Short Communications

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The crystal structure of HoZn₃. By DAVID J. MICHEL and EARLE RYBA, *Metallurgy Section, Department of Materials Science, The Pennsylvania State University, University Park, Pennsylvania,* 16802, *U.S.A.*

HoZn₃ was found by single-crystal techniques to be isostructural with YZn₃. The space group is *Pnma* with $a = 6.697$, $b = 4.366$, $c = 10.099$ Å.

The crystal structure of HoZn₃ has been determined by single-crystal X-ray diffraction techniques, and it was found to be isostructural with YZn₃ (Sree Harsha & Ryba, 1964). The alloy was prepared by melting stoichiometric amounts of 99·5 + % holmium and 99·999% zinc in a sealed tantalum crucible. The resulting alloy contained minor amounts of two secondary phases, which suggests that HoZn₃ forms by a peritectic reaction. From a Debye–Scherrer photograph (Cu *Kα* radiation: $\lambda = 1.54178$ Å) of this alloy, the orthorhombic lattice parameters were found from a least-squares fit to the data, using the Nelson–Riley extrapolation function, to be (25°C):

$$a = 6.697 \pm 0.003, \quad b = 4.3655 \pm 0.0014, \quad c = 10.099 \pm 0.003 \text{ Å} .$$

Weissenberg photographs of a well-formed single crystal from the alloy revealed that all *hk*0 reflections with $h = 2n + 1$ and 0*kl* reflections with $k + l = 2n + 1$ are absent; thus, the space group is $Pn2_1a$ or $Pnma$.

The intensities of 412 *hkl* ($k = 0$ to 6) reflections were measured on an equi-inclination Weissenberg counter diffractometer with Mo *Kα* ($\lambda = 0.71069$ Å) radiation and an ω scan. Data were recorded out to $\sin \theta = 0.5$. Intensities were corrected for absorption by the crystal, a rectangular prism $0.06 \times 0.08 \times 0.25$ mm in size, according to the method of Burnham (1966).

Since the lattice parameters and space group possibilities indicated that HoZn₃ is isostructural with YZn₃, a trial structure was refined on this basis, giving the positional and thermal parameters shown in Table 1. The full-matrix least-squares program of Busing, Martin & Levy (1962), modified for the IBM System 360/67, was used, and atomic scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1962). Unit weights were assigned to all reflections. For all observable reflections, the residual, based on *F*'s, was

8·4%. An *h*0*l* electron density map confirmed the correctness of the structure.

*h*0*l* structure factors and interatomic distances are given in Tables 2 and 3, respectively. The standard deviations for the interatomic distances were calculated by taking into account the standard deviations in both the positional parameters and the lattice parameters.

Table 2. *Observed and calculated h0l structure factors for* HoZn₃

hkl	F₀	Fc	hkl	F₀	Fc
002	28	−47	403	62	57
004	231	−234	404	68	−56
006	187	178	405	177	186
008	44	−32	406	56	60
0·0·10	131	−131	407	83	−85
0·0·12	67	72	408	43	−45
0·0·14	43	−40	409	43	−43
101	19	18	4·0·10	34	−38
102	98	82	4·0·11	98	111
103	84	−72	4·0·12	36	44
104	225	−231	501	64	66
105	104	89	502	25	−16
106	70	−60	503	30	−33
107	74	80	504	127	−105
108	79	79	505	88	77
109	116	−99	508	61	61
1·0·10	121	−114	509	100	−108
1·0·12	27	−15	5·0·10	59	−60
1·0·13	48	48	5·0·12	20	−22
1·0·14	84	92	600	120	−120
200	142	−166	601	120	122
201	18	19	602	35	30
202	31	30	603	22	18
203	14	−10	604	71	58
204	37	−25	605	160	−146

Table 1. *Final positional parameters for* HoZn₃ *from the least-squares refinement*

	Equipoint	x	y	z	B
Zn(1)	4(c)	0·2169 ± 0·0008	0·250	0·0432 ± 0·0005	0·99 ± 0·07 Å²
Zn(2)	4(c)	0·9177 ± 0·0007	0·250	0·8524 ± 0·0005	0·99 ± 0·07
Zn(3)	4(c)	0·5370 ± 0·0008	0·250	0·8966 ± 0·0005	1·06 ± 0·07
Ho	4(c)	0·2796 ± 0·0003	0·250	0·3370 ± 0·0002	0·65 ± 0·02

Table 2 (cont.)

hkl	F_o	F_c	hkl	F_o	F_c
205	35	−31	606	94	−87
206	182	−171	609	16	−17
208	119	107	6·0·10	72	71
209	83	−49	701	123	−123
2·0·10	137	130	702	52	−47
2·0·11	30	−5	703	126	117
2·0·12	57	−55	705	57	−49
2·0·13	52	52	707	85	−79
302	188	−244	708	20	20
303	103	90	709	114	119
304	182	192	800	27	−25
305	7	6	801	48	−35
306	140	136	803	44	58
307	31	−31	804	20	17
308	92	−93	805	96	89
309	61	54	807	71	−62
3·0·10	79	74	901	88	85
3·0·12	32	32	903	82	−72
400	170	190	904	29	−12
401	96	−106			

The existence of $REZn_3$ compounds (RE = rare earth) has been established in the Y–Zn (Chiotti, Mason & Gill, 1963), Ce–Zn (Chiotti & Mason, 1965), Dy–Zn (Sree Harsha, 1964), Sm–Zn (Chiotti & Mason, 1967a), and Ho–Zn systems. Table 4 gives the available crystallographic data for YZn_3, $DyZn_3$ and $CeZn_3$. Only $DyZn_3$ and $HoZn_3$ have so far been found to have the YZn_3-type structure, but all $REZn_3$ compounds probably have the same structure except for $CeZn_3$, which has a slightly different structure (Lott & Chiotti, 1966), $YbZn_3$, which has been reported not to exist (Chiotti & Mason, 1967b), and possibly $EuZn_3$. The interatomic distances in YZn_3 and $HoZn_3$ are similar, but there are significant differences between them even though the CN12 radius of Ho is only 2·7% smaller than that of Y. In addition, the Ho–Ho and Y–Y distances are longer than expected, while many Zn–Zn distances are contracted. The structure appears to be predominantly controlled by the coordination of the zinc atoms. Fig. 1 shows (a) the basic layer of the structure, which lies in a plane perpendicular to the b axis, and (b) the coordination of the Ho atoms. The zinc atoms in the basic layer form chains

of side sharing pentagons and the holmium atoms occupy the space between these chains. Adjacent layers fit together so that the holmium atoms partially occupy the holes in the centers of the zinc atom pentagons.
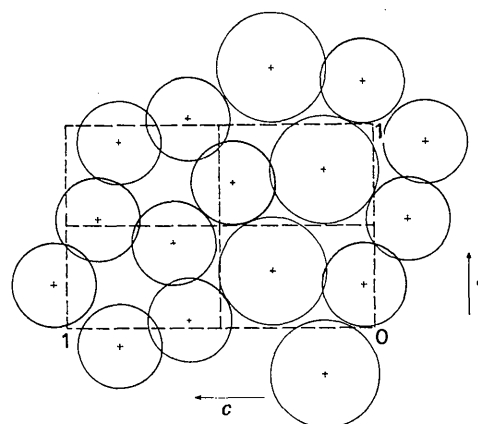
(a)
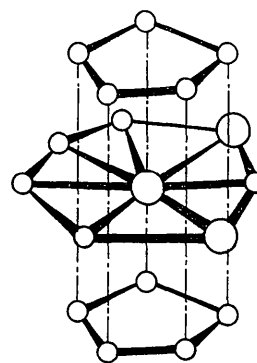
(b)

Fig. 1. Atom arrangement in $HoZn_3$. (a) Basic layer (size of circles corresponds to CN12 radii); (b) Holmium atom coordination.

Table 3. *Interatomic distances in* $HoZn_3$

Ho–2Ho	3·782 ± 0·003 Å	Zn(2)–1Ho	3·270 ± 0·005 Å
Ho–1Zn(1)	3·958 ± 0·006	Zn(2)–2Ho	3·189 ± 0·004
Ho–1Zn(1)	3·169 ± 0·006	Zn(2)–2Ho	2·983 ± 0·004
Ho–2Zn(1)	3·017 ± 0·004	Zn(2)–1Zn(1)	2·780 ± 0·007
Ho–1Zn(1)	2·997 ± 0·006	Zn(2)–2Zn(1)	2·586 ± 0·004
Ho–1Zn(2)	3·270 ± 0·005	Zn(2)–2Zn(2)	3·856 ± 0·006
Ho–2Zn(2)	3·189 ± 0·004	Zn(2)–1Zn(3)	2·638 ± 0·007
Ho–2Zn(2)	2·983 ± 0·004	Zn(2)–1Zn(3)	2·588 ± 0·007
Ho–2Zn(3)	3·441 ± 0·004		
Ho–1Zn(3)	3·143 ± 0·006	Zn(3)–2Ho	3·441 ± 0·004
Ho–2Zn(3)	3·102 ± 0·004	Zn(3)–1Ho	3·143 ± 0·006
		Zn(3)–2Ho	3·102 ± 0·004
Zn(1)–1Ho	3·958 ± 0·006	Zn(3)–2Zn(1)	2·802 ± 0·005
Zn(1)–1Ho	3·169 ± 0·006	Zn(3)–1Zn(2)	2·638 ± 0·007
Zn(1)–2Ho	3·017 ± 0·004	Zn(3)–1Zn(2)	2·588 ± 0·007
Zn(1)–1Ho	2·997 ± 0·006	Zn(3)–2Zn(3)	3·062 ± 0·005
Zn(1)–1Zn(2)	2·780 ± 0·007		
Zn(1)–2Zn(2)	2·586 ± 0·004		
Zn(1)–2Zn(3)	2·802 ± 0·005		
Zn(1)–1Zn(3)	2·605 ± 0·007		

Table 4. *Crystallographic data for* REZn₃ *compounds*[*]

YZn₃
$a = 6\cdot690 \pm 0\cdot005$, $b = 4\cdot405 \pm 0\cdot003$, $c = 10\cdot111 \pm 0\cdot009$ Å
Pnma

	Equipoint	x	y	z	B
Zn(1)	4(*c*)	$0\cdot2152 \pm 0\cdot0014$	$0\cdot25$	$0\cdot0449 \pm 0\cdot0009$	$1\cdot22 \pm 0\cdot17$ Å²
Zn(2)	4(*c*)	$0\cdot9162 \pm 0\cdot0014$	$0\cdot25$	$0\cdot8549 \pm 0\cdot0009$	$1\cdot27 \pm 0\cdot17$
Zn(3)	4(*c*)	$0\cdot5362 \pm 0\cdot0013$	$0\cdot25$	$0\cdot8956 \pm 0\cdot0009$	$1\cdot20 \pm 0\cdot16$
Y	4(*c*)	$0\cdot2773 \pm 0\cdot0009$	$0\cdot25$	$0\cdot3387 \pm 0\cdot0006$	$0\cdot62 \pm 0\cdot10$

DyZn₃
$a = 6\cdot700$, $b = 4\cdot398$, $c = 10\cdot06$ Å
Pnma

	Equipoint	x	y	z	B
Zn(1)	4(*c*)	$0\cdot216$	$0\cdot25$	$0\cdot042$	$1\cdot4$ Å²
Zn(2)	4(*c*)	$0\cdot961$	$0\cdot25$	$0\cdot853$	$1\cdot1$
Zn(3)	4(*c*)	$0\cdot535$	$0\cdot25$	$0\cdot897$	$0\cdot9$
Dy	4(*c*)	$0\cdot279$	$0\cdot25$	$0\cdot336$	$2\cdot2$

CeZn₃
$a = 4\cdot62 \pm 0\cdot01$, $b = 10\cdot43 \pm 0\cdot01$, $c = 6\cdot64 \pm 0\cdot01$ Å
C2cm, Cmc2, or *Cmcm*

[*] YZn₃: Sree Harsha & Ryba (1964)
DyZn₃: Sree Harsha (1964)
CeZn₃: Lott & Chiotti (1966)

Sree Harsha (1967) has investigated the structure of CeZn₃, but full details are not yet available. The lattice parameters are similar to those of the other REZn₃ compounds, and it is suspected that only slight atom shifts are necessary to change the symmetry.

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The crystal structure of tris- (2-dimethylaminoethyl)aminemanganese (II), -iron (II) and -zinc (II) bromides.

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The crystal structures of the isomorphous compounds Mn(Me₆tren)Br₂, Fe(Me₆tren)Br₂ and Zn(Me₆tren)Br₂ [Me₆tren = N(CH₂CH₂N(CH₃)₂)₃] have been investigated by three-dimensional X-ray analysis and refined to final R values of $0\cdot067$, $0\cdot055$ and $0\cdot065$ respectively. Crystals of the three complexes are cubic, space group $P2_13$, with $a = 12\cdot216 \pm 0\cdot007$, $12\cdot185 \pm 0\cdot004$ and $12\cdot105 \pm 0\cdot003$ Å for the manganese(II), iron(II) and zinc(II) compounds respectively; $Z = 4$. The three structures consist of M(Me₆tren)Br⁺ and Br⁻ ions, arranged in a distorted NaCl type arrangement. The coordination polyhedron about the metal atoms is a trigonal bipyramid with C_3 crystallographic symmetry. The structure is essentially identical with that of the cobalt(II), nickel(II) and copper(II) analogues. The manganese(II) compound represents the first example of pentacoordination for this ion so far described by X-ray methods. The iron(II) complex is the first structure determined by X-rays, with trigonal bipyramidal arrangement about this ion.

A series of five-coordinated high spin complexes with general formula $M^{II}(Me_6tren)X_2$, where $M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn$ and $Me_6tren = $ tris-(2-dimethylaminoethyl)-amine, N(CH₂CH₂N(CH₃)₂)₃, and X = Cl, Br, I, NO₃ or

ClO₄, has been prepared by Ciampolini & Nardi (1966a, b).

As a part of an X-ray structural investigation of the isomorphous series of the complex bromides, we have previously reported the structures of the cobalt(II) (Di Vaira