

ZINC-RICH PHASES OF THE RARE-EARTH-ZINC ALLOYS

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SUMMARY

The crystal structures of the intermetallic compounds in the composition range 89–100% at. % zinc have been investigated for the rare earth (RE)–Zn systems. Five crystal structure types have been found, corresponding to the formulae: REZn_{13} , REZn_{12} , REZn_{11} and $\text{RE}_2\text{Zn}_{17}$. The existence of the different structures appears to be closely related to the dimensions of the RE atoms. Eu and Yb behave as divalent elements.

INTRODUCTION

In the present work, the zinc-rich side of all RE–Zn systems (89–100 at. % Zn) has been studied, mainly structurally, in order to define the composition and the structure of the existing phases and to examine the variations resulting from the differences in the atomic dimensions of the RE metals, and from the different valencies of Eu and Yb. Some zinc compounds of Sr, Ca, Th and U have been examined for comparison.

EXPERIMENTAL

The RE metals were obtained from the Michigan Co., the Nuclear Co., the Lindsay Co., and the Gallard Schlesinger Co. of the U.S.A. and had a purity of 99.4–99.6%; Ca and Sr supplied by the Fluka Soc., Switzerland, had a purity of 99.5%, while U (99.7%) and Th (99.9%) were obtained from the Koch-Light Laboratories Ltd., England.

With the exception of those phases having the composition M_2Zn_{17} , nearly all the remaining compounds decomposed before melting, losing zinc until reaching the composition M_2Zn_{17} . Consequently, in preparing the compounds richest in zinc, prolonged heating of the two metals at low temperatures to complete the reaction appeared to be the most convenient procedure, especially in view of the high reaction rate between zinc and the other metals, even at temperatures as low as 400°C.

Thorium powder, turnings of the RE metals and Ca, Sr and U, prepared under inert-gas atmosphere, were mixed with filings of zinc in various stoichiometric ratios, pressed, and heated either in glass vessels *in vacuo* for low temperatures (up to 600°C),

or in tantalum containers, closed under argon, for higher temperatures. The time of heating was sufficient to ensure complete reaction. The intermediate and final products of reaction were examined by X-ray diffraction ($\text{CuK}\alpha$ or $\text{FeK}\alpha$ radiation). In the majority of those cases in which it was impossible to obtain single crystals (MZn_{13} , MZn_{12} , MZn_{11} phases), the powder method was employed.

As the reactions were performed in sealed vessels it was assumed that there were no losses and that the constituent proportions were unchanged after reacting.

RESULTS

X-ray examination of the samples showed the existence of five structure types corresponding to four compositions, which are discussed below.

Irrespective of the initial composition, the first reaction products obtained at low temperature ($400^\circ\text{--}450^\circ\text{C}$) corresponded to the compounds richest in zinc existing for a given element at this temperature. These compounds have the formulae: MZn_{13} for Sr, Ca, La, Eu, Yb; MZn_{12} for Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu; MZn_{11} for Ce, Pr, Nd, and M_2Zn_{17} for Th and U.

MZn_{13} phases

These phases were prepared by prolonged heating of stoichiometric quantities of the two metals between 450° and 600°C *in vacuo*. In many cases, after the first reaction the samples were again pressed and reheated. The NaZn_{13} structure type¹ was found for SrZn_{13} , EuZn_{13} , CaZn_{13} (already known) and also for LaZn_{13} and YbZn_{13} . For the other RE metals, mixtures of zinc with the phases REZn_{11} or REZn_{12} were obtained. The phases REZn_{13} seem therefore, to exist only for the compounds of RE with La, Eu, Yb.

TABLE I

LATTICE CONSTANTS (\AA) OF MZn_{13} PHASES (NaZn_{13} TYPE)

	SrZn_{13}	EuZn_{13}	CaZn_{13}	YbZn_{13}	LaZn_{13}
This work ($\pm 0.005 \text{ \AA}$)	12.238	12.216	12.185	12.172	12.096
Other values	12.240 ³	12.216 ⁴	12.155 ³	—	{ From 12.096 to 12.079 ⁵

The MZn_{13} compounds are not all stable with increasing temperature. SrZn_{13} and EuZn_{13} could be melted without decomposition, but LaZn_{13} and YbZn_{13} decomposed respectively to $\text{LaZn}_{11} + \text{Zn}$ and $\text{YbZn}_{11} + \text{Zn}$ between 650° and 750°C . In one phase diagram of the La-Zn system², relating to a pressure of 10 atm, only LaZn_{13} appears; for this composition two arrests were observed at 710°C and 844°C and these are now interpreted as corresponding to two peritectic points, the first for LaZn_{13} , the second for LaZn_{11} .

Lattice constant values are reported in Table I, together with the values obtained by other authors.

MZn_{12} phases

The REZn_{12} phases only are formed by the elements from Sm to Lu, with the

exceptions of Eu, Yb, Ca and Sr, by heating the two metals for several days at 450°–500°C.

Their crystal structures are of the ThMn₁₂ type¹; Table II gives the structural data. The corresponding space group is the tetragonal $I4/mmm$ and the positions are: 2 RE in 2(a), 8 Zn in 8(f), 8 Zn in 8(i), and 8 Zn in 8(j). The last two positions contain two parameters (x and x' respectively) to be determined; these have been carried out from the reflection intensities on the powder photographs of TmZn₁₂. Geometrical

TABLE II

LATTICE CONSTANTS (Å) OF REZn₁₂ PHASES (ThMn₁₂ TYPE)

Compound	This work		Other values	
	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
	±0.003	±0.002		
SmZn ₁₂	8.927	5.215	—	—
GdZn ₁₂	8.898	5.210	—	—
TbZn ₁₂	8.884	5.200	8.856	5.199 ⁶
DyZn ₁₂	8.877	5.198	8.872	5.204 ⁶
HoZn ₁₂	8.868	5.195	—	—
ErZn ₁₂	8.863	5.193	8.850	5.195 ⁶
TmZn ₁₂	8.852	5.190	—	—
LuZn ₁₂	8.848	5.186	—	—

TABLE III

OBSERVED AND CALCULATED INTENSITIES FOR TmZn₁₂ (ThMn₁₂ TYPE)

<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}	<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}	<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}
110	1.1	—	303	12.0	10	552	19.7	20
101	0.7	—	600	2.9	—	712		
200	0.01	—	512	10.8	10	404	35.8	35
211	9.7	10	323	32.0	30	613	3.9	—
220			611	14.1	15	642	42.1	40
310	4.6	5	620			651	24.7	25
002	13.7	15	413	1.8	—	800		
301	28.6	30	442	2.5	2	334	4.7	—
112	1.0	—	541	1.9	—	424	15.9	15
202	48.0	50	532	15.9	15	543	2.6	—
321	100.0	100	004	15.7	15	741	14.0	15
400			602	75.2	75	811		
330	3.4	2	631			820	0.6	—
222	21.0	25	114	0.5	—	732		
411	15.4	15	550	8.2	10	633	55.0	55
420			710			660	25.6	20
312	5.4	5	204	0.04	—	514	18.7	15
510	7.2	5	433	9.3	10	105	0.5	—
103	0.3	—	503			750	0.5	—
402	1.4	—	622	2.1	—	703	4.4	—
431	9.0	10	701			802	4.1	—
501			640	1.4	—	831	86.7	85
332	4.6	5	224			215	7.1	—
213	3.1	2	523	2.7	5	444	23.1	25
422	9.5	10	721	8.9	10	723	26.9	30
521	7.7	10	314	3.7	5	822	35.7	35
440			730	0.2	—	840	34.4	35
530	9.3	10				534	63.2	60

considerations lead to x values from 0.350 to 0.356 and of x' values from 0.290 to 0.296. The calculations were carried out on an IBM 1620 computer for nine pairs of values and the best agreement was obtained for $x=0.353$ and $x'=0.293$. The observed and calculated intensities are reported in Table III.

Figure 1 shows three sections of the unit cell, at heights of $z=0$, $z=\frac{1}{2}$, $z=\frac{1}{4}; \frac{3}{4}$. Each RE atom is surrounded by 4 Zn (i) at 3.13 Å, 8 Zn (j) at 3.18 Å and 8 Zn (f) at 3.39 Å. The Zn atoms have inter-atomic distances varying from 2.60 to 2.90 Å. Taking the values of the atomic radii of Tm and Zn with co-ordination numbers 8 and 12⁷, the calculated distances are 3.05–3.12 Å (Tm–Zn) and 2.68–2.74 Å (Zn–Zn).

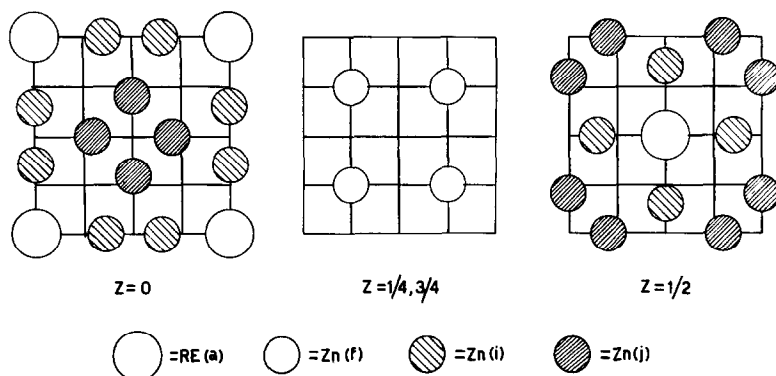


Fig. 1. ThMn_{12} type; sections of the unit cell.

MZn_{11} phases

Samples having the composition MZn_{11} were similarly prepared at temperatures up to 600°C. CaZn_{11} , LaZn_{11} , PrZn_{11} , NdZn_{11} , EuZn_{11} and YbZn_{11} (not SrZn_{11}) appear as homogeneous phases with the crystal structure of BaCd_{11} type⁸: for all other RE metals, X-ray patterns corresponding to the REZn_{12} phases were obtained. The phase diagram of the Ca–Zn system published by MESSING *et al.*⁹, shows the presence of the compound CaZn_{13} , which decomposes at 669°C, and of the compound CaZn_{11} having a melting point of 724°C, with which the present results are in agreement.

TABLE IV

LATTICE CONSTANTS (Å) OF MZn_{11} PHASES (BaCd_{11} TYPE)

Compound	This work		Other values	
	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
EuZn_{11}	± 0.004	± 0.003	10.72	6.877 ⁶
CaZn_{11}	10.719	6.874	—	—
YbZn_{11}	10.699	6.830	—	—
LaZn_{11}	10.637	6.822	10.66	6.838 ⁶
LaZn_{11}	10.686	6.881	10.68	6.87 ⁸
CeZn_{11}	—	—	10.66	6.86 ⁸
PrZn_{11}	10.626	6.835	10.662	6.855 ¹⁰
NdZn_{11}	10.608	6.828	10.65	6.85 ⁸
NdZn_{11}	—	—	10.64	6.842 ⁶

Table IV reports our lattice constant values for these phases together with those already known, and others published in the course of this work.

M_2Zn_{17} phases

These phases can be formed by the decomposition of the zinc-rich RE-Zn alloys and by direct reaction. They can be melted in closed containers under argon without decomposition. Attempts to prepare Sr_2Zn_{17} , Ca_2Zn_{17} and Eu_2Zn_{17} were unsuccessful, mixtures of MZn_5 with MZn_{11} or MZn_{13} being obtained. In the systems La-Zn and Ce-Zn referred to by GSCHNEIDNER², his suggestion that the compositions $REZn_8$ or $REZn_9$ must be replaced by RE_2Zn_{17} is then justified.

Each of the preceding phases, MZn_{13} , MZn_{12} , MZn_{11} , and M_2Zn_{17} shows a very restricted homogeneity range. Different preparations always gave identical X-ray photographs and their denomination as "compounds" thus appears to be justified. In the course of this investigation the recent work of VELEKIS *et al.*⁵, was kindly brought to our notice by the authors. By means of a recording effusion balance and by X-ray diffraction they have examined the systems of zinc with La, Ce, Pr, Nd and Y. Their results are in complete agreement with ours and show the existence of the phases: $REZn_{13}$ for La; $REZn_{11}$ for La, Ce, Pr, Nd; $REZn_{12}$ for Y, and RE_2Zn_{17} for all of the RE systems examined.

The crystal structure determination of the RE_2Zn_{17} compounds was performed on single crystals of Ho_2Zn_{17} , obtained from a melted sample. After some difficulties, due to the ease of twinning, a single crystal was found which showed rhombohedral symmetry, with lattice constants referred to hexagonal axes: $a \cong 8.97$ and $c \cong 13.15$ Å and with 3 formula units per unit cell. The possible space groups were: $R3m$; $R\bar{3}m$, and a discussion of the different possible positions suggested the already known structure of the Th_2Zn_{17} type¹², ($R\bar{3}m$). Powder photographs of a sample of Th_2Zn_{17} showed complete similarity with those of all RE_2Zn_{17} compounds. The atomic positions, in the space group $R\bar{3}m$ are¹³:

6 Ho in	6(c)	: 00z	... with $z = \frac{1}{3}$
6 Zn in	6(c)	: 00z'	... with $z' = 0.097$
9 Zn in	9(d)	: $\frac{1}{2}\frac{1}{2}0$...
18 Zn in	18(f)	: x00	... with $x = \frac{1}{3}$
18 Zn in	18(h)	: x'x'z	... with $x' = \frac{1}{6}$ and $z = \frac{1}{2}$

A first calculation of the intensities for a powder photograph of Gd_2Zn_{17} with the preceding values gave results that were not wholly satisfactory. As the distances between zinc atoms in 18(f) were greater than the sum of the atomic radii, the intensities were recalculated with various x values, giving, for $x = 0.30$, results which are in good agreement with the observed ones, as shown in Table V. This divergence from $x = \frac{1}{3} = 0.333$ produces an approach of zinc atoms at distances of 2.70 Å to form hexagons around the couples of zinc in 6(c). Table VI contains the lattice constant values.

This structure may be considered as formed by atomic layers of four types, as in the following graph (Fig. 2), with the stacking sequence: ADBDCDA...

Another crystal form has been observed by VELEKIS *et al.*⁵ for some RE_2Zn_{17} compounds prepared at about 500°C (U_2Zn_{17} type), and also by KUZ'MA *et al.*⁶ (Th_2Ni_{17} type¹¹). These two structure types are closely related to Th_2Zn_{17} , as they

TABLE V

OBSERVED AND CALCULATED INTENSITIES FOR Gd_2Zn_{17} (Th_2Zn_{17} TYPE)

<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}	<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}	<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}
101	0.04	—	330	5.5	5	508	1.0	—
102	0.2	—	325	4.2	5	3.1.10	0.4	20
110	0.2	—	421	0.1	—	440	21.5	
003	0.1	—	009	0.3	—	517	2.0	30
201	0.6	—	422	0.4	—	614	0.4	
202	1.7	—	218	1.0	—	606	42.8	
113	12.0	10	333	21.2	20	2.1.11	0.4	—
104	1.2	2	317	0.1		701	1.0	20
211	0.4	—	504	1.3	—	419	19.5	
212	1.6	—	511	0.6	6	702	0.5	—
300	20.9	20	119	6.5		428	1.0	—
204	2.8	5	512	1.2	2	0.0.12	14.0	
105	1.9		407	0.01	—	4.0.10	0.7	5
220	36.1	100	424	1.2	5	443	5.0	
303	63.9		416	1.2		526	1.4	—
214	3.4	25	505	1.9	—	615	1.0	—
006	21.6		318	0.1		621	1.2	—
205	3.6	—	600	28.0	25	622	2.3	5
311	0.2	—	1.0.10	0.1		518	2.5	
312	0.01	—	327	1.6	5	1.1.12	0.01	—
223	19.9	20	514	2.4		3.2.10	0.3	
116	3.1	5	425	2.1	30	437	0.1	—
215	4.7		431	0.7		704	0.1	—
401	0.6	—	309	31.6	2	339	42.1	40
402	0.1	—	432	0.3		3.1.11	0.01	
107	0.2	—	408	0.01	—	710	3.0	2
314	0.5	—	2.0.10	0.02		624	5.6	
321	0.9	2	520	0.5	—	705	0.01	—
322	1.9	—	603	0.3	—	4.0.11	0.2	—
410	0.7	—	336	2.4	5	438	0.2	20
207	0.9	—	515	3.6		3.0.12	21.4	
404	0.01	8	229	4.5	5	5.0.10	0.2	—
306	7.4		328	1.8	—	713	33.3	
315	1.2	—	2.1.10	0.01	—	617	0.2	25
108	0.2		523	9.0	10	1.0.13	0.02	
413	11.3	13	507	0.9		446	53.3	70
217	1.1		434	0.01	—	625	11.1	
324	3.2	20	611	0.1	—	541	1.5	—
226	18.0		1.0.11	0.02	—	3.2.11	2.6	—
405	0.1	—	612	0.01	—	542	4.3	70
501	0.4	—	427	0.8	—	2.2.12	77.7	
502	0.7	2	435	0.1	—	4.2.10	0.01	—
208	0.7		2.0.11	0.3	—	2.0.13	1.1	—

are formed by the same layers as in Fig. 2, but with different stacking sequences; the U_2Zn_{17} type corresponding to ADBDCDADCDBA..., the Th_2Ni_{17} to BDCDB..., both with hexagonal symmetry. The U_2Zn_{17} type was reported by MAKAROV AND VINOGRADOV^{12,14}, but a detailed study by VOLD AND PETERSON¹⁵ showed for U_2Zn_{17} the existence of a rhombohedral modification (β) (Th_2Zn_{17} type), and of a hexagonal one, (α), but of the Th_2Ni_{17} type.

We have examined this structure type for samples of RE metals and zinc, reacted for 5 days at 500°C in proportions corresponding to the composition RE_2Zn_{17} and for comparison, we have prepared U_2Zn_{17} similarly. All these products give

TABLE VI

LATTICE CONSTANTS (Å) OF $\text{RE}_2\text{Zn}_{17}$ PHASES ($\text{Th}_2\text{Zn}_{17}$ TYPE)

Compound	hexagonal axes		Ref.
	<i>a</i>	<i>c</i>	
	± 0.004	± 0.005	
$\text{La}_2\text{Zn}_{17}$	9.131	13.334	
$\text{Ce}_2\text{Zn}_{17}$	9.088	13.290	
$\text{Pr}_2\text{Zn}_{17}$	9.066	13.274	
$\text{Nd}_2\text{Zn}_{17}$	9.052	13.236	
$\text{Sm}_2\text{Zn}_{17}$	9.017	13.211	
$\text{Gd}_2\text{Zn}_{17}$	8.994	13.169	
$\text{Tb}_2\text{Zn}_{17}$	8.977	13.161	
$\text{Dy}_2\text{Zn}_{17}$	8.967	13.139	
$\text{Ho}_2\text{Zn}_{17}$	8.956	13.133	
$\text{Er}_2\text{Zn}_{17}$	8.942	13.118	
$\text{Tm}_2\text{Zn}_{17}$	8.937	13.110	
$\text{Yb}_2\text{Zn}_{17}$	9.040	13.216	
$\text{Lu}_2\text{Zn}_{17}$	8.920	13.096	
$\text{Th}_2\text{Zn}_{17}$	{ 9.060 9.03	{ 13.234 13.20	this work 12
U_2Zn_{17}	{ 8.983 8.978	{ 13.161 13.160	this work 15

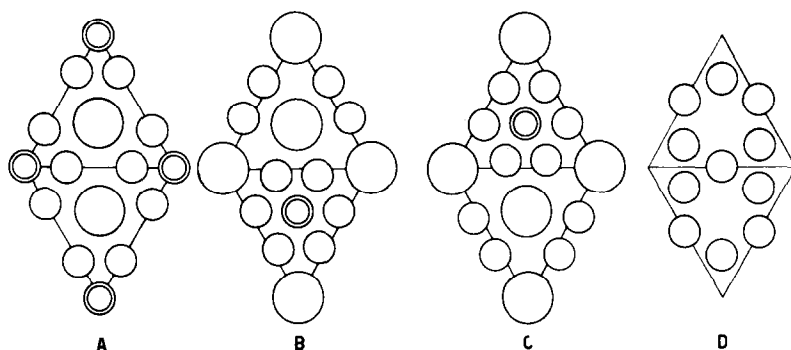


Fig. 2. Atomic layers in the M_2Zn_{17} structures. Large circles are M atoms, small circles zinc atoms. Double circles represent pairs of zinc atoms above and below the plane of the others.

similar X-ray powder photographs, little different from those of the $\text{Th}_2\text{Zn}_{17}$ type. For Eu, Yb, La only REZn_{11} and REZn_{13} phases are formed.

The powder photographs of this low temperature form could be indexed as a hexagonal cell corresponding to $\text{Th}_2\text{Ni}_{17}$ type, and the structure was determined by calculating the reflection intensities of $\alpha\text{-Dy}_2\text{Zn}_{17}$ using the original values¹¹ of the parameters. This first calculation did not give good agreement. Following the same dimensional considerations employed in determining the structure of the β form, the intensities were recalculated with the same change in the positions of a part of the zinc atoms. A better, but not wholly satisfactory result was obtained; somewhat surprisingly the agreement in the two cases was better for the reflections with $h-k=3n$; for the others it was possible to observe on the powder photographs only five very faint reflections, while from the calculated intensities about twenty-five weak, but again detectable, reflections must be present.

TABLE VII

OBSERVED AND CALCULATED INTENSITIES FOR $\text{Dy}_2\text{Zn}_{17}$ ($\text{Th}_2\text{Ni}_{17}$ TYPE)

hkl	$I_{\text{calc.}}$	$I_{\text{obs.}}$	hkl	$I_{\text{calc.}}$	$I_{\text{obs.}}$
110	0.2	—	520	0.5	—
002	0.1	—	602	0.2	—
112	11.6	10	334	2.6	3
300	20.1	20	226	4.9	3
220	35.5	100	522	10.8	10
302	64.5		440	23.7	20
004	21.6	20	604	47.3	45
222	18.0	25	416	20.5	18
114	2.9	3	008	16.1	15
410	0.8	—	442	4.8	6
304	6.6	6	524	1.4	—
412	13.0	12	118	0.1	—
224	18.5	20	336	45.4	50
330	5.8	6	710	3.7	—
006	0.3	—	308	28.7	30
332	23.0	25	712	42.9	40
116	6.6	6	444	62.7	60
414	1.1	—			
600	29.7	30			
306	33.4	30			

TABLE VIII

LATTICE CONSTANTS (\AA) OF $\text{RE}_2\text{Zn}_{17}$ PHASES ($\text{Th}_2\text{Zn}_{17}$ TYPE)

Compound	This work		Other values		Ref.
	a	c	a	c	
	± 0.004	± 0.004			
$\text{Ce}_2\text{Zn}_{17}$	9.088	8.856	—	—	
$\text{Pr}_2\text{Zn}_{17}$	9.063	8.847	—	—	
$\text{Nd}_2\text{Zn}_{17}$	9.042	8.838	—	—	
$\text{Sm}_2\text{Zn}_{17}$	9.010	8.807	8.979	8.876	6
$\text{Gd}_2\text{Zn}_{17}$	8.994	8.779	8.987	8.828	6
$\text{Tb}_2\text{Zn}_{17}$	8.978	8.768	8.984	8.770	6
$\text{Dy}_2\text{Zn}_{17}$	8.956	8.776	8.980	8.801	6
$\text{Ho}_2\text{Zn}_{17}$	8.949	8.758	8.963	8.747	6
$\text{Er}_2\text{Zn}_{17}$	8.947	8.745	—	—	
$\text{Tm}_2\text{Zn}_{17}$	8.935	8.752	8.939	8.736	6
$\text{Lu}_2\text{Zn}_{17}$	8.925	8.738	—	—	
$\text{Th}_2\text{Zn}_{17}$	9.032	8.929	—	—	
U_2Zn_{17}	8.974	8.804	8.962	8.809	15

This disagreement may be explained, as for the hexagonal form of U_2Zn_{17} ¹⁵, by assuming stacking faults of the layers A, B, C of Fig. 2, corresponding to sequences BDCDB..., ADBDA..., ADCDA... If so, the reflections with $h-k=3n$ are unaffected while the others are lowered and enlarged. In Table VII only the observed and calculated intensities for the reflections of the first kind are reported and only those with $l=2n$, as for l odd, have about zero intensity. With the following values of the positions and of the parameters, in the space group $P6_3/mmc$, a reasonable agreement may be observed:

2 Dy in 2(b) :	$00\frac{1}{4}$...
2 Dy in 2(d) :	$\frac{1}{2}\frac{2}{3}\frac{3}{4}$...
4 Zn in 4(f) :	$\frac{1}{3}\frac{2}{3}z$... with $z=0.11$
6 Zn in 6(g) :	$\frac{1}{2}00$...
12 Zn in 12(k) :	$x, 2x, 0$... with $x=\frac{1}{6}$
12 Zn in 12(j) :	$x, y, \frac{1}{4}$... with $x=0.033, y=\frac{2}{3}$

Table VIII contains the lattice constant values for α -RE₂Zn₁₇ compounds. Here, and also in Table VI, the values for U₂Zn₁₇ and Th₂Zn₁₇ are reported. For U₂Zn₁₇, contrary to VOLD AND PETERSON¹⁵, we were only able to obtain the α -form by reaction of the two metals for 15 days at 550°C, while the β -form appeared in melted samples (about 1100°C), as in the case of the RE₂Zn₁₇ compounds. For Th, the hexagonal α -form (not yet known) was obtained at low temperature (540°C) for compositions having zinc a little in excess of the composition Th₂Zn₁₇.

For all M₂Zn₁₇ compounds examined, the α -form appears to be a polytypic rather than a polymorphic modification. While the β -form can always be obtained from the α -form by heating, it seems impossible to revert from β to α : a sample of β -Ho₂Zn₁₇ gave an identical powder photograph after annealing for 10 days at 500°C. Furthermore, the α -form seems to be stabilised by a little excess zinc, as in the case of Th₂Zn₁₇. For Dy, samples obtained by reaction at 500°C for one month, having the compositions DyZn₈, Dy₂Zn₁₇, and DyZn₉, showed that the first had the rhombohedral structure whereas the two latter were hexagonal.

DISCUSSION

The five structure types found for the compounds richest in zinc are characterised by the formation of a network of zinc atoms containing a certain number of nearly spherical holes in which the RE, or other atoms, may be arranged. The diameter and the number of the holes vary according to the structure, and the whole is stabilised through the introduction of M atoms in the corresponding positions. Hence the structure and the formula change if the dimensions of the M atoms become too large or too small.

In the proposed scheme (Fig. 3), where the various types are reported for the M atoms arranged in order of decreasing atomic radius, it is apparent that the ranges of existence for the various structure types are closely related to the dimensions of the M atoms.

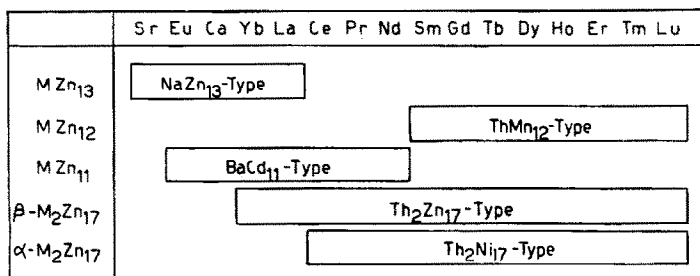


Fig. 3. Existence ranges for the examined zinc compounds.

The number of zinc atoms surrounding each M atom is: 24 for NaZn_{13} type; $8+10$ (+4) for BaCd_{11} type; $12+8$ for ThMn_{12} type, and $6+12$ for all M_2Zn_{17} types. The two values correspond to increasing M-Zn distances, which may be much greater than the sum of the atomic radii (*e.g.* in NaZn_{13} type). This makes it difficult to define a "coordination number" for M atoms and to discuss the different structures more quantitatively. A criterion of stability for a certain structure based on the atomic size is not sufficient. For the Th-Zn system, various attempts to prepare phases richer in zinc than $\text{Th}_2\text{Zn}_{17}$ were unsuccessful, although the radius of Th is the same as

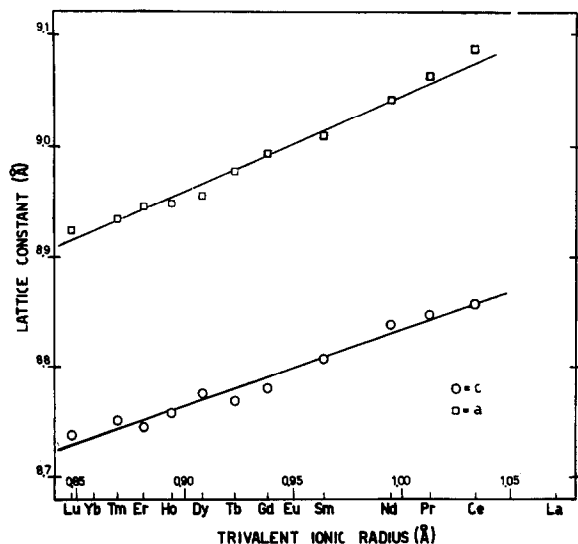


Fig. 4. Lattice constants of $\alpha\text{-RE}_2\text{Zn}_{17}$ compounds *vs.* RE trivalent ionic radii.

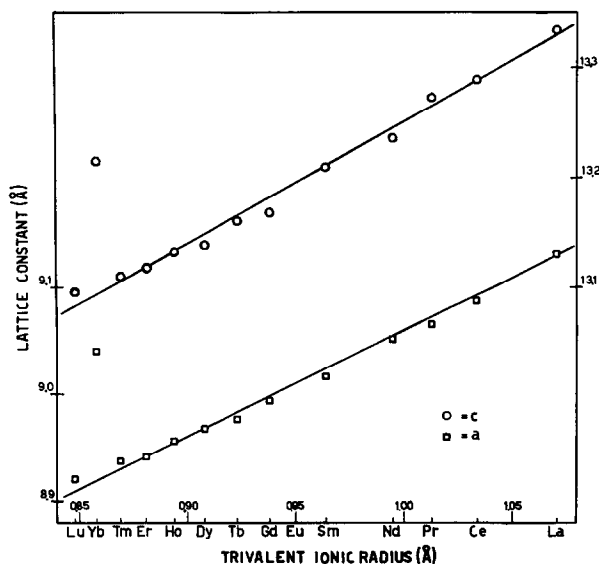


Fig. 5. Lattice constants of $\beta\text{-RE}_2\text{Zn}_{17}$ compounds *vs.* RE trivalent ionic radii.

that of Nd or Sm and the formation of ThZn_{11} or ThZn_{12} should thus be dimensionally possible.

For the various compounds of trivalent RE examined, the decrease of lattice dimensions from La to Lu, as for other series, follows those of the trivalent ionic radii; this can be seen for the most complete series of REZn_{12} and $\text{RE}_2\text{Zn}_{17}$ compounds. In Figs. 4 and 5 the lattice constants *vs.* the values of the trivalent ionic radii for α - and β - $\text{RE}_2\text{Zn}_{17}$ are shown and a regular linear variation is observed. For REZn_{12} compounds two straight lines should again result, but with very little slope.

In Fig. 3, Eu and Yb are placed between Sr, Ca and La, taking the values of the atomic radii which correspond to divalent elements. Their divalency has been confirmed by magnetic measurements on EuZn_{13} , YbZn_{13} , EuZn_{11} , YbZn_{11} and $\text{Yb}_2\text{Zn}_{17}$, the values of magnetic susceptibilities and the moments corresponding to Eu^{2+} and Yb^{2+} . This behaviour of Eu and Yb is observed in many other intermetallic compounds; the existence of Eu^{3+} and of Yb^{3+} appears to be the exception.

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