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On the rare-earth palladium aluminides LnPdAl

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Abstract

A hexagonal ZrNiAl- or Fe_2P-type high-temperature modification was identified for the compounds LnPdAl with Ln = Sm, Gd ... Tm, Lu, Y. YbPdAl and its Pt analogue were obtained only in the orthorhombic TiNiSi structure, LaPdAl only in the orthorhombic LaNiAl structure. CePdAl transformed to an unknown low-temperature modification, while PrPdAl and NdPdAl retained the ZrNiAl structure on annealing at 700 °C. ScPdAl crystallizes in the hexagonal $MgZn_2$ structure. Antiferromagnetic ordering was observed in hexagonal TbPdAl, whereas DyPdAl and HoPdAl appear to undergo a transition to ferromagnetic order.

Keywords: Aluminium; Palladium; Rare earth metals

Ten years ago Dwight [1] reported the structures of the ternary lanthanide aluminides LnPdAl (Ln = Sm, Gd ... Tm, Y) and LnPtAl (Ln = Sm, Gd ... Tm, Lu, Y). He found all these compounds to crystallize in the orthorhombic TiNiSi-type structure, an ordered version of the Co_2Si type.

Interested in finding a relation between the $LnPd_2X$, $LnPt_2X$ and the LnPdX, LnPtX phases, we tried to complete the latter rare-earth series [2]. The results on the LnPdAl series turned out to be exceptional. While we failed to index the X-ray patterns of LaPdAl and EuPdAl, the patterns of the compounds with Ln elements between La and Eu were compatible with the hexagonal ZrNiAl type, an ordered version of the Fe_2P type. Surprisingly, we found the same hexagonal structure in LuPdAl. We then conjectured that the discrepancy might be due to the different preparation method. Dwight had prepared his samples also by arc-melting, and annealed them for an unknown time at 800 °C. Our samples, however, were not annealed.

A preliminary confirmation of our assumption, that the annealed samples of Dwight represented the low-temperature modification while our more or less quenched samples retained the high-temperature structure, was found in our hexagonal ErPdAl sample. In order to provide a full proof of this hypothesis, we decided to investigate Dwight's series in the quenched and annealed state. Thus, one part of the samples was kept at 750 °C for seven weeks. Indeed, all the rapidly cooled samples turned out to be hexagonal whereas the annealed samples were orthorhombic (Tables 1 and 2). As far as we can judge from intensity calculations with LAZY PULVERIX [3], and based on average site parameters [4], the ordering appears to be fairly complete in all the hexagonal modifications. YbPdAl was synthesized in a closed tantalum tube after an attempt by arc-melting had failed. Either the cooling was too slow or a hexagonal high-temperature modification does not

Table 1
Structural parameters at $T = 295$ K of the hexagonal compounds *Ln*PdAl. ZrNiAl type, space group $P\bar{6}2m$ (No. 189), $Z = 3$, hP9, for all *Ln* except Sc. ScPdAl: $MgZn_2$ type, space group $P6_3/mmc$ (No. 194), $Z = 4$, hP12. The standard deviations of the last digit, added in parentheses, refer to the statistical error only. The additional uncertainty due to calibration, impurities and deviation from ideal stoichiometry may be larger

Ln	a (Å)	c (Å)	c/a	V (Å^3)	d_X (g cm^{-3})
Ce*	7.2198(2)	4.2329(2)	0.58629(6)	191.08(2)	7.131
Pr*	7.2004(3)	4.2141(4)	0.58526(7)	189.22(4)	7.222
Nd*	7.1864(4)	4.1857(3)	0.58245(7)	187.21(4)	7.388
Sm	7.1427(3)	4.1491(3)	0.58088(5)	183.32(3)	7.711
Gd	7.2003(7)	4.0359(6)	0.5605(2)	181.21(6)	7.990
Tb	7.1869(6)	3.9957(6)	0.5560(2)	178.73(5)	8.148
Dy	7.1863(3)	3.9589(3)	0.55089(6)	177.06(3)	8.325
Ho	7.1830(4)	3.9378(3)	0.54820(6)	175.95(3)	8.447
Er*	7.1787(4)	3.9062(4)	0.54414(8)	174.33(5)	8.592
Tm	7.1693(4)	3.8837(3)	0.54171(6)	172.88(3)	8.712
Lu*	7.1565(4)	3.8498(5)	0.53795(9)	170.76(5)	8.996
Y	7.2216(3)	3.9419(3)	0.54585(6)	178.03(3)	6.221
Sc	5.2846(3)	8.4977(6)	1.6080(2)	205.52(4)	5.764

* Data from Ref. [2].

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Table 2
Room-temperature structural parameters of the orthorhombic modifications of *Ln*PdAl and YbPtAl. LaPdAl: LaNiAl type, space group *Pnma* (No. 62), $Z=8$, oP24. All remaining compounds: TiNiSi type, same space group, $Z=4$, oP12. The data of Dwight [1] and Cordier et al. [5] are added in italics for comparison. As for the error, see Table 1

*LnT*Al	a (Å)	b (Å)	c (Å)	V (Å^3)	d_X (g cm^{-3})
LaPdAl	7.3277(4)	4.3209(2)	16.4990(11)	522.39(6)	6.925
SmPdAl	7.0069(4)	4.4727(3)	7.7898(4)	244.13(4)	7.720
	7.013	*4.493*	*7.766*	*244.70*	
GdPdAl	6.9602(4)	4.4482(3)	7.7630(5)	240.34(5)	8.033
	6.975	*4.446*	*7.754*	*240.46*	
TbPdAl	6.9166(5)	4.4297(3)	7.7429(4)	237.23(5)	8.185
	6.915	*4.43*	*7.746*	*237.29*	
DyPdAl	6.8807(5)	4.4157(3)	7.7366(5)	235.06(4)	8.361
	6.884	*4.415*	*7.733*	*235.03*	
HoPdAl	6.8544(3)	4.4049(2)	7.7254(3)	233.25(2)	8.495
	6.851	*4.405*	*7.729*	*233.25*	
ErPdAl	6.8192(7)	4.3905(3)	7.7200(6)	231.13(5)	8.640
	6.826	*4.408*	*7.713*	*232.08*	
TmPdAl	6.7909(4)	4.3754(2)	7.7142(3)	229.22(3)	8.761
	6.790	*4.380*	*7.712*	*229.36*	
YbPdAl	6.8079(3)	4.3473(2)	7.7889(3)	230.52(3)	8.830
	6.819(2)	*4.350(1)*	*7.801(2)*	*231.4(2)*	
LuPdAl	6.7401(7)	4.3543(4)	7.7150(7)	226.42(6)	9.046
YPdAl	6.9136(4)	4.4298(3)	7.7119(3)	236.18(3)	6.252
	6.89	*4.415*	*7.73*	*235.1*	
YbPtAl	6.7511(5)	4.3384(3)	7.6736(5)	224.75(4)	11.677
	6.769(2)	*4.348(1)*	*7.690(2)*	*226.3(2)*	

exist: the X-ray pattern of YbPdAl (and YbPtAl) showed mainly the orthorhombic phase reported recently by Cordier et al. [5]. Several faint lines were neither indexable on the basis of a hexagonal ZrNiAl-type cell nor based on the orthorhombic CaPdAl type [6]. The latter structure could be expected for YbPdAl with purely divalent Yb.

As can be deduced from Figs. 1 and 2, Yb is not trivalent either. Moreover, we can see that it is impossible to derive an effective radius for the Yb "ion", which points to the influence of the valence-electron concentration. From the c axis alone one would derive an effective Yb radius similar to that of Pr^{3+}, which would imply a valence only slightly larger than +2 (according to Shannon [7] the ionic radius of Yb^{2+} is 1.02 Å, only 0.01 Å larger than the radius of Ce^{3+}, 1.01 Å). From the a axis and the cell volume, on the other hand, one would derive a valence close to +3, whereas from the b axis a totally unreasonable valence greater than three would result. The intermediate valence of Yb is confirmed by the magnetic and electrical measurements of Cordier et al. [5].

The influence of the valence-electron concentration is demonstrated also by ThPdAl [8] with tetravalent Th. Its volume corresponds to that of the hexagonal CePdAl, the a axis would suggest a Th radius larger than that of La^{3+}, the c axis corresponds to Pm^{3+}, whereas Shannon's Th^{4+} radius (0.94 Å) is nearly the same as that of Gd^{3+} (0.938 Å). For YbPtAl, on the other hand, the lattice parameters point to trivalent Yb. The differences between our values and those of Cordier et al. [5] may be due to impurities, annealing and slightly different stoichiometry.

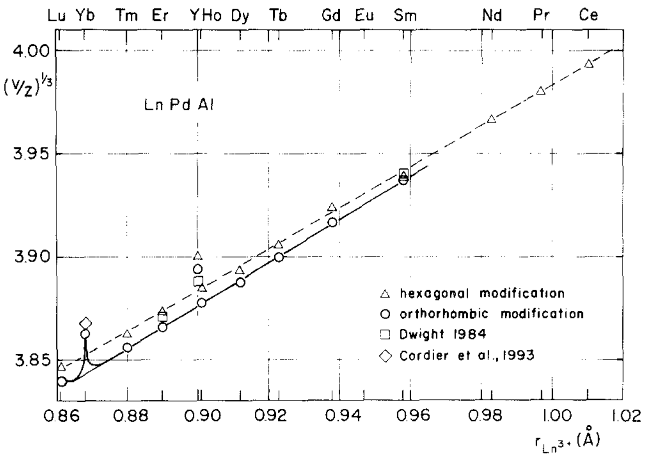

Fig. 1. Comparison of the specific volumes of the hexagonal high-temperature and the orthorhombic low-temperature modifications of the LnPdAl compounds. The cube root of the unit-cell volume per formula unit is plotted vs. the rare-earth radius [7].

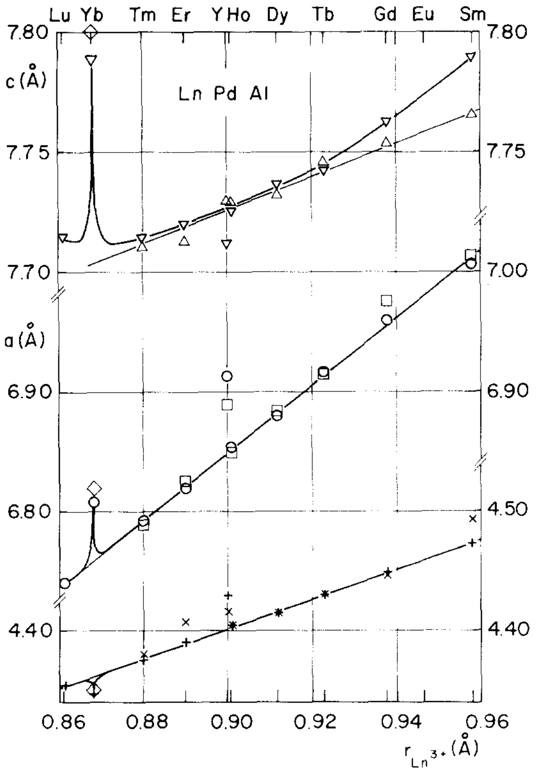

Fig. 2. Dependence of the lattice parameters a, b and c of the LnPdAl low-temperature modifications on the size of the Ln element. The radii of the trivalent six-coordinated rare-earth ions of Shannon [7] are used. Faint symbols: data from Refs. [1,5].

Another stray shot is due to yttrium. In this case our lattice parameters deviate even more than those of Dwight [1], particularly those of the hexagonal phase. This may be due to deviations in the stoichiometry, since an energy-dispersive X-ray analysis revealed no remarkable impurities.

An attempt to prepare orthorhombic low-temperature modifications of CePdAl, PrPdAl and NdPdAl was not successful. After four weeks at 700 °C, CePdAl had transformed to an unknown structure (which appears to be different from that of LaPdAl) while PrPdAl and NdPdAl had retained the hexagonal ZrNiAl structure. Their transformation temperature thus must be lower than 700 °C. LaPdAl also remained unchanged. Its X-ray pattern was indexed based on the orthorhombic LaNiAl-type structure [9].

The Sc^{3+} ion is distinctly smaller than Lu^{3+}, so that we were prepared to meet a different structure in ScPdAl. Our ScPdAl sample (probably not phase-pure, since our starting scandium metal contained non-negligible amounts of tantalum) was found to crystallize in the hexagonal $MgZn_2$ structure like ScNiAl [4]. This structure type occurs also in the LnNiAl series (with Ln = Sm, Gd ... Lu, including Yb^{3+}) when prepared at high pressure [10], whereas the normal-pressure phases with Ln = Pr, Nd, Sm ... Tm crystallize in the ZrNiAl structure. The $MgZn_2$ structure is also adopted by ZrPdAl and HfPdAl [11], which both contain one additional valence electron per formula unit.

Hexagonal TbPdAl was found to be antiferromagnetic below $T_N = 43$ K. At 4 K a magnetic transition was observed near 6.5 kOe; ferromagnetic saturation was reached near 13.5 kOe (5.2 μ_B for the polycrystalline sample, constant up to 100 kOe). DyPdAl and HoPdAl both appear to be ferromagnetic below 24 K and 6.5 K, respectively.

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