The structure of some ternary intermetallic compounds of the rare earths

A. Iandelli

Istituto di Chimica Fisica, Università di Genova, Corso Europa, Palazzo delle Scienze, I-16132 Genova (Italy)

Abstract

Ternary phases with compositions RPdMg, RAgMg, RPdPb and RPdHg (R = rare earth) have been prepared and their crystal structure has been investigated. The majority of them adopt the structure of the ZrNiAl type. Numerical data are reported and briefly discussed.

1. Introduction

During a study on the structure types of ternary equiatomic intermetallic phases of the rare earths, other compounds of the very common [1–3] ZrNiAl type were found. In the present paper the results for the compounds RPdMg, RAgMg, RPdPb and RPdHg are reported.

2. Experimental details

The rare earth metals used had a nominal purity of 99.7%–99.9% (Koch–Light, Rare Earth Products). The other metals were commercial products with a minimum purity of 99.99%.

The compounds RPdMg, RAgMg and RPdPb were prepared as described previously [4] from mixtures of turnings of the metals enclosed by soldering under argon in tantalum crucibles, heated by induction to about 1200 °C and annealed for 10–12 days at 750 °C (compounds with Pd) or 700 °C (RAgMg). The compounds RPdHg were prepared from mixtures of turnings of R and Pd with a drop of the equivalent quantity of mercury put into a crucible of alumina and enclosed in another crucible of iron under argon. The latter was heated to 1100 °C and annealed at 450 °C.

For the compounds of Table 1, micrographic examination of some samples showed their homogeneity, which was confirmed by X-ray photographs. The latter were obtained either with a Guinier camera or with a standard camera for the oxidizable RPdHg compounds. The intensities for selected compounds were measured with an X-ray diffractometer.

3. Results and discussion

The X-ray reflections of the compounds reported in Table 1 can be indexed with a hexagonal cell similar to that of the ZrNiAl type. Ytterbium behaves irregularly: only YbPdPb is isostructural with the others; YbPdMg and YbAgMg crystallize with a different structure not yet investigated. It has not been possible to obtain homogeneous YbPdHg and the same applies to DyPdHg, ErPdHg and YPdHg.

From Table 1 a volume concentration upon formation from the elements is always observed, with the exception of the first three compounds of the RAgMg series. On the other hand, the RAgMg compounds have melting points lower than the corresponding ones of RAgPd.

In the structure of the ZrNiAl (or HoNiAl) type (space group $P\bar{6}2m$) the Zr (or Ho) atoms are located in the positions $3g$: $x,0,\frac{1}{2}$; Al in $3f$: $x',0,0$; Ni in $2c$: $\frac{1}{3},\frac{2}{3},0$ and $1b$: $0,0,\frac{1}{2}$.

By assuming this structure type for the compounds of Table 1, the intensities of reflections have been calculated for some of them belonging to the four series, taking $x = 0.60$ and $x' = 0.25$ and with the three atomic types in various positions. Only by putting the R atoms in $3g$, Pd or Ag in $2c + 1b$ and the others (Mg, Pb, Hg) in the $3f$ positions is it possible to obtain sufficiently good agreement with the observed intensities: particularly Pd and Ag must be in the prismatic positions $2c + 1b$. For the isostructural RAgSi compounds [5], on the contrary, the Ag atoms are in the $3f$ positions. This appears to be linked to the dimensions, the atomic radii being in the sequence: $r_{Mg} > r_{Ag} > r_{Si}$.

The values of the parameters have been obtained for representative compounds from the intensities measured with a Philips diffractometer or, for the RPdHg

TABLE 1. Lattice constants (a, c) and unit cell volumes (V_u) of ZrNiAl-type phases

Phase	a (Å)	c (Å)	c/a	V_u(obs.) (Å³)	V(calc.) (Å³)	ΔV(calc. − obs.) (%)
LaPdMg	7.718(0)	4.141(0)	0.537	71.21	75.39	5.55
CePdMg	7.651(1)	4.103(1)	0.536	69.33	73.55	5.74
PrPdMg	7.636(2)	4.085(1)	0.535	68.76	72.53	5.20
SmPdMg	7.554(1)	4.050(0)	0.536	66.71	71.11	6.18
GdPdMg	7.502(1)	4.042(1)	0.539	65.67	71.04	7.56
DyPdMg	7.425(1)	4.025(1)	0.542	64.06	69.58	7.94
ErPdMg	7.373(1)	4.018(0)	0.545	63.05	68.68	8.20
YPdMg	7.430(1)	4.054(1)	0.546	64.61	69.51	7.06
LaAgMg	7.853(2)	4.370(2)	0.556	77.80	77.70	−0.13
CeAgMg	7.823(2)	4.331(1)	0.554	76.51	75.86	−0.86
PrAgMg	7.797(3)	4.293(3)	0.551	75.34	74.84	−0.67
SmAgMg	7.730(1)	4.224(1)	0.546	72.86	73.42	0.76
GdAgMg	7.679(1)	4.189(1)	0.546	71.31	73.35	2.78
DyAgMg	7.645(2)	4.130(2)	0.540	69.68	71.89	3.07
ErAgMg	7.626(0)	4.074(1)	0.534	68.39	70.99	3.66
YAgMg	7.661(2)	4.138(1)	0.540	70.11	71.82	2.39
LaPdPb	7.789(5)	4.178(4)	0.536	73.17	82.48	11.29
CePdPb	7.750(5)	4.140(4)	0.534	71.78	80.64	10.99
PrPdPb	7.728(1)	4.106(1)	0.531	70.79	79.62	11.10
SmPdPb	7.691(1)	4.016(2)	0.522	68.58	78.20	12.30
GdPdPb	7.715(2)	3.925(1)	0.509	67.44	78.13	13.68
DyPdPb	7.713(2)	3.853(2)	0.500	66.17	76.67	13.70
ErPdPb	7.714(1)	3.798(2)	0.492	65.24	75.77	13.90
YbPdPb	7.846(0)	3.802(2)	0.485	67.56	86.28	21.69
CaPdPb	7.845(1)	3.883(1)	0.495	68.99	88.56	22.10
YPdPb	7.717(1)	3.854(1)	0.499	66.25	76.60	13.51
LaPdHg	7.761(5)	4.015(4)	0.517	69.81	75.54	7.58
CePdHg	7.728(5)	3.953(3)	0.512	68.15	73.70	7.53
PrPdHg	7.705(4)	3.927(2)	0.510	67.30	72.68	7.41
SmPdHg	7.673(4)	3.836(2)	0.500	65.20	71.25	8.50
GdPdHg	7.649(4)	3.782(3)	0.494	63.88	71.19	10.27

compounds, from the photographs. In the compounds containing Mg, since its positions hardly influence the intensities, x_{Mg} has been fixed at 0.25. The best values thus obtained are: YAgMg, $x_Y = 0.59_5$, $x_{Mg} = 0.25$; YPdMg, $x_Y = 0.59_2$, $x_{Mg} = 0.25$; YPdPb, $x_Y = 0.59_7$, $x_{Pb} = 0.26_0$; SmPdHg, $x_{Sm} = 0.60$, $x_{Hg} = 0.26$.

Since the dimensions of YbPdPb appear anomalous, the compound CaPdPb has been prepared for comparison. It is isostructural with YbPdPb and its lattice constants are reported in Table 1. Considering the dimensions of the two compounds, it appears evident that Yb behaves as a divalent element.

Good agreement between the observed and calculated intensities is obtained by putting the Ca atoms in 3g ($x_{Ca} = 0.60_5$), Pb in 3g ($x_{Pb} = 0.26_0$) and Pd in $2c + 1b$. In contrast, considerable disagreement is found for the other five possible dispositions of the Ca, Pd and Pb atoms in the same three positions. The atoms placed in the positions 3g, 3f and $2c + 1b$ have decreasing dimensions as in other cases and for all the compounds reported here.

References

1 E. Parthé and B. Chabot, *Handbook of the Physics and Chemistry of Rare Earths*, Vol. 6, North-Holland, Amsterdam, 1984, pp. 113–334.
2 E.I. Gladishevskii and O.B. Bodak, *Kristallokhimia Intermetallicheskikh Soedimenii Redkozemelnykh Metallov*, Vischa Shkola, L'vov, 1982.
3 P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society for Metals, Metals Park, OH, 1985.
4 A. Iandelli, *J. Alloys Comp.*, 182 (1992) 87.
5 A. Iandelli, *J. Less-Common Met.*, 113 (1985) L27.