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Magnetic properties of PrPdSb and NdPdSb compounds

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Abstract. Magnetometric and neutron diffraction measurements performed for PrPdSb and NdPdSb (hexagonal, LiGaGe-type crystal structure) indicate the absence of any long-range magnetic order in PrPdSb at 1.5 K and a sine-modulated order in NdPdSb described by the wave-vector $k = |0.1418(4), 0, 0|$, stable below the Néel point at 10 K. The magnetic moment of 2.51(6) μ_B is localized on the Nd ion. Below $T_\tau = 5.8$ K, additional magnetic reflections appear pointing at a square-modulated magnetic structure. The magnetic moment at 1.67 K is 3.16(5) μ_B. In both magnetic phases of NdPdSb the moments are parallel to the hexagonal c-axis.

1. Introduction

RPdSb compounds (R—a lanthanide element) crystallize in two types of structure. The hexagonal $CaIn_2$-type structure has been found in compounds containing R = La–Tb (excluding Eu), while the samples containing R = Dy–Tm show the cubic MgAgAs-type structure [1, 2]. CePdSb orders ferromagnetically, while NdPdSb, SmPdSb, GdPdSb, TbPdSb, DyPdSb and HoPdSb have been reported to be antiferromagnets [2–5].

The magnetic behaviour of these phases seemed to us to be so interesting that we have decided to carry out a new study, including neutron diffraction experiments. At first, PrPdSb and NdPdSb have been chosen. The results of these studies are presented below.

2. Experiment

The samples of PrPdSb and NdPdSb were synthesized by arc melting in an argon atmosphere the starting materials: praseodymium and neodymium (3N purity), palladium and antimony (4N). After melting, the samples were sealed in quartz capsules and annealed for one week at 800 °C. X-ray measurements were performed using Cu Kα radiation. The observed lines were indexed assuming the hexagonal $CaIn_2$-type structure. The lattice parameters determined are as follows: $a = 4.5792(7)$ Å and $c = 7.7260(9)$ Å, $c/a = 1.6872$ for NdPdSb, and $a = 4.588(8)$ Å and $c = 7.836(9)$ Å, $c/a = 1.7079$ for PrPdSb. The ac susceptibility was measured using a mutual inductance bridge. The magnetization data

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were collected by means of a vibrating-sample magnetometer in magnetic fields up to 50 kOe and a ballistic magnetometer in the Bitter-type magnet in magnetic fields up to 140 kOe. A SQUID magnetometer was adopted to perform additional measurements in low magnetic fields.

Neutron diffractions patterns were run in the temperature range 1.5 to 20 K on the E6 diffractometer installed at the BER II reactor in the Hahn-Meitner Institute, Berlin. The neutron wavelength was 2.40 Å. Data processing was performed by using the Fullproff program [6]. Neutron scattering lengths were adopted after reference [7]. The magnetic form factor Nd^{3+} were taken from reference [8].

3. Results

3.1. Crystal structure

X-ray and neutron diffraction patterns recorded for both samples in the paramagnetic state (see figure 1) confirm that all observed peaks are indexable according to a hexagonal unit cell. Additional peaks of small intensities corresponding to indefinite phases. Two models of the atomic distribution are possible:

(i) either $CaIn_2$ type (space group $P6_3/mmc$), with

(a) two R atoms in 2(b) sites: 0, 0, 1/4; 0, 0, 3/4;

(b) two Pd and two Sb atoms randomly distributed in 4(f) sites: 1/3, 2/3, z; 2/3, 1/3, $\bar{z}$; 2/3, 1/3, $1/2 + z$; 1/3, 2/3, $1/2 - z$;

(ii) or LiGaGe type (space group $P6_3mc$), with

(c) two R atoms in 2(a) sites: 0, 0, z_1; 0, 0, $1/2 + z_1$;
(d) two Pd atoms in 2(b) sites: 1/3, 2/3, z_2; 2/3, 1/3, $1/2 + z_2$;
(e) two Sb atoms in 2(b) sites: 1/3, 2/3, z_3; 2/3, 1/3, $1/2 + z_3$.

z_1 was chosen at 0.25 to define the origin.

Table 1. Crystal data for PrPdSb and NdPdSb.

	PrPdSb				NdPdSb	
	$CaIn_2$ type of crystal structure		LiGaGe type of crystal structure		$CaIn_2$ type of crystal structure	LiGaGe type of crystal structure
T (K)	1.5	12	1.5	12	13.1	13.1
a (Å)	4.5626(16)	4.5619(16)	4.5687(15)	4.5620(15)	4.5265(38)	4.5265(38)
c (Å)	7.7338(38)	7.7343(39)	7.7335(38)	7.7343(38)	7.5840(90)	7.5839(91)
a/c	0.5900	0.5898	0.5900	0.5898	0.5968	0.5968
z	0.031(1)	0.031(1)			0.0356(16)	
z_1			0.25	0.25		0.25
z_2			0.063(4)	0.065(4)		0.044(18)
z_3			0.500(4)	0.503(4)		0.473(18)
R_{profile}	8.30	8.49	7.80	7.87	5.72	5.70
R_{Bragg}	6.22	6.66	4.79	4.51	1.91	1.81

The reliability factors R for both compounds are slightly better for the second model of the crystal structure in which Pd and Sb atoms are occupying separate sites. The crystal structure parameters determined for both models and both compounds are listed in table 1.

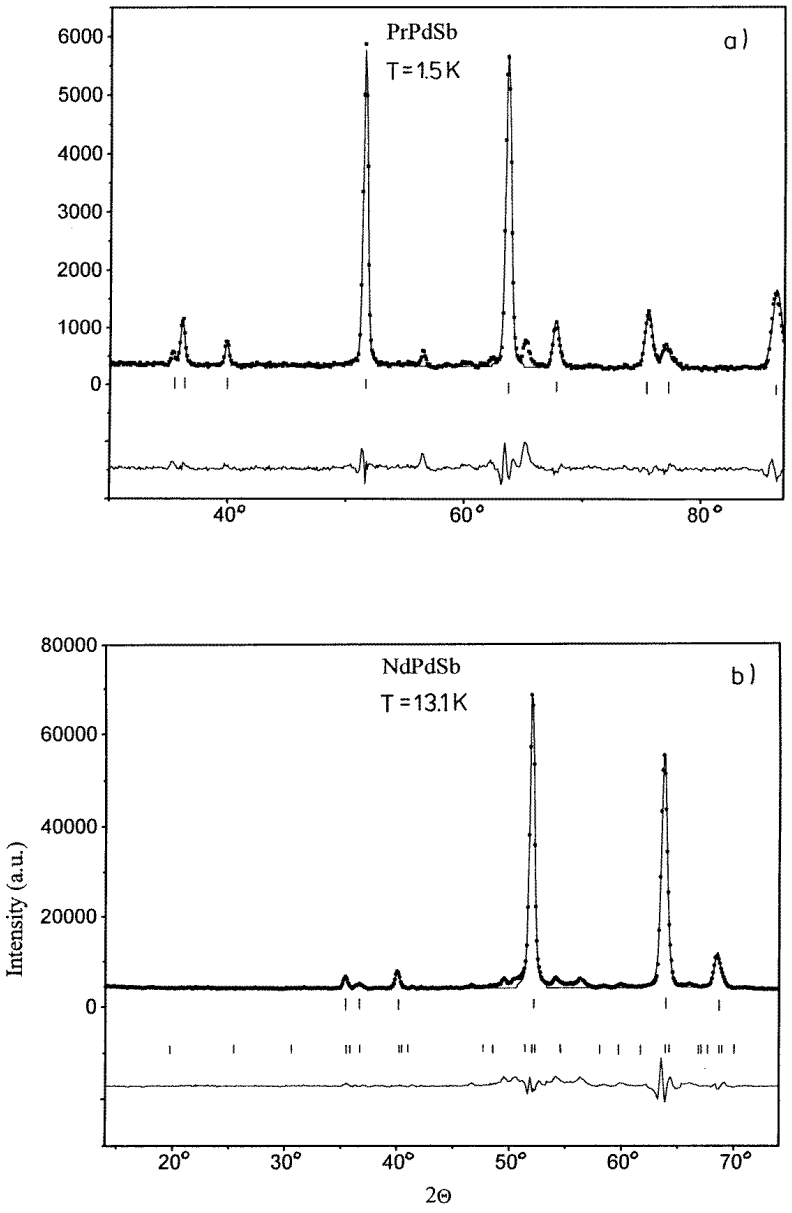

Figure 1. Plots of the observed and calculated patterns of (a) PrPdSb at 1.5 K and (b) NdPdSb at 13.1 K. The first row corresponds to the reflections of the nuclear structure of the hexagonal LiGaGe type of crystal structure. The second row in the NdPdSb pattern corresponds to the orthorhombic crystal structure proposed in reference [9].

The *R*-factors for the two compounds differ considerably. The possible reason for this is the different number of peaks used in the Rietveld profile refinement. The larger values of the *R*-factors obtained for PrPdSb at both temperatures result from the concentration of the additional phase in this compound being greater than that in NdPdSb.

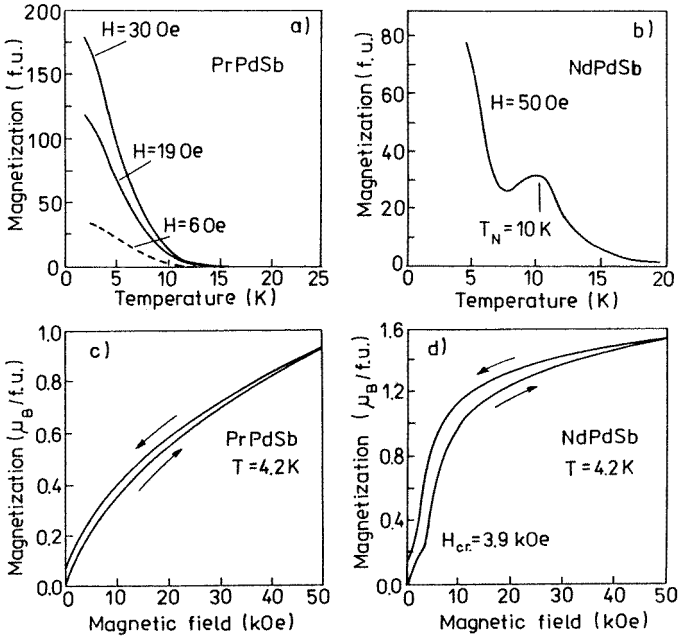

Figure 2. Temperature dependences of the magnetization in low magnetic fields for (a) PrPdSb and (b) NdPdSb. Magnetization curves at $T = 4.2$ K and in magnetic fields rising up to 50 kOe and decreasing to zero for (c) PrPdSb and (d) NdPdSb.

3.2. Magnetic properties

The temperature dependence of the magnetization of PrPdSb and NdPdSb in low magnetic fields is shown in figure 2. For PrPdSb, a strong increase of the magnetization is observed below $T = 12$ K. Its magnetization is also a function of the external field.

Table 2. Magnetic data for PrPdSb and NdPdSb. (M: data from magnetization measurements; ND: data from neutron diffraction measurements.)

						μ_S (μ_B)			
	$T_{C,N}$ (K)			μ_{eff} (μ_B)		Experiment		Theory	
Compound	M	ND	θ_p(K)	Experiment	Theory	M	ND		H_C (kOe)
PrPdSb	10?	—	+5	3.32	3.58	0.9	—	3.2	—
NdPdSb	10	10.5	+9	2.95	3.62	1.55	3.15	3.27	3.9

For NdPdSb a maximum typical for a transition from an antiferromagnetic to a paramagnetic state is observed at $T_N = 10$ K. An additional phase transition at $T_\tau = 5.8$ K can be deduced from the temperature dependence of the ac magnetic susceptibility (figure 3). The reciprocal magnetic susceptibilities of both compounds satisfy the Curie–Weiss law. The values determined for the paramagnetic Curie temperature θ_p and effective magnetic moments are listed in table 2. The positive values of the paramagnetic Curie temperatures indicate that the ferromagnetic interactions are dominant.

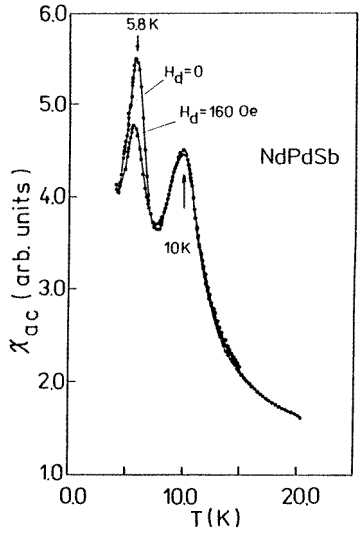

Figure 3. Temperature dependence of the ac magnetic susceptibility for NdPdSb.

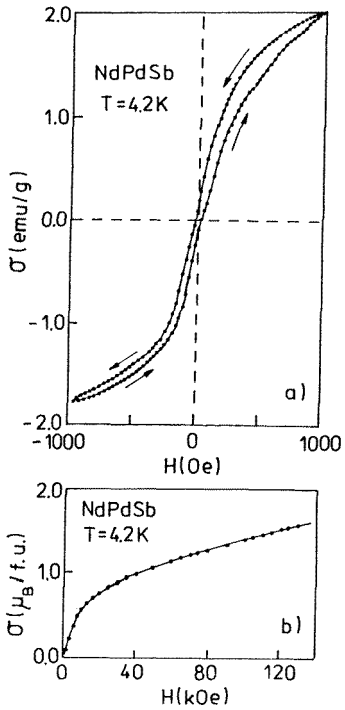

Figure 4. NdPdSb. (a) The hysteresis curve and (b) the magnetization curve in high magnetic fields at $T = 4.2$ K.

The magnetization curve at 4.2 K for PrPdSb (see figure 2) is typical for a paramagnet, whereas for NdPdSb it has more complex character. A non-linear increase in low fields suggests the non-collinear antiferromagnetic structure in the magnetic field below the critical field $H_{cr} = 3.9$ kOe. Above this field the change to a ferromagnetic state is observed. A small hysteresis can be noticed. The value of the magnetic moment on the Nd ion at 4.2 K and $H = 50$ kOe is 1.55 μ_B, i.e. much smaller that the free-ion value ($gJ = 3.27$ μ_B). This magnetization curve does not attain saturation in the magnetic field of 140 kOe (figure 4(b)). Magnetic measurements indicate ferromagnetic properties at $T = 4.2$ K (see figure 4(a)).

Figure 1(a) shows the neutron diffraction pattern of PrPdSb recorded at 1.5 K with the Rietveld fit to this crystallographic structure. The absence of any magnetic contribution follows clearly from this fit. The R-factor for $T = 1.5$ K has a similar value to that obtained at $T = 12$ K. In figure 5 a differential pattern of PrPdSb taken at $T = 1.5$ K and 12 K is compared with the theoretical patterns calculated for the ferromagnetic ordering of the Pr moments placed along the [001] direction and in the (001) plane. A large difference between theoretical and experimental patterns precludes the existence of any ferromagnetic ordering at 1.5 K. We therefore conclude that the observed small increase (near 4%) of the (102) and (110) strong nuclear reflections results from the change in the positional parameters of the atoms.

Neutron diffraction patterns recorded for NdPdSb at 7.1 K (see figure 6) show that additional peaks of magnetic origin which could be indexed by the wavevector $\boldsymbol{k} =$

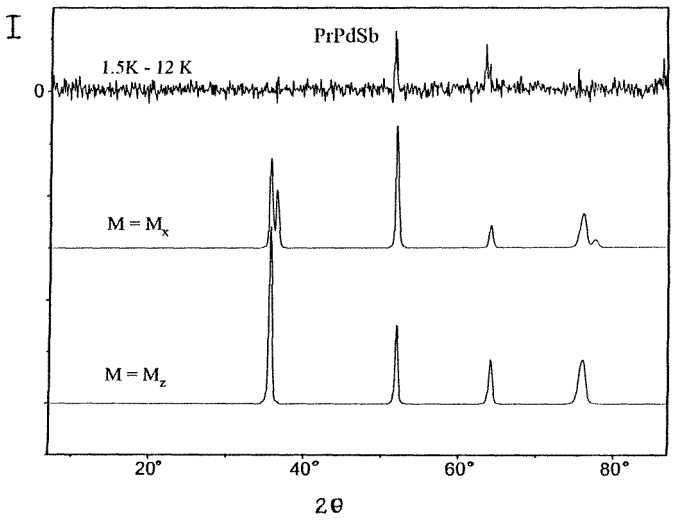

Figure 5. Differential neutron diffraction patterns of PrPdSb between 1.5 and 12 K and the theoretical patterns calculated for the ferromagnetic ordering of the Pr moments placed along the [001] direction and in the (001) plane.

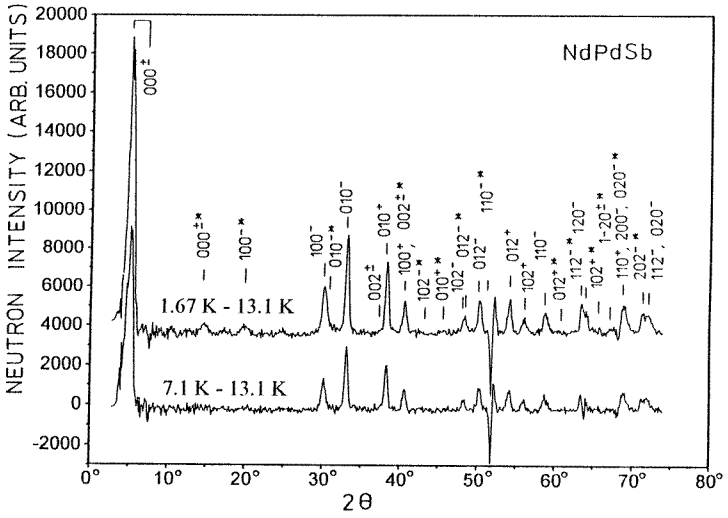

Figure 6. Differential neutron diffraction patterns of NdPdSb: 13.1 K patterns subtracted from the 1.67 K and 7.1 K diffractograms.

$(0.1416(4), 0, 0)$ or $\boldsymbol{k} \approx (1/7, 0, 0)$ corresponding to the hexagonal unit cell. The best agreement between the observed and calculated magnetic intensities was obtained for magnetic ordering represented by a sinusoidal transverse spin wave schematically displayed in figure 7(a). The magnetic moment distribution is described by $gJ \cos 2\pi \boldsymbol{k} \cdot \boldsymbol{r}$, where gJ is the maximum ordered moment per Nd^{3+} ion amounting to 2.51(6) μ_B, and r is the real-space distance. The magnetic moments are aligned along the c-axis. Two other models for

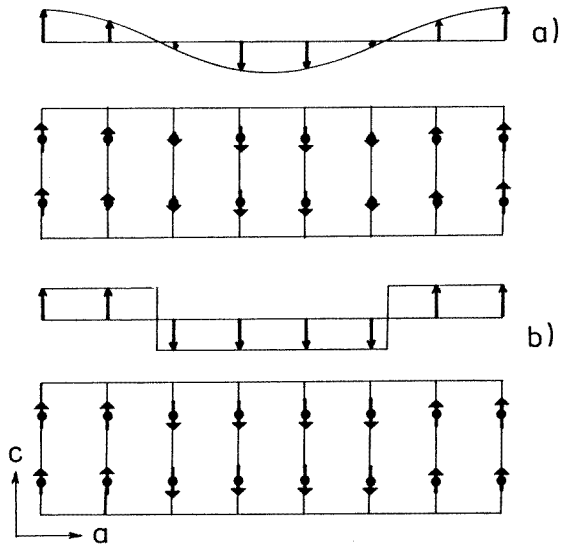

Figure 7. Magnetic structures of NdPdSb projected onto the a–c plane; (a) the sine-modulated structure observed in the temperature region $T_\tau < T < T_N$ and (b) the square-modulated structure observed below T_τ.

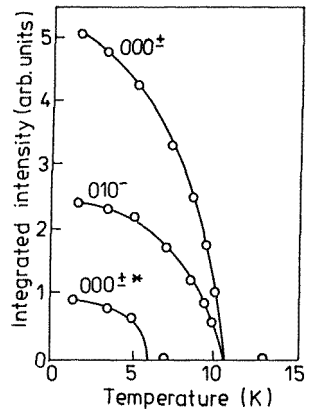

Figure 8. Temperature dependences of the integrated intensities of the $000^{\pm}$, 010^{-} and $000^{\pm *}$ reflections.

the 7.1 K ordering were considered as possible alternatives: moments located in the basal plane and helicoidal ordering of moments. The first model gave the R-factor of 39.9%; the other yielded $R = 24.8\%$. The sinusoidal transverse amplitude of spins pointing along the [001] direction seems therefore the most probable, since it gives $R = 5.6\%$.

The neutron diffraction pattern of NdPdSb at 1.67 K (see figure 6) contains the same peaks of magnetic origin as at 7.1 K, due to the structure with the wavevector $\boldsymbol{k} = (0.1418(4), 0, 0)$. In addition, new magnetic reflections corresponding to the wavevector $3\boldsymbol{k}$ were found. This indicates the square-modulated structure at low temperatures with the magnetic moment equal to 3.15(5) μ_B for the fundamental and 1.03(5) μ_B for the third harmonic. The moments are parallel to the c-axis (see figure 7(b)). The proposed antiphase structure consists of ferromagnetic layers perpendicular to the vector $\boldsymbol{k}$. The magnetic moments in successive planes follow the sequence $(3, \bar{4}, 3, \bar{4})$, i.e. 3 moments 'up' followed by 4 moments 'down', according to the commensurate value of the k_x-component which is 1/7 within the accuracy of the experiment.

Table 3. The Bragg angles and intensities of the magnetic reflections for NdPdSb at 1.67 and 7.1 K.

	$T = 1.67$ K			$T = 7.1$ K		
hkl	2θ	I_{calc}	I_{obs}	2θ	I_{calc}	I_{obs}
$000^{\pm}$	4.85	27 979.3	26 974.9	4.85	17 525.5	16 897.1
$000^{\pm}$*	14.95	839.4	750.6			
100^{+}*	20.25	480.2	468.5			
100^{-}	30.45	1991.7	2461.1	30.45	1249.9	1118.7
010^{-}*	30.85	413.8				
010^{-}	33.30	3321.6	3259.0	33.30	2083.8	1892.4
$002^{\pm}$	37.25	40.4	46.4	37.22	25.4	31.0
010^{+}	38.5	2484.2	2209.8	38.5	1563.0	1346.8
$002^{\pm}$*	40.0	29.6	1064.7			
100^{+}	40.9	1103.7		40.9	692.9	622.7
102^{-}*	42.4	43.2	33.2			
010^{+}*	45.6	189.2	212.2			
012^{-}*	48.8	116.8	659.6			
102^{-}	48.55	547.0		48.54	343.6	355.4
110^{-}*	49.95	158.2	190.			
012^{-}	50.55	1122.4	972.4	50.53	704.8	658.8
100^{+}*	51.7	73.7	76.9			
012^{+}	54.4	1117.2	1084.4	54.36	701.6	654.6
110^{-}	59.0	1067.6	1223.6	59.04	669.6	685.7
012^{+}*	60.0	116.0	83.6			
112^{-}*	63.65	111.2	1110.4			
$1\text{-}20^{-}$	64.2	912.4		64.2	572.4	558.6
102^{+}*	65.2	54.6	68.4			
020^{-}*	76.9	87.6	107.2			
110^{+}	69.2	792.8	1221.0	69.18	498.4	740.0
200^{-}	69.25	396.0		69.28	248.5	
202^{-}*	70.4	51.0	78.0			
112^{-}	71.67	937.6	1609.6	71.67	588.8	524.0
020^{-}	72.5	727.0		72.5	456.4	470.2
R (%)		5.	0			5.6

* The magnetic peaks corresponding to the $3\boldsymbol{k}$ wavevector.

A comparison of the calculated and observed magnetic intensities at 1.67 and 7 K is presented in table 3. The temperature dependence of the magnetic peak intensities corresponding to the vectors $\boldsymbol{k}$ and $3\boldsymbol{k}$ gives the temperature of the phase transition at $T_\tau = 5.8$ K and the Néel temperature at 10.5 K (see figure 8). Both transitions are observed in the ac susceptibility versus temperature plot (figure 3).

4. Discussion

Our results show that both title compounds crystallize in the hexagonal LiGaGe-type structure. The orthorhombic structure of NdPdSb claimed in reference [9] has not been confirmed (see figure 1(b)).

In contrast to the specific heat and susceptibility data reported in reference [10], our results indicate that even at 1.5 K PrPdSb does not show any long-range magnetic order. A large value of the electronic coefficient of the specific heat γ found for PrPdSb amounting to 75 mJ mol^{-1} K^{-2} [10] suggests that the hybridization of 4f electrons of Pr^{3+} ions with

conduction electrons, the 4d electrons of Pd and the sp electrons of Sb, may take place. This effect is a possible reason for the absence of long-range magnetic order at low temperatures, similarly to what was detected in some cerium compounds [11]. However, like in $PrCu_2$ (orthorhombic, $CeCu_2$-type structure), the absence of magnetic order in PrPdSb may be explained as connected with the action of a crystal electric field (CEF). In the former compound, magnetic susceptibility, specific heat and thermal expansion data point to the non-magnetic singlet as the ground state [12].

The magnetic ordering in NdPdSb at 1.67 K is a square-modulated structure. It transforms into a sine-modulated structure as the temperature rises. This effect can be interpreted in terms of the self-consistent periodic-field model [13].

The analysis of interatomic distances in NdPdSb shows that each Nd ion has six Nd neighbours in the (001) plane at 4.526 Å and two others along the [001] direction at 3.792 Å. These are fairly long distances to exclude any direct magnetic coupling. The RKKY mechanism seems thus to be responsible for the stability of both of the observed magnetic ordering schemes.

The magnitude of the magnetic moment localized on the Nd^{3+} ion is close to its free-ion value (see table 2). This suggests that the CEF action is probably negligible. No data are as yet available concerning either the magnitudes of CEF parameters as defined by Hutchings [14] or their signs which are connected with the orientation of the magnetic moment with respect to the hexagonal axis. In isostructural CePdSb [3] and CePtSb [15], the cerium moment is in the basal plane and the CEF parameters B_2^0 and B_4^3 were found to be positive, but B_4^0 is negative. Since in NdPdSb the moment is aligned along the hexagonal axis, the sign of B_0^2 may be negative.

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