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MAGNETIC PROPERTIES AND STRUCTURES OF PrPt and NdPt

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The magnetic properties of the CrB-type orthorhombic phase of PrPt and NdPt are presented. Below their ordering temperature which is 15 and 23 K respectively, these compounds exhibit a ferromagnetic behaviour. The magnetic structures determined by neutron diffraction are collinear. While in PrPt, the magnetic moments are parallel to **c**, in NdPt, the moments lie in the (**a**, **c**) plane and make an angle of 22° with **a**. These properties and especially the peculiar moment direction in NdPt are discussed in terms of crystalline electric field effects on the rare earth ion.

1. INTRODUCTION

THE CRYSTALLOGRAPHIC structure of the equiatomic R–Pt compounds (R = rare earth) was first studied by Dwight *et al.* [1]. They have shown that LaPt and CePt crystallize in the CrB-type orthorhombic structure while the other equiatomic rare earth platinum compounds crystallize in the FeB-type orthorhombic structure. However, in 1978 Le Roy *et al.* [2] have shown that samples of PrPt and NdPt quenched from high temperatures have the CrB-type structure. In this paper we present the results obtained on quenched PrPt and NdPt. This CrB-type structure (as well as the FeB-type) can be built from trigonal prisms where the corners are occupied by rare earth atoms and the center by a platinum atom. Platinum does not contribute to the magnetism of the compounds because the Stoner criterion for onset of $5d$ electrons magnetism is far to be satisfied. The magnetic interactions between rare earth atoms are of RKKY type and occur through polarization of the conduction band. Because of the spin–orbit coupling the magnetocrystalline anisotropy is very high ($L \neq 0$). Magnetic properties observed in this type of compounds result from the competition between these two effect.

2. EXPERIMENTAL

The rare earth elements used were 99.9% pure, and the platinum was 99.99% pure. Polycrystalline samples were induction melted in a cold crucible. The quenched CrB-phase was obtained by switching off the induction furnace while the alloy was in the liquid phase. Magnetic measurement between 4.2 and 300 K were performed at the S.N.C.I. (Service National des Champs Intenses, Grenoble) in fields up to 150 kOe. Magnetic structures were studied at the Laboratoire de Diffraction Neutronique du Centre d'Etudes Nucléaires de Grenoble.

3. CRYSTALLOGRAPHIC STRUCTURE

The CrB-type [2] structure of PrPt and NdPt belongs to the orthorhombic *Cmcm* space group. The cell parameters are: PrPt: a = 3.891 Å, b = 10.899 Å, c = 4.569 Å and NdPt: a = 3.846 Å, b = 10.769 Å, c = 4.542 Å. This cell which contains two unit cells has four rare earth atoms and four Pt atoms lying in the $4c$ site. These atoms are numbered (1) in $(0, y, 1/4)$, (2) in $(0, \bar{y}, 3/4)$, and those deduced with the 1/2, 1/2, 0 translation: (3) in $(1/2, 1/2 + y, 1/4)$ and (4) in $(1/2, 1/2 - y, 3/4)$. The 1/2, 1/2, 0 translation leads to the selection rule $h + k = 2n$ for all the (hkl)'s. The inversion operation which associates (1) to (2) as well as (3) to (4) leads to the selection rule $l = 2n$ for the $(h0l)$ reflections. From the intensities of the neutron diffraction patterns performed above the ordering temperatures we have refined the atomic positions: y (Pr) = 0.132 and y (Pt) = 0.409 in PrPt and y (Nd) = 0.131 and y (Pt) = 0.416 in NdPt.

4. MAGNETIC MEASUREMENTS

The field dependences of the magnetizations at 4.2 K are shown in Fig. 1. Both compounds exhibit a ferromagnetic behaviour: a spontaneous magnetization appears, however in fields higher than 5 kOe a strong field dependence of the magnetization is observed. For that reason, the determination of the spontaneous magnetizations leads to difficulties. The estimated values are $1.02 \pm 0.04\,\mu_B$ and $1.44 \pm 0.08\,\mu_B$ per formula unit in PrPt and NdPt respectively. The Curie temperatures were deduced from the thermal variations of the a.c. susceptibility measured on a Hartshorn bridge; they are 15 and 23 K respectively for PrPt and NdPt.

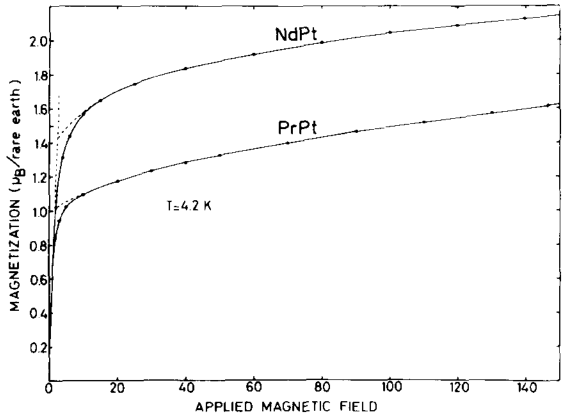

Fig. 1. Magnetization vs applied field at 4.2 K in PrPt and NdPt.

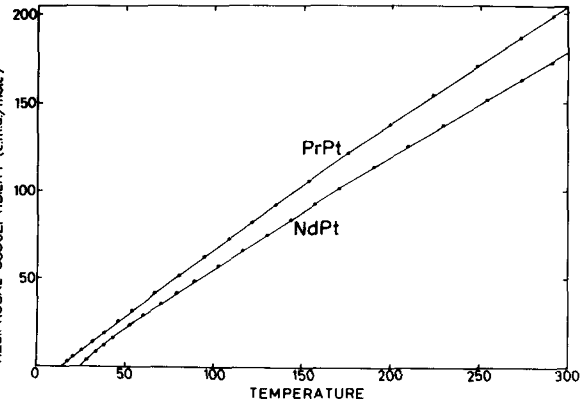

Fig. 2. Thermal variation of the reciprocal susceptibility of PrPt and NdPt above their Curie temperature.

The thermal variations of the reciprocal susceptibilities measured in the paramagnetic domain are shown in Fig. 2. These variations exhibit a weak negative curvature below 180 K and are almost linear above this temperature. The effective moments deduced from the slopes of the linear variations are 3.46 and $3.68\,\mu_B$ respectively for PrPt and NdPt. These values are in close agreement with the free Pr^{3+} and Nd^{3+} ion values (3.52 and $3.68\,\mu_B$ respectively).

5. MAGNETIC STRUCTURES

5.1. PrPt

The neutron diffraction patterns performed at 46 and 4.2 K are shown in Fig. 3. At 46 K, the observed peaks are characteristic of the CrB-type crystallographic structure. Especially, the selection rules of the crystallographic *Cmcm* space group are satisified: the Bragg peaks (hkl), with $h + k = 2n + 1$, and $(h0l)$, with $l = 2n + 1$ do not appear. The calculated intensities with the Fermi lengths $b_{Pr} = 0.44 \times 10^{-2}$ cm and $b_{Pt} = 0.95 \times 10^{-2}$ cm are compared in Table 1 with the observed ones. The reliability factor is:

$$R = \frac{\Sigma\,|I_{obs} - I_{cal}|}{I_{obs}} = 3.4\%.$$

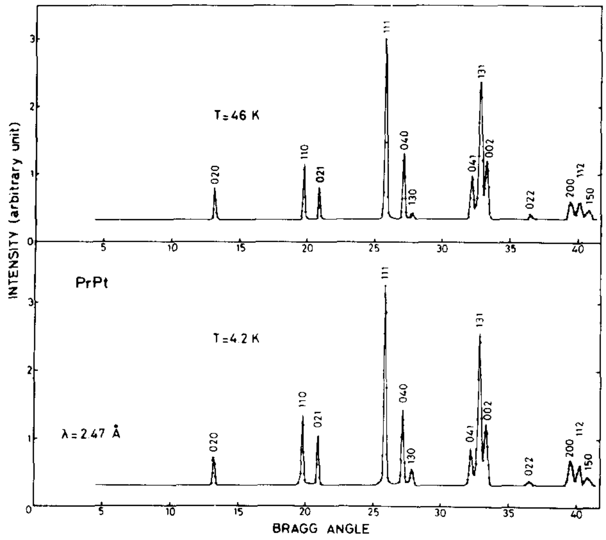

Fig. 3. PrPt: Neutron diffraction patterns at 4.2 and 46 K.

At 4.2 K, the pattern exhibits only a small increase of almost all the nuclear peaks. The extinction rules are still satisfied. For the (hkl) reflections with $h + k = 2n + 1$, this means that the translation is still present. For the $(h0l)$ reflections with $l = 2n + 1$, this means that the (1) and (2) rare earth moments are parallel. Then PrPt exhibits a collinear ferromagnetic structure. The macroscopic method proposed by Bertaut [3] leads to the following conclusions: with the $K = [0, 0, 0]$ propagation vector for the elementary unit cell, only the coupling between the atoms (1) and (2)

Table 1. PrPt: *Observed and calculated neutron diffraction intensities at* 46 *and* 4.2 K

hkl	θ	46 K		4.2 K		
		$I_{N_{\text{cal}}}$	$I_{N_{\text{obs}}}$	$I_{M_{\text{cal}}}$	$I_{M_{\text{cal}}} + I_{N_{\text{cal}}}$	I_{obs}
020	13.20	3.93	3.84	0.07	4.00	3.95
110	19.76	16.02	14.88	8.35	24.37	20.08
021	20.92	11.66	8.79	7.31	18.97	16.44
111	25.82	89.84	97.03	11.03	100.87	108.79
040	27.17	35.83	38.51	8.00	43.83	46.61
130	27.87	2.76	4.10	10.32	13.08	13.39
041	32.20	39.67	42.96	0.35	40.02	39.98
131	32.83	245.47	246.77	8.38	253.85	261.92
002	33.32					
022	36.50	7.78	8.20	0.02	7.80	5.44
200	39.53	61.01	49.72	6.97	67.98	61.85
112	40.16	31.72	36.14	3.46	35.18	36.92
150	40.81	29.28	24.34	3.93	33.21	28.09
		$R = 7.1\%$		$R = 6.3\%$		

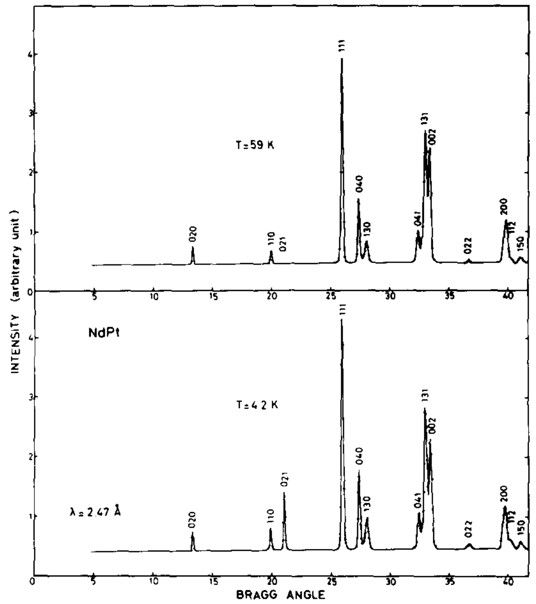

Fig. 4. NdPt: Neutron diffraction patterns at 4.2 and 59 K.

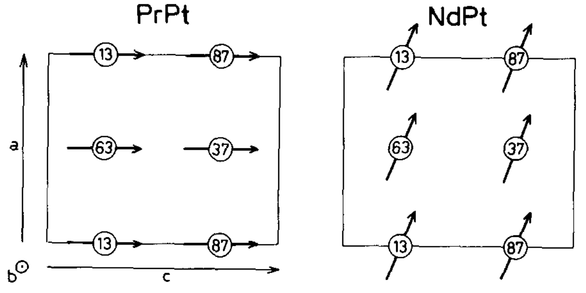

Fig. 5. Magnetic structures of PrPt and NdPt at 4.2 K. Inscribed numbers correspond to y parameters multiplied by 100. Pt atoms are not shown because they lie in the same x, z positions as the rare earth atoms.

must be examined. There are two basis vectors $\mathbf{F} = \mathbf{S}_1 + \mathbf{S}_2$ and $\mathbf{A} = \mathbf{S}_1 - \mathbf{S}_2$. We can show that only one basis vector is associated with each irreducible representation of the G_K group: A_a, A_b, A_c, F_a, F_b or F_c. As a first step we must try one of the three ferromagnetic configurations. The refinement of the observed magnetic intensities has led to the F_c configuration: the moments are along c and reach $M(\text{Pr}) = 2.2 \pm 0.2\,\mu_B$. This structure which is shown in Fig. 4 belongs to the magnetic space group $Cm'c'm$; it is identical to that observed in PrNi [4]. The observed and calculated intensities are compared in Table 1. From the value of the Pr magnetic moment $M(\text{Pr})$ one can expect a value of $M(\text{Pr})/2 = 1.1 \pm 0.1\,\mu_B/\text{Pr}$ for the magnetization measurements on a polycrystalline sample and extrapolated in zero internal field; the value is in agreement with the observed one.

5.2. NdPt

The neutron diffraction patterns performed on this compound at 59 and 4.2 K are shown in Fig. 5. As for PrPt at 59 K the pattern is characteristic of the CrB-type crystallographic structure. Using the Fermi lengths $b_{\text{Nd}} = 0.769 \times 10^{-12}$ cm and $b_{\text{Pt}} = 0.95 \times 10^{-12}$ cm the comparison between the observed and calculated intensities leads to a reliability factor of 4.6% (Table 2).

At 4.2 K, one observed an increase of almost all the nuclear peaks. Especially, the (0 2 1) peak which is

Table 2. NdPt: *Observed and calculated neutron diffraction intensities at* 59 *and* 4.2 K

hkl	θ	59 K		4.2 K		
		$I_{N_{\text{cal}}}$	$I_{N_{\text{obs}}}$	$I_{M_{\text{cal}}}$	$I_{M_{\text{cal}}} + I_{N_{\text{cal}}}$	I_{obs}
020	13.25	5.25	3.12	0.07	5.32	3.51
110	19.94	5.69	4.98	2.58	8.27	7.72
021	21.04	0.24	n.o.	20.99	21.23	21.01
111	26.03	138.68	132.28	11.47	150.15	158.95
040	27.30	49.69	47.73	10.63	60.32	57.81
130	28.07	22.18	23.76	7.94	30.12	34.09
041	32.37	55.51	50.05	0.45	55.96	50.14
131	33.07	350.87	350.40	19.34	370.21	360.94
002	33.53					
022	36.73	10.39	7.51	0.10	10.49	9.25
200	39.96	104.50	118.19	13.37	117.87	125.38
112	40.47					
150	41.09	10.58	14.49	4.70	15.28	18.09
		$R = 4.6\%$		$R = 5.3\%$		

very weak at 59 K becomes much larger than the (1 1 0) peak. However, as for PrPt, we do not observe new peaks and the selection rules of the crystallographic structure are satisfied. The magnetic structure is then collinear and ferromagnetic. The strong value of the (0 2 1) peak and the very weak value of the (1 1 0) peak show that there is a strong component of the magnetic moment along the a-axis. However, it is not possible to give account for the neutron diffraction pattern using the F_a basis vector alone and consequently the refinement of the intensities led to magnetic moments which lie in the (a, c) plane. The value of the Nd magnetic moments is $2.34 \pm 0.20\,\mu_B$ and the angle between these moments and the a-axis is $\varphi = 22° \pm 5°$. The observed intensities and the calculated ones with these moments are compared in Table 3. The reliability factor is 5.3%. The symmetry of this magnetic structure which is shown in Fig. 5 is lower than that of PrPt; the magnetic space group is Cc'.

Table 3. Crystal field parameters $B_l^m = \theta_l\, V_l^m$ *calculated in* PrPt *and* NdPt *using the point charge model. The multipoles of the* 4f *shell* $\theta_l(\alpha_J, \beta_J$ *and* $\gamma_J)$ *are also given*

	PrPt	NdPt
B_2^0 (cm^{-1})	-0.52	-0.22
B_2^2 (cm^{-1})	-0.29×10^{1}	-0.66
B_4^0 (cm^{-1})	-0.80×10^{-2}	-0.28×10^{-2}
B_4^2 (cm^{-1})	-0.97×10^{-1}	0.34×10^{-1}
B_4^4 (cm^{-1})	0.45×10^{-1}	0.16×10^{-1}
B_6^0 (cm^{-1})	-0.46×10^{-4}	0.19×10^{-4}
B_6^2 (cm^{-1})	-0.52×10^{-3}	0.26×10^{-3}
B_6^4 (cm^{-1})	0.26×10^{-3}	-0.13×10^{-3}
B_6^6 (cm^{-1})	-0.48×10^{-3}	0.25×10^{-3}
α_J	-2.101×10^{-2}	-0.643×10^{-2}
β_J:	-7.364×10^{-4}	-2.911×10^{-4}
γ_J	60.994×10^{-6}	-37.988×10^{-6}

This direction of the magnetic moments can appear to be surprising but it is close to that observed in the isomorphous NdNi compound. Indeed in this last compound, neutron diffraction experiments and magnetization measurements on a single crystal have shown that the Nd magnetic moment reach $2.55\,\mu_B$ and make an angle of 24.50° with the a-axis [3].

With the values $M(\text{Nd}) = 2.34\,\mu_B$ and $\varphi = 22°$ we can expect a value of $N(\text{Nd})/2\ (\sin\varphi + \cos\varphi) = 1.46 \pm 0.12\,\mu_B$ for the magnetization extrapolated in zero internal field and measured on a polycrystalline sample. The observed value $(1.44\,\mu_B)$ is in agreement with this last value. If the Nd moment was along *a* or *c* the spontaneous magnetization on a polycrystal would be $M(\text{Nd})/2 = 1.17 \pm 0.10\,\mu_B$, a value which is smaller than observed.

6. DISCUSSION

In order to understand the magnetic properties and especially the magnetic structures of PrPt and NdPt, as well as those of PrNi and NdNi, we can examine the crystalline electric field (CEF) effects in these compounds. In the point symmetry (mm) of the rare earth site the CEF perturbing Hamiltonian has nine terms:

Table 4. Calculated magnetization on rare earth atoms along each crystallographic direction (a, b, c) when a field of 1 kOe is applied along this direction. B_l^m's are those reported in Table 3. We have verified that at the maximum moment direction was associated the minimum of the energy

		M_a (μ_B)	M_b (μ_B)	M_c (μ_B)	Easy axis
PrPt	All B_l^m's	0.14	0.003	0.31	z
	B_2^m's only	0.67	0.001	0.02	x
	B_4^m's only	0.006	0.15	0.17	z
	B_6^m's only	0.11	0.09	0.16	z
NdPt	All B_l^m's	1.13	0.32	2.39	z
	B_2^m's only	2.00	0.36	1.85	x
	B_4^m's only	0.90	1.52	1.86	z
	B_6^m's only	1.91	1.02	1.22	x

$$\mathcal{H}_c = V_2^0\alpha_J O_2^0 + V_2^2\alpha_J O_2^2 + V_4^0\beta_J O_4^0 + V_4^2\beta_J O_4^2 + V_4^4\beta_J O_4^4 + V_6^0\gamma_J O_6^0 + V_6^2\gamma_J O_6^2 + V_6^4\gamma_J O_6^4 + V_6^6\gamma_J O_6^6,$$

where the O_l^m's are the equivalent Stevens operators, the V_l^m's are the CEF coefficients which depend essentially on the surroundings and the θ_l's ($\alpha_J, \beta_J, \gamma_J$) are coefficients characteristic of the multipoles of the $4f$ shell of the ion [5]. The simplest way to calculate the V_l^m's is the point charge model which generally fails for the fourth and sixth order terms but gives rather well account for the second order terms. We have considered a charge $+3e$ on rare earth atoms and a zero change for Pt. In order to take into account the screening by the $5s^2 6p^1$ electrons, the V_l^m's terms were multiplied by the factor 0.5 as generally used. The B_m^1's ($B_l^m = V_l^m \times \theta_l$) then obtained are reported on Table 3. With such CEF coefficients we have calculated the effect of a field of 1 kOe applied along **a**, **b** and **c**. The results are reported in Table 4. We have also performed this calculation considering separately the second, fourth and sixth order terms.

Considering all the V_l^m's, the magnetization values obtained show that **c** is the easy magnetization direction, in agreement with the magnetic structure of PrPt. In PrPt (as well as in PrNi) this model shows that the anisotropy which is high between the **a** and **c** directions is more important between the **b** and **c** directions. We note that the second order terms give rise to a big anisotropy between the **b** direction and the (a, c) plane. As well, the calculated values of the magnetization for Nd tend to show that the anisotropy in the (a, c) plane is lower in NdPt than in PrPt. The main difference between PrPt and NdPt arises from the change of the easy direction (**c** in PrPt, **a** in NdPt) when only the sixth order terms are considered. This difference arises from the opposite sign of those terms in both compounds due to the γ_J coefficient. This result allows to understand why moments are in the (a, c) plane in NdPt. The point charge model favours the **c**-axis in NdPt but we can show that increasing the fourth and sixth order terms makes the easy direction along the **a**-axis in NdPt, whereas it remains along **c** in PrPt. In conclusion, the change of the magnetization direction between PrPt and NdPt (as well as between PrNi and NdNi) arises from the change of sign of the γ_J coefficient between Pr^{3+} and Nd^{3+} ions. The intermediate direction in NdPt is a result of the competition between second and sixth order terms which favour the **a**-axis and the fourth order terms which favour the **c**-direction.

In both compounds the value of the magnetization is smaller than the free ion value ($3.20\,\mu_B$ for Pr^{3+} and $3.27\,\mu_B$ for Nd^{3+}). In the molecular field approximation the ordering temperature leads to molecular field of 305 and 439 KOe acting on the rare earth ions respectively in PrPt and NdPt. With these values and the point charge model, the values of the magnetization are 2.82 and $3.21\,\mu_B$ on Pr^{3+} and Nd^{3+} respectively. This result shows that the B_l^m values must be higher than those given with the point charge model, especially fourth and sixth order terms, as it has been suggested above. This is in agreement with the experimental values determined in cubic and hexagonal compounds [6–8].

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