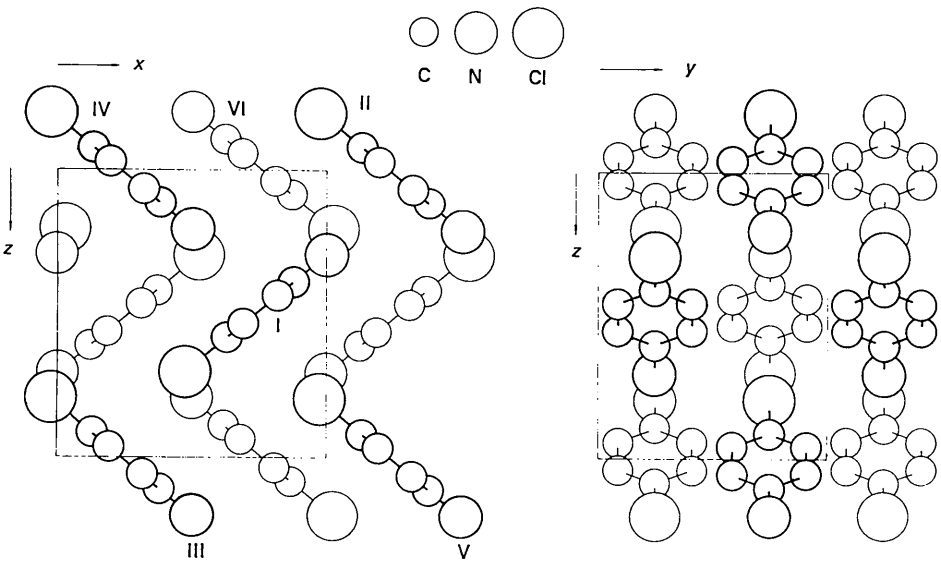

Fig. 2. The crystal structure of *p*-chloroaniline projected along the *a* and *b* axes.

relation to one another. All distances shorter than 4 Å are listed in Table 4, the molecules being labelled as in Fig. 2.

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The Crystal Structures of $LuMn_5$ and the RMn_{12} Compounds (where R = Gd, Tb, Dy, Ho, Er and Tm)

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By means of single-crystal and powder X-ray diffraction methods, the crystal structures of six RMn_{12} compounds (where R is a rare earth element) have been shown to be isostructural with that of $ThMn_{12}$. These RMn_{12} compounds were found in the following systems: Gd–Mn, Tb–Mn, Dy–Mn, Ho–Mn, Er–Mn and Tm–Mn.

A hitherto unreported and unexpected compound, $LuMn_5$ ($P6_3mc$) with cell dimensions $a = 5{\cdot}18$, $c = 8{\cdot}56$ Å, has been found in the Lu–Mn system in which the expected compound '$LuMn_{12}$' is absent. The structure of $LuMn_5$ is a variation of the $C14$ ($MgZn_2$ type) structure represented by $LuMn_2$.

Introduction

There has been considerable interest in both the crystal and magnetic structures of the intermediate phases between the rare earth elements and manganese. The crystal structures of the RMn_2 (Laves phase) compounds have been summarized by Elliott (1964) and the magnetic structures were reported by Nesbitt, Williams, Wernick & Sherwood (1963), and Corliss & Hastings (1964). Recently Wang & Holden (1965) identified the R_6Mn_{23} compounds as isostructural with Th_6Mn_{23}–$Fm3m$ (Florio, Rundle & Snow, 1952) and explained the absence of 'Eu_6Mn_{23}' and 'Yb_6Mn_{23}' based on the 'enveloping effects'. The unique magnetic properties of the R_6Mn_{23} compounds were found and qualitatively explained by DeSavage, Bozorth, Wang & Callen (1965).

The existence of $GdMn_{12}$ and $DyMn_{12}$, and the possibility that their structures would be isostructural with that of $ThMn_{12}$, was originally suggested but never confirmed by Moriarty & Baenziger (1959; see also Moriarty, 1960). Recently Mykelbust & Daane (1962) have shown in their phase diagram study of the Y–Mn system that YMn_{12} crystallizes in a body-centered tetragonal structure. In the present study, similar compounds have been sought in all of the rare earth–Mn systems (except promethium).

Experimental

The purity of the elements and detailed procedures for the preparation of alloys have been described earlier (Wang & Holden, 1965). It is our experience that in the alloying of rare earths with manganese, the use of crucibles made of 'stabilized zirconia', supplied by Laboratory Equipment Corp., St. Joseph, Michigan, as reaction vessels is quite satisfactory. No detectable reaction has been observed between the rare earth and ZrO_2. We have also used 'recrystallized alumina', which has been suggested by Nester & Schroeder (1965) as a perfect crucible material. Our results with this material are no different than those obtained with 'stabilized zirconia'. In each charge, the atom ratio between the rare earth element and manganese was $R:Mn=1:12$ and a constant weight, 3 g, of rare earth metal was used.

Because the formation of RMn_{12} compounds is of the peritectic type (Mykelbust & Daane, 1962), it was necessary to anneal the samples at about 900° to 1000°C for as long as eight hours, followed by slow cooling (2°C per minute). In spite of such precautions, the alloy matrices were never completely free of manganese. As a result, the lattice constants for the RMn_{12} compounds reported in this paper are less precise than those obtained for the R_6Mn_{23} compounds (Wang & Holden, 1965), as shown in Table 2. The lattice constants for the RMn_{12} compounds were determined from powder through use of a Norelco Debye–Scherrer type camera (circumference 360 mm) and Fe $K\alpha_1$ (1·93597 Å) and Fe $K\alpha_2$ (1·93991 Å) radiation. The technique of collecting data was essentially that of Straumanis (1949). Cohen's (1936) least-squares method was applied to the four high angle diffraction lines: 642, 404, 633 and 802. The lattice constants of $LuMn_5$ were obtained from an $h0l$ Weissenberg photograph which had been calibrated against NaCl lines ($a=5·6394$ Å). In the single-crystal studies, both Weissenberg and Buerger precession cameras were used. The methods used in the collection of intensity data and its conversion to $k\cdot|F_o|^2$ were essentially the same as those described in the identification of Gd_6Mn_{23} (Wang, Gilfrich, Ernst & Hubbard, 1964).

The X-ray 63 system (Stewart, 1965) was used for Fourier summations and least-squares refinement and UCRL-7196 (Smith, 1963) for calculation of theoretical powder patterns on an IBM 7090 computer.

Structure determination

$DyMn_{12}$ single crystals of approximately spherical shape (diameter 0·03 mm), obtained from the alloy matrix with the composition ratio $Dy:Mn=1:12$, showed diffraction symmetry $4/mmm$ (tetragonal). The only systematic extinction was $h+k+l=2n$. From the $h0l$ Weissenberg photograph, the lattice constants $a=8·68$ and $c=4·76$ Å were obtained. The close similarity between these preliminary data for the present compound and those of $ThMn_{12}$ (Florio *et al.*, 1952), warranted the use of the space group and the atomic positions given for $ThMn_{12}$ as a starting point for the subsequent least-squares refinements. Three cycles of isotropic least-squares refinement on 212 symmetry independent diffraction planes (hkl, $1=0$ through 4) gave an agreement index $R(F)$, $\Sigma||F_c|-|F_o||/\Sigma|F_o|=0·12$, confirming that the structure of $DyMn_{12}$ has space group $I4/mmm$ and is isostructural with $ThMn_{12}$. The crystallographic data and the interatomic distances are given in Table 1.*

Table 1. *Crystallographic data for* $DyMn_{12}$

$DyMn_{12}$: $I4/mmm$ (2 formula weights per unit cell).
Unit-cell dimensions (±0·02 Å)
$a=8·67$, $c=4·76$ Å.

Atom positions (add $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$):
2 Dy(a) 0, 0, 0
8 Mn(f) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{1}{4}, \frac{1}{4}$
8 Mn(i) $x=0·349$ (±0·003)
8 Mn(j) $x=0·281$ (±0·002)

Interatomic distances: (standard deviation, ±0·02 Å)

Dy(a)	8 Mn(f)	3·28 Å
	4 Mn(i)	3·02
	8 Mn(j)	3·04
Mn(f)	4 Mn(f)	2·38
	4 Mn(i)	2·61
	2 Mn(j)	2·48
	2 Dy(a)	
Mn(i)	4 Mn(i)	2·68
	1 Mn(i)	2·61
	4 Mn(f)	2·61
	2 Mn(j)	2·62
	2 Mn(j)	2·63
	1 Dy(a)	
Mn(j)	2 Mn(i)	2·62
	2 Mn(i)	2·63
	4 Mn(f)	2·48
	2 Mn(j)	2·68
	2 Dy(a)	

* Since calculated structure factors and powder patterns for $ThMn_{12}$ type compounds have been given in a number of previous papers (Florio *et al.*, 1952; Raeuchel & Batchelder, 1955; Gladyshevskii & Kripyakevich, 1957), comparable data for the RMn_{12} compounds are not included in this paper.

RMn_{12} *compounds* ($GdMn_{12}$, $TbMn_{12}$, $HoMn_{12}$, $ErMn_{12}$ *and* $TmMn_{12}$)

The identification of the structures of these compounds was made by comparing the powder patterns of these alloys with that of $DyMn_{12}$. The final lattice constants for the RMn_{12} compounds and those of the RMn_2 and R_6Mn_{23} compounds previously reported are summarized in Table 2.

$LuMn_5$

The powder diagram from the composition ratio 1:12 alloy of Lu and Mn contained the pattern of manganese plus a new pattern different from that of RMn_{12}. Single crystals of the compound were found in an alloy of about the same composition. Single-crystal data obtained with Mo radiation showed a Laue symmetry $6/mmm$ (hexagonal) with lattice constants $a=5{\cdot}18$ and $c=8{\cdot}56$ Å. The only systematic extinction was $h-k=3n$ for $l=2n+1$, which limited the possible space groups to $P6_322$, $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$ for which these extinctions exist for certain special positions (*e.g.* $\frac{1}{3}$, $\frac{2}{3}$, z: *etc.*). Consideration of atomic* and unit-cell volumes, together with the space group requirements and approximate alloy composition, resulted in placing two Lu atoms at $\frac{1}{3}$, $\frac{2}{3}$, z and $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}+z$. This assignment was substantiated by a three-dimensional Patterson synthesis which moreover showed that:

(1) There were no mirror planes at $z=\frac{1}{4}$ and $\frac{3}{4}$ in the real cell (this conclusion is based on the analysis of (0, 0, w) Harker line). This led to the elimination of space groups $P\bar{6}2c$ and $P6_3/mmc$.

(2) The arrangement of the triangularly clustered Mn atoms was incompatible with space group $P6_322$.

* The values for atomic volumes are from the table recently compiled by Rudman (1965).

Table 3. *Crystallographic data for* $LuMn_5$

$LuMn_5$: $P6_3mc$ (2 formula weights per unit cell)
$a=5{\cdot}186$ ($\pm0{\cdot}005$) Å
$c=8{\cdot}566$ ($\pm0{\cdot}008$)

Atom positions			Temperature factor, B
2 Lu(b)	$z=$	0·250 (±0·004)	0·523 Å^2
2 Mn(a)	$z=$	0·185 (±0·004)	1·515
2 Mn(b)	$z=$	0·358 (±0·007)	0·824
6 Mn(c)	$x=$	0·167 (±0·003)*	1·787
	$z=$	−0·047 (±0·002)	

Interatomic distances:
(standard deviation, ±0·012 Å)

Lu(b)	3 Mn(a)	3·045 Å
	3 Mn(b)	3·133
	1 Mn(b)	3·357
	3 Mn(c)	2·951
	6 Mn(c)	3·119
Mn(a)	3 Mn(b)	3·016
	3 Mn(c)	2·487
	3 Mn(c)	2·740
	3 Lu(b)	
Mn(b)	3 Mn(c)	3·052
	6 Mn(c)	3·054
	3 Lu(b)	
Mn(c)	4 Mn(c)	2·593
	2 Mn(a)	2·740
	3 Mn(b)	3·054
	3 Lu(b)	

* The standard deviation for this parameter is based on all reflections other than those for which $h-k=3n$ where $l=2n+1$. The structure factor calculations showed that, within the limits set by the standard deviation, the extinctions $h-k=3n$ where $l=2n+1$ apply. For this reason, the $h-k=3n$ where $l=2n+1$ reflections are not listed in Table 4.

Table 2. *The intermediate phases of the rare earths and manganese and their lattice constants*

Atomic number	R (Rare earth)	RMn_2* (Laves phase)	R_6Mn_{23}† $Fm3m$, a (±0·004 Å)	RMn_{12}‡ $I4/mmm$, a, c (±0·018 Å)
21	Scandium	$C14$	n	unknown
39	Yttrium	$C15$, $a=7{\cdot}68$ Å	$a=12{\cdot}438$ Å	§ $a=8{\cdot}54$, $c=4{\cdot}78$ Å
57	Lanthanum	n	n	n
58	Cerium	n	n	n
59	Praseodymium	unknown	n	n
60	Neodymium	$C14$	$a=12{\cdot}657$ Å	n
61	Promethium	—	—	—
62	Samarium	unknown	$a=12{\cdot}558$ Å	n
63	Europium	unknown	n	n
64	Gadolinium	$C15$, $a=7{\cdot}73$ Å	$a=12{\cdot}532$ Å	$a=8{\cdot}72$, $c=4{\cdot}78$ Å
65	Terbium	$C15$, $a=7{\cdot}62$ Å	$a=12{\cdot}396$ Å	$a=8{\cdot}68$, $c=4{\cdot}78$ Å
66	Dysprosium	$C15$, $a=7{\cdot}57$ Å	$a=12{\cdot}361$ Å	$a=8{\cdot}67$, $c=4{\cdot}76$ Å
67	Holmium	$C15$, $a=7{\cdot}51$ Å	$a=12{\cdot}324$ Å	$a=8{\cdot}62$, $c=4{\cdot}75$ Å
68	Erbium	$C14$, $a=5{\cdot}28$, $c=8{\cdot}62$ Å	$a=12{\cdot}275$ Å	$a=8{\cdot}56$, $c=4{\cdot}74$ Å
69	Thulium	$C14$, $a=5{\cdot}24$, $c=8{\cdot}56$ Å	$a=12{\cdot}226$ Å	$a=8{\cdot}54$, $c=4{\cdot}73$ Å
70	Ytterbium	unknown	n	n
71	Lutetium	$C14$, $a=5{\cdot}20$, $c=8{\cdot}51$ Å $LuMn_5$ ($P6_3mc$) $a=5{\cdot}18$, $c=8{\cdot}56$ Å	$a=12{\cdot}187$ Å	n

* Results summarized by Elliott (1964).
† Wang and Holden (1965).
‡ Present investigation.
§ Mykelbust and Daane (1962).
n Non-existent.

Therefore, by process of elimination, space group $P6_3mc$ was chosen for the compound. This space group was also found to be compatible with all the Mn atom positions found from a complete analysis of the Patterson vectors and their peak heights*. After three cycles of isotropic least-squares refinement based on all the atom positions found from the Patterson map, an $R(F)$ of 0·09 was obtained. The atomic positional parameters, together with the interatomic distances, are given in Table 3. The calculated and observed structure factors are given in Table 4. These atomic positions gave the formula $LuMn_5$ for the compound with two formula weights per unit cell. By using the atomic volumes 29·5 and 12·2 Å³ for Lu and Mn, the unit-cell volume based on Lu_2Mn_{10} was calculated to be 181·0 Å³, which is in close agreement with the observed 184·7 Å³.

A density measurement was not made, because of the consistent manganese contamination. Owing to the lack of knowledge of the phase diagram, no attempts were made to prepare an alloy of pure phase.

Discussion

The 15 AB_{12} ($ThMn_{12}$ type) compounds known to exist as of this writing are listed in Table 5. The atom radius ratios* of these compounds range from 1·12 (Cr/Be) to 1·32 (Th/Mn). It is shown in this investigation that RMn_{12} compounds do not exist in the La–Mn, Ce–Mn, Pr–Mn, Nd–Mn, Sm–Mn, Eu–Mn, Yb–

* Although positions 6(c) in $P6_3mc$ do not show any special extinctions for arbitrary values of the parameter, the six manganese atoms occupying the set (c) are consistent with the extinction, $h-k=3n$ for $l=2n+1$, because their x parameter is very close to $\frac{1}{6}$.

Table 5. *Known* AB_{12} *compounds* ($ThMn_{12}$ *type*) *and their lattice constants*

	a_0	c_0	R/r	Reference
$CrBe_{12}$	7·21 Å	4·16 Å	1·12	(*a*)
$NdMg_{12}$	10·31	5·93	1·14	(*b*)
VBe_{12}	7·25	4·18	1·18	(*a*)
$MoBe_{12}$	7·27	4·23	1·21	(*c*), (*d*)
WBe_{12}	7·22	4·22	1·24	(*d*)
$TmMn_{12}$	8·54	4·73	1·26	(*e*)
$ErMn_{12}$	8·56	4·74	1·27	(*e*)
$NbBe_{12}$	7·35	4·24	1·28	(*a*)
$HoMn_{12}$	8·62	4·75	1·28	(*e*)
$DyMn_{12}$	8·67	4·76	1·28	(*e*)
$TaBe_{12}$	7·32	4·24	1·28	(*d*)
$TbMn_{12}$	8·68	4·78	1·29	(*e*)
YMn_{12}	8·53	4·78	1·30	(*f*)
$GdMn_{12}$	8·72	4·78	1·31	(*e*)
$ThMn_{12}$	8·74	4·95	1·32	(*g*)

(*a*) Kripyakevich & Gladyshevskii (1955).
(*b*) Evdokimenko & Kripyakevich (1963).
(*c*) Raeuchle & Batchelder (1955).
(*d*) Gladyshevskii & Kripyakevich (1957).
(*e*) Present investigation.
(*f*) Mykelbust & Daane (1962).
(*g*) Florio, Rundle & Snow (1952).

* The atomic radii used throughout this paper are from *Tables of Interatomic Distances and Configuration in Molecules and Ions* (1959).

Table 4. *Observed and calculated structure factors of* $LuMn_5$

H K	Fo	Fc	A	B
L = 0				
2 0	84.8	88.5	-88.5	0.0
3 0	127.2	120.2	120.2	0.0
4 0	63.7	56.6	-56.6	0.0
5 0	28.1	20.8	-20.8	0.0
6 0	83.0	98.2	98.2	0.0
7 0	19.9	17.4	-17.4	0.0
8 0	24.0	21.9	-21.9	0.0
9 0	31.2	34.3	34.3	0.0
10 0	14.7	13.4	-13.4	0.0
11 0	13.9	9.1	-9.1	0.0
12 0	12.9	18.0	18.0	0.0
1 1	139.6	153.0	153.0	0.0
2 1	26.1	22.7	-22.7	0.0
3 1	28.9	22.3	-22.3	0.0
4 1	91.6	88.0	88.0	0.0
5 1	22.3	20.0	-20.0	0.0
6 1	22.1	18.2	-18.2	0.0
7 1	41.3	47.4	47.4	0.0
8 1	•	14.5	-14.5	0.0
9 1	•	12.4	-12.4	0.0
10 1	16.5	23.8	23.8	0.0
2 2	164.5	192.8	192.8	0.0
3 2	37.6	21.6	-21.6	0.0
4 2	52.3	41.8	-41.8	0.0
5 2	59.0	62.7	62.7	0.0
6 2	32.1	26.5	-26.5	0.0
7 2	•	15.2	-15.2	0.0
8 2	41.3	40.3	40.3	0.0
9 2	•	11.1	-11.1	0.0
10 2	•	10.5	-10.5	0.0
11 2	17.3	16.0	16.0	0.0
3 3	79.1	77.7	77.7	0.0
4 3	20.4	19.1	-19.1	0.0
5 3	•	17.6	-17.6	0.0
6 3	44.9	43.6	43.6	0.0
7 3	•	13.7	-13.7	0.0
8 3	•	11.7	-11.7	0.0
9 3	24.2	22.2	22.2	0.0
4 4	68.4	75.9	75.9	0.0
5 4	•	16.0	-16.0	0.0
6 4	•	19.0	-19.0	0.0
7 4	27.7	29.5	29.5	0.0
5 5	37.5	37.0	37.0	0.0
6 5	•	12.4	-12.4	0.0
7 5	•	10.5	-10.5	0.0
8 5	16.1	19.5	19.5	0.0
6 6	31.0	28.4	28.4	0.0
7 7	11.7	16.0	16.0	0.0
L = 1				
1 0	74.3	72.1	-71.2	11.5
2 0	135.9	137.6	95.9	98.6
4 0	85.6	84.3	-64.9	-53.7
5 0	32.4	40.9	40.9	-1.0
7 0	•	21.3	-20.4	-0.9
8 0	38.5	30.3	27.8	12.0
10 0	23.7	18.5	-17.8	-5.0
2 1	60.9	58.5	-58.2	6.2
3 1	44.3	50.8	50.6	-3.6
5 1	41.7	37.3	-37.3	0.2
6 1	•	32.0	32.0	0.6
8 1	•	22.6	-22.5	-1.3
9 1	•	18.7	18.6	1.3
3 2	34.6	45.3	-45.3	2.0
4 2	70.8	60.5	49.7	34.5
6 2	41.7	36.9	-33.0	-13.6
7 2	•	24.1	24.0	1.3
9 2	•	16.5	-16.5	-1.2
10 2	14.2	14.0	13.7	2.9
4 3	•	24.7	-21.5	-2.6
5 3	•	29.7	29.7	0.9
7 3	•	21.1	-21.1	-1.3
8 3	•	17.5	17.5	1.3
5 4	•	25.8	-25.8	-1.2
6 4	25.7	25.3	23.7	8.8
8 4	16.6	16.0	-15.6	-3.8
6 5	•	12.4	11.3	-2.8
7 5	•	18.8	-17.5	-6.2
7 6	•	13.1	-13.0	-1.1
8 6	8.7	10.9	10.8	1.8
L = 2				
1 0	49.7	53.8	53.7	-1.8
2 0	•	23.2	-4.0	22.9
3 0	117.4	140.7	-129.5	54.9
4 0	•	18.3	6.8	16.9
5 0	33.8	28.9	28.8	-1.7
6 0	45.0	40.9	-40.6	5.4
7 0	•	20.5	20.4	-1.6
8 0	•	11.5	11.3	2.2
9 0	40.4	33.3	-32.3	8.0
1 1	166.1	182.4	-166.1	75.3
2 1	55.9	42.9	42.8	-1.8
3 1	39.0	36.7	36.6	-1.8
4 1	91.3	98.2	-91.8	35.0
5 1	29.6	26.1	26.0	-1.7
6 1	•	12.4	12.3	-1.7
7 1	51.3	47.9	-15.0	13.5
8 1	•	15.3	15.2	-1.4
9 1	•	12.5	12.4	-1.2
10 1	23.4	22.5	-22.0	4.5
2 2	65.7	52.3	-52.1	4.7
3 2	34.7	32.3	32.2	-1.8
4 2	•	14.3	10.2	9.9
5 2	70.7	66.0	-62.6	20.9
6 2	•	12.2	11.6	3.7
7 2	•	16.4	16.3	-1.4
8 2	•	16.2	-14.8	4.0
3 3	72.7	85.0	-79.8	29.1
4 3	•	14.3	14.2	-1.7
5 3	•	20.5	20.4	-1.6
6 3	44.6	43.5	-41.9	11.8
7 3	•	14.3	14.2	-1.3
8 3	•	11.7	-11.7	-1.1
9 3	16.8	20.9	-20.5	4.1
4 4	30.8	36.3	-36.0	5.0
5 4	•	17.6	17.5	-1.5
6 4	•	10.8	10.7	1.2
7 4	28.6	28.3	-27.5	6.3
8 4	18.6	8.3	8.3	0.0
5 5	36.4	36.3	-35.1	9.1
6 5	•	12.5	12.4	-1.2
7 5	•	10.3	10.2	-1.0
8 5	15.5	18.2	-17.9	3.3
L = 3				
1 0	137.0	140.8	133.2	45.5
2 0	52.3	48.1	-42.5	22.3
4 0	56.7	40.6	39.2	-10.4
5 0	70.1	67.9	-65.5	-17.6
7 0	49.6	43.6	42.5	9.6
8 0	21.0	25.8	-25.8	-0.2
10 0	16.4	18.4	18.4	1.1
11 0	16.8	16.9	-16.7	-2.4
2 1	100.3	109.4	104.3	33.0
3 1	98.5	90.8	-87.0	-25.9
5 1	64.9	60.0	58.1	14.9
6 1	49.7	48.2	-46.9	-11.0
8 1	30.5	30.5	30.0	5.8
9 1	24.3	24.1	-23.7	-4.1
11 1	11.8	14.8	14.6	2.0
3 2	82.9	77.8	74.8	21.1
4 2	39.7	36.0	-35.6	5.1
6 2	19.9	28.8	28.8	-0.6
7 2	30.2	33.2	-32.5	-6.5
9 2	19.6	21.8	20.5	3.3
10 2	•	15.3	-15.2	-1.2
4 3	47.3	53.6	52.0	12.8
5 3	37.7	43.6	-42.5	-9.6
7 3	21.7	28.1	27.7	5.1
8 3	19.8	22.4	-22.0	-3.7
10 3	10.6	13.8	13.7	1.8
5 4	34.3	36.2	35.4	7.4
6 4	19.9	23.1	-23.0	-0.7
8 4	•	17.0	17.0	1.3
9 4	12.5	14.8	-14.6	-2.0
6 5	22.5	24.1	23.7	4.1
7 5	18.6	19.4	-19.1	-3.0
7 6	14.8	15.8	15.6	2.2
8 6	5.6	11.7	-11.7	-0.9
L = 4				
1 0	41.7	49.5	-33.2	-36.8
2 0	40.0	51.4	-49.4	14.2
3 0	46.4	53.1	51.9	-11.4
4 0	•	26.9	-24.3	8.5
5 0	39.9	24.7	-21.2	-12.8
6 0	56.8	55.3	45.6	-31.4
1 1	•	23.4	18.9	-15.3
2 1	39.7	39.1	-27.8	-26.5
3 1	34.1	32.7	-25.6	-20.3
4 1	•	24.3	23.4	-8.6
5 1	•	22.6	-19.9	12.0
2 2	120.3	103.9	74.7	-72.1
3 2	36.4	28.2	-23.2	-16.0
4 2	•	21.2	-20.5	2.4
3 3	•	12.7	11.8	-2.7
4 3	•	10.4	-12.4	2.9
4 4	53.4	43.5	37.5	-22.0
L = 5				
1 0	68.1	83.2	-82.7	8.3
2 0	137.1	149.6	149.6	-0.2
4 0	99.5	103.5	-103.5	0.6
5 0	61.6	51.6	51.5	-3.8
7 0	37.6	36.8	-36.7	2.2
8 0	35.0	39.6	39.5	-0.7
10 0	24.3	23.4	-23.4	0.5
11 0	12.1	16.1	16.1	-0.6
2 1	87.2	71.6	71.3	-6.5
3 1	72.1	63.4	-63.2	5.3
5 1	51.2	47.1	47.0	-3.3
6 1	43.2	39.8	-39.7	2.5
8 1	26.9	27.4	-27.4	1.4
9 1	19.6	22.3	22.3	-1.0
11 1	10.3	14.3	-14.2	0.5
3 2	55.6	56.9	56.7	-4.5
4 2	73.6	77.4	-77.4	0.8
6 2	53.6	48.4	48.4	-0.8
7 2	26.0	29.4	29.4	-1.5
9 2	18.3	19.5	-19.5	0.6
10 2	18.6	17.3	17.3	-0.4
4 3	43.6	43.2	43.1	-2.6
5 3	31.8	30.8	-30.7	2.2
7 3	22.1	25.6	-25.5	1.2
8 3	16.9	20.9	20.8	-0.9
10 3	9.4	13.4	-13.4	0.4
5 4	28.3	31.6	31.6	-1.7
6 4	35.3	32.8	-32.8	0.7
8 4	22.4	20.1	-20.1	0.5
9 4	11.6	14.3	14.2	-0.5
6 5	21.3	22.3	22.3	-1.0
7 5	15.8	18.3	18.3	-0.7
L = 6				
1 0	46.2	51.9	50.0	13.5
2 0	63.3	71.4	53.7	47.4
3 0	45.7	45.0	-44.6	9.3
4 0	52.8	49.4	38.8	30.6
5 0	26.7	29.6	-28.8	7.0
6 0	44.5	42.0	-36.7	-20.3
7 0	26.5	19.8	19.3	4.2
8 0	27.3	18.3	16.5	7.9
9 0	15.8	20.4	-20.4	-0.9
10 0	16.6	10.8	10.3	3.4
1 1	49.5	50.4	-48.7	13.2
2 1	46.6	43.4	42.4	11.1
3 1	39.8	37.9	36.7	9.4
4 1	37.6	38.6	-38.3	4.6
5 1	29.4	26.5	25.8	6.1
6 1	•	22.5	21.9	5.0
7 1	21.2	25.9	-25.9	-0.1
8 1	•	14.7	14.2	2.9
9 1	•	11.7	11.5	2.2
10 1	•	15.8	-15.7	-1.1
2 2	71.1	68.4	-53.1	-43.1
3 2	37.3	33.3	32.3	8.0
4 2	39.6	36.6	30.1	20.9
5 2	27.1	31.3	-31.2	1.3
6 2	24.2	27.4	19.8	10.7
7 2	21.7	15.9	15.5	3.3
8 2	•	21.8	-20.4	-8.2
9 2	•	10.7	10.0	1.8
10 2	10.1	8.1	7.8	2.0
3 3	31.2	35.8	-35.7	3.2
4 3	19.1	23.0	23.3	3.4
5 3	•	20.5	20.0	4.5
6 3	•	15.7	-12.4	-2.4
7 3	•	13.6	13.3	2.7
8 3	•	10.9	10.7	2.0
4 4	37.5	34.7	-31.4	-14.7
5 4	•	17.2	16.8	3.0
6 4	23.3	14.2	14.0	5.0
7 4	13.7	18.2	-18.2	-1.0
8 4	•	9.8	9.3	2.9
5 5	•	17.1	-17.0	-0.8
6 5	•	11.7	11.5	2.2
7 5	•	9.3	-8.2	4.5
6 6	18.9	16.6	-16.3	-3.7
L = 7				
1 0	77.3	83.0	79.0	-25.4
2 0	•	16.7	-16.6	2.6
3 0	31.3	26.6	26.6	-0.2
5 0	52.6	49.2	-47.5	12.8
7 0	43.9	33.4	32.5	-9.6
2 1	65.1	71.2	-68.1	20.8
3 1	59.3	67.2	59.7	-17.5
5 1	39.7	44.3	42.8	-11.1
6 1	33.5	36.1	-35.5	8.6
3 2	58.9	55.1	51.0	-14.9
4 2	•	12.6	-12.6	1.4
6 2	•	12.7	12.4	-2.3
7 2	•	18.3	-18.2	4.9
4 3	•	12.0	10.6	-5.2
5 3	•	15.0	-15.0	2.7
5 4	•	19.6	16.8	-2.6
6 4	•	15.7	-14.6	2.2
6 5	•	20.3	20.0	-3.5
7 5	•	16.6	-16.3	2.9
L = 8				
1 0	48.4	62.3	-61.5	-10.1
2 0	38.7	39.1	-38.7	8.6
3 0	67.7	68.6	65.7	17.6
4 0	31.4	31.6	-31.2	5.1
5 0	43.8	36.1	-35.7	-5.2
6 0	31.4	30.7	30.6	-2.2
7 0	32.3	23.6	-23.4	-3.0
8 0	•	16.7	-16.7	0.3
9 0	26.0	24.7	24.4	3.9
10 0	•	11.1	-11.1	-0.3
11 0	•	9.5	-9.5	-1.0
1 1	65.6	77.6	73.9	23.9
2 1	52.3	53.3	-52.7	-8.4
3 1	49.4	46.4	-45.8	-7.0
4 1	59.4	55.4	53.5	14.2
5 1	37.1	32.2	-31.9	-4.5
6 1	28.6	26.1	-25.8	-3.4
7 1	27.6	33.1	32.5	6.6
8 1	24.6	16.4	-16.3	-1.9
9 1	19.0	16.7	-16.8	-1.4
10 1	17.5	17.0	17.0	0.3
2 2	38.1	36.4	36.2	-8.6
3 2	44.7	40.7	-40.3	-6.0
4 2	28.7	26.0	-25.4	6.0
5 2	39.1	42.1	41.1	9.4
6 2	•	19.5	-19.5	0.9
7 2	25.6	17.9	-17.8	-2.1
8 2	•	15.4	14.9	-2.7
9 2	•	11.8	-11.7	-1.3
3 3	50.4	50.3	48.8	12.2
4 3	37.8	28.9	-28.6	-3.9
5 3	28.3	23.6	-23.4	-3.0
6 3	26.4	30.7	30.2	5.5
7 3	•	16.1	-16.0	-1.9
8 3	•	12.7	-12.6	-1.4
9 3	16.5	16.7	16.6	2.0
4 4	22.7	28.0	27.9	-0.8
5 4	34.3	19.6	-19.4	-2.4
6 4	•	14.5	-14.5	0.0
7 4	21.6	21.6	21.4	3.1
8 4	•	9.7	-9.7	-0.3
9 4	7.5	7.8	-7.7	-0.7
5 5	25.9	26.5	26.2	4.3
6 5	16.4	12.9	-12.8	-1.4
7 5	•	11.0	-10.9	-1.2
8 5	14.5	14.7	14.6	1.7
6 6	•	17.5	17.4	1.0
7 6	7.5	8.3	-8.3	-0.7

• -reflections too weak to be observed.

Mn and Lu–Mn systems, even though the atom radius ratios appear favorable. Their absence in the La–Mn and Ce–Mn systems is in agreement with the phase diagram investigations of Rolla & Iandelli (1952) and Mirgalovskaya & Strelnikova (1957)*. Inasmuch as the X-ray powder diagrams of the Pr–Mn, Nd–Mn and Sm–Mn alloys close to the composition ratio R:Mn = 1:12 showed a mixture of the respective rare earth and Mn lines, an immiscibility gap in the manganese-rich end of these systems is suspected. In the Eu–Mn and Yb–Mn systems, diffraction patterns different from those of the RMn_{12} compounds were observed. Since the atomic radii of Eu and Yb are considerably larger than those of the rest of the rare earth elements, the existence of R_2Mn_{17} (Th_2Ni_{17} type, Florio, Baenziger & Rundle, 1956) compounds in place of RMn_{12} compounds in these two systems is anticipated* and is being investigated.

* Though the claim of an immiscibility gap by Rolla & Iandelli was disputed by Mirgalovskaya & Strelnikova, both investigations are in agreement that no intermediate phase exists in the Ce–Mn system.

Within the limitations of the method used in preparing the alloys, the expected compound '$LuMn_{12}$' is absent. Because the atomic radius ratio of Lu/Mn, 1·26, falls within the limits set by other AB_{12} compounds (Table 5) and there is no reason to suspect an abrupt change in the atomic orbitals between Tm and Lu, the absence of '$LuMn_{12}$' is not easily understood. However, the unique existence of $LuMn_5$ in the Lu–Mn system suggests that there is a significant difference between the Lu–Mn phase diagram and those of the other R–Mn systems. For this reason, the absence of

* For details of the reasoning and evidence, see Evdokimenko & Kripyakevich (1963).

Table 6. *Calculated powder patterns of* $LuMn_2$ *and* $LuMn_5$

	$LuMn_2$ ($C14$, $MgZn_2$ type) $P6_3/mmc$ $a=5·20$, $c=8·51$ Å		$LuMn_5$ (Prototype to $C14$) $P6_3mc$ $a=5·18$, $c=8·57$ Å	
$hk.l$	d	I_o*	d	I_o*
1 0 0	4·503	565·2	4·486	57·2
0 0 2	4·255	347·7	4·285	135·3
1 0 1	3·980	392·5	3·974	974·1
1 0 2	3·092	438·3	3·098	315·9
1 1 0	2·600	1936·3	2·590	833·9
1 0 3	2·400	2651·8	2·409	1225·2
2 0 0	2·251	408·4	2·243	198·2
1 1 2	2·218	2435·4	2·216	1655·6
2 0 1	2·176	1142·6	2·169	887·0
0 0 4	2·127	127·2	2·142	233·1
2 0 2	1·990	0·3	1·987	41·1
1 0 4	1·923	76·6	1·933	96·4
2 0 3	1·763	91·8	1·764	45·6
2 1 0	1·702	20·6	1·695	1·4
2 1 1	1·669	45·1	1·663	90·0
1 1 4	1·646	0·3	1·650	44·0
1 0 5	1·592	317·3	1·601	166·0
2 1 2	1·580	125·3	1·576	73·7
2 0 4	1·546	6·0	1·549	63·7
3 0 0	1·501	341·8	1·495	155·8
3 0 1	1·478	0·9	1·473	0·0
2 1 3	1·459	1032·5	1·458	487·2
0 0 6	1·418	86·3	1·428	31·5
3 0 2	1·415	546·2	1·411	358·0
2 0 5	1·357	670·3	1·361	407·2
1 0 6	1·352	93·2	1·361	49·4
2 1 4	1·329	41·7	1·329	53·4
3 0 3	1·326	0·4	1·324	0·0
2 2 0	1·300	540·0	1·295	311·2
3 1 0	1·249	47·7	1·244	8·2
1 1 6	1·245	91·3	1·250	43·9
2 2 2	1·243	104·3	1·239	45·6
3 1 1	1·235	44·5	1·231	86·6
3 0 4	1·226	0·1	1·226	48·2
2 1 5	1·203	456·8	1·205	181·8
2 0 6	1·200	188·6	1·204	95·1
3 1 2	1·198	71·1	1·194	47·0
1 0 7	1·173	93·3	1·181	132·3
3 1 3	1·143	745·9	1·140	320·6

* $I_o=|F_o|^2 . \mathrm{Lp} . M$
where Lp = Lorentz & polarization factor
M = multiplicity factor

'$LuMn_{12}$' should not be considered final until the complete phase diagram has been determined.

The structure of $LuMn_5$ given here is derivable from that of $LuMn_2$ ($C14$, $MgZn_2$ type)*. One obtains the structure of $LuMn_5$ by taking the parameters given for $LuMn_2$ (Dwight, 1960), shifting the origin by 0·185 along z, and placing Mn atoms in one-half of the Lu positions. The situation here is analogous to that of the prototype structure $AuBe_5$ ($C15_b$) which is derivable from the $C15$ ($MgCu_2$ type) structure (Pearson, 1958).

Inasmuch as the lattice constant, Laue symmetry and atomic positions are similar in $LuMn_2$ and $LuMn_5$, the identification of one compound from the other, based on powder patterns alone, necessarily requires some care. For this reason, the theoretical powder patterns of both the $LuMn_2$ and $LuMn_5$ are listed side by side in Table 6 for future reference.

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* The fact that $LuMn_5$ is the prototype structure of $C14$ ($MgZn_2$ type) was pointed out to us by one of the reviewers.

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