic structures of these compounds are collinear with the wave vectors $\mathbf{k} = (1/2, 0, 0)$ for R = Tb–Ho and $\mathbf{k} = (1/3, 0, 0)$ for R = Er. Below the respective Néel temperatures, the transitions to incommensurate structures are observed in the compounds with R = Tb, Ho and Er [4, 6].

This study has been also motivated by the results obtained for isostructural NdAgSn [5] and NdAuSn [7] in which collinear antiferromagnetic order has been observed. On the

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other hand, a sine modulated antiferromagnetic structure was detected in PrAgSn [5] while PrAuSn exhibits a collinear antiferromagnetic order [7].

In order to obtain further information on the magnetism of RCuSn phases we have performed a study of PrCuSn and NdCuSn, including the determination of their magnetic structures by neutron diffraction. The results are reported below.

2. Experiment

Both title compounds were synthesized by arc melting of respective high-purity elements in the atmosphere of purified argon. Annealing was carried out at 600 °C for 100 h in evacuated quartz tubes. X-ray powder diffraction patterns have shown that the samples exhibit hexagonal structure. The obtained lattice parameters agree fairly well with those given in [8]. Very weak peaks corresponding to R₆Cu₈Sn₈ impurity phases were found on x-ray diffractograms.

Magnetic properties were measured using the Cryogenics S100 SQUID susceptometer in external magnetic fields of 10 Oe in the temperature range from 2 to 300 K. Additional magnetization data were obtained at 4.2 K in the presence of magnetic field up to 120 kOe using a vibrating sample Oxford Instruments VSM 12 T magnetometer.

The neutron diffraction experiment was performed at BENSC Hahn-Meitner-Institute (Berlin) with the E6 diffractometer ($\lambda = 2.3823 \text{ \AA}$) in the temperature range 1.6–12 K. The neutron diffraction data were analysed using the Rietveld-type FULLPROF program [15]. Neutron scattering length values were taken from [16], the form-factors for Pr³⁺ and Nd³⁺ ions were adopted after [17].

3. Results

3.1. Crystal structure

Neutron diffraction peaks observed at temperatures above the respective Néel points were easily indexed on a hexagonal unit cell.

Two types of crystal structures for the title compounds have been considered: either CaIn₂ type, space group $P6_3/mmc$ with

2R atoms in the 2(b) site: $0, 0, 1/4; \quad 0, 0, 3/4;$

2Cu and 2Sn atoms at random in the 4(f) site:

$1/3, 2/3, z; \quad 2/3, 1/3, \bar{z}; \quad 2/3, 1/3, 1/2 + z; \quad 1/3, 2/3, 1/2 - z;$

or LiGaGe-type, space group $P6_3mc$ with

2R atoms in the 2(a) site: $0, 0, z_1; \quad 0, 0, 1/2 + z_1;$

2Cu atoms in the 2(b) site: $1/3, 2/3, z_2; \quad 2/3, 1/3, 1/2 + z_2;$

2Sn atoms in the 2(b) site: $1/3, 2/3, z_3; \quad 2/3, 1/3, 1/2 + z_3.$

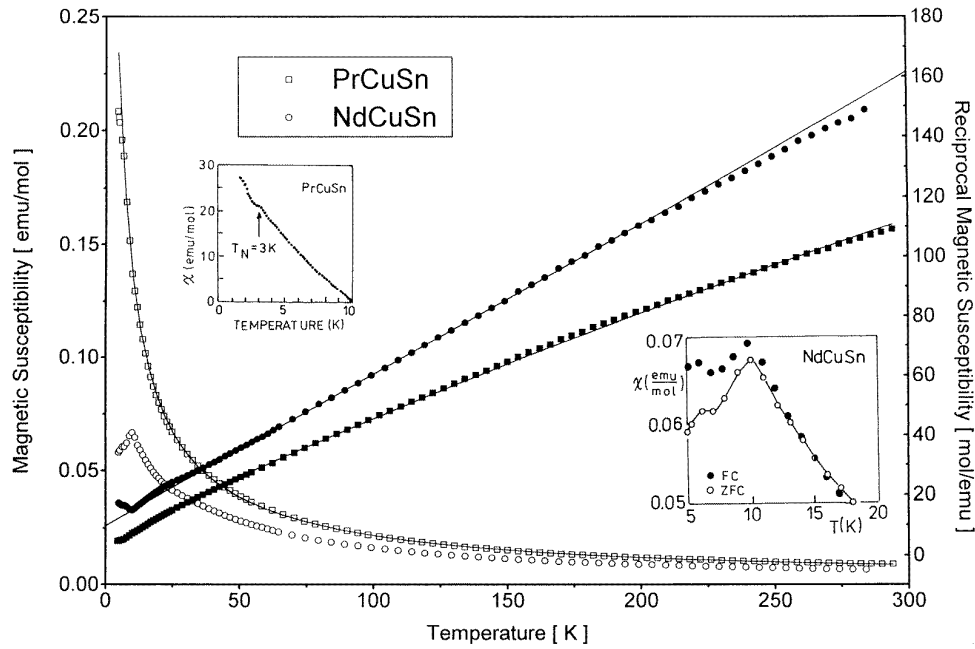
Fairly good agreement between observed and calculated nuclear intensities is obtained for CaIn₂-type crystal structure. The determined parameters related to the crystal structure are listed in table 1.

3.2. Magnetic data

Figure 1 shows the temperature dependence of the magnetic susceptibility and reciprocal magnetic susceptibility for both compounds. At $T_N = 3 \text{ K}$ (PrCuSn) and at $T_N = 10 \text{ K}$ (NdCuSn) the characteristic maximum for the transition from antiferro- to paramagnetic

Table 1. Crystal data for PrCuSn and NdCuSn compounds.

	PrCuSn		NdCuSn	
	$T = 1.6$ K	$T = 6$ K	$T = 1.5$ K	$T = 12$ K
a (Å)	4.5927(9)	4.5892(11)	4.5727(14)	4.5768(16)
c (Å)	7.7240(22)	7.7159(27)	7.6044(27)	7.6147(38)
V (Å ³)	141.105(85)	140.731(154)	137.705(130)	138.136(166)
c/a	1.6818(8)	1.6813(10)	1.6630(11)	1.6638(15)
z	0.0262	0.0262(5)	0.0270	0.0270(7)
R_{Bragg} (%)	5.49	6.87	6.28	5.51
R_{prof} (%)	6.64	5.85	3.77	4.47

**Figure 1.** Temperature dependence of the magnetic susceptibility χ and reciprocal susceptibility χ^{-1} for RCuSn (R = Pr and Nd). The inset shows the χ versus T plot at low temperatures.

state is observed. At $T = 6$ K an additional anomaly was found for NdCuSn. A difference between zero-field cooling (ZFC) and field cooling (FC) curves is observed.

For NdCuSn the reciprocal magnetic susceptibility above the Néel temperature obeys the modified Curie–Weiss law: $\chi = \chi_0 + N\mu_{eff}^2/k_B(T - \theta_p)$, where N is the Avogadro number, k_B is Boltzmann's constant, θ_p is a paramagnetic Curie temperature, μ_{eff} is the effective magnetic moment and $\chi_0 = \chi_{dia} + \chi_{Pauli} + \chi_{vv}$ is a temperature-independent part of the magnetism including the diamagnetic core correction χ_{dia} , the Pauli susceptibility of the electron gas χ_{Pauli} and the Van Vleck temperature-independent paramagnetism χ_{vv} . The reciprocal susceptibility for PrCuSn is strongly curvilinear above its Néel point. The molar Curie constant for this compound has been given as [18]:

$$C_M = \frac{g_J^2 \mu_B^2 N}{k_B} \frac{m_{1eff}^2 + m_{2eff}^2 e^{-\Delta E/k_{BT}}}{1 + e^{-\Delta E/k_{BT}}}$$

where g_J is the Landé splitting factor, μ_B is the Bohr magneton, m_{1eff} and m_{2eff} are the effective quantum number of the ground and the first excited levels and ΔE is the energy gap between them. Fitting the experimental data to the above relation gives the following values: $m_{1eff} = 1.83(15)$, $m_{2eff} = 2.781(5)$, $\Delta E = 84.4(25)$ K, $\theta_p = -3.4(7)$ K. For both compounds the paramagnetic Curie temperatures are negative indicating the predominance of antiferromagnetic interactions. The effective magnetic moment values are larger than for the respective free R^{3+} ion values. The χ_0 values are equal to 1.49×10^{-3} emu mol $^{-1}$ for PrCuSn but almost zero for NdCuSn.

Figure 2 illustrates how the magnetization at 4.2 K depends on the applied magnetic fields up to 120 kOe. The curve for PrCuSn is typical for a paramagnet while for NdCuSn the metamagnetic phase transitions at critical fields of 10 and 40 kOe are observed. The magnetic moments of both compounds determined at 4.2 K and $H = 120$ kOe are smaller than the respective free R^{3+} ion values.

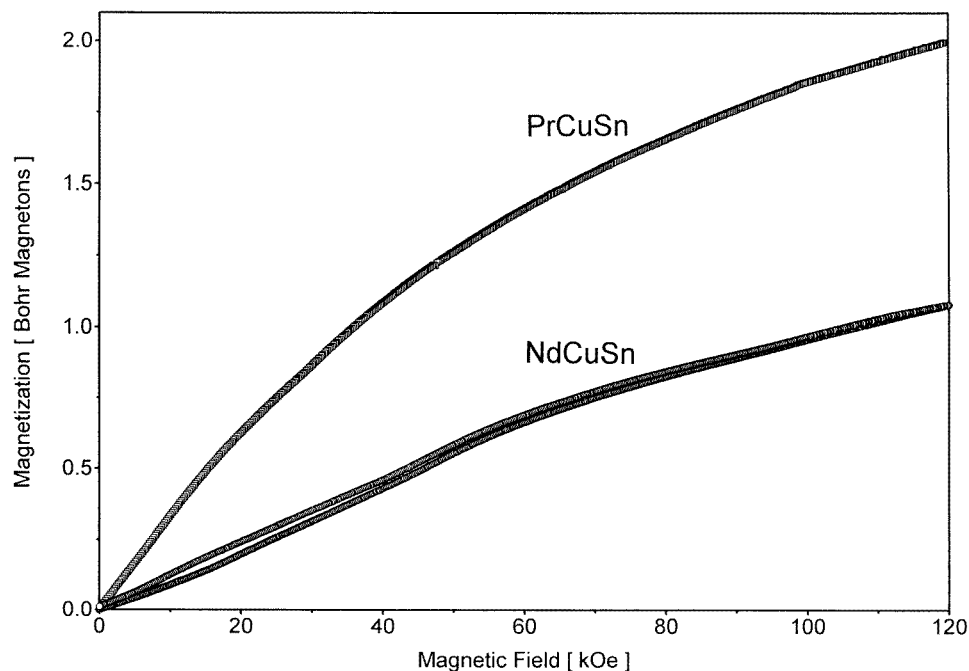
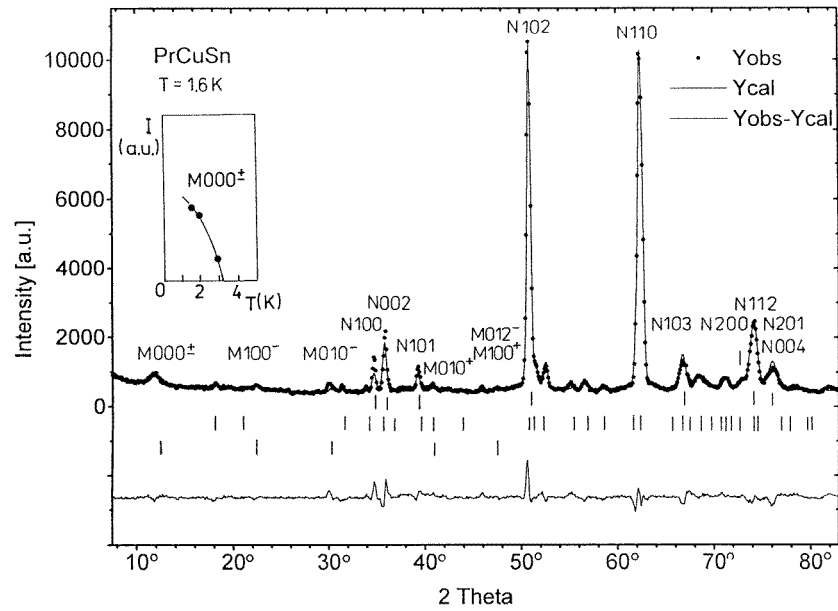


Figure 2. Magnetization–magnetic field strength functions for RCuSn (R = Pr and Nd) recorded at $T = 4.2$ K.

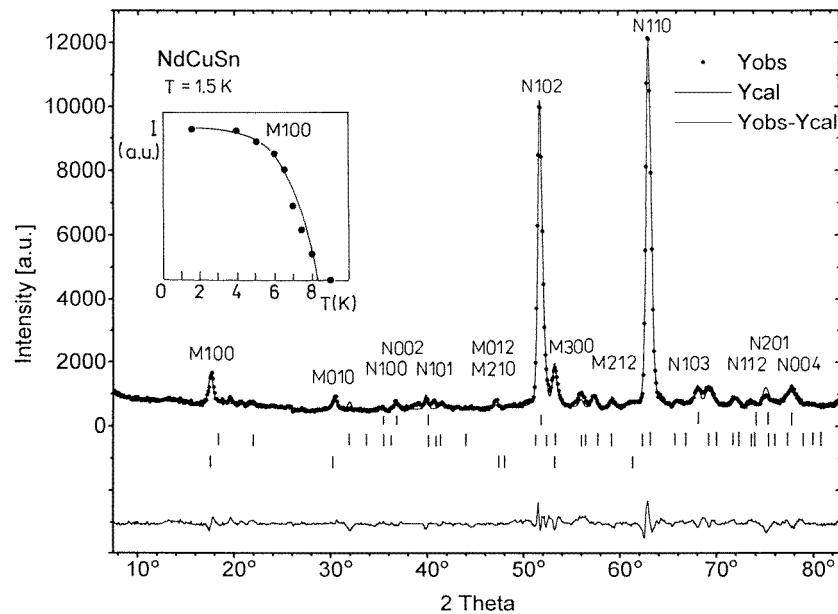
3.3. Magnetic structure

Neutron diffraction patterns recorded at 1.5 K for both samples contain low-intensity diffraction peaks of magnetic origin (see figure 3). These peaks are indexed by the wave vector $\mathbf{k} = (0.349(1), 0, 0)$ corresponding to the (a, a, c) unit cell for PrCuSn and their intensities indicate a sine modulated magnetic structure.

The neutron diffraction pattern of NdCuSn contains the magnetic peaks which could be indexed with the wave vector $\mathbf{k} = (1/2, 0, 0)$. This corresponds to the magnetic unit cell: $a_m = \sqrt{3}a_h$, $b_m = a_h$ and $c_m = c_h$ and a collinear magnetic structure. The magnetic unit cell contains neodymium magnetic moments situated at the following sites:



(a)



(b)

Figure 3. Neutron diffraction patterns observed at $T = 1.5$ K and calculated for (a) PrCuSn and (b) NdCuSn. The open squares represent the observed points, the solid lines the calculated profiles. Below, the difference between observed and calculated data is shown. The upper row indices correspond to the reflections related to the crystal structure of the hexagonal CaIn_2 type second row correspond the orthorhombic $\text{Pr}(\text{Nd})_6\text{Cu}_8\text{Ge}_8$ type. The lower row corresponds to the magnetic structure described in hexagonal (PrCuSn) and orthorhombic (NdCuSn) unit cells. The inset shows the temperature dependence of the 000^\pm (PrCuSn) and 100 (NdCuSn) magnetic reflections.

$S_1(0, 0, 1/4)$, $S_2(0, 0, 3/4)$, $S_3(1/2, 1/2, 1/4)$ and $S_4(1/2, 1/2, 3/4)$.

Group theory considerations [19] point to three possible antiferromagnetic ordering schemes:

$$A = S_1 + S_2 - S_3 - S_4 \quad C = S_1 - S_2 + S_3 - S_4 \quad G = S_1 - S_2 - S_3 + S_4.$$

The best agreement with the experimental magnetic peaks intensities has been obtained for a structure corresponding to the A mode.

The magnetic moment at 1.5 K is equal to 1.19(4) μ_B (PrCuSn) and to 1.25(4) μ_B (NdCuSn). In both compounds it is parallel to the c -axis.

The temperature dependence of the magnetic peaks gives the Néel temperature at 3.2 K (PrCuSn) and at 8.3 K (NdCuSn). In both compounds the magnetic structures between 1.5 K and relevant Néel temperatures do not change.

4. Discussion

Both title compounds crystallize in the hexagonal, CaIn_2 -type crystal structure and order antiferromagnetically at low temperatures.

The antiferromagnetic structure of NdCuSn is collinear and similar to the structures observed in other NdTSn compounds (see table 3). On the other hand, the sine-modulated magnetic order detected in PrCuSn is different from the magnetic structures found in other PrTSn compounds; it is similar to the magnetic structure observed in PrCuGe [20].

Table 2. Magnetic data for PrCuSn and NdCuSn.

Compound	T_N (K)		θ_p (K)	μ_{eff} (μ_B)		μ (μ_B)			Ref.
	M	ND		Exp.	Theor.	Exp.			
						M*	ND	Theor.	
PrCuSn	3	3.2	-3.4 -9	3.84(6) 3.64	3.58	2.0 ^a	1.19(4)	3.20	This work [8]
NdCuSn	10	8.3	-19.5 -14 -15	3.84(5) 3.8 3.6	3.62	1.1	1.25(4)	3.27	This work [8] [9]

M—magnetization measurements in $H = 10$ Oe.

M*—magnetization measurements in $H = 120$ kOe and 4.2 K.

ND—neutron diffraction experiment in $H = 0$ and 1.5 K.

^a Data in paramagnetic state.

The obtained results for NdCuSn are different from those reported in [9]. Spin glass behaviour is claimed on the basis of the large difference between field cooling (FC) and zero-field cooling (ZFC) magnetization curves recorded below $T = 10$ K (see figure 4 in [9]) and preliminary neutron experiment. At the same time the hyperfine field on ^{119}Sn nuclei is observed at low temperatures. Above 8 K, the hyperfine field rapidly decreases as the temperature rises, and vanishes at 12(1) K [9].

Our results indicate also a difference between ZFC and FC curves below $T = 10$ K. The similar effect of thermomagnetic irreversibility has been observed in collinear antiferromagnetic DyCu_2Si_2 and UNi_2Ge_2 compounds. In this case the difference between FC and ZFC curves results from random orientation of crystallites, and anisotropy [21, 22].

The results of our neutron diffraction experiment indicate the presence of long-range magnetic ordering up to $T = 8.3$ K, in agreement with the temperature change of the

Table 3. Magnetic data for RTSn and RCuGe (R = Pr, Nd, T = Cu, Ag, Au) compounds.

Compound	c/a	T_N (K)	μ (μ_B)	gJ	k	Direction of mag. mom.	Ref.
PrCuSn	1.681	3	1.19(4)	3.2	(0.349, 0, 0)	$\parallel c$	This work
PrAgSn	1.593	3.8	1.88		(1/3, 1/3, 0)	$\parallel c$	[5]
PrAuSn	1.614	3.5	0.64		(1/2, 0, 0)	$\parallel c$	[7]
PrCuGe	1.822	1.8	1.45(9)		(1/3, 0, 0)	$\perp c$	[20]
NdCuSn	1.663	10	1.25(4)		(1/2, 0, 0)	$\parallel c$	This work
NdAgSn	1.591	11.5	1.97(5)	3.27	(1/2, 0, 0)	$\parallel c$	[5]
NdAuSn	1.607	14	1.96		(1/2, 0, 0)	$\parallel c$	[7]
NdCuGe	1.816	3.5	1.24(5)		(1/2, 0, 0)	$\perp c$	[20]

hyperfine field (see figure 4 in [9]).

It is possible to describe the magnetic ordering in NdCuSn by a simple model of exchange interactions taking into account the interactions between the nearest and next-nearest moments located on the hexagonal (001) plane (see figure 8 in [23]). On the other hand, the magnetic structure of PrCuSn can be deduced when the interaction with the third-nearest neighbour is allowed for [24].

In both title compounds the determined magnitudes of ordered moments localized on the lanthanide ions are much smaller than the free ion values. Table 3, in which selected magnetic data for PrTSn and NdTSn (T = Cu, Ag, Au) are listed, shows that this effect appears in all the above compounds. The reduction of the value of magnetic moment is usually explained as due to the action of crystalline electric field. For RTSn (R = rare earth, T = Cu, Ag, Sn) the crystal field parameters have been determined only for Ce compounds [25]. The Ce^{3+} ground state moments calculated from the crystal electric field wavefunctions gives values of nearly 50% of the free Ce^{3+} ion values. This result is in fair agreement neutron diffraction data [5] and the magnetic measurements performed for CeAgSn [25].

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