

It is interesting to note that the structural sequences, viz. (221212)<sub>3</sub> and (2221212)<sub>3</sub>, of types 30R and 42R respectively, closely resemble each other. In fact, as indicated earlier, the structure of type 42R could be calculated relatively easily by anticipating that it could be similar to that of type 30R. Whether this resemblance is purely a matter of chance or is indicative of the existence of a structural series of the form [(22)<sub>n</sub>(12)<sub>2</sub>]<sub>3</sub> for rhombohedral polytypes of cadmium iodide is difficult to say at present. The issue can be decided only after more rhombohedral modifications of cadmium iodide are discovered and their structures worked out. Nevertheless, this point may be of great help in the determination of the structures of any future rhombohedral types.

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## The Crystal Structure of Gd<sub>13</sub>Zn<sub>58</sub>

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By single-crystal X-ray diffraction methods, a compound, Gd<sub>13</sub>Zn<sub>58</sub>, has been identified in the Gd-Zn system and its crystal structure determined. Gd<sub>13</sub>Zn<sub>58</sub> is a complex structure with 142 atoms (two units of Gd<sub>13</sub>Zn<sub>58</sub>) in a unit cell of space group *P6<sub>3</sub>mc* with dimensions  $a = 14.35$ ,  $c = 14.21$  Å.

#### Introduction

A<sub>6</sub>B<sub>23</sub> (Th<sub>6</sub>Mn<sub>23</sub>-type; Florio, Rundle & Snow, 1952) compounds have been found to exist both in the R (rare earths)–Mn (Wang, Gilfrich, Ernst & Hubbard, 1964; Wang & Holden, 1965) and R–Fe (Kripyakevich & Frankevich, 1965) systems. The basic atomic arrangement in these compounds is the octahedrally clustered group of six rare earth atoms. The limitation to the formation of A<sub>6</sub>B<sub>23</sub> compounds of such a geometrical arrangement has been discussed (Wang & Holden, 1965). Because the atomic radii of Mn and Zn are nearly equal (Mn 1.36 Å, Zn 1.33 Å)\*, based on the 'size factor' consideration alone, the existence of A<sub>6</sub>B<sub>23</sub> compounds in the R–Zn systems would be expected. This paper is a partial report on the efforts

which have been made to find A<sub>6</sub>B<sub>23</sub>-type compounds or compounds with similar atomic arrangements such as SrMg<sub>4</sub> (Wang, Kanda, Miskell & King, 1965) in the R–Zn systems.

The complexities of R–Zn systems are exemplified by the works of Rolla & Iandelli (1941) on the La–Zn system, Chiotti, Mason & Gill (1963) on the Y–Zn system and Chiotti & Mason (1965) on the Ce–Zn system. While the numbers of intermediate phases reported to exist in these three systems differ, there is a profound similarity in the general features of the three reported phase diagrams. Therefore, it is likely that the three systems have the same number of intermediate phases and that these phases have the same crystal structures. Extension of this reasoning suggests that the same crystal structures will be found for the intermediate phases between all the rare earths (except perhaps Eu and Yb) and zinc.

\* The atomic radii used throughout this paper are from *Tables of Interatomic Distances* (1958).

Until the recent single-crystal work of Sree Harsha (1964) on  $YZn_2$ ,  $YZn_3$ , and  $Y_3Zn_{11}$ , the crystal structure determinations of the intermediate phases between the rare earths and zinc have been limited to  $RZn$  (CsCl type),  $RZn_5$  (CaCu<sub>5</sub> type) and  $RZn_{11}$  (BaCd<sub>11</sub> type) based on powder pattern methods as summarized by Gschneidner (1961). Meanwhile the crystallographic data for the cerium-zinc compounds have been given by Lott & Chiotti (1966) very recently.

### Experimental

The gadolinium metal in ingot form, supplied by Michigan Chemical Corp. (St. Louis, Michigan) was guaranteed by the supplier to be at least 99.9 wt.% pure (traces of silicon, calcium and other minor constituents present on occasion, not to be more than 0.05 wt.%) as shown by spectrographic analysis. Zinc metal in rod form supplied by United Mineral and Chemical Corporation (New York, N.Y.) has a purity of 99.9998 wt.% according to the supplier. Because of the relatively low melting point and high vapor pressure of zinc metal, it was considered ideal to alloy zinc with gadolinium in 'quartz' (fused silica) tubing under argon atmosphere. Experimentally, through electron microprobe analysis, it was found that (1) at 800°C zinc readily diffused into gadolinium and that (2) no significant amount of silicon was detected in the alloy to indicate possible chemical reaction between the alloying elements and the 'quartz' tubing.

A sample with the atomic composition ratio Gd:Zn = 1:4 (with 3 g Gd), was sealed under an argon at-

mosphere in 'quartz' tubing and held at 800°C for 48 hours. Electron microprobe analysis across the sample surface showed that there were two predominant regions in which the Zn/Gd ratio approximated 3.7 and 4.3 respectively. Therefore, the alloy prepared in this manner was a two-phase alloy. The crystal used in the present investigation was obtained from the matrix which was found to have a zinc to gadolinium ratio of 4.3.

Both Weissenberg and Buerger precession cameras were used in the single-crystal studies. The methods used in the collection of intensity data and its conversion to  $k|F_o|^2$  were essentially the same as those described in the identification of  $Gd_6Mn_{23}$  (Wang, Gilfrich, Ernst & Hubbard, 1964). With the use of Mo radiation, the lattice constants were obtained from  $hk0$  and  $h0l$  Weissenberg photographs which had been calibrated against NaCl lines ( $a = 5.6394 \text{ \AA}$ ).

The 'X-ray 63 system' (Stewart, 1964) was used for Fourier summations and least-squares refinement. For the least-squares refinement of those atomic positions in which the  $y$  positional parameter is equal to the negative value of  $x$ , a 'patch' was written and added to the 'X-ray 63 system'; during each cycle of refinement, the  $y$  parameters were held constant and subsequently replaced by the newly adjusted negative values of  $x$  prior to the next cycle of refinement. The atomic scattering factors given by Thomas & Umeda (1957) were used and no dispersion corrections were applied. The weighting scheme adopted in the calculation was that patterned after the method suggested by Hughes (1941). Observed reflections were given

Table 1. *Crystallographic data including the final atomic coordinates and isotropic temperature factors*

(Average standard deviation of coordinates  $\pm 0.02 \text{ \AA}$  for Gd and  $\pm 0.04$  for Zn)

$Gd_{13}Zn_{58}$  (two formula units per unit cell)

Space group:  $P6_3mc$

Lattice constants:  $a = 14.352$ ,  $c = 14.218 \text{ \AA}$  ( $\pm 0.008 \text{ \AA}$ )

Density: exp.  $7.57 \text{ g.cm}^{-3}$ , cal.  $7.63 \text{ g.cm}^{-3}$

Position	Atom	$x$	$\sigma(x) \times 10^4$	$y$	$\sigma(y) \times 10^4$	$z$	$\sigma(z) \times 10^4$	$B$	$\sigma(B)$
6(c)	Gd(1)	0.1316	14	-x	—	0.0	—	1.63	0.13
6(c)	Gd(2)	0.4538	15	-x	—	0.0165	24	1.16	0.20
6(c)	Gd(3)	-0.2102	12	-x	—	0.2206	16	1.08	0.19
2(a)	Gd(4)	0.0	—	0.0	—	0.2650	31	1.66	0.17
6(c)	Gd(5)	0.1993	17	-x	—	0.3282	21	1.98	0.19
2(b)	Zn(1)	0.3333	—	-0.3333	—	0.0052	9	2.15	0.25
2(a)	Zn(2)	0.0	—	0.0	—	0.0141	13	2.19	0.24
12(d)	Zn(3)	0.3695	16	0.0856	16	0.0248	25	2.03	0.27
6(c)	Zn(4)	-0.2730	36	-x	—	0.0336	42	2.24	0.31
6(c)	Zn(5)	0.2264	44	-x	—	0.1052	39	2.19	0.27
6(c)	Zn(6)	-0.1051	33	-x	—	0.1167	29	2.22	0.33
6(c)	Zn(7)	-0.4346	26	-x	—	0.1410	27	1.61	0.28
12(d)	Zn(8)	0.3272	26	0.3576	27	0.1769	26	1.73	0.25
2(b)	Zn(9)	-0.3333	—	0.3333	—	0.1780	47	2.49	0.26
6(c)	Zn(10)	0.3968	23	-x	—	0.2273	26	1.05	0.22
6(c)	Zn(11)	0.5064	32	-x	—	0.2779	36	2.62	0.28
12(d)	Zn(12)	0.1779	36	-0.0244	39	0.2861	40	2.10	0.27
2(b)	Zn(13)	0.3333	—	-0.3333	—	0.3148	52	2.13	0.31
6(c)	Zn(14)	-0.3844	32	-x	—	0.3376	33	2.07	0.29
12(d)	Zn(15)	0.3803	24	0.0428	25	0.3778	26	2.52	0.24
6(c)	Zn(16)	-0.2444	45	-x	—	0.4207	42	2.05	0.30
6(c)	Zn(17)	0.0772	40	-x	—	0.4305	37	2.20	0.29
6(c)	Zn(18)	0.4380	40	-x	—	0.4386	35	1.23	0.31

weight 1.0 if  $|F_o|$  was less than 30 and  $30/|F_o|$  if  $|F_o|$  was equal to or greater than 30. The relative magnitude of the observed reflections ranged from 3 to 352.

**Structure determination**

Single crystals of approximately spherical shape (approximate diameter 0.03 mm), obtained from an alloy matrix with the composition ratio Zn/Gd-4.3, showed diffraction symmetry  $6/mmm$  (hexagonal) with lattice constants  $a=14.35$  and  $c=14.21$  Å. The only systematic extinction observed in the eight layers of Weissenberg photographs,  $hk \cdot l$  for  $0 \leq k \leq 7$ , (532 symmetry-independent observed reflections) was  $l=2n+1$  for  $hh \cdot l$  reflections. Therefore, the possible space groups are limited to  $P6_3/mmc$ ,  $P\bar{6}2c$  and  $P6_3mc$ . Although, in space group  $P6_322$ , these extinctions apply for cer-

tain special positions, the space group was not considered possible for the following reasons. If all the atoms were to be found in these special positions, the space group would be  $P6_3/mmc$ . On the other hand, owing to the large unit cell size, spatially it would be impossible to have the majority of the atoms in these special positions and leaving a small number of atoms in the positions other than these special positions such as to account for the apparent extinction.

A three-dimensional Patterson synthesis showed that there are no mirror planes perpendicular to the  $c$  axis in the real cell (based on an analysis of the  $(0,0,w)$  Harker line). This eliminated space groups  $P\bar{6}2c$  and  $P6_3/mmc$ . Therefore, by process of elimination, space group  $P6_3mc$  was chosen for the compound. This space group was eventually found to be compatible with all the atom positions found by analysis of the three-dimensional Patterson vectors and their peak heights.

Initial analysis of the Patterson map revealed 24 Gd and 22 Zn atoms which gave an agreement index,  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ , of 31% and confirmed the correct identification of these atomic positions. A subsequent difference Fourier map from which the 24 Gd and 22 Zn atoms were subtracted yielded positions for 2 Gd and 58 Zn atoms. The ensuing structure factor calculations based on the 26 Gd and 80 Zn atoms gave an agreement factor,  $R(F)$ , of 19% and served as the basis for a further difference Fourier synthesis. Thirty-six more Zn atoms were located from this map giving a total of 26 Gd and 116 Zn atoms in the unit cell.

After four cycles of isotropic full-matrix least-squares refinement an  $R(F)$  of 0.13 was obtained. The  $z$  parameter of the three Gd(1) atoms was set equal to zero in the least-squares refinement in order to establish the origin of the unit cell. The crystallographic data and the final atomic positional parameters are given in Table 1. The interatomic distances and coordination numbers, following the definition of Frank & Kasper (1958), are given in Table 2. In Table 3 the calculated and observed structure factors are listed. These atomic positions gave the formula  $Gd_{13}Zn_{58}$  for the compound with two formula weights per unit cell. The density of the compound was found by the displacement method (in water and in air) to be  $7.57 \text{ g.cm}^{-3}$ . This value compares favorably with the calculated value,  $7.63 \text{ g.cm}^{-3}$  based on two units of  $Gd_{13}Zn_{58}$  per unit cell.

**Discussion**

While there are five crystallographically different kinds of Gd atom in  $Gd_{13}Zn_{58}$ , from the basis of coordination geometry, they can be considered in three physically distinct groups. These are: (a) Gd(1) and Gd(2) - total C.N. (coordination number) is 16, includes one gadolinium atom; (b) Gd(3) and Gd(5) - total C.N. is 18, includes no gadolinium atom; and (c) Gd(4) - total C.N. is 17, includes three gadolinium atoms. Taking the atomic radii of Gd and Zn in metal as

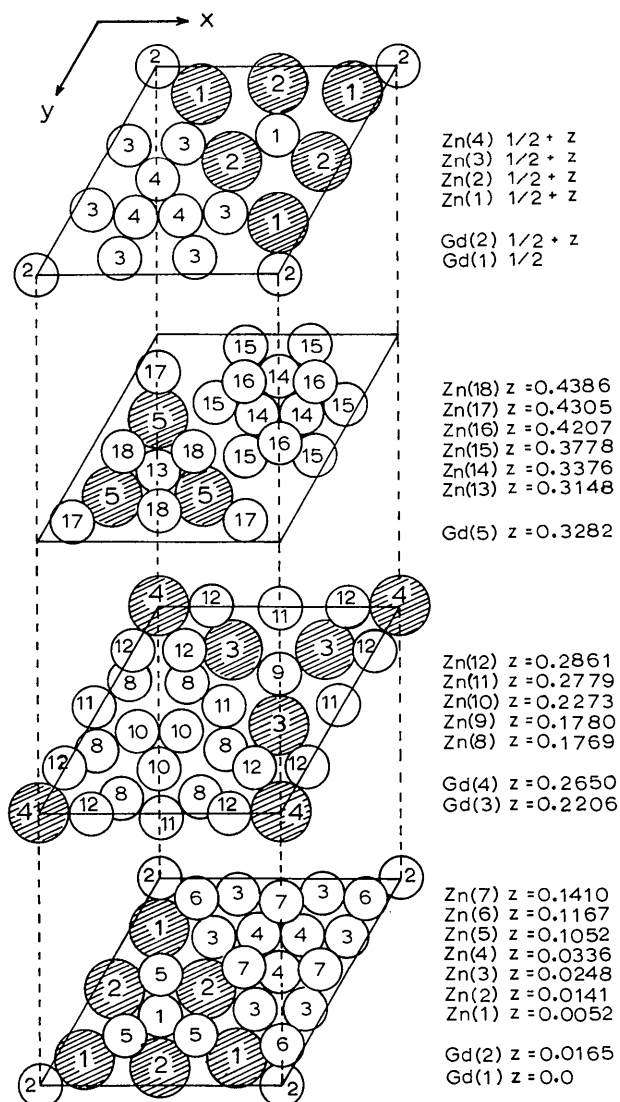


Fig. 1. Projection of the atoms onto the  $xy$  plane (full cell) at various levels of  $z$ . Shaded circles Gd; open circles Zn.

1.78 and 1.33 Å respectively, the atomic sizes observed in this structure are reasonable with the exception of Zn(12) and Zn(17). The radii of the zinc atoms belonging to these two groups appear to have contracted by as much as 17% of metallic radii. These contrac-

tions are manifested in the following interatomic distances in which atoms are in direct contact: Zn(12)–Zn(12) 2.20 Å, Zn(12)–Gd(4) 2.76 Å, Zn(12)–Gd(5) 2.74 Å, Zn(12)–Zn(17) 2.40 Å and Zn(17)–Zn(2) 2.35 Å. It is interesting to note that both Zn(12) and Zn(17)

Table 2. *Interatomic distances*

Gd(1) - 1Gd(2) 4.37Å	Zn(1) - 3Gd(2) 3.00Å	- 2Zn(8) 3.06	- 3Zn(4) 3.45
- 1Zn(2) 3.27	- 3Zn(5) 3.01	- 1Zn(9) 2.57	- 3Zn(10) 2.32
- 2Zn(3) 3.29	- 3Zn(10) 3.53	- 1Zn(11) 2.43	- 3Zn(18) 2.82
- 1Zn(5) 2.79	- 3Zn(14) 2.70	- 1Zn(18) 2.88	
- 2Zn(6) 3.42	- 3Zn(16) 2.51		
- 2Zn(8) 3.49		Zn(8) - 1Gd(1) 3.49Å	Zn(14) - 1Gd(2) 3.07Å
- 2Zn(12) 3.60		- 1Gd(2) 3.30	- 2Gd(3) 3.13
- 2Zn(15) 3.10	Zn(2) - 3Gd(1) 3.27Å	- 1Gd(3) 3.08	- 1Zn(1) 2.70
- 1Zn(16) 3.02	- 2Gd(4) 3.54	- 1Gd(5) 3.07	- 1Zn(9) 2.60
- 2Zn(17) 2.96	- 3Zn(6) 2.99	- 1Zn(3) 2.61	- 1Zn(11) 2.84
	- 3Zn(17) 2.35	- 1Zn(5) 2.64	- 2Zn(14) 2.32
		- 1Zn(7) 3.06	- 1Zn(15) 3.14
		- 1Zn(10) 3.22	- 2Zn(16) 2.25
		- 1Zn(11) 2.73	
		- 1Zn(12) 2.68	Zn(15) - 1Gd(1) 3.10Å
		- 1Zn(15) 3.00	- 1Gd(2) 2.89
Gd(2) - 1Gd(1) 4.37Å	Zn(3) - 1Gd(1) 3.29Å		- 1Gd(3) 3.11
- 1Zn(1) 3.00	- 1Gd(2) 3.33	Zn(9) - 3Gd(3) 3.12Å	- 1Gd(5) 3.20
- 2Zn(3) 3.33	- 1Gd(3) 3.19	- 3Zn(4) 2.54	- 1Zn(8) 3.00
- 2Zn(5) 3.10	- 1Zn(3) 2.84	- 3Zn(7) 2.57	- 1Zn(11) 2.50
- 1Zn(7) 3.29	- 1Zn(4) 2.61	- 3Zn(14) 2.60	- 1Zn(12) 2.87
- 2Zn(8) 3.30	- 1Zn(6) 2.76		- 1Zn(14) 3.14
- 1Zn(10) 3.31	- 1Zn(7) 3.03		- 1Zn(16) 2.58
- 1Zn(14) 3.07	- 1Zn(8) 2.61		- 1Zn(18) 3.02
- 2Zn(15) 2.89	- 1Zn(17) 3.25		
- 2Zn(16) 3.01	- 1Zn(18) 2.81		
- 1Zn(18) 2.90			
		Zn(10) - 1Gd(2) 3.31Å	Zn(16) - 1Gd(1) 3.02Å
Gd(3) - 2Zn(3) 3.19Å	Zn(4) - 1Gd(3) 3.08Å	- 2Gd(5) 3.22	- 2Gd(2) 3.01
- 1Zn(4) 3.08	- 1Gd(5) 3.44	- 1Zn(1) 3.53	- 1Gd(3) 2.96
- 1Zn(6) 3.00	- 2Zn(3) 2.61	- 2Zn(5) 2.89	- 1Zn(1) 2.51
- 2Zn(7) 3.04	- 2Zn(4) 2.59	- 2Zn(8) 3.22	- 1Zn(5) 2.66
- 2Zn(8) 3.08	- 2Zn(7) 2.67	- 2Zn(10) 2.73	- 2Zn(14) 2.25
- 1Zn(9) 3.12	- 1Zn(9) 2.54	- 1Zn(11) 2.82	- 2Zn(15) 2.58
- 2Zn(11) 3.70	- 1Zn(13) 3.45	- 1Zn(13) 2.32	
- 2Zn(12) 3.55	- 2Zn(18) 2.63		
- 2Zn(14) 3.13			
- 2Zn(15) 3.11			
- 1Zn(16) 2.96	Zn(5) - 1Gd(1) 2.79Å	Zn(11) - 2Gd(3) 3.70Å	Zn(17) - 2Gd(1) 2.96Å
	- 2Gd(2) 3.10	- 2Gd(5) 3.87	- 1Gd(4) 2.95
	- 1Gd(5) 3.24	- 1Zn(7) 2.43	- 1Gd(5) 3.26
	- 1Zn(1) 3.01	- 2Zn(8) 2.73	- 1Zn(2) 2.35
Gd(4) - 3Gd(1) 4.67Å	- 2Zn(8) 2.64	- 1Zn(10) 2.82	- 2Zn(3) 3.25
- 2Zn(2) 3.54	- 2Zn(10) 2.89	- 1Zn(14) 2.84	- 2Zn(12) 2.40
- 3Zn(6) 2.96	- 1Zn(16) 2.66	- 2Zn(15) 2.50	
- 6Zn(12) 2.76		- 1Zn(18) 2.84	
- 3Zn(17) 2.95			
	Zn(6) - 2Gd(1) 3.42Å		
	- 1Gd(3) 3.00	Zn(12) - 1Gd(1) 3.60Å	Zn(18) - 1Gd(2) 2.90Å
Gd(5) - 2Zn(3) 3.15Å	- 1Gd(4) 2.96	- 1Gd(3) 3.55	- 2Gd(5) 3.41
- 1Zn(4) 3.44	- 1Zn(2) 2.99	- 1Gd(4) 2.76	- 1Zn(3) 2.81
- 1Zn(5) 3.24	- 2Zn(3) 2.76	- 1Gd(5) 2.74	- 2Zn(4) 2.63
- 2Zn(8) 3.07	- 2Zn(12) 2.93	- 1Zn(8) 2.68	- 1Zn(7) 2.88
- 2Zn(10) 3.22		- 2Zn(12) 2.20	- 1Zn(11) 2.84
- 2Zn(11) 3.87		- 1Zn(15) 2.87	- 1Zn(13) 2.82
- 2Zn(12) 2.74		- 1Zn(17) 2.40	- 2Zn(15) 3.02
- 1Zn(13) 3.33	Zn(7) - 1Gd(2) 3.29Å		
- 2Zn(15) 3.20	- 2Gd(3) 3.04		
- 1Zn(17) 3.26	- 2Zn(3) 3.03		
- 2Zn(18) 3.41	- 2Zn(4) 2.67	Zn(13) - 3Gd(5) 3.33Å	

\* Average standard deviation of interatomic distances;  $\pm 0.01\text{\AA}$  between Gd-Gd,  $\pm 0.03\text{\AA}$  between Gd-Zn and  $\pm 0.05\text{\AA}$  between Zn-Zn.

Table 3. The observed and calculated structure factors

\* Unobserved reflections;  $\alpha$  is the phase angle expressed in degrees-minutes.

Table with 4 columns of data (h, I, F0, Fc, alpha) repeated 10 times, containing numerical values for structure factors and phase angles.

are coordination atoms to Gd(4) and that both have the smallest C.N. of 9 among the zinc atoms.

Although the Gd atom arrangement in  $Gd_{13}Zn_{58}$  in each of the four layers shown in Fig. 1 resembles that in the  $CaZn_5$  ( $D2_d$ ) type, the stacking of these layers in the  $z$  direction has no precedent. In three dimensions the Gd atoms arrange themselves in such a manner as to eliminate completely any direct contact. The recent structure work of Sree Harsha (1964) on the intermetallic compounds between yttrium and zinc over the composition range  $Zn/Y = 2$  through 4 also showed the lack of either trigonal or octahedral clustering of the rare earth atoms.\* These observations tend to indicate that the  $A_6B_{23}$  type compounds as found in the R-Mn systems should be absent in the R-Zn systems†.

The latest summary of the intermediate phases between rare earths (with the exception of Pm, Eu and Yb) and manganese (Wang & Holden, 1965; Wang & Gilfrich, 1966) shows that only three ( $RMn_2$ ,  $R_6Mn_{23}$  and  $RMn_{12}$ ) or possibly four (including  $RMn_5$  prototype to  $C14$ ,  $MgZn_2$ ) compounds exist in each R-Mn system. In sharp contrast to this, as many as nine compounds may exist in a given R-Zn system as shown by the work of Lott & Chiotti (1966) on the Ce-Zn system. Undoubtedly,  $Gd_{13}Zn_{58}$  corresponds to the compounds, 'CeZn<sub>4.5</sub>' (hexagonal,  $a = 14.60$ ,  $c = 14.11$  Å) identified by these authors as well as 'YZn<sub>5</sub>' (hexagonal,  $a = 14.28$ ,  $c = 14.08$  Å) identified by Sree Harsha (1964). These observations strongly suggest that the interaction between rare earth and zinc atoms is considerably stronger than that between rare earth atoms or between zinc atoms. Such strong rare-earth-zinc interactions can and will prevent clustering of rare earth atoms and consequently the formation of  $A_6B_{23}$ -

\* According to Sree Harsha, the rare earth atoms form straight or zigzag chains in these compounds.

† Recently, Kuz'ma, Kripyakevich & Frankevich (1965) reported the existence of  $A_6B_{23}$  compounds in the lanthanide-zinc series based on powder pattern methods. However, in the light of the single-crystal results and the fact that  $Y_3Z_{11}$  (Sree Harsha, 1964) has lattice constants  $a = 4.40$ ,  $b = 8.90$ ,  $c = 12.93$  Å which are closely related to that reported for 'Y<sub>6</sub>Zn<sub>23</sub>' (Kuz'ma *et al.*, 1965),  $a = 12.69$  Å, confirmation of the existence of  $A_6B_{23}$  compounds in the lanthanide-zinc systems should await single-crystal results.

type compounds in the R-Zn systems. The absence of the commonly found Laves phase as well as the uncommon crystal structures assumed by the intermetallic compounds in both the Y-Zn system (Sree Harsha, 1964) and the Ce-Zn system (Lott & Chiotti, 1966), strongly support this reasoning.

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