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Report on the crystal structure of Gd_6Mn_{23}.

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$GdMn_2$ (Laves phase) is the only intermediate phase in the Gd–Mn system whose structure has been definitely characterized (Endter & Klemm, 1943). In the course of a study of the magnetic properties of alloys of Gd with some of the transition elements (Hubbard, Adams & Gilfrich, 1960) we found it necessary to carry out structure determinations on these alloys to support the magnetic study. This is a partial report of that structure investigation.

Initial investigation of the alloy containing 62·3 wt.% (81·6 at.%) Mn by the powder method (using a counter-diffractometer) showed the possibility of indexing the pattern based on a face-centered cubic cell with a lattice constant of $a_0 = 12{\cdot}5$ Å. However, the study of the Gd–Mn system by various authors (Nassau, 1959; Klemm, 1948; Moriarty & Baenziger, 1959; Nassau, Cherry & Wallace, 1960) revealed no cubic phase in this composition range of the system. Therefore, it was decided to carry the investigation further by single-crystal methods. A single crystal of irregular shape (best approximated as spherical) with an average diameter of approximately 0·10 mm was picked out of the alloy matrix. Even though there were obvious advantages in using a Mo $K\alpha$ radiation, a few initial Weissenberg photographs showed this to be impractical owing to the large cell constant. By the use of Cu $K\alpha$ (Ni-filtered) radiation and the equi-inclination method, zero through 6th layer Weissenberg photographs were obtained. The observation of the regular absence of mixed odd and even Miller indices and the *m*3*m* diffraction symmetry confirmed the crystal structure, face-centered cubic, as previously indicated in the powder pattern. From a zero-layer Weissenberg photograph which had been calibrated against superimposed NaCl lines ($a_0 =$ 5·6394 Å assumed) a lattice constant of $a_0 = 12{\cdot}578 \pm 0{\cdot}003$ Å was obtained.

At this time, the structure of Th_6Mn_{23} (Florio, Rundle & Snow, 1952) came to our attention. The closeness of the two compounds, in their atomic radius ratio (1·32 for (Th/Mn) and 1·31 for (Gd/Mn)) and in their lattice constants, ($a_0 = 12{\cdot}523$ Å for Th_6Mn_{23} and $a_0 = 12{\cdot}578$ Å for the present compound), and the fact that both compounds are face-centered cubic, strongly suggested that the two compounds are isostructural. Estimation of the relative intensities of a total of 116 symmetry independent reflections was achieved by the multiple-film technique and a standard scale made from the same crystal. Owing to the irregular shape of the crystal, several of the diffraction data, such as 200, 220, 311 *etc.*, which fall in the extreme high absorption area (detectable by the shade of the background) were rejected even though they were observed*. After the usual Lorentz–polarization and absorption corrections were applied to the estimated intensities, the observed $|F_o|^2$ values were correlated and scaled statistically. Based on the average diameter, 0·10 mm, of the crystal and the atomic composition of Gd:Mn = 6:23, the spherical absorption correction ($\mu R = 13{\cdot}1$; extrapolation of the table given in *International Tables for X-ray Crystallography*, 1959) was applied*. Subsequently the space group, *Fm*3*m*, and the atomic positions given for Th_6Mn_{23} by Florio *et al.* (1952) were used as the starting point for a least-squares refinement. After four cycles of isotropic least-squares refinement in which the over-all temperature factor, $B_0 = 1{\cdot}6$ obtained from the Wilson (1942) plot was held constant (because of the possible erroneous refinement due to the high absorption) an $R(F)$, $\{\Sigma||F_o|-|F_c||/\Sigma|F_o|\}$, of 0·13 was obtained. This confirms that the present compound is isostructural with Th_6Mn_{23} and its formula is therefore Gd_6Mn_{23}.

The final atomic parameters are given in Table 1 and

* These actions were deemed justified in view of the fact that the objective of the present work is to prove that Th_6Mn_{23} and the present compound are isostructural, and is not an original structure determination.

Table 1. *Atomic positions and parameters in* Gd_6Mn_{23}.

Standard deviation of the parameters (Å), in parenthesis

Space group *Fm*3*m*

24 Gd	in (*e*)	with $x = 0{\cdot}1954 \pm 0{\cdot}0014$	($\pm 0{\cdot}017$)
4 Mn	in (*b*)	special positions	
24 Mn	in (*d*)	special positions	
32 Mn(1)	in (*f*)	with $x = 0{\cdot}1778 \pm 0{\cdot}0020$	($\pm 0{\cdot}025$)
32 Mn(2)	in (*f*)	with $x = 0{\cdot}3759 \pm 0{\cdot}0019$	($\pm 0{\cdot}024$)

Table 2. *Observed and calculated structure factors of* Gd_6Mn_{23}.

H	K	$\|F_o\|$	F_c
(L = 0)			
4	0	202	122
6	0	372	405
8	0	227	227
10	0	189	172
12	0	128	113
14	0	15	-24
16	0	79	81
4	2	27	31
6	2	34	-35
8	2	<10	10
10	2	59	55
12	2	71	67
14	2	47	47
4	4	297	358
6	4	99	81
8	4	21	18
10	4	77	87
12	4	128	131
14	4	29	28
6	6	176	185
8	6	48	-51
10	6	94	98
12	6	59	60
8	8	141	178
10	8	14	22
12	8	52	-55
10	10	88	95
12	10	26	29
(L = 1)			
5	1	318	289
7	1	99	-89
9	1	<10	-25
11	1	104	99
13	1	<10	8
15	1	27	22
3	3	185	-150
5	3	87	-72
7	3	95	-83
9	3	65	52
11	3	82	-73
13	3	86	-77
15	3	50	43
5	5	141	136
7	5	61	61
9	5	91	88
11	5	76	73
13	5	26	-34
15	5	67	67
7	7	94	-99
9	7	51	-53
11	7	<10	15
13	7	33	-29
9	9	28	21
11	9	27	27
13	9	26	22
11	11	18	20
(L = 2)			
4	2	127	-143
6	2	27	28
8	2	199	-201
10	2	24	25
12	2	52	-61
14	2	37	-39
4	4	50	-46
6	4	<10	-3
8	4	99	-111
10	4	<10	12
12	4	55	42
14	4	33	-35
6	6	<10	14
8	6	47	-39
10	6	52	60
12	6	69	-66
14	6	83	79
8	8	142	-169
10	8	29	-26
12	8	70	-72
10	10	26	22
12	10	25	-23
(L = 3)			
3	3	298	-314
5	3	47	42
7	3	163	-197
9	3	139	-202
13	3	111	-100
15	3	91	-89
7	5	47	-50
9	5	21	23
7	7	58	-49
9	7	42	-41
11	7	62	-67
13	7	93	-103
11	11	24	-23
(L = 4)			
8	4	104	132
10	4	78	60
12	4	< 10	-12
14	4	14	-6
10	6	59	57
12	6	27	-26
14	6	28	25
8	8	53	-62
10	8	<10	1
12	8	52	54
10	10	57	60
(L = 5)			
5	5	207	263
7	5	< 10	-12
9	5	40	26
11	5	133	141
13	5	57	53
9	7	20	22
11	7	< 10	2
13	7	38	-41
9	9	80	92
(L = 6)			
6	6	190	205
8	6	37	-40
10	6	87	91
12	6	60	57
8	8	< 10	-4
10	8	<10	0
12	8	52	-54
10	10	83	91

the observed $|F_o|$ values are compared with the calculated F_c values in Table 2. The density of the compound was found by the displacement method (in water and in air) to be 7·39 g.cm^{-3}. This value compares favorably with the calculated value, 7·36 g.cm^{-3}, based on four Gd_6Mn_{23} units per unit cell. This then, adds another member to the family of A_6B_{23}-type compounds which includes Th_6Mn_{23} (Florio *et al.*, 1952), Sr_6Li_{23} (Wang, King & Kanda, 1962) and Sr_6Mg_{23}, Ba_6Mg_{23} (Gladyshevskii, Kripyakevich, Kuzma & Teslyuk, 1962; Wang, Kanda, Miskell & King, 1963).

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The crystal data for sodium carbonate decahydrate.

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Dr J. W. Visser (of Technisch-Physische Dienst T.N.O. en T.H., Delft) has kindly informed us of the results of his accurate determination of the crystal data for $Na_2CO_3.10H_2O$. This has drawn our attention to a mistake in transcription which led to errors in the *b* parameter and space-group symbol reported by us (Dunsmore & Speakman, 1963), as well as to a possible source of confusion affecting the crystal data for this substance. Because it is pseudo-hexagonal, there are three very similar choices of *a* and *c* axes. These are listed in Table 1 on the basis of our own (corrected) measurements. Cell (i), which has the value of β nearest to 90°, is that chosen by Visser, whose parameters are given in the last column. Cell (ii) is the one adopted in our note, with an emendation of space-group symbol. Cell (iii) corresponds most closely with the axial ratios and β value recorded by Groth (Vol. II, 1908), as is seen by comparing the figures in columns 5 and 6. (We have chosen the centrosymmetric space group No. 15, instead of No. 9, because the goniometric data imply the point group $2/m$.) D_x is now 1·460.

We are indebted to Dr Visser for permission to publish his results for the decahydrate, and also parameters for $Na_2CO_3.7H_2O$ ($a = 19{\cdot}498$, $b = 7{\cdot}0157$, $c = 14{\cdot}483$ Å) which agree well with our own.

Reference

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Table 1. *Crystal data for* $Na_2CO_3.10H_2O$, *with translations in* Å

				Ratios		
	(i)	(ii)	(iii)	(iii)	(Groth)	Visser
a	12·761	12·571	12·761	1·4165	1·4186	12·754
b	9·009	9·009	9·009	1	1	9·009
c	12·571	13·470	13·470	1·4951	1·4828	12·597
β	115° 46′	121° 26′	122° 48′	—	122° 20′	115° 51′
S.G.	*C*2/*c*	*I*2/*a*	*C*2/*c*			*C*2/*c*