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On new ternary gallides $LnPd_2Ga$ with the YPd_2Si-type structure

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Abstract

The compounds $LnPd_2Ga$ (Ln ≡ La, Ce, Pr, Nd, Sm, Gd, Tb, Dy) were found to crystallize in the orthorhombic YPd_2Si-type structure (space group, *Pnma; Z* = 4; *oP*16) an ordered variant of the Fe_3C type. The compounds with Ln ≡ Ce, Nd, Sm, Gd, Tb, Dy order magnetically with ordering temperatures of 3–24 K. No superconductivity was detected down to 1.6 K.

1. Introduction

Three basic types of crystal structure are known for the ternary compounds LnT_2X, where Ln ≡ La, ..., Lu, Y, Sc; T ≡ Ni, Pd, Pt and Cu, Ag, Au; X ≡ Al, Ga, In, Tl, Si, Ge, Sn, Pb [1]. The dominating structure type is the cubic $MnCu_2Al$ (Heusler) type. The second frequent type is the orthorhombic YPd_2Si type [2], an ordered version of the Fe_3C type which is very common among the Ln_3T phases. The YPd_2Si type has been found up to now in $LnPd_2Si$ [2] and $LnPd_2Ge$ [3] and in the heavy rare earth $LnPt_2Si$ [2] members as well as in YPd_2Ga [3]. The third structure type, the hexagonal $GdPt_2Sn$ type (also known as the $ZrPt_2Al$ type [4]), an ordered version of the TiAs type [5], is found with the heavier rare earth elements in the series $LnPt_2In$ and $LnPt_2Sn$, and in $LaPd_2In$ [6] and $CePd_2In$. In the $LnPd_2In$ series the members with the smaller Ln atoms Sm, Gd, ..., Tm, Lu adopt the Heusler-type structure. To our knowledge, in no LnT_2X series with Ln ≡ La, ..., Lu, Y, Sc were all three structure types identified up to now. In the series $LnPd_2In$ and $LnPt_2In$ a change from the $ZrPt_2Al$ type to the Heusler type occurs with decreasing Ln radius while in the $LnPd_2Ga$ series a transition from the YPd_2Si type to the Heusler type must occur somewhere between yttrium and scandium. As a preliminary result of our investigations on these systems we report our findings in the $LnPd_2Ga$ system.

2. Experimental details

Polycrystalline samples of these alloys were prepared by reacting the constituent elements (minimum 99.9% grade) in an argon arc furnace. The resulting buttons have a silvery metallic lustre and are rather brittle. The compounds with the lighter Ln appear to melt congruently. Increasing difficulties in obtaining homogeneous single-phase samples with Ln ≡ Dy, Y appeared to indicate a peritectic reaction for the representatives with the smaller rare earth elements. Most of the isotypic germanides form peritectically between 910 and 1065 °C [3]. Annealing of the polyphase "$DyPd_2Ga$" sample at 800 or 650 °C, however, destroyed the YPd_2Si-type phase completely and its Guinier pattern looked very similar to that of "$HoPd_2Ga$". Remelting of the annealed $DyPd_2Ga$ sample reproduced the impure YPd_2Si-type phase. Thus the YPd_2Si-type $DyPd_2Ga$ is a high temperature phase. It may decompose at lower temperatures or transform to a low temperature modification of the type met in $HoPd_2Ga$. In the case of $HoPd_2Ga$, no trace of a YPd_2Si-type phase was detectable in a rapidly cooled sample or in an annealed sample.

The room-temperature lattice parameters were derived from Guinier patterns taken with Cu $K\alpha_1$ radiation and silicon as internal standard (assuming that a = 5.43047 Å at 22 °C). As we started with the cerium compound we had no problems with foreign lines in indexing the Guinier patterns. Magnetic measurements were carried out from 1.6 K to room temperature in magnetic fields of 0.2, and 2–98 kOe.

3. Results and discussion

Intensity calculations with LAZY PULVERIX [7] using the site parameters of YPd_2Si led to fair agreement with our Guinier patterns. Nevertheless, confirmation of our structure assignment by a complete structure determination on single crystals is highly desired. The

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lattice parameters are listed in Table 1. In Fig. 1 we compare our data for the $LnPd_2Ga$ compounds with those obtained by Jorda *et al.* [3] for the $LnPd_2Ge$ compounds. The lattice parameters and the unit-cell volumes are plotted *vs.* the rare earth ionic radii r derived by Shannon [8] (except lanthanum) from oxides. In both gallides and germanides, $a(r)$ and $b(r)$ are fairly linear whereas $c(r)$ is curved, strongest in the gallides, less in the germanides and least in the silicides [2] (not shown). In the gallium compounds, a is smaller, while b and (although less pronounced) c are larger than in the corresponding germanium compounds. However, the unit-cell volumes are virtually the same. The values for the yttrium compound deviate distinctly for both gallium and germanium (those of Jorda *et al.* [3] for YPd_2Ga disagree even more). This might be due to deviations in stoichiometry, as it occurred (in the other direction) also in our first sample of $SmPd_2Ga$, where we observed a weight loss as a consequence of the evaporation of samarium. An explanation for the deviation of the values of $LaPd_2Ga$ may be found in an instability of the structure. Possibly the lanthanum radius is nearly too large for the YPd_2Si structure (in the $LnPd_2Si$ and $LnPt_2Si$ series the upper limits of existence are at $Ln \equiv Ce$ and $Ln \equiv Gd$ respectively [2]). As pointed out by Moreau *et al.* [2] the ternary Fe_3C-type derivatives differ from the binary Ln_3T representative by $b/a < 1$ compared with $b/a > 1$ for the latter. The coordination of the atoms, however, is still similar. Although the structures of quite a number of compounds are assigned to the YPd_2Si type the only structure determination is that of the prototype. In YPd_2Si the silicon atom is located near the centre of a three-capped (Y + 2Pd) trigonal prism [Y_2Pd_4]. These prisms

TABLE 1. Room-temperature (295 K) lattice parameters and X-ray densities of the YPd_2Si-type $LnPd_2Ga$ compounds (space group *Pnma* (No. 62)), where the data of Jorda *et al.* [3] for YPd_2Ga are added for comparison and the estimated standard deviations are given in parentheses

Ln	a (Å)	b (Å)	c (Å)	V (Å^3)	d_x (g cm^{-3})
La	7.5759(6)	7.0598(4)	5.8782(4)	314.39(6)	8.908
Ce	7.5574(7)	7.0478(6)	5.7902(5)	308.41(8)	9.106
Pr	7.5200(9)	7.0521(8)	5.7576(7)	305.3(2)	9.22
Nd	7.4844(9)	7.0549(9)	5.7264(6)	302.4(2)	9.38
Sm	7.4139(7)	7.0587(8)	5.6766(5)	297.07(8)	9.682
Gd	7.3629(6)	7.0703(7)	5.6414(4)	293.68(8)	9.951
Tb	7.3212(7)	7.0718(7)	5.6164(4)	290.78(7)	10.087
Dy	7.292(2)[a]	7.069(3)[a]	5.604(2)[a]	288.9(4)	10.24
	7.289(2)[b]	7.063(2)[b]	5.604(2)[b]	288.5(3)	
Y	7.3217(9)	7.0671(7)	5.5914(9)	289.3(2)	8.53
	7.351 [3]	7.058 [3]	5.612 [3]	291.2	

[a]Rapidly cooled.
[b]After annealing at 800 °C, remelting and fast cooling.

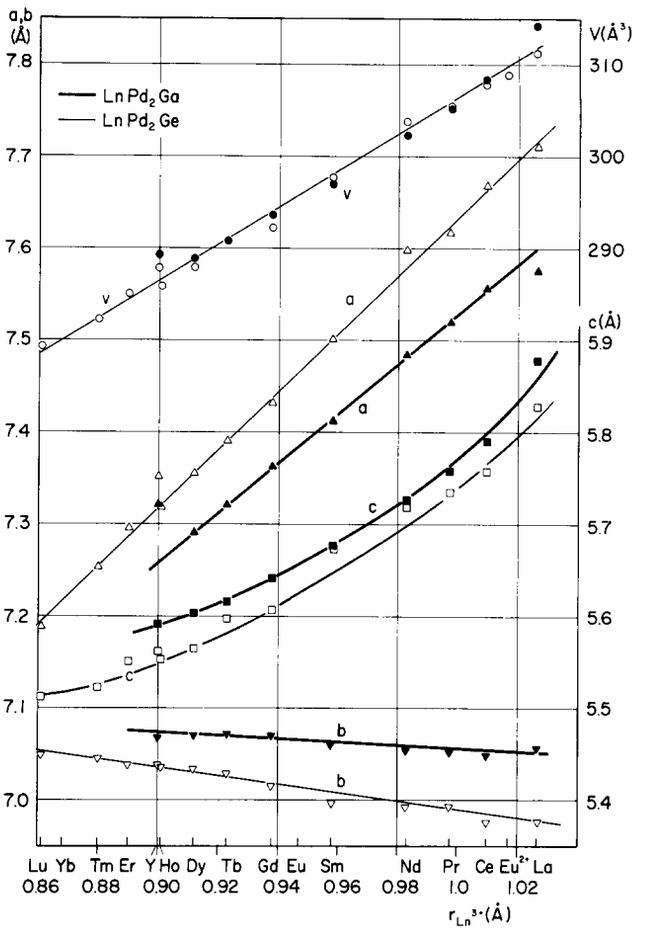

Fig. 1. Rare earth radius dependence of the lattice parameters and unit-cell volumes of the YPd_2Si-type $LnPd_2Ga$ compounds (full symbols). The corresponding data for the isotypic $LnPd_2Ge$ compounds [3] (open symbols) are added for comparison.

are deformed as the edges are of different length and not parallel. They are connected via corners so that layers parallel to (a, b) are formed consisting of silicon-centred and empty oblique prisms. Neighbouring layers are correlated via mirror symmetry relative to the unit-cell centre. The coordination of the yttrium atoms may be described by a pentagonal prism of palladium atoms (although two edges are longer) capped by 3Si + 2Y in the equatorial plane. In the yttrium sublattice the yttrium atoms are surrounded by a deformed yttrium tetrahedron which is part of two slightly different crossing zigzag chains (they would be identical if $a = b$ and $z_Y = \frac{1}{8}$). Palladium, finally, has three silicon, four palladium and three (or four?) yttrium neighbours. The segment of the YPd_2Si structure given in the review by Parthé and Chabot [9] and reproduced in ref. 3 shows such a layer in an idealized version, namely with parallel prism edges (this already requires $z_{Pd} = 0.5 + z_{Ln}$) and the silicon atoms located in the equatorial plane. We wondered whether such a symmetrization is realistic for the $LnPd_2Ga$ representatives or not. If we make

TABLE 2. Coordinates for YPd_2Si

	Calculated coordinates			Coordinates from single-crystal data [2]		
Pd 8d	0.1784	0.0475	0.6233	0.1767(5)	0.0517(5)	0.5928(8)
Y 4c	0.0353	¼	0.1233	0.0303(9)	¼	0.144(2)
Si 4c	0.3922	¼	0.8767	0.363(3)	¼	0.853(5)

such symmetry assumptions and claim that the three Ln–Ga distances are of equal length and that the equatorial plane of one prism coincides with the top plane of the upper and lower prism, then we obtain conditions for the site parameters which (with the exception of YPd) only depend on the ratio c/a:

$$x_{Ln} = \frac{c}{a}\tan\alpha\, z_{Ln} \quad y_{Ln} = \tfrac{1}{4} \quad z_{Ln} = 0.5\cos(2\alpha) - 0.25$$

$$x_{Ga} = 0.5 - \frac{c}{a}\tan\alpha\,(0.5 - z_{Ln}) \quad y_{Ga} = \tfrac{1}{4} \quad z_{Ga} = 1 - z_{Ln}$$

$$x_{Pd} = \frac{c}{a}\tan\alpha\,(0.5 + z_{Ln}) \quad y_{Pd} = ? \quad z_{Pd} = 0.5 + z_{Ln}$$

with $\sin(2\alpha) = a/2c$, where α is the angle between the prism edge and the a axis. For the parameter y_{Pd} we need an additional condition, preferably one that connects the two layers. Of course, the resulting Pd–Pd distance along the b direction in the triangular prism faces has to be at least as large as the diameter of the palladium atom. In YPd_2Si this distance indeed corresponds to the diameter of metallic palladium. We chose another distance to fix the y_{Pd} parameter. The four distances Ga–Pd in one prism should be equal to the two distances Ga–Pd with palladium of a neighbouring layer. This leads to the value

$$y_{Pd} = (x_{Ga} + x_{Pd} - 4x_{Ga}x_{Pd} - 0.25)\left(\frac{a}{b}\right)^2 + (0.25 - 2z_{Ln})^2\left(\frac{c}{b}\right)^2$$

For YPd_2Si we obtain with the idealized positional parameters the coordinates in Table 2.

Our condition equalizes the Pd–Si distances (2.40(2) and 2.69(2) Å within the prism and 2.49(2) Å to the neighbouring prism, [2]) to 2.517 Å and changes also the Y–Y distances (3.832 Å, prism edge along the a axis; 3.829 Å, along the b axis) to 3.907 Å and 3.750 Å respectively. Either our condition for y_{Pd} or the whole symmetrization is non-realistic. Intensity calculations based on our model site parameters showed distinctly less agreement than with the experimental values [2] of YPd_2Si.

The results of our preliminary magnetic measurements are summarized in Table 3. $TbPd_2Ga$ undergoes a first-order transition to ferromagnetic order at 24 K; all other compounds with magnetic Ln ions, except praseodymium, become antiferromagnetic with Néel temperatures higher than 1.6 K. Above the ordering temperature, crystal field effects give rise to deviations from the Curie–Weiss law, which are pronounced in the cerium compound and, in particular, in the samarium compound where, however, the main disturbance stems from the $^6H_{7/2}$ state. In a crude estimate, neglecting the splitting of ground state and first excited state, we obtain for the $^6H_{7/2}$–$^6H_{5/2}$ separation about 1300 K, a value which at least is of the correct order of magnitude. The ordering temperatures do not fit a de Gennes relation although the magnetic interactions are expected to be mediated, at least to a great part, by the conduction electrons (Ln–Ln about 3.9 Å in the stretched zigzag chains). Surprisingly, measurements of the spontaneous magnetization of $TbPd_2Ga$ led to the same value with both a polycrystalline bulk sample and loose fine powder. The observed magnetic moment is less than half that expected for collinear Tb^{3+} moments. In the antiferromagnetic gadolinium compound the saturation moment is also too small. In both compounds, no further magnetic transition is observed up to 98 kOe.

In the $LnPd_2Ga$ compounds we did not detect any indication of superconductivity down to 1.6 K. This behaviour is similar to that of the $LnPd_2Ge$ compounds which were found to be normal down to 1.1 K [3]. On the contrary, quite a number of Heusler-type LnT_2X

TABLE 3. Preliminary magnetic data for the $LnPd_2Ga$ compounds (polycrystalline samples): Néel temperature T_N, Curie temperature T_C, paramagnetic Curie temperature Θ_p and effective Bohr magneton number n_p derived from the Curie–Weiss (CW)-like part of $1/\chi(T)$

Ln	T_N (K)	T_C (K)	Θ_p (K)	n_p (μ_B)	Remarks
Ce	3		−8	2.65	057μ_B near T_N; CW law 250–300 K
Pr	<1.6		−10	3.53	No order; CW law above 100 K
Nd	3		−8	3.60	CW law 100–300 K
Sm	6				0.5μ_B (6–8 K); 0.97μ_B (10–30 K)
Gd	21		+21	8.05	At 3 K ferromagnetism saturated in 41 kOe; 4.1μ_B
Tb		24	+25	9.50	Spontaneous magnetization 4.2μ_B at 2.6 K; CW law 50–300 K
Dy	19				The sample contained two foreign phases

analogues with the heavier B elements are superconducting at low temperatures: YPd_2In [10], $ScPd_2Sn$ [9, 10], $LuPd_2Sn$ [11], YPd_2Pb [10], YPd_2Sb [10], YAu_2Sn [12], and even compounds with magnetic rare-earth elements such as $TmPd_2Sn$ and $YbPd_2Sn$ [11], the latter exhibiting the coexistence of superconductivity and antiferromagnetism.

It is noteworthy that the YPd_2Si type of structure is not stable through the whole $LnPd_2Ga$ series. We do not yet know whether one or two different novel structure types occur with the smaller Ln atoms holmium, erbium and thulium (the Guinier patterns of the erbium and thulium sample were similar but different from that of holmium), or rather a stability gap. With the distinctly smaller scandium the cubic Heusler type appears [1].

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