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Equiatomic ternary compounds of rare earths with the Fe_2P or ZrNiAl structure type

A. Iandelli
Istituto di Chimica fisica, Universitá di Genova, Palazzo delle Scienze, 16132 Genova (Italy)

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Abstract

Ternary phases of the composition RNiZn, RPdZn, RPdCd and RCuCd (R = rare earth) have been prepared and their structures investigated. We found that the majority of these compounds adopt the structure of the Fe_2P or the ZrNiAl type. Structural data are reported and briefly discussed.

1. Introduction

Many ternary phases of the rare earths with the composition RXZ and with the structure of the ordered ZrNiAl or of the Fe_2P type are known [1–3]. They are generally formed by X elements of the $VIII^0$ group of the periodic system, and some of them also by copper, silver and gold, while the Z elements belong to the IIIB or IVB groups.

It is possible to take as Z elements also those of the IIB group. In this work some compounds with the formulae RNiZn, RPdZn, RPdCd and RCuCd have been prepared and their structures examined.

2. Experimental details

R ≡ La, Ce, Pr, Sm, Gd, Dy, Er have been considered as representative elements. All R metals had a nominal purity of 99.8–99.9% (Rare Earth Products, Koch Light), and the others (nickel, palladium, copper, zinc and cadmium) a minimum purity of 99.9% (Koch Light, Fluka).

The compounds have been prepared by melting together the components, mixed in fine turnings, in tantalum crucibles soldered under argon. Alternatively the compounds were prepared without crucibles by induction heating of a compact of the mixture of the components under an argon pressure of 180–200 atm. In this way the speed of vaporization of zinc and cadmium is strongly reduced and the alloy is obtained almost without loss.

After melting, the alloys were annealed, generally at 750 °C, for 8–10 days. In the case of the RCuCd compounds, which have low melting points,

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the annealing temperature was 600 °C. Generally the quenched and annealed alloys were examined using an X-ray technique. In many cases a micrographic examination was made.

Powder photographs were taken with standard and Guinier cameras; the intensities were measured in typical cases with a Philips diffractometer.

3. Results and discussion

For the majority of the studied compounds (Table 1) the X-ray diffractograms can be completely indexed with a hexagonal cell, corresponding to the Fe_2P or ZrNiAl type. In Table 1 the lattice constants are given together with the values of the corresponding volumes V_u per formula unit. From the observed values and the values calculated on the basis of the atomic volumes the relative contraction was estimated.

The lattice constants decrease regularly from the lanthanum to the erbium compounds, with the exception of CeNiZn. A low temperature form has been

TABLE 1

Unit-cell constants of ZrNiAl-type compounds

	a (Å)	*c* (Å)	*c*/*a*	V_u (Å^3)		ΔV (%)
				Observed	Calculated	
LaNiZn	7.308(1)	3.952(1)	0.540	60.93	63.56	4.13
CeNiZn	7.141(1)	3.888(1)	0.544	57.23	61.72	7.28
PrNiZn	7.194(1)	3.896(0)	0.542	58.21	60.70	4.10
SmNiZn	7.111(2)	3.831(2)	0.539	55.92	59.29	5.68
GdNiZn	7.097(2)	3.798(1)	0.535	55.22	59.21	6.73
DyNiZn	7.046(3)	3.765(2)	0.534	53.96	57.75	6.56
ErNiZn	6.994(1)	3.746(1)	0.536	52.90	56.89	7.01
CePdZn	7.399(0)	4.014(0)	0.543	63.44	64.29	1.33
PrPdZn	7.387(1)	3.990(1)	0.540	62.85	64.49	2.54
SmPdZn	7.330(3)	3.922(2)	0.535	60.83	63.06	3.54
GdPdZn	7.299(2)	3.877(3)	0.531	59.63	63.00	5.35
DyPdZn	7.246(3)	3.837(2)	0.530	58.16	61.54	5.49
ErPdZn	7.247(0)	3.799(0)	0.524	57.60	60.64	5.02
CeCuCd	7.596(2)	4.116(2)	0.542	68.56	68.93	0.54
PrCuCd	7.565(6)	4.070(3)	0.538	67.24	67.91	0.94
SmCuCd	7.509(1)	4.014(1)	0.535	65.34	66.49	1.73
GdCuCd	7.466(4)	3.980(3)	0.533	64.04	66.42	3.73
DyCuCd	7.410(2)	3.927(2)	0.530	62.25	64.96	4.18
LaPdCd	7.723(1)	4.104(1)	0.531	70.66	73.73	4.16
CePdCd	7.677(0)	4.058(0)	0.529	69.04	71.89	3.97
PrPdCd	7.662(1)	4.029(1)	0.526	68.28	70.87	3.66
SmPdCd	7.604(3)	3.953(2)	0.520	65.98	69.45	4.99
GdPdCd	7.582(6)	3.929(3)	0.518	65.20	69.38	6.02

observed for SmPdZn, CePdCd and GdPdZn after annealing at 750 °C. The values reported in Table 1 refer to the high temperature modification.

The other compounds examined – YbNiZn, LaPdZn, LaCuCd, ErCuCd, DyPdCd and ErPdCd – do not have the same structure. An attempt was made to prepare the compounds CeNiCd, SmNiCd and ErNiCd with no success. For these compositions, heterogeneous, two-phase alloys were obtained.

It is known that the unit cell of the ZrNiAl or HoNiAl type (space group, $P\bar{6}2m$), derived from the Fe_2P type, contains three formula units with the following positions: three R in 3g, $x\ 0\ \frac{1}{2}$ ($x \approx 0.6$); three aluminium in 3f, $x\ 0\ 0$ ($x \approx 0.25$); two nickel in 2c, $\frac{1}{3}\ \frac{2}{3}\ 0$; one nickel in 1b, $0\ 0\ \frac{1}{2}$ (equivalent description: three R in 3f; three aluminium in 3g; two nickel in 2d; one nickel in 1a).

For the compounds obtained in the present investigation the intensities of the diffraction lines are in good agreement with those calculated on the basis of the ZrNiAl type by again placing the large rare earth atom in 3g, zinc or cadmium in 3f and nickel or palladium or copper in 2c + 1b. Significant differences are found for the calculated X-ray intensities if we exchange the positions of zinc with those of palladium in RPdZn or the positions of copper and cadmium in RCuCd. That does not occur when exchanging nickel and zinc in RNiZn and palladium and cadmium in RPdCd, owing to the small differences between the scattering factors of nickel and zinc and those of palladium and cadmium respectively.

The intensities were measured with a powder diffractometer for PrNiZn, PrPdZn, PrPdCd and GdCuCd and were compared with those calculated with different values of the parameters. The best values thus obtained are as follows. For PrNiZn, $x_{Pr}=0.58_5$, $x_{Zn}=0.24_5$; for PrPdZn, $x_{Pr}=0.59_2$, $x_{Zn}=0.25_0$; for PrPdCd, $x_{Pr}=0.59_0$, $x_{Cd}=0.25_0$; for GdCuCd, $x_{Gd}=0.58_8$, $x_{Cd}=0.25_0$.

The calculation of the intensities for various values of the atomic position parameters in PrPdZn and GdCuCd, after exchange of the positions of palladium with zinc and of copper with cadmium (*i.e.* by putting the palladium and copper atoms in the 3f positions) leads to complete disagreement with the observed values. Therefore in these compounds the palladium and copper atoms occupy the trigonal prismatic positions 2c + 1b.

The same method cannot be followed for the compounds RNiZn and RPdCd, but the occupation of the prismatic sides by the smaller atoms nickel and palladium is quite probable considering the dimensions of the atomic sites. The space available around the positions 2c + 1b, 3f and 3g is progressively larger and should accommodate atoms with increasing sizes, *i.e.* Ni–Zn–R and Pd–Cd–R respectively. Otherwise the distances R–Zn and R–Cd would become strongly contracted, while the distances R–Ni and R–Pd would be comparatively larger.

The studied compounds again show that there is not a rule for the valence electron concentration for the formation of ZrNiAl structure type. For many RXZ compounds the relative radii of X and Z are rather important. Structures of the TiNiSi type are observed if the atomic radii ratio r_X/r_Z or

TABLE 2

Lattice constants of $SmNi_{2-x}Zn_x$ alloys

		a (Å)	c (Å)	V_u (Å^3)
$SmNi_{1.2}Zn_{0.8}$	Heterogeneous	7.094(3)	3.832(3)	55.67
$SmNi_{1.1}Zn_{0.9}$	Homogeneous	7.103(2)	3.831(2)	55.80
SmNiZn	Homogeneous	7.111(2)	3.831(2)	55.92
$SmNi_{0.9}Zn_{1.1}$	Homogeneous	7.142(1)	3.834(2)	56.45
$SmNi_{0.8}Zn_{1.2}$	Heterogeneous	7.148(4)	3.838(3)	56.61

r_Z/r_X (larger/smaller) is less than about 1.1. If it is higher, the ZrNiAl type is preferred. This criterion is satisfied for the compounds RNiZn ($r_{Zn}/r_{Ni} = 1.12$), RPdCd ($r_{Cd}/r_{Pd} = 1.14$), RCuCd ($r_{Cd}/r_{Cu} = 1.23$), but not for RPdZn ($r_{Zn}/r_{Pd} = 1.01$).

For the compounds of ZrNiAl type there is the possibility of solid solutions. This has been briefly studied in the system $SmNi_{2-x}Zn_x$ for the compositions given in Table 2, corresponding to homogeneous or heterogeneous alloys.

Only the lattice constant a increases, while c remains almost unchanged. These alloys are too brittle for micrographic examinations; therefore the boundaries of the solid solution around SmNiZn can be evaluated to lie between $SmNi_{\approx 1.15}Zn_{\approx 0.85}$ and $SmNi_{\approx 0.85}Zn_{\approx 1.15}$.

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