

RARE-EARTH INTERMEDIATE PHASES WITH ZINC

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SUMMARY

The existence and the structure of the rare earth-zinc intermediate phases in the range 75–88 at.% Zn has been investigated: the compositions MZn_3 , M_3Zn_{11} , MZn_4 , $M_{13}Zn_{58}$, MZn_5 , M_3Zn_{17} and M_3Zn_{22} were examined. A part of the Er-Zn system has been studied by differential thermal analysis.

The different types of structure occurring in these intermetallic phases were correlated through the coordination number of the component atoms. The trend of the rare-earth coordination number appears to be related to the existence of ranges of the different phases.

In the series of isomorphous compounds, the known, linear dependence of the lattice dimensions upon the rare-earth trivalent ionic radii is confirmed.

INTRODUCTION

In recent years a number of reports on the alloying behaviour of the rare earths with zinc have been published. Full structural data on the MZn and MZn_2 compounds are available^{1,2}. For Zn-rich alloys, crystal structures have been found corresponding to the formulae M_2Zn_{17} , MZn_{11} , MZn_{12} , and MZn_{13} ³.

The alloy phase diagrams of Zn with La, Ce, Pr, Nd, Sm, Yb, and Y are known⁴⁻⁸ and are generally characterized by a large number of intermetallic phases.

In this work, an attempt has been made to define, as completely as possible, the existence and the structure of the intermediate phases occurring in the range 75–88 at.% Zn. The compositions 1:3, 3:11, 1:4, 13:58, 1:5, 3:17 and 3:22 have been examined and a part of the Er-Zn system has been studied by differential thermal analysis (DTA).

EXPERIMENTAL

The rare-earth metals were supplied by Michigan Co. and Gallard-Schlesinger Co., U.S.A. and were 99.5–99.9 wt.% pure; the zinc was a commercial product of 99.99 wt.% purity.

The preparation of the samples was carried out by mixing filings of the two

metals and sealing in pyrex tubes under vacuum. The powders obtained after a preliminary reaction at low temperature (400°C) were pressed into pellets, placed in tantalum containers, and sealed in quartz tubes under a reduced pressure of argon. The samples were sintered at temperatures between 600° and 700°C or melted and annealed.

The Er-Zn alloys were studied by differential thermal analysis, being contained in molybdenum crucibles and sealed under an argon atmosphere. As no losses in weight were detected after the preparation, chemical analyses were only carried out in some cases. All the specimens were examined by metallography and X-ray diffraction. The X-ray analyses were principally carried out by the powder method using $FeK\alpha$ radiation and a 114.6 mm diam. camera, but in some cases, single-crystal techniques, using Mo or $CuK\alpha$ radiation were employed. GANDOLFI'S device^{9,10} was always used to obtain Debye patterns from single crystals. In all cases it was confirmed that the crystals had the same composition as the nonhomogeneous bulk from which they were chosen.

Table I summarizes the results obtained together with the values published by other authors. Data on the observed and calculated intensities of the powder patterns referred to in the text are available from this laboratory.

TABLE I

A - STRUCTURAL DATA FOR MZn_3 COMPOUNDS

Compound	Structure type	Lattice parameters (Å)			Ref.
		a	b	c	
CeZn ₃	<i>A</i> mma (derived from YZn ₃)	6.644	4.627	10.437	This work
PrZn ₃	YZn ₃	6.655	4.589	10.380	This work
PrZn ₃	YZn ₃	6.656	4.591	10.379	4
NdZn ₃	YZn ₃	6.717	4.544	10.284	This work
NdZn ₃	YZn ₃	6.709	4.551	10.292	4
SmZn ₃	YZn ₃	6.725	4.489	10.199	This work
GdZn ₃	YZn ₃	6.718	4.439	10.158	This work
TbZn ₃	YZn ₃	6.690	4.411	10.104	This work
DyZn ₃	YZn ₃	6.700	4.398	10.06	12
HoZn ₃	YZn ₃	6.697	4.365	10.099	12
ErZn ₃	YZn ₃	6.678	4.350	10.024	This work
TmZn ₃	YZn ₃	6.661	4.330	9.997	This work
LuZn ₃	YZ ₁₁₃	6.650	4.300	9.974	This work
YZn ₃	YZn ₃	6.690	4.405	10.111	11

B - STRUCTURAL DATA FOR M_3Zn_{11} COMPOUNDS

Compound	Structure type	Lattice parameters (Å)			Ref.
		a	b	c	
Ce ₃ Zn ₁₁	La ₃ Al ₁₁	4.519	13.444	8.883	This work
Ce ₃ Zn ₁₁	La ₃ Al ₁₁	4.521 ₅	13.463	8.885 ₅	5
Pr ₃ Zn ₁₁	La ₃ Al ₁₁	4.500	13.390	8.868	This work
Pr ₃ Zn ₁₁	La ₃ Al ₁₁	4.502	13.392	8.871	4
Nd ₃ Zn ₁₁	La ₃ Al ₁₁	4.485	13.318	8.855	This work
Nd ₃ Zn ₁₁	La ₃ Al ₁₁	4.484	13.322	8.858	4
Sm ₃ Zn ₁₁	La ₃ Al ₁₁	4.452	13.179	8.838	This work
Gd ₃ Zn ₁₁	La ₃ Al ₁₁	4.423	13.063	8.842	This work

TABLE I (Continued)

Compound	Structure type	Lattice parameters (\AA)			Ref.
		<i>a</i>	<i>b</i>	<i>c</i>	
Tb ₃ Zn ₁₁	La ₃ Al ₁₁	4.408	12.989	8.825	This work
Dy ₃ Zn ₁₁	La ₃ Al ₁₁	4.395	12.922	8.830	This work
Yb ₃ Zn ₁₁	La ₃ Al ₁₁	4.421	13.122	8.889	This work
Yb ₃ Zn ₁₁	La ₃ Al ₁₁	4.421	13.127	8.891	8
Y ₃ Zn ₁₁	La ₃ Al ₁₁	4.402	12.934	8.906	11
Y ₃ Zn ₁₁	La ₃ Al ₁₁	4.388	12.925	8.866	4
Y ₃ Zn ₁₁	La ₃ Al ₁₁	4.388	12.929	8.871	This work

C - STRUCTURAL DATA FOR MZn₄ COMPOUNDS

Compound	Structure type	Lattice parameters (\AA)			Ref.
		<i>a</i>	<i>b</i>	<i>c</i>	
LaZn ₄	orthorh.	6.33	10.29	6.11	This work

D - STRUCTURAL DATA FOR M₁₃Zn₅₈ COMPOUNDS

Compound	Structure type	Lattice parameters (\AA)		Ref.
		<i>a</i>	<i>c</i>	
Ce ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.60	14.11	5
Pr ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.57	14.15	This work
Nd ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.53	14.09	This work
Sm ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.40	14.07	This work
Gd ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.35	14.21	16
Tb ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.31	14.07	This work
Dy ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.24	13.99	This work
Ho ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.21	13.97	This work
Er ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.20	13.98	This work
Tm ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.14	13.94	This work
Yb ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.32	14.15	This work
Lu ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.09	13.89	This work
Y ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	14.28	14.08	11

E - STRUCTURAL DATA FOR MZn_{5~} COMPOUNDS

Compound	Structure type	Lattice parameter (\AA)		Ref.
		<i>a</i>	<i>c</i>	
ErZn _{5~}	rhombohedr. <i>R3c</i> or <i>R3c</i>	15.32	27.53	This work
HoZn _{5~}	} isomorphous with ErZn _{5~}			This work
TmZn _{5~}				
LuZn _{5~}				
YZn _{5~}				

F - STRUCTURAL DATA FOR M₃Zn₁₇ COMPOUNDS

Compound	Structure type	Lattice parameters (\AA)		Ref.
		<i>a</i>	<i>c</i>	
Yb ₃ Zn ₁₇	Ru ₃ Be ₁₇	14.291 ± 0.003		This work

G - STRUCTURAL DATA FOR M₃Zn₂₂ COMPOUNDS

Compound	Structure type	Lattice parameter (\AA)		Ref.
		<i>a</i>	<i>c</i>	
La ₃ Zn ₂₂	Ce ₃ Zn ₂₂	8.97	21.48	26
Ce ₃ Zn ₂₂	Ce ₃ Zn ₂₂	8.94	21.33	26
Pr ₃ Zn ₂₂	Ce ₃ Zn ₂₂	8.88	21.07	26
Nd ₃ Zn ₂₂	Ce ₃ Zn ₂₂	8.886	21.251	This work
Sm ₃ Zn ₂₂	Ce ₃ Zn ₂₂	8.856	21.175	This work
Gd ₃ Zn ₂₂	Ce ₃ Zn ₂₂	8.831	21.118	This work

MZn₃ compounds

The occurrence of a MZn_3 phase with the orthorhombic YZn_3 type of structure has been established for Dy, Ho and Y^{11,12}. Single crystal data, reported by LOTT AND CHIOTTI⁵ show, for $CeZn_3$, an orthorhombic C -centered cell with three possible space groups: $C2cm$, $Cmc2$ or $Cmcm$, while the $PrZn_3$ and $NdZn_3$ phases, previously reported as isomorphous with $CeZn_3$ ⁴, appear isotypic with YZn_3 ¹³. Yb does not form this phase⁸.

The 1:3 composition was examined for almost all of the rare-earth metals. The $ErZn_3$ phase was prepared by melting in a tantalum crucible, and X-ray investigation of isolated single crystals showed symmetry, systematic extinctions, and lattice parameters consistent with the YZn_3 structure type. The 1:3 phases of Pr, Nd, Sm, Gd, Tb, Tm and Lu were prepared by sintering at 700°C. These compounds are also isomorphous with YZn_3 . The lattice constants were obtained from powder photographs and the $DyZn_3$ atomic parameters were used to perform the crystal structure analysis.

Samples with the composition $LaZn_3$ were prepared, but micrographically they appeared to be heterogeneous; the powder patterns exhibited the reflections of $LaZn_2$ ($CeCu_2$ type) and those of another phase, subsequently identified as $LaZn_4$. In the case of Eu, the diffraction pattern of an alloy with 78.6 at. % Zn gave the reflections of the 1:2 and 1:5 phases, thus excluding the occurrence of phases with intermediate composition.

Samples of $CeZn_3$, prepared by sintering at 700°C, gave Debye-Scherrer photographs nearly identical to those of $PrZn_3$. They were indexed according to the YZn_3 type and the following lattice constants (in Å) were obtained: $a=6.644$; $b=4.627$; $c=10.437$. On examining the powder patterns of all the MZn_3 compounds with the YZn_3 structure it is observed that the intensity of the hkl reflections with $h+l=2n+1$ decreases from Lu to Pr. For $PrZn_3$, very few reflections of this type are observed, while for $CeZn_3$ they are completely absent. This suggests that the atomic parameters actually shift so that a gradual approach to an A -centered lattice results. With this in mind, attempts were made by successive refinements, to determine for $CeZn_3$ the best values of the positional parameters in the space group $Pnma$.

The following atomic positions were obtained:

4 Ce	4(c)	$x, \frac{1}{4}, z$ with	$x=0.250$;	$z=0.350$;
4 Zn	4(c)		$x'=0.250$;	$z'=0.060$;
4 Zn	4(c)		$x''=0.945$;	$z''=0.870$;
4 Zn	4(c)		$x'''=0.555$;	$z'''=0.870$.

These values of the parameters are consistent with the space group $Amma$; by means of a simple interchange of the crystallographic axes ($xyz \rightarrow zxy$) one obtains the symmetry of the $Cmcm$ space group indicated by LOTT AND CHIOTTI⁵. The lattice constants reported by these authors ($a=4.62$ Å; $b=10.43$ Å; $c=6.64$ Å) actually correspond to the values obtained in the present work, provided the alternative setting of the unit cell is taken into account.

M₃Zn₁₁ compounds

The existence of the M_3Zn_{11} compounds for Ce, Pr, Nd, Sm, Yb, and Y has been established and, except for Sm_3Zn_{11} , their lattice constants, based on a body-centered orthorhombic cell, were already known^{4-6,8,11}. All the above mentioned

compounds were prepared together with Gd_3Zn_{11} , Tb_3Zn_{11} and Dy_3Zn_{11} , by melting and subsequently annealing at $700^\circ C$. All these phases are isomorphous and belong to the type of structure found by GOMES DE MESQUITA AND BUSCHOW¹⁴ for the La_3Al_{11} compound. This structure corresponds to that found by HARSHA AND RYBA¹¹ for Y_3Zn_{11} if two crystallographic axes (y and z) are interchanged. The space group is $D^{25}_{2h}-Immm$ with the following atomic positions:

$$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$$

$$2 M \text{ in } 2(a): 0, 0, 0;$$

$$4 M \text{ in } 4(g): 0, y, 0; 0, \bar{y}, 0;$$

$$2 Zn \text{ in } 2(c): \frac{1}{2}, \frac{1}{2}, 0$$

$$4 Zn \text{ in } 4(j): \frac{1}{2}, 0, z'; \frac{1}{2}, 0, \bar{z}'$$

$$8 Zn \text{ in } 8(l): 0, y'', z''; 0, \bar{y}'', \bar{z}''; 0, \bar{y}'', z''; 0, y'', \bar{z}''$$

$$8 Zn \text{ in } 8(l): 0, y''', z'''; 0, \bar{y}''', \bar{z}'''; 0, \bar{y}''', z'''; 0, y''', \bar{z}'''$$

The intensities obtained from powder patterns were used for the atomic parameters refinement in the case of Gd_3Zn_{11} . The best agreement between the calculated and observed intensities correspond to the following values of the parameters:

$$y_{Gd} = 0.295 \quad z'_{Zn} = 0.687$$

$$y''_{Zn} = 0.340 \quad z''_{Zn} = 0.354$$

$$y'''_{Zn} = 0.133 \quad z'''_{Zn} = 0.287$$

This composition was also examined for Eu, Ho, Er, and Tm, but no evidence for the existence of the 3:11 phase was found. In the case of Er, its absence was confirmed by the equilibrium phase diagram. The magnetic susceptibility measurements indicate the divalency of ytterbium in Yb_3Zn_{11} .

MZn₄ compounds

The results obtained in the present work are consistent with those reported in the literature^{4,15}: the metallographic and chemical analysis confirm the existence of the $LaZn_4$ compound. Between the 1:2 and 1:5 compositions no other phase forms with zinc.

X-ray analysis of single crystals showed orthorhombic symmetry with the following lattice constants (in Å): $a = 6.33$; $b = 10.29$; $c = 6.11$.

The observed reflections obeyed the conditions $h + k = 2n$ for hkl and $l = 2n$ for hol ; thus, the possible space groups are $Cmc2_1$, $C2cm$ and $Cmcm$.

The density of the samples was found to be 6.65 g/cm^3 , which is consistent with the value calculated for 4 units of formula/cell (6.69 g/cm^3). The photographs obtained from powders of $LaZn_4$ were similar to that of $ThZn_4$, which has the tetragonal $BaAl_4$ -type of structure. However, splitting of several reflections was observed so that the structure of $LaZn_4$ is probably an orthorhombic distortion of the $BaAl_4$ -type.

M₁₃Zn₅₈ compounds

In the Ce-Zn alloy system LOTT AND CHIOTTI identified a $CeZn_{4.5}$ compound having hexagonal symmetry⁵. Phases of the same composition were found for Pr, Nd, Sm, Yb, and Y^{4-6,8}. WANG determined the crystal structure of the $Gd_{13}Zn_{58}$ compound (space group $P6_3mc$)¹⁶ and LARSON AND CROMER proposed a quite similar structure for $Pu_{13}Zn_{58}$ (space group $P6_3/mmc$)¹⁷. We examined this composition for all the rare-earth metals from Ce to Lu, excluding Eu. The alloys were prepared by sintering at $700^\circ C$ and single crystals, isolated from melted samples of $Nd_{13}Zn_{58}$ and $Er_{13}Zn_{58}$,

gave structural data consistent with the $Gd_{13}Zn_{58}$ structure-type. An isomorphous phase was recognized for all the other rare earths covered. The lattice constants were determined from photographs of crystal powders of the samples mixed with KI as an internal standard. The atomic parameters calculated by WANG for $Gd_{13}Zn_{58}$ were used for the crystal structure analysis of the isomorphous phases. As confirmed by WANG in a private communication, the z atomic parameter for Zn(13) is erroneously listed in Table I of his work¹⁶, the exact value being 0.362, while in Table II of his paper, the coordination numbers for Gd(1) and Gd(2) should be 17 instead of 16.

The magnetic susceptibility measurements indicate the divalency of ytterbium in $Yb_{13}Zn_{58}$.

MZn₅ compounds

Previous work indicates that the 1:5 phase occurs for La, Ce, and Eu, and has the $CaZn_5$ -type of structure¹⁸⁻²⁰; it also occurs for Y but with an unknown structure⁴. In no case was evidence found of the existence of a definite phase with this composition for Nd, Sm and Yb^{4,6,8}. However, the behaviour of Pr and the remaining rare-earth metals remained unsolved. Repeated attempts were made in the course of the present work to confirm the existence of a phase near the stoichiometric composition $PrZn_5$, but the powder photographs could not be satisfactorily interpreted. However, this is not regarded as proof of the non-existence of the compound.

Alloys of the same composition for Tb, Dy, Ho, Er, Tm, Lu, and Y, were prepared by sintering or melting. In the case of Tb and Dy, the samples appeared heterogeneous and the powder patterns showed the reflections of the known 13:58 and 2:17 phases. The rare earths Ho, Er, Tm, Lu, and Y, however, form isostructural phases, the composition of which could be estimated as being very close to the 1:5 ratio, as judged from the investigation carried out on the Er-Zn alloys. A single crystal was isolated from an Er-83.3 at.% Zn alloy, which appeared from metallographic examination to be homogeneous, and was therefore employed for X-ray analysis. The Laue photographs of this crystal showed hexagonal symmetry. Rotation patterns were made with the crystal rotated about the c and a axes and the following lattice spacings were determined: $a = 15.32 \text{ \AA}$; $c = 27.53 \text{ \AA}$.

All the indices obtained from Weissenberg photographs satisfied the rhombohedral extinction conditions; moreover only the hol reflections with $l = 2n$ were observed. Therefore the possible space groups are $R3c$ and $R\bar{3}c$. It must be noted that the very weak intensity of some layer lines on the rotating crystal photographs is such as to result in a pronounced hexagonal subcell, with $a = 8.847$ and $c = 9.177 \text{ \AA}$. These values are, respectively, $1/3$ and 3 times smaller than the spacings reported above.

M₃Zn₁₇ compounds

IANDELLI²¹ found a cubic Yb-Zn compound near the 1:6 composition, isotypic with $CeCd_6$ ^{22,23}. The existence of an ytterbium phase between 80 and 85 at.% zinc was also reported by KUZMA and coworkers²⁴. We examined sintered and melted samples of $YbZn_6$; the compound has a body-centered cubic cell with $a = 14.291 \text{ \AA}$, and its structure was found to be isotypic with that of Ru_3Be_{17} ²⁵. The occurrence of this phase was sought for La, Pr, Sm, Eu, Gd, and Dy with Zn, but only Yb_3Zn_{17} was found to exist. Magnetic susceptibility measurements indicated the divalency of ytterbium in this compound.

M₃Zn₂₂ compounds

The existence of a phase of this composition was reported by KRIPYAKEVICH and coworkers²⁶ for La, Ce, and Pr. The crystal structure belongs to the space group *I*₄₁/*amd* and is the same as Pu₃Zn₂₂²⁷.

The alloys with Nd, Sm, Eu, Gd, Tb, Dy, Er, and Y were examined in this work, and were prepared by sintering at 700°C. The 3:22 compounds exist only for Nd, Sm and Gd, and have the Ce₃Zn₂₂ structure. The atomic parameters of Ce₃Zn₂₂ were employed to provide intensity data and in carrying out the structural analysis.

Er-Zn alloy system

In order to confirm the different behaviour between the lighter- and heavier rare-earth metals, several compositions were examined in the range 73.7–89.5 at. % Zn in the Er-Zn system. The X-ray diffraction data along with differential thermal and metallographic analysis were employed to establish the composition and the structure of the intermediate phases occurring in the system. The metals in the desired proportions were sealed in Mo crucibles by welding under an argon atmosphere. The peritectic formation of the following phases was observed: ErZn₃ (880°C), Er₁₃Zn₅₈ (870°C), ErZn₅ (845°C) and Er₂Zn₁₇ (818°C). The metallographic examination excluded the occurrence of other intermediate phases in this range of composition. As previously reported, single crystals of ErZn₃, Er₁₃Zn₅₈ and ErZn₅ were isolated and employed for the X-ray analysis.

DISCUSSION

A survey of all available data is shown in Table II, in which the horizontal lines correspond to non-existence of the compounds. Yttrium has been included between Tb and Dy, according to the order of the lattice constant values in all compounds. Likewise, Yb would be placed between Nd and Sm, but it appears more logical to set Yb and Eu apart because of their divalency.

In the range 0–50 at. % Zn, no phase seems to exist in any R.E.-Zn system. All the R.E. metals form isomorphous compounds with the formula MZn (CsCl type)

TABLE II
RARE EARTH-ZINC INTERMEDIATE PHASES

M:Zn	Eu	Yb	La	Ce	Pr	Nd	Sm	Gd	Tb	Y	Dy	Ho	Er	Tm	Lu	TYPE OF STRUCTURE
1:1	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨ CsCl
1:2	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" CeCu ₂
1:3	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" YZn ₃ ▨ CeZn ₃
1:3.67	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" La ₃ Al ₁₁
1:4	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" orthorhombic
1:4.46	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" Gd ₁₃ Zn ₅₈
1:5	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" CaZn ₅ ▨ rhombohedral
1:5.67	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" Ru ₃ Be ₁₇
1:7.33	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" Ce ₃ Zn ₂₂
1:8.5	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" Th ₂ Zn ₁₇ ▨ Th ₂ Ni ₁₇
1:11	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" BaCd ₁₁
1:~11	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" SmZn ₁₂
1:12	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" ThMn ₁₂
1:13	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	" NaZn ₁₃

and MZn_2 ($CeCu_2$ type). For the alloys richer in Zn, wide isomorphism only occurs for MZn_3 (YZn_3 type), $M_{13}Zn_{58}$ ($Gd_{13}Zn_{58}$ type) and M_2Zn_{17} (Th_2Zn_{17} and Th_2Ni_{17} type) series. Several phases exist with the R.E. metals of greater atomic dimensions: MZn_{13} ($NaZn_{13}$ type), for Eu, Yb and La; MZn_5 ($CaZn_5$ type), for Eu, La and Ce; MZn_{11} ($BaCd_{11}$ type), for Eu, Yb, La, Ce, Pr and Nd; M_3Zn_{22} (Ce_3Zn_{22} type), from La to Gd; M_3Zn_{11} (La_3Al_{11} type), from Ce to Dy. Two series of isomorphous compounds also exist for R.E. metals of smaller atomic sizes: MZn_{12} ($ThMn_{12}$ type), from Sm to Lu; $MZn_{5\sim}$ (rhombohedral, unknown structure), from Ho to Lu.

VELECKIS and coworkers found a high-temperature hexagonal modification for $NdZn_{12}$ and $SmZn_{12}$ ²⁸. Recently, the crystal structure of the corresponding Sm phase with approximate composition $SmZn_{11\sim}$ was determined²⁹.

Several structure types occurring in the rare earth-zinc phases show geometrical relations which have already been noticed by different authors^{3,30}. In a previous investigation, we examined the relationships amongst the $CeCu_2$, YZn_3 , La_3Al_{11} and $BaAl_4$ types of structure³¹. JOHNSON AND SMITH³² surveyed the relationships amongst the structures which can be geometrically derived from the D_{2d} type ($CaZn_5$), namely, Pu_3Zn_{22} , Ce_5Mg_{42} , Th_2Zn_{17} , Th_2Ni_{17} and $ThMn_{12}$. From the geometrical point of view, the crystal structures of the other rare earth-zinc phases do not appear to belong to one of these structural families.

It is well known that in the formation of intermetallic compounds the effects of the following factors are important: (a) the difference between the electronegativity of the component atoms; (b) the difference between their atomic dimensions; (c) the electron/atom concentration which the stoichiometric ratio and electronic structures provide. The extent of overlap of these factors determines the existence and the properties of a phase. Table II emphasizes the complexity of the interactions between these factors and indicates that even in a series of elements so closely similar as the lanthanides, alloying behaviour can vary considerably.

The dimensional factor can be very significant, as previous authors have pointed out for the 1:11, 1:12 and 1:13 compounds.

As the coordination of atoms characterizes the type of structure and is related to the atomic dimensions, we examined the coordination number for rare earth and zinc atoms ($c.n.M$ and $c.n.Zn$, respectively) in the different phases. In defining the coordination number, the question arises as to how far the neighbouring atoms ought to be counted. The most widely employed criterion is that of FRANK AND KASPER³³. This was used by us, but as a further possibility, the atomic distribution around one atom was calculated and represented by plotting the number of surrounding atoms at a distance " d " against the ratio $d/\sum r$, where $\sum r = r_{\text{central at.}} + r_{\text{surr. at.}}$ (employing the Goldschmidt metallic radii for the coordination 12).

Some results are reported in Fig. 1, and in all cases it will be observed that a gap in the atomic distribution occurs. The horizontal dashed lines indicate the atoms belonging to the FRANK AND KASPER coordination polyhedron. In some cases this atomic distribution plot allows the gradual variation of coordination caused by atomic parameter shifts to be considered. The coordination number may be found by counting all the atoms before the gap; where some uncertainty arises because the gap is less well marked, the counting of the atoms does not exceed $d/\sum r = 1.25$. If a component atom is present in the unit cell with several crystallographic positions, the weighted average of the respective coordination numbers is taken.

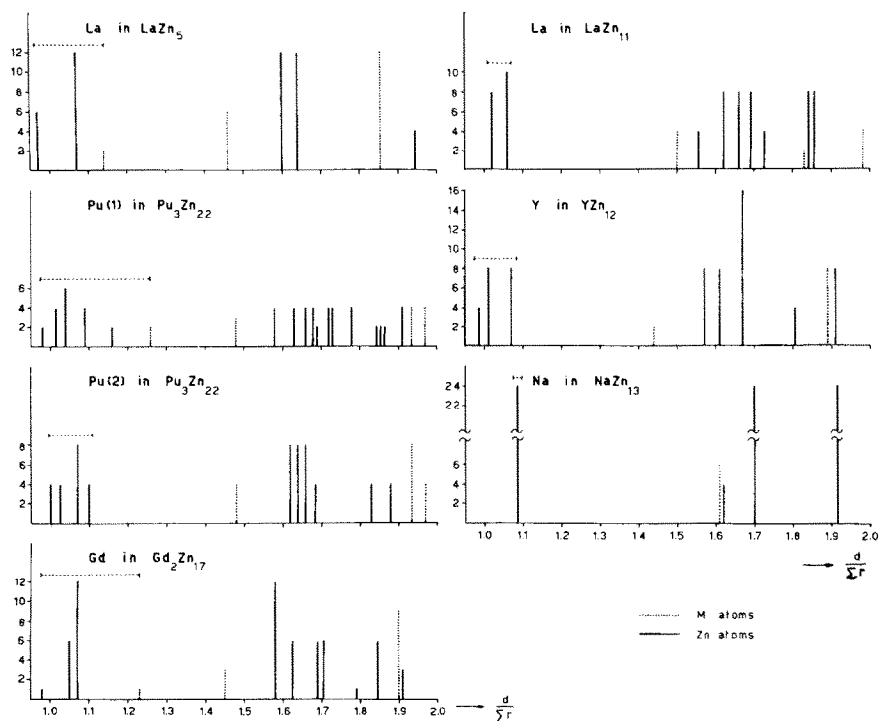


Fig. 1. Atomic distribution around the M atoms in some M-Zn phases.

TABLE III

COORDINATION NUMBERS FOR THE M-Zn PHASES

Compound	Structure type	<i>c.n.M</i> after FRANK AND KASPER	<i>c.n.M</i>	<i>c.n.Zn</i>
LaZn	CsCl	14	14	8
LaZn ₂	CeCu ₂	16	16	10
HoZn ₃	YZn ₃	17	16	10.7
CeZn ₃	CeZn ₃	17	17	10.3
Gd ₃ Zn ₁₁	La ₃ Al ₁₁	19.3	19.3	10.7
Gd ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	17.5	18.2	11.9
LaZn ₅	CaZn ₅	20	20	12
Pu ₃ Zn ₂₂	Pu ₃ Zn ₂₂	20	20	12
Gd ₂ Zn ₁₇	Th ₂ Zn ₁₇	20	20	12.2
LaZn ₁₁	BaCd ₁₁	22	22	12.2
YZn ₁₂	ThMn ₁₂	20	20	12.7
NaZn ₁₃	NaZn ₁₃	24	24	12

A comparison of the two values obtained in this way with the FRANK AND KASPER criterion shows very good agreement, as may be seen from Table III.

Figure 2 shows, graphically, the trend of the coordination numbers *vs.* the logarithm of the zinc/rare earth stoichiometric ratio ($\log m$). The coordination number of zinc, *c.n.Zn*, gradually increases from 8 (1:1 phase) to 11.9 (13:58 phase); it then remains constant at this value up to the phase richest in zinc (1:13). The coordination

number of the R.E. atom, $c.n._M$, increases with zinc content. It is noteworthy that the $c.n._M$ values reported in Fig. 2 for the 1:1, 1:2, 1:3, 1:3.58 and 2:17 phases, which are formed for almost all the R.E. elements, show a regular and nearly linear trend. This suggests that the $c.n._M$ values for the other phases, which do not lie on this line, can be considered abnormally high or low. In effect, the compounds 3:11, 1:5 (CaZn₅ type), 3:22, 1:11 and 1:13 which have higher $c.n._M$ values correspond to a range of existence limited to the larger rare-earth atoms, while the compounds 1:12, having lower $c.n._M$ values, exist only for the smaller rare-earth atoms. The crystal structure determination for the 1:5 phase formed from Ho to Lu will establish whether this case agrees with the $c.n._M$ trend.

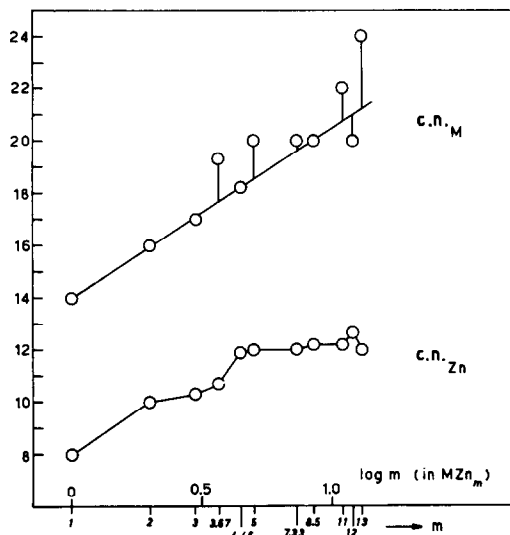


Fig. 2. A plot of the coordination numbers of R.E. ($c.n._M$) and Zn ($c.n._{Zn}$) atoms as a function of the Zn/R.E. stoichiometric ratio.

It is clear that the relationship between the coordination number and the range of existence of a phase provides only rough qualitative information. For example, La shows a particular behaviour because it does not form the 1:3, 3:11 and 1:3.58 phases, but is the only one to form a 1:4 compound. Moreover, Yb does not form the 1:5 (CaZn₅ type) phase and is the only R.E. to form a 3:17 phase. Its behaviour cannot be explained by simple dimensional considerations.

If one examines the behaviour of R.E. atoms in every series of isomorphous compounds, it is found that in almost all cases the lattice dimensions are linearly related to the trivalent ionic radius of the R.E. elements. This was previously noted by IANDELLI^{1,34,35} for several series of intermetallic and semimetallic R.E. compounds. The plots of the cube root of the cell volume divided by the number of R.E. atoms in the elementary cell ($\sqrt[3]{V/n_M}$) vs. the ionic radii $r_{M^{3+}}$ shown in Fig. 3 enable the dimensional variations in the different isostructural series to be compared. A linear trend is observed, with decreasing slope from the 1:1 to the 1:11 phases, except for the MZn₁₂ compounds for which the influence of the R.E. ionic size appears to be very weak, the points lying on a smooth and rather flat curve.

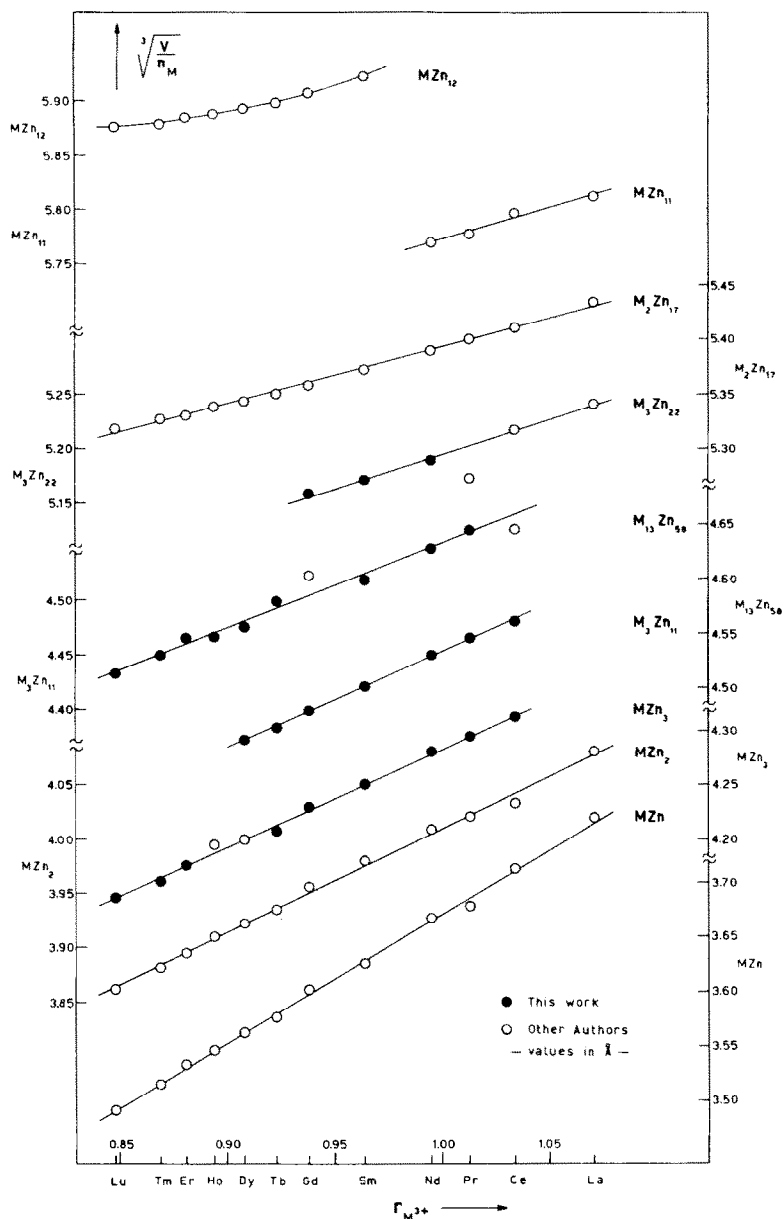


Fig. 3. Cubic root of the unit cell volume (V) divided by the number of R.E. atoms (n_M) vs. R.E. trivalent ionic radii.

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