

THERMODYNAMIC AND CRYSTALLOGRAPHIC PROPERTIES OF REPd INTERMETALLIC COMPOUNDS

A. PALENZONA AND S. CIRAFICI

Istituto di Chimica Fisica, Università di Genova, Genova (Italy)

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ABSTRACT

REPd phases have been extensively studied both by thermal, crystallographic, thermodynamic and micrographic methods. As a result of this investigation a possible sequence of structures is proposed which is correlated with the thermal and thermodynamic data.

Europium is a divalent rare earth in EuPd while ytterbium in YbPd seems to be present with a certain, fixed percentage of atoms in the trivalent state.

INTRODUCTION

As a part of a research dealing with the study of the alloying behaviour of the rare earths (RE) with the transition metals, after the determination of the Eu-Pd¹, Yb-Pd² phase diagrams and of the crystallographic and thermodynamic properties of the RE₆₈Pd₂₈ compounds^{3,4}, we have directed our attention to the REPd equiatomic composition in order to determine the crystal structures of such phases, their polymorphism and if possible the heats of formation together with other thermodynamic properties which could provide a measure of their relative stability.

Data on these compounds are scarce and can be summarized in Table 1. Moreover the works of Loebich and Raub⁵ indicate the presence of polymorphic transformation in the solid state and the existence of small ranges of homogeneity for

TABLE 1
CRYSTALLOGRAPHIC PROPERTIES OF
REPd PHASES FROM LITERATURE

l = low temperature modification; h = high temperature modification.

<i>Comp.</i>	<i>Struct. type</i>	<i>Ref.</i>	<i>Comp.</i>	<i>Struct. type</i>	<i>Ref.</i>
SmPd (l)	CrB	5	ErPd (h)	CsCl	5
GdPd (l)	CrB	6	TmPd	CsCl	8
EuPd	CrB	1, 7	YbPd	CsCl	2
DyPd (h)	CsCl	5	LuPd	CsCl	8
HoPd (h)	CsCl	5			

these phases. It was therefore considered that a more detailed investigation on this subject would be worthwhile.

EXPERIMENTAL

The RE metals and Pd used in this research, both for crystallographic and thermodynamic study were commercial products with a purity of 99.5 and 99.9%, respectively.

REPd compounds for the crystallographic study were prepared by direct synthesis of the two metals in arc-welded molybdenum crucibles. The samples were heated above the melting temperature, well shaken to ensure homogenization and allowed to cool to room temperature.

Differential thermal analysis (DTA) was carried out, up to 1500°C, using a conventional DTA apparatus and standard procedures on 1-g samples. Several thermal cycles were carried out to ensure reproducibility of the data. Characteristic temperatures were correct to within $\pm 5^\circ\text{C}$.

Thermodynamic properties were determined by means of the dynamic differential calorimetric method (DDC) previously described⁹ and used to evaluate the heats of formation, and the heats and entropies of fusion of REX_3 compounds, where X = Sn, Pb, In, Tl¹⁰ and other RE-Pd phases⁴. Values reported in Table 4 are the average values of, at least, three or four determinations. The total error of these results is evaluated to be of the order of 5 to 6%.

An X-ray powder diffraction investigation was carried out on cast and annealed samples using Cu or Cr $K\alpha$ radiation; no single crystal could be obtained to support structure determination.

Samples for microscopic examination were prepared on silicon carbide papers and diamond polishing; as etching agent a 10% Nital solution was employed.

Thermal analysis results

Table 2 collects all thermal data obtained from DTA analysis for these phases obtained in the present work together with the known values.

Melting points increase almost linearly with RE atomic number except for EuPd and YbPd, due to the divalent or partially trivalent character of Eu and Yb, respectively, in these compounds. The values for Tm and Lu have been evaluated by extrapolation.

Transformation temperatures have a more irregular trend and show a sharp difference, if detected on heating or cooling curves, which increase for heavier RE compounds. For Ho and Er the transformation on cooling is no more detectable. Also Loebich and Raub⁵ found a small difference in these transformation temperatures but ascribe this difference to samples of slight different composition in the solid solution range. This seems not the case for our samples as they have been prepared on the equiatomic composition and it is an almost improbable reversible change in composition during the thermal cycles. Probably the observed differences can be

TABLE 2
THERMAL PROPERTIES FOR REPd PHASES

(+) = RE richer composition; (-) = Pd richer composition; T_m = melting point; n.o. = not observed.

<i>This work</i>			<i>Literature</i>			
<i>Comp.</i>	T_m	<i>Transf. temp. (°C)</i>	T_m	<i>Transf. temp. (°C)</i>		<i>Ref.</i>
		<i>heat. cool.</i>		(+)	(-)	
LaPd	1080	1015-1000	—	—	—	—
CePd	1130	1010-1005	1150	—	—	11
PrPd	1175	1020-1000	—	—	—	—
NdPd	1220	1045-1030	—	—	—	—
SmPd	1275	985-950	1270	982-960	—	5
EuPd	—	—	855	no transf.	—	1
GdPd	1380	1015-970	1380	1038-1005	—	5
TbPd	1420	885-790	—	—	—	—
DyPd	—	795-665	1450	798-770	—	5
HoPd	—	700-n.o.	1480	697-665	—	5
ErPd	—	560-n.o.	1540	565-548	—	5
TmPd	1570*	no transf.	—	—	—	—
YbPd	—	—	1460	no transf.	—	2
LuPd	1650*	no transf.	—	—	—	—

* Extrapolated value.

ascribed to the kinetic and to the kind of the transformation itself. Finally Tm, Yb, Lu and Eu show no transformation in the solid state.

The thermal effect observed for the solidification, if detected at high sensitivity, is not as sharp as might be expected but shows a faint second effect, close to the first (about 10°C below), which, excluding a change in the initial composition, could be ascribed to another transformation, near the melting point, for these alloys. This behaviour is not unusual as we have a similar situation for REAu compounds¹².

Crystallographic results

Table 3 contains the results obtained by X-ray investigation. From La to Tb, the low temperature modification of the REPd phases crystallizes with the CrB type of structure, as already found by Pierre and Siaud⁶ for GdPd. It should be pointed out that these patterns were difficult to obtain from powder specimens. The alloys are somewhat ductile and could not be easily crushed into powders. Preparation of powders by filing apparently destroyed the crystalline nature of the samples, and X-ray photographs could only be obtained after prolonged heat treatment (50 days at 400°C) of the filings. With this procedure the resulting powder patterns were adequate for identification of the structure involved; all the patterns were indexed on the basis of a CrB type of structure and the lattice parameters were refined with the aid of a computer. Single crystals were not obtained from any of these alloys; the structure could thus not be verified in this manner. In order to identify the high

TABLE 3

CRYSTALLOGRAPHIC DATA FOR REPd PHASES

R = cubic root of the unit formula volume.

Comp.	Struct. type	Lattice constants (Å)			<i>R</i>	Ref.
		<i>a</i>	<i>b</i>	<i>c</i>		
LaPd (I)	CrB	3.945	11.032	4.660	3.701	this work
CePd (I)	CrB	3.890	10.910	4.635	3.664	this work
PrPd (I)	CrB	3.850	10.826	4.614	3.636	this work
NdPd (I)	CrB	3.832	10.776	4.609	3.624	this work
SmPd (I)	CrB	3.771	10.666	4.574	3.583	this work
		3.77	10.65	4.56	—	5
EuPd	CrB	4.097	11.121	4.447	—	1
		4.092	11.075	4.450	—	7
GdPd (I)	CrB	3.745	10.597	4.558	3.563	this work
		3.736	10.55	4.548	—	6
TbPd (I)	CrB	3.722	10.523	4.554	3.546	this work
DyPd (h)	CsCl	3.486	—	—	—	this work
		3.486	—	—	—	5
HoPd (h)	CsCl	3.469	—	—	—	this work
		3.467	—	—	—	5
ErPd (h)	CsCl	3.459	—	—	—	this work
		3.455	—	—	—	5
TmPd	CsCl	3.440	—	—	—	this work
		3.440	—	—	—	8
YbPd	CsCl	3.447	—	—	—	2
LuPd	CsCl	3.417	—	—	—	this work
		3.417	—	—	—	8

temperature modification, samples of these phases were quenched from the melt but always without success.

The structure of the high temperature modification of Dy, Ho and Er compounds corresponds to the CsCl type⁵ and this work confirms the result. The low temperature form, obtained after annealing the powders at 400°C, gives powder patterns of poor resolution; most of the lines could be tentatively indexed with the orthorhombic FeB type of structure, as this structure is related geometrically with the CrB type and both these modifications are often present for the same compound, but without the support of single crystal investigation such results are inconclusive. Finally Eu, Tm, Yb and Lu show no structural modification in the range of temperatures explored (up to 1500°C) and crystallize with the CrB or CsCl type of structure.

Thermodynamic results

Table 4 shows the results obtained from thermodynamic measurements on REPd phases. The reaction between elemental RE's and Pd takes place at temperatures (*T_r*) of about 600°C below the melting point of the corresponding compound and the same, almost linear trend is observed for melting temperatures. The reaction

TABLE 4

THERMODYNAMIC PROPERTIES OF REPd PHASES,
OBTAINED IN THE PRESENT WORK

T_r = temperature at which the reaction starts; ΔH_r = heat of formation at T_r ; ΔH_t = heat of transformation; ΔS_t = entropy of transformation.

<i>Comp.</i>	<i>Struct. type</i>	T_r ($^{\circ}\text{C}$)	ΔH_r (kcal g-at.^{-1})	ΔH_t (kcal g-at.^{-1})	ΔS_t ($\text{cal deg}^{-1} \text{g-at.}^{-1}$)
LaPd (l)	CrB	610	-13.5	0.4	0.3
CePd (l)	CrB	555	-15.2	1.2	0.9
PrPd (l)	CrB	600	-15.1	1.1	0.8
NdPd (l)	CrB	640	-16.1	1.0	0.8
SmPd (l)	CrB	685	-15.1	0.9	0.7
GdPd (l)	CrB	765	-15.0	0.7	0.6
TbPd (l)	CrB	800	-14.6	0.6	0.5
DyPd (h)	CsCl	835	-14.6	0.6	0.5
HoPd (h)	CsCl	885	-14.4	0.4	0.4
ErPd (h)	CsCl	910	-14.3	0.3	0.3
TmPd	CsCl	930	-14.2	—	—
LuPd	CsCl	970	-14.0	—	—

Note: from La to Tb the transformation corresponds to the change from the CrB to the FeB, TbNi or related structure while from Dy to Er from this last type to the CsCl one.

is very fast, highly exothermic and the heat evolved is sufficient to melt the samples which, in most cases, appeared homogeneous and single phase. Now, due to the existence of solid-state transformations, the problem arises to which of these modifications the measured heats of formation refer. From La to Gd and with some uncertainty for Tb, the reaction between RE's and Pd begins and ends in a temperature range which is always lower than the transformation temperature. The heat of formation can therefore be attributed to the low temperature modification. X-ray powder patterns taken on the samples so obtained, even of poor resolution, show the lines of this type of structure (CrB). From Dy to Er, however, the "reaction temperature" is always higher than the transformation temperature, so that the heats of formation refer to the high temperature modification (CsCl) and again the powder photographs show only the line of this type of structure. It should be remembered that as soon as the reaction is ended the sample is air-cooled to room temperature so that a quenching effect is observed with retention of this high temperature modification. For TmPd and LuPd there is no problem of this kind as these compounds have no transformation in the solid state, at least up to 1500 $^{\circ}\text{C}$.

At the transition temperatures we have also determined the heats of transformation and hence the entropy involved; these two values are almost unchanged if evaluated on heating or cooling curves although the temperature differences were detected in the two thermal cycles. The heats of formation of the unknown modifications can thus be determined by summing or subtracting the corresponding heats of formation and of transformation, bearing in mind that at the transformation

temperature the heats of formation of the high temperature phase is less exothermic than that of the low temperature phase.

We have also tried to determine heats and entropies of fusion for alloys, with melting points not higher than 1300°C due to the limits of our instruments, but some additional uncertainties arise for the overlapping of a "second" thermal effect to the solidification effect (see DTA results). These values range from 2.4 to 2.9 kcal g-at.⁻¹ for the heats of fusion and from 1.7 to 1.9 cal K⁻¹ g-at.⁻¹ for the corresponding entropies.

DISCUSSION

So far the situation for REPd phases has not been completely clarified as regards the complications arising from the ease with which polymorphic transformations in the solid state take place. The two structure types found (CrB and CsCl) and the other one (FeB), for which there are some indications, have often been encountered among the equiatomic compounds of RE's with VIII and I B group metals and, at a lesser extent, with the IIIA and IVA group elements. Moreover, in the case of the REAu phases the three structures are present not only along the "series" but also for the same RE. On the basis of these considerations the following scheme can be proposed for the possible sequence of structures for the REPd phases:

La Ce Pr Nd Sm Gd Tb Dy Ho Er Tm Lu
CsCl-type
FeB, TbNi or related structure
CrB-type

EuPd crystallizes with the CrB type of structure, like SrPd and BaPd¹, according to the divalent state of Eu atoms in this phase¹ and with lattice constant values considerably higher than those of the neighbouring, trivalent REPd compounds.

A singular behaviour is presented by YbPd: the structure type adopted and the lattice constant value seem to indicate for Yb an intermediate valency state in this phase. By using the concept¹³ of "apparent radius" (lattice constants of CsCl type compounds can be evaluated by summing the ionic RE radius with an "apparent radius" of the partner elements and multiplying this value by $2/\sqrt{3}$), it is possible to calculate the relative percentages of trivalent and divalent Yb in YbPd, assuming that YbPd follows a hypothetical Vegard's law between Yb²⁺Pd and Yb³⁺Pd. From the lattice constant values of the REPd phases, CsCl type, it is possible to extrapolate a

value for Yb^{3+}Pd which is the same as that calculated from the apparent radius for Pd, valid when alloyed with trivalent elements and the ionic radius for Yb^{3+} (Table 5). From CaPd, CsCl type, the corresponding value, for Pd alloyed with divalent elements, is obtained and with the values of the ionic radius of divalent Yb it is

TABLE 5

OBSERVED AND CALCULATED LATTICE CONSTANT VALUES WITH IONIC AND APPARENT RADII (Å) FOR MPd PHASES

Compound	a	$r_{\text{ion.}}(M)$	$r_{\text{app.}}(\text{Pd})$
Yb^{3+}Pd (calc.)	3.428	0.858	2.111
Yb^{2+}Pd (calc.)	3.517	0.993	2.053
CaPd (obs.)	3.522	0.997	2.053
YbPd (obs.)	3.447	—	—

possible to evaluate the lattice constant for the Yb^{2+}Pd compound. Now, with the relation:

$$a_{\text{obs.}}(\text{YbPd}) = a(\text{Yb}^{3+}\text{Pd}) \cdot X + a(\text{Yb}^{2+}\text{Pd}) \cdot (1 - X)$$

where X is the fraction of trivalent Yb, one can obtain for X the value of 0.79. This value is in very good agreement with the preliminary results of magnetic measurements on YbPd which can be explained by the presence in YbPd of 80% of the Yb atoms in the trivalent state, in the temperature range -180 to $+500^\circ\text{C}$.

A further proof, even though much more empirical, can be derived from melting points which indeed reflect the bond strengths and then the valency state of Yb. The melting point of Yb^{3+}Pd can be obtained as intermediate value between TmPd and LuPd (1610°C) while CaPd has been found to melt at 860°C . With a similar relation we can write:

$$T_f(\text{YbPd}) = T_f(\text{Yb}^{3+}\text{Pd}) \cdot X + T_f(\text{CaPd}) \cdot (1 - X)$$

and again X is found to be 0.80.

As observed in many series of RE intermetallic compounds, the lattice constants or the cube roots of the unit formula volumes (R) decrease linearly with RE trivalent ionic radii (Fig. 1). The increase in the volume contraction at Tb is in part responsible for the change of structure.

Heats of formation for REPd phases, with the exception of La and Nd, range from -14.0 to -15.2 kcal g-at $^{-1}$ and show a regular decrease from Ce to Lu. CrB-type phases have a little higher heats of formation due to the higher average contraction in the RE-Pd bond lengths observed in this type of structure compared with the CsCl type. These values together with those obtained for $\text{RE}_{68}\text{Pd}_{28}$ phases can be used to predict heats of formation for other RE-Pd alloys; from the thermodynamic diagram of Fig. 2 it can be seen that the heat of formation for Er_3Pd_2 should not be lower than -12 kcal g-at $^{-1}$ and so on.

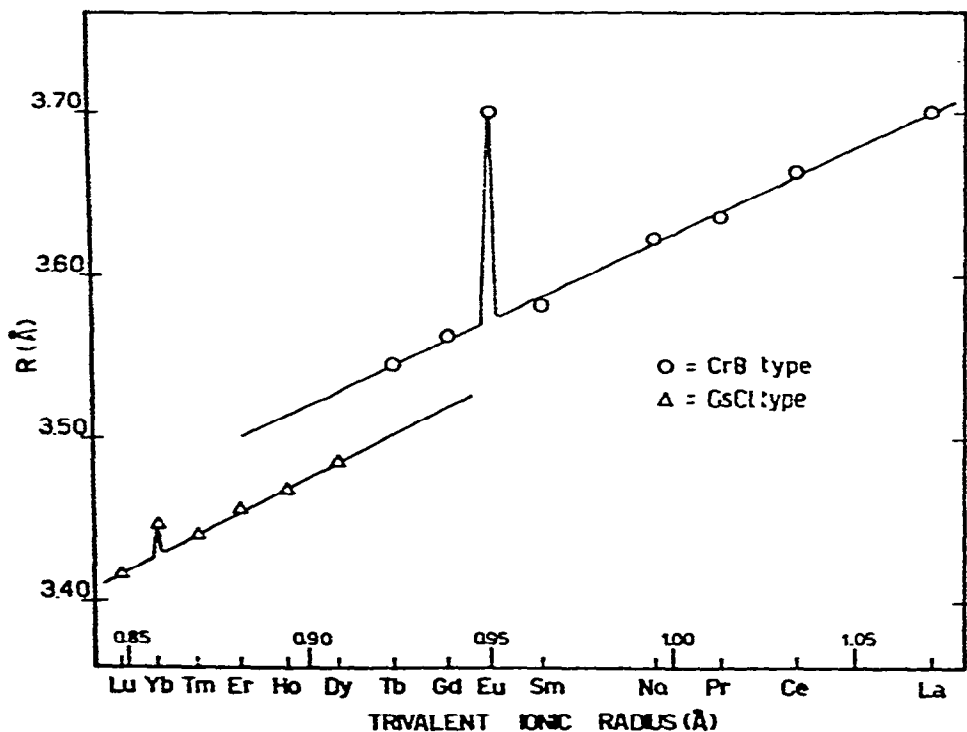


Fig. 1. Lattice constant or cube root of the unit formula volume (R) vs. trivalent ionic radius of the RE's.

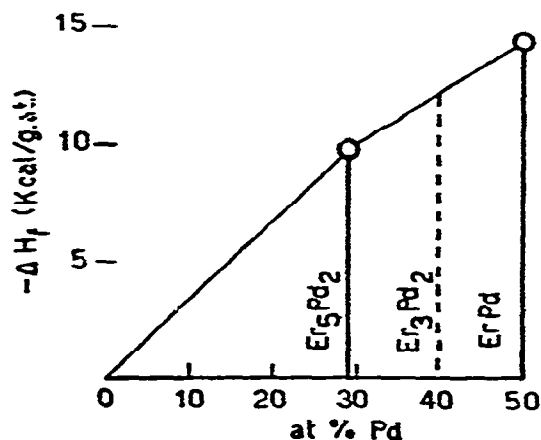


Fig. 2. Thermodynamic phase diagram for the Er-Pd system.

For $EuPd$ and $YbPd$ we could not determine the heats of formation as the reaction between these two RE and Pd is not so exothermic as for other RE and leads to non-homogeneous products. For $YbPd$ this fact can be explained: as already observed by Gschneidner¹⁴ the heat of promotion of the 4f extra electron of Yb to

the valency band is about $9 \text{ kcal g-at.}^{-1}$, so that for our compound, if completely trivalent, it is possible to extrapolate between TmPd and LuPd a value of $-14.1 \text{ kcal g at.}^{-1}$, and to obtain a value of

$$\Delta H_f = -14.1 - (-9 \times 0.8) = -6.9 \text{ kcal g-at.}^{-1}$$

which is too low.

Finally, heats of transformation and involved entropies, show again a regular decrease from lighter to heavier RE in agreement with the disappearance of transformations for Tm and Lu.

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