The Crystal Structures of Sr_6Mg_{23}, $SrMg_4$, Ba_6Mg_{23} and $BaLi_4$

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The crystal structures of Sr_6Mg_{23}, Ba_6Mg_{23}, $SrMg_4$ and $BaLi_4$ have been determined by the single-crystal X-ray diffraction method. Sr_6Mg_{23} and Ba_6Mg_{23} are isomorphous with Th_6Mn_{23} and Sr_6Li_{23} and crystallize in space group $Fm3m$, with unit-cell dimensions $a_0 = 14\cdot91$ and $a_0 = 15\cdot26$ Å, respectively. $SrMg_4$ is complex with 90 atoms in a unit cell of space group $P6_3/mmc$, with unit-cell dimensions $a_0 = 10\cdot51$, $c_0 = 28\cdot36$ Å. $BaLi_4$, the only compound in the Ba–Li system, has been completely characterized, (including all Li atom positions). Its space group is $P6_3/mmc$ with cell dimensions, $a_0 = 11\cdot02$, $c_0 = 8\cdot89$ Å.

The atomic arrangements of $SrMg_4$, Sr_6Mg_{23}, Ba_6Mg_{23} and $BaLi_4$ are closely related although their crystal structures are different.

Introduction

The investigation of the Sr–Mg phase diagram by Vosskühler (1939), Klemm & Kinkelacker (1947) and Ray (1947) disclosed the existence of four compounds, which were assigned the formulae $SrMg_2$, $SrMg_3$, $SrMg_4$ and $SrMg_9$, and disproved the existence of the compound SrMg reported by Nowotny (1942). $SrMg_2$ was investigated by Hellner & Laves (1943) who found the structure to be a 'Laves phase' of the C_{14} type. The crystal structure investigation of $SrMg_9$ by Miskell (1948) was inconclusive as far as the atomic positions were concerned. The formula $SrMg_9$ was later proved to be incorrect by Kripyakevich & Evdokimenko (1962) and Wang, Kanda, Miskell & King (1963), both of whom assigned the formula Sr_2Mg_{17} to this compound.

In many respects the Ba–Mg phase diagram, determined by Klemm & Kinkelacker (1947), Zeek (1955) and Weibke & Schmidt (1940), is similar to that of the Sr–Mg system. Except for the non-existence of $BaMg_3$, the Ba–Mg system duplicates the series of compounds, $SrMg_2$, $SrMg_4$, and $SrMg_9$ found in the Sr–Mg system. The structure of $BaMg_2$ was found to be isomorphous with that of $SrMg_2$ by Hellner & Laves (1943). Miskell (1948) reported that $BaMg_9$ was isomorphous with $SrMg_9$; Goldish & Marsh (1955) reported that it was a disordered phase which possessed a stoichiometric Ba:Mg ratio of 1:10·5. However, both proposed structures for $BaMg_9$ were independently proven to be in error by Kripyakevich & Evdokimenko (1962) and Wang *et al.* (1963), who concluded that $BaMg_9$ is not isomorphous with $SrMg_9$ (correct formula Sr_2Mg_{17}) and should be assigned the formula Ba_2Mg_{17}.

The current investigation was carried out to clarify the structural relationships between the intermediate

phases of the two systems Sr–Mg and Ba–Mg. Consideration of the similarity of the physical properties of Mg and Li (Hume-Rothery, 1962) led to the extension of this structure study to include $BaLi_4$, which had been reported by Keller (1958) in his phase diagram study.

Experimental

In a previous paper (Wang, Kanda & King, 1962), the purity of the metals and the method of sample preparation were discussed in detail. For the crystal structure studies of the Sr–Mg system, four alloys of composition 50, 25, 15 and 8 at.% Sr were prepared. These compositions were chosen so that they fell between the compound compositions indicated by the phase diagram. X-ray powder diffraction patterns of samples from the top and bottom portions of the 50 at.% Sr alloy showed that the bottom portion consisted of Sr(f.c.c.); whereas the top portion consisted of a mixture of Sr(f.c.c.) and $SrMg_2$ (hexagonal). Similar investigations were carried out with the remaining alloys and these studies confirmed that only four compounds did exist in this system. Analogous procedures carried out for the alloys of the Ba–Mg system revealed that only three compounds existed in this system. Single crystals were mechanically extracted under oil from each alloy matrix which had been shown by a powder pattern to consist of a distinct phase. Owing to the irregular shapes of the crystals, the error due to absorption was minimized by selecting crystals of small size (0·05–0·10 mm average diameter) rather than by application of an absorption correction. Equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation. Precise lattice constants were determined from zero layer Weissenberg photographs calibrated against NaCl. Density measurements were made by the flotation method, using carbon tetrachloride and methylene iodide as two miscible liquids. The results

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Table 1. *Preliminary crystallographic data*

Compound	$SrMg_4$	$BaLi_4$	Sr_6Mg_{23}	Ba_6Mg_{23}
Diffraction symmetry	$6/mmm$	Same as $SrMg_4$	$m3m$	Same as Sr_6Mg_{23}
Extinction	$hk\cdot L$: no restriction $hh\cdot L$: $L \neq 2n$ $h\bar{h}\cdot L$: no restriction $h0\cdot L$: no restriction	Same as $SrMg_4$	hkL: $h+k$, $k+L$, $(h+L) \neq 2n$	Same as Sr_6Mg_{23}
Space group	$P6_3/mmc$	Same as $SrMg_4$	$Fm3m$	Same as Sr_6Mg_{23}
Lattice constants	$a_0 = 10\cdot511 \pm 0\cdot008$ Å $c_0 = 28\cdot362 \pm 0\cdot011$ Å	$a_0 = 11\cdot026 \pm 0\cdot023$ Å $c_0 = 8\cdot891 \pm 0\cdot010$ Å	$a_0 = 14\cdot914 \pm 0\cdot015$ Å	$a_0 = 15\cdot263 \pm 0\cdot018$ Å
Density	Calc. $2\cdot03$ g.cm^{-3} Obs. $2\cdot11$ g.cm^{-3}	Calc. $1\cdot77$ g.cm^{-3} Obs. $1\cdot75$ g.cm^{-3}	Calc. $2\cdot18$ g.cm^{-3} Obs. $2\cdot15$ g.cm^{-3}	Calc. $2\cdot58$ g.cm^{-3} Obs. $2\cdot52$ g.cm^{-3}

of this preliminary investigation are given in Table 1. Intensities were estimated visually with the use of the multiple film technique and a graduated intensity scale prepared from the same crystal. The reflection data, obtained in this manner, were corrected to $|F_o(hkL)|^2$ then scaled statistically. The ERFR–2 (Sly, Shoemaker & Van den Hende, 1962) and ORFLS (Busing, Martin & Levy, 1962) programs were used for the computations of three-dimensional Fourier syntheses and least-square refinements on an IBM 7094 computer.

Structure determination

Sr_6Mg_{23} *and* Ba_6Mg_{23}

Careful side by side comparison of the powder pattern of Sr_6Li_{23} with that of the top portion of the 25 at.% Sr conclusively proved that the two structures were isomorphous.* Single crystals were obtained from the alloy matrix, and Weissenberg photographs were taken about the c axis of the zero through eighth layer. From these photographs, the intensities of a total of 195 symmetry independent reflections were obtained.

Previously, Sr_6Li_{23} had been found to be isomorphous with Th_6Mn_{23} (Florio *et al.*, 1952) and its atomic parameters had been determined (Wang, King & Kanda, 1962). Since this compound is isomorphous with Th_6Mn_{23} and Sr_6Li_{23}, its space group is $Fm3m$ and its empirical formula is Sr_6Mg_{23}. The equivalent atomic positions found for Sr_6Li_{23} were used as the starting point of a least-squares refinement. After three cycles of isotropic refinement, a reliability index, $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ (hereafter to be denoted $R(F)$) of $0\cdot16$ was obtained. The final atomic parameters are given in Table 2 and the F_o's are compared with the F_c's in Table 5. The existence of Ba_6Mg_{23} as well as its isomorphism with Sr_6Li_{23} was established solely by the careful investigation and comparison of powder patterns. The atomic arrangement of 50 Mg

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* About the time the preliminary publication of this work (Wang *et al.*, 1963) was submitted, Gladyschevskii, Kripyakevich, Kuzma & Teslyuk (1962) confirmed independently by the powder method that Sr_6Mg_{23} and Ba_6Mg_{23} are isomorphous with Th_6Mn_{23} (Florio, Rundle & Snow, 1952).

atoms surrounding 6 octahedrally arranged Sr atoms is shown in Fig. 1(*a*).

Table 2. Sr_6Mg_{23}

(*a*) Atomic positions and parameters

(standard deviations of parameters in Å in parenthesis)
Space group; $Fm3m$

24 Sr(*e*);	with $x = 0\cdot2041 \pm 0\cdot0012 (\pm 0\cdot018$ Å)
4 Mg(*b*);	special positions
24 Mg(*d*);	special positions
32 Mg(*f*)$_1$;	with $x = 0\cdot3741 \pm 0\cdot0042 (\pm 0\cdot062$ Å)
32 Mg(*f*)$_2$;	with $x = 0\cdot1774 \pm 0\cdot0041 (\pm 0\cdot061$ Å)

(*b*) Interatomic distances

Sr(*e*)	−Sr(*e*)	$4\cdot303 \pm 0\cdot036$ Å
Sr(*e*)	−Mg(*d*)	$3\cdot778 \pm 0\cdot060$
Sr(*e*)	−Mg(*f*)$_1$	$3\cdot667 \pm 0\cdot058$
Sr(*e*)	−Mg(*f*)$_2$	$3\cdot766 \pm 0\cdot049$
Mg(*b*)	−Mg(*f*)$_1$	$3\cdot247 \pm 0\cdot079$
Mg(*d*)	−Mg(*f*)$_1$	$3\cdot224 \pm 0\cdot080$
Mg(*d*)	−Mg(*f*)$_2$	$3\cdot056 \pm 0\cdot072$
Mg(*f*)$_1$	−Mg(*f*)$_2$	$3\cdot464 \pm 0\cdot081$

$SrMg_4$

It has been shown above that four compounds exist in this system, three of which are $SrMg_2$, Sr_2Mg_{17} and Sr_6Mg_{23}. There is little doubt that the structures determined for $SrMg_2$ and Sr_2Mg_{17} correspond to the compounds $SrMg_2$ and $SrMg_9$ indicated by the phase diagram. Furthermore, in view of the fact that compounds of the type A_6B_{23} (*e.g.* Th_6Mn_{23}, Sr_6Li_{23}) were originally assumed to be AB_4 in the phase diagram studies, one is inclined to assign the structure of Sr_6Mg_{23} to the diagram-predicted compound, $SrMg_4$. If these assignments are correct, the remaining compound indicated by the phase diagram should be $SrMg_3$. However, the number of molecules in a unit cell based on the postulated formula Sr_6Mg_{18} was calculated to be $3\cdot58$. This suggested that the true formula for the compound was not $SrMg_3$. A series of varied formulae, Sr_6Mg_{19}, Sr_6Mg_{20}, Sr_6Mg_{21}, Sr_6Mg_{22} used in a similar calculation indicated that the number of molecules in a unit cell approached the whole number 3 as the ratio of Sr atoms to Mg atoms approached one to four. This fact, along with the similarity of its density ($2\cdot11$ g.cm^{-3}) to the $2\cdot15$
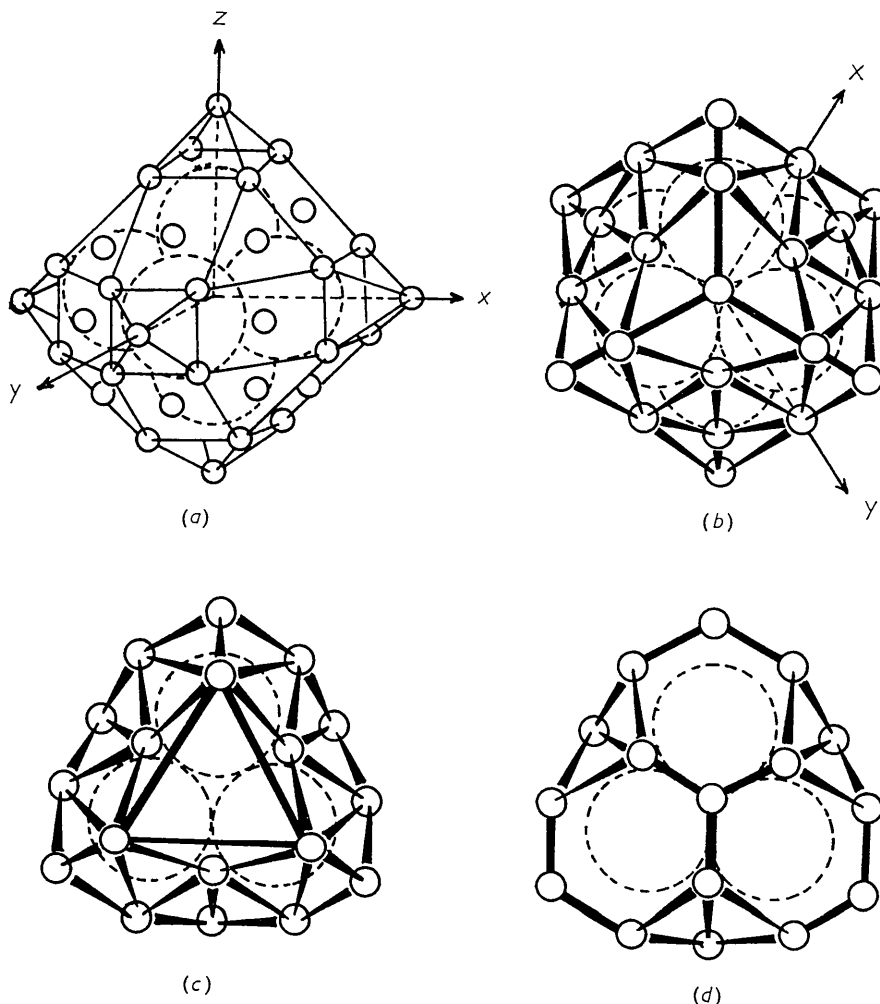
Fig. 1. (a), (b) Octahedral cluster of 6 Sr atoms surrounded by 50 Mg atoms in Sr_6Mg_{23} (f.c.c.) and $SrMg_4$ (hexagonal). (c) Triangular cluster of 3 Sr atoms surrounded by 33 Mg atoms in $SrMg_4$. (d) Triangular cluster of 3 Ba atoms surrounded by 29 Li atoms in $BaLi_4$.

g.cm^{-3} density of Sr_6Mg_{23} crystals, suggested the possible existence of an allotropic modification of Sr_6Mg_{23}. It was decided, therefore, to determine the structure first and then deduce the formula. Five layers of Weissenberg photographs, rotated about the orthohex axis and 3 layers rotated about the c axis yielded a total of 581 symmetry independent reflections. A three-dimensional Patterson synthesis computed from these reflection data immediately showed that the vectors form two octahedral clusters of six Sr atoms (orientated as shown in Fig. 1(b)), in the u–v planes at w levels of 0/120, 17/120 and 43/120. The extinctions observed (Table 1) together with the fact that two octahedral clusters of this type can only be placed at $\pm (x, 2x, z; \; 2\bar{x}, \bar{x}, z; \; x, \bar{x}, z; \; x, 2x, \frac{1}{2}-z; \; 2\bar{x}, \bar{x}, \frac{1}{2}-z; \; x, \bar{x}, \frac{1}{2}-z)$ led to the selection of space group $P6_3/mmc$ for this structure. In seeking the remaining Sr atomic positions, a misinterpretation

of Patterson vectors was made, leading to the erroneous assignment of the atoms: 2 Sr in (c) and 4 Sr in (f) with $z = -21.5/120$. This error was due to a certain degree of homometry between this structure and the true structure. After several cycles of three-dimensional least-squares refinement on the false structure, the $R(F)$ remained at 0.47; whereas after three cycles of similar refinement on the true structure, the $R(F)$ value was reduced to 0.32. A three-dimensional difference Fourier synthesis, from which the contribution of the 18 Sr atoms had been subtracted, showed the location of 72 Mg atoms. This confirmed that the formula was $SrMg_4$, ruling out the possibility of an allotropic form of Sr_6Mg_{23}. The final three-dimensional isotropic least-squares refinement based on all atoms reduced the $R(F)$ to 0.12 after three cycles. The final atomic parameters and interatomic distances are given in Table 3.

Table 3. SrMg₄

(a) Atomic positions and parameters
(standard deviations of parameters in Å in parenthesis)

Space group; $P6_3/mmc$

12 Sr(k);	with x =	$0.1369 \pm 0.0004(\pm 0.004$ Å$)$
	z =	$0.0625 \pm 0.0001(\pm 0.003)$
6 Sr(h);	with x =	$0.0478 \pm 0.0005(\pm 0.005)$
4 Mg(e);	with z =	$0.1580 \pm 0.0011(\pm 0.031)$
4 Mg(f)₁	with z =	$0.0373 \pm 0.0010(\pm 0.028)$
4 Mg(f)₂;	with z =	$-0.1427 \pm 0.0010(\pm 0.028)$
6 Mg(g);	special positions	
6 Mg(h);	with x =	$-0.1011 \pm 0.0015(\pm 0.015)$
12 Mg(k)′;	with x =	$\frac{1}{2}$ (special position)
	z =	$0.1177 \pm 0.0005(\pm 0.014)$
12 Mg(k)₁;	with x =	$-0.2321 \pm 0.0011(\pm 0.011)$
	z =	$0.0546 \pm 0.0005(\pm 0.014)$
12 Mg(k)₂;	with x =	$-0.1677 \pm 0.0010(\pm 0.010)$
	z =	$0.1540 \pm 0.0005(\pm 0.014)$
12 Mg(k)₃;	with x =	$0.1772 \pm 0.0010(\pm 0.010)$
	z =	$0.1897 \pm 0.0005(\pm 0.014)$

(b) Interatomic distances

Sr(k)	–Sr(k)	4.316 ± 0.012 Å
Sr(h)	–Sr(h)	4.255 ± 0.009
Sr(k)	–Mg(g)	3.779 ± 0.019
Sr(k)	–Mg(k)₁	3.685 ± 0.016
Sr(k)	–Mg(f)₁	3.646 ± 0.022
Sr(k)	–Mg(e)	3.675 ± 0.020
Sr(k)	–Mg(k)′	3.687 ± 0.031
Sr(k)	–Mg(k)₃	3.678 ± 0.022
Sr(h)	–Mg(k)₂	3.860 ± 0.032
Sr(h)	–Mg(k)₃	3.714 ± 0.021
Sr(h)	–Mg(h)	3.675 ± 0.030
Sr(h)	–Mg(k)′	3.794 ± 0.038
Mg(g)	–Mg(k)₁	3.067 ± 0.048
Mg(g)	–Mg(k)′	3.338 ± 0.089
Mg(g)	–Mg(f)₁	3.209 ± 0.082
Mg(k)₁	–Mg(k)₁	3.192 ± 0.080
Mg(k)₁	–Mg(k)′	3.198 ± 0.078
Mg(k)₂	–Mg(k)′	3.193 ± 0.092
Mg(k)₂	–Mg(e)	3.055 ± 0.086
Mg(k)₂	–Mg(k)₃	3.316 ± 0.084
Mg(e)	–Mg(h)	3.193 ± 0.081
Mg(f)₂	–Mg(k)′	3.116 ± 0.089
Mg(f)₂	–Mg(k)₃	3.138 ± 0.075

Sr(h) z = 1/4
Mg(h) z = 1/4
Mg(k)₃ z = 0.1897

Mg(e) z = 0.1580
Mg(k)₂ z = 0.1540
Mg(f)₂ z = 0.1427
Mg(k)′ z = 0.1177

Sr(k) z = ±0.0625
Mg(k)₁ z = 0.0546
Mg(f)₁ z = 0.0373
Mg(g) z = 0

Fig. 2. SrMg₄; Projection of the atoms onto the xy plane (full cell) at various levels of z.

Table 4. BaLi₄

(a) Atomic positions and parameters
(standard deviations of parameters in Å in parenthesis)

Space group; $P6_3/mmc$

6 Ba(h);	with x =	$0.4720 \pm 0.0002(\pm 0.0017$ Å$)$
2 Li(a);	special positions	
4 Li(f);	with z =	$0.5808 \pm 0.0076(\pm 0.083)$
6 Li(h);	with x =	$0.1027 \pm 0.0057(\pm 0.050)$
12 Li(k);	with x =	$0.1621 \pm 0.0087(\pm 0.077)$
	z =	$0.5615 \pm 0.0117(\pm 0.103)$

(b) Interatomic distances

Ba(h)	–Ba(h)	(intra-triangular)	4.586 ± 0.021 Å
Ba(h)	–Ba(h)	(inter-triangular)	4.571 ± 0.018
Ba(h)	–Li(h)		3.838 ± 0.072
Ba(h)*	–Li(f)		3.947 ± 0.068
Ba(h)†	–Li(f)		4.012 ± 0.056
Ba(h)*	–Li(k)		3.605 ± 0.068
Ba(h)†	–Li(k)		3.873 ± 0.069
Li(a)	–Li(k)		3.138 ± 0.089
Li(h)	–Li(k)		2.969 ± 0.096
Li(a)	–Li(h)		2.963 ± 0.110
Li(f)	–Li(k)		3.255 ± 0.088

* Atom located at $z = \frac{1}{4}$.   † Atom located at $z = \frac{3}{4}$.

The F_c's based on these parameters are compared with the F_o's in Table 5. Projections of the atomic arrangements on the xy plane at various z levels within the interval of $z = 0$ to $z = \frac{1}{4}$ are shown in Fig. 2. The 18 Sr atoms are grouped in two octahedral and two triangular clusters. The Mg atomic arrangement surrounding the octahedrally clustered Sr atoms is the same as the arrangement of Mg atoms in Sr₆Mg₂₃ despite the fact that the octahedral groups in SrMg₄ share different Mg atoms. These arrangements are shown in Fig. 1(a) and (b).

BaLi₄

The present investigation, by the single-crystal method, gave hexagonal unit cell dimensions (Table 1) which substantiated the lattice constants given by Keller (1958). Keller, using only powder diffraction data, assigned the space group $P6_3/mmc$ to the structure, and placed the six Ba atoms in the special positions in (g) which required a special condition

for limiting possible reflections: $hk·L$; $L=2n$ (Li scattering is regarded as negligible). But in the single crystal data, such a condition was not observed and thus ruled out the special position assignment. From six layers of Weissenberg photographs, rotated about the orthohex axes, a total of 334 independent reflections were obtained.

Based on the consistent atomic arrangement found for the heavy atoms in Sr$_6$Mg$_{23}$, Ba$_6$Mg$_{23}$ and SrMg$_4$ (*i.e.* in clusters of six or three), the following was postulated: The six Ba atoms in the unit cell exist in triangular groups of three, parallel to the xy plane, and located at $z=\frac{1}{4}$ and $\frac{3}{4}$. This postulate was con-

sidered to be reasonable because the length of the c_0 axis is 8·89 Å, just about equal to four times the radius of the Ba atom, 2·17 Å. To test the correctness of this postulate, two Harker sections, $w=0$ and $\frac{1}{2}$, were computed. The result confirmed that the Ba atoms are clustered in triangular groups. This provided the basis for assigning the space group $P6_3/mmc$, which determined the relative positions of the two triangular clusters. The agreement between $F_o^2(hk·L)$ and $F_c^2(hk·L)$ based on these six Ba atoms was 30%, which further confirmed the accuracy of the initial postulate. Owing to the relatively low atomic scattering power of the Li atoms, a difference Fourier synthesis

Table 5. *Observed and calculated structure factors for* Sr$_6$Mg$_{23}$, SrMg$_4$ *and* BaLi$_4$

Table 5 (cont.)

Column 1

L	OBS	CAL
13	102	62-
14	65	54-
15	190	215-
16	143	120
17	149	145
18	109	83
19	104	89
29	64	79-
(2,5·L)		
0	143	202-
3	377	342
4	56	49-
5	94	108
6	166	145
7	150	150
8	77	55
9	154	150-
11	124	124-
12	67	77-
13	278	296-
16	226	245-
18	68	46-
19	287	298
21	101	8-
22	125	143
23	123	119
25	120	130-
26	78	69
27	81	98-
29	146	221-
(2,6·L)		
0	72	5:-
1	107	133
2	42	64
3	69	104
4	54	64-
5	135	105
8	148	155
9	151	165
10	176	164
24	229	232-
18	120	122
20	80	60-
21	154	165
24	105	111
25	48	14
26	75	99
27	70	103-
(2,7·L)		
0	145	135-
1	126	181-
2	70	105-
3	88	121-
5	376	305-
6	169	189
10	145	136
11	231	239
13	85	111
15	180	180
16	145	149-
17	145	131-
21	145	199-
22	78	84
(2,8·L)		
0	140	129
3	156	204-
4	144	161-
7	100	112-
8	104	110
9	125	131
10	64	104
13	167	187
16	105	128-
19	131	193-
(3,3·L)		
0	445	353
2	47	58
4	188	150
6	319	254-
8	139	111-
10	491	377-
12	86	54
16	216	192
20	234	152
22	157	125-
26	255	223-
28	64	56

Column 2

L	OBS	CAL
(3,4·L)		
0	216	135-
1	168	136
2	219	187-
5	295	185
6	180	154
7	67	43-
10	150	101
1:	195	152-
12	78	65
14	85	72-
15	135	88-
16	163	141-
17	199	156
18	125	117-
21	120	107
22	72	37
23	78	48-
26	84	101
27	159	189-
(3,5·L)		
0	53	24-
1	88	55
2	302	261-
3	244	174
4	87	111
5	167	160
7	103	57
8	248	195
9	75	90-
11	250	196-
:2	217	181
:3	214	159-
:4	209	162-
:8	214	182-
:9	200	186
20	101	102
21	295	180
22	97	81-
23	82	49
24	161	160
27	87	108-
(3,6·L)		
0	:30	129-
4	74	41-
6	139	90
7	76	54
8	78	21
:6	189	162-
:8	74	48-
:9	65	40-
22	63	68
23	61	46
(3,7·L)		
:	121	103-
2	:98	164-
3	172	126-
4	120	98
5	172	187-
7	64	32-
8	100	93
9	52	66
10	110	104-
::	233	214
:2	105	98
13	165	122
14	175	145-
17	69	86-
18	88	103-
19	129	150-
20	108	141
2:	145	200-
(3,8·L)		
0	132	118-
1	131	118-
5	197	155-
11	86	94
15	131	125
16	88	116-
17	65	91-
(3,9·L)		
0	206	220
4	61	63
6	138	153-
8	69	108-
:0	169	196-

Column 3

L	OBS	CAL
(4,4·L)		
0	464	390
4	145	124-
6	205	186
10	100	35-
20	161	108
26	130	186
(4,5·L)		
2	201	174
3	93	85
4	70	59-
6	87	69-
7	105	69-
8	305	258-
9	73	88-
10	135	132-
11	136	86
13	96	84-
14	210	180
18	201	186
21	53	71-
22	76	75-
23	69	86
24	146	175-
25	58	84-
26	67	85-
(4,6·L)		
2	170	164
3	120	146-
4	81	88-
9	92	93-
10	113	93
11	131	126
12	53	50-
13	96	109
14	116	109
16	101	89
17	83	89
18	190	197
20	95	100-
21	77	85-
(5,5·L)		
0	395	369
4	148	122
6	319	277-
8	125	141-
10	361	328-
12	136	113
14	62	50
16	272	278
20	94	95
22	175	236-
24	63	108-

BaLi4

L	OBS	CAL
(00·L)		
2	230	291-
4	316	268
6	248	246-
8	183	185
10	182	175-
(01·L)		
2	97	101
3	95	76-
4	77	77-
5	40	48
6	65	73
7	3:	46-
8	42	61-
9	30	46
10	45	53
(02·L)		
0	165	261
2	253	262-
4	252	228
6	190	180-
8	175	176
10	150	142-
(03·L)		
0	118	122-
1	194	188
2	104	121
3	147	174-
4	89	105-
5	129	147

Column 4

L	OBS	CAL
6	77	93
7	99	130-
8	43	75-
9	84	114
10	45	75
11	83	98-
(04·L)		
0	166	142
1	129	151-
3	17	28
4	107	137
6	88	105-
8	86	111
10	54	86-
(05·L)		
0	153	130-
1	290	220
2	139	125
3	175	187-
4	78	109-
5	175	187
6	86	106
7	129	159-
8	67	85-
9	96	135
10	54	80
(06·L)		
0	69	64
1	84	75-
3	71	71
4	20	32
5	49	64-
6	28	42-
7	40	57
9	26	51-
(07·L)		
0	151	105-
1	242	180
2	119	118
3	206	181-
4	92	130-
5	148	157
6	73	94
7	118	144-
8	48	86-
9	95	134
(08·L)		
0	56	48-
1	147	120-
2	38	36
3	112	105
4	34	34-
5	100	112-
6	30	42
7	61	89
(09·L)		
0	69	60-
1	153	131
2	56	62
3	143	133-
4	44	58-
5	104	116
6	34	55
7	77	112-
(0,10·L)		
0	90	80-
:	204	:43-
2	70	7C
3	169	146
4	55	67-
5	123	126-
6	56	72
(0,11·L)		
L	83	79
3	70	64-
(0,12·L)		
0	:13	71-
1	225	144-
(1,1·L)		
0	46	71-
10	28	46
2	58	72

Column 5

L	OBS	CAL
4	45	61-
6	43	53
8	30	41-
(1,2·L)		
0	47	88-
7	110	135-
10	22	49
11	66	123-
11	42	65
2	65	88
3	77	93
4	52	70-
5	83	99-
6	49	69
7	55	80
8	38	54-
9	43	65-
(1,3·L)		
0	20	3-
1	20	36-
3	30	48
(1,4·L)		
0	24	29-
1	108	116-
2	24	34
3	72	111
5	61	95-
7	50	86
9	51	76-
10	31	25
(1,5·L)		
0	65	63
1	56	61-
2	48	57-
3	30	43
4	41	59
5	40	54-
6	36	45-
7	37	43
8	36	45
(1,6·L)		
1	71	78-
3	61	85
5	48	66-
7	40	62
9	28	60-
(1,7·L)		
0	123	100
1	25	28-
2	100	93-
3	22	30
4	72	88
6	58	81-
8	52	77
(1,8·L)		
0	33	33
2	33	32-
(1,9·L)		
0	125	105
2	113	96-
4	91	98
6	64	86-
(1,10·L)		
1	42	38
3	:28	33-
5	28	36
(1,11·L)		
0	57	64
1	24	28
2	48	63-
3	26	36-
(2,2·L)		
0	172	222
2	126	158-
4	143	160
6	128	153-
8	75	110
10	70	112-
(2,3·L)		
0	95	93-
1	214	183

Column 6

L	OBS	CAL
2	95	102
3	208	183-
4	65	82-
B	30	41-
5	130	150
6	61	78
7	110	135-
8	44	69-
9	87	24
10	37	58
(2,4·L)		
0	66	76
1	29	32-
2	92	87-
3	14	18
4	74	79
5	30	34-
6	44	57-
8	43	68
10	31	48-
(2,5·L)		
0	106	103-
1	211	183
2	112	105
3	205	179-
4	96	96-
5	171	156
6	79	87
7	140	145-
8	72	73-
9	110	129
(2,6·L)		
0	22	22-
:	67	69-
3	74	76
5	51	54-
6	13	20
7	51	63
9	41	51-
(2,7·L)		
0	76	91-
1	161	152
2	87	88
3	:45	130-
4	76	79-
5	153	138
6	65	81
7	95	119-
8	44	65-
(2,8·L)		
0	46	45-
1	112	111-
2	76	78
3	::3	107
4	58	8:-
5	:06	100-
6	41	48
7	74	92
(2,9·L)		
0	26	33-
1	71	83
2	43	45
3	78	87-
4	33	34-
5	54	75
6	26	35
(2,10·L)		
0	71	86-
1	129	138-
2	51	77
3	114	128
4	5:	74-
(3,1·L)		
0	140	97
2	59	88-
4	63	82
6	47	72-
8	40	68
10	33	51-
(3,4·L)		
0	61	58-
1	165	145-
2	45	57
3	94	121
4	26	48

Column 7

L	OBS	CAL
5	98	:27-
6	37	52
7	8:	107
8	22	40-
9	59	92-
(3,5·L)		
0	211	150
2	169	139-
4	115	137
6	103	118-
8	81	109
(3,6·L)		
0	40	35-
1	55	55-
2	34	39
3	52	58
4	33	35-
5	41	47-
6	24	33
7	30	47
(3,7·L)		
0	228	157
2	254	153-
4	195	150
6	126	132-
(3,8·L)		
0	24	23-
1	26	21
2	21	22
3	20	13-
4	24	24-
5	20	19
6	22	24
(3,9·L)		
0	158	:37
2	127	128-
4	:25	125
(3,10·L)		
0	34	40-
:	66	68
2	32	37
(4,4·L)		
0	22:	29
(4,5·L)		
0	112	73-
1	180	::4
2	115	8:
3	158	117-
4	71	7:-
5	97	:00.
6	58	68
7	61	93-
8	42	64-
(4,6·L)		
0	:5	::-
1	42	40-
2	55	50
3	29	31
4	40	47-
5	33	41-
6	38	54
7	17	2P
(4,7·L)		
0	76	64-
1	75	64
2	75	66
3	66	72-
4	58	62-
5	43	58
6	43	59
(4,8·L)		
0	71	74-
1	77	80-
2	65	65
3	71	P3
4	53	52-
5	54	69-
(4,9·L)		
0	29	30-
2	17	25

Column 8

L	OBS	CAL
(5,5·L)		
0	246	187
2	242	177-
4	231	170
6.	175	158-
8	151	146
(5,6·L)		
0	52	63-
2	52	59
4	52	53-
6	41	57
(5,7·L)		
0	239	183
2	213	177-
4	171	174
(5,8·L)		
0	41	54-
1	41	57
2	45	57
3	45	49-
4	4:	53-
(6,6·L)		
0	47	41-
2	69	68
4	55	55-
(6,7·L)		
0	46	43-
1	22	20-
2	56	55
3	:7	14
4	6:	45-

was not attempted. Instead, a three-dimensional Patterson synthesis was computed, from which all Ba · · · Ba interactions had been subtracted by using $|F_o^2 - F_c^2|$ as coefficients. All the Ba · · · Li vectors were identified in this synthesis which led to the location of all Li atoms. After three cycles of isotropic least-squares refinement, including all atoms, the $R(F)$ value was reduced to 0·14. The final atomic parameters and atomic distances are given in Table 4. The projection of the atomic positions onto the xy plane is shown in Fig. 3(a) and (b). The arrangement of Li atoms surrounding the three Ba atoms is pictorially shown in Fig. 1(d). The only feature which makes the atomic arrangement of the small atoms (Li) around the large atoms (Ba) distinct from that found in Sr_6Mg_{23} and $SrMg_4$ is that the clusters of three Ba atoms at $z = \frac{1}{4}$ and $\frac{3}{4}$ are not completely enveloped

Ba(h) $z = 1/4, 3/4$
Li(h) $z = 1/4, 3/4$

Li(a) $z = 0$
Li(f)* $z = 0.5808$
Li(k)* $z = 0.5615$

(a) (b)

Fig. 3. (a), (b) BaLi₄; Projection of Ba (large circles) and Li (small circles) onto the xy plane (full cell) at two levels of z. Parameters marked with an asterisk refer to Li atoms represented by light circles.

by small atoms (Li), but rather are touching each other in the z direction.

Discussion

Since the Mg content of the compounds $SrMg_4$ and Sr_6Mg_{23} differs by only 0·69 at.% (1·06 wt.%), it was reasonable to assume that they were allotropic forms of the same compound. However, this structure determination proves that not only are the two compounds different, but that $SrMg_4$ contains triangularly as well as octahedrally clustered Sr atoms; whereas Sr_6Mg_{23} contains only octahedrally clustered Sr atoms. Therefore, the phase diagram, especially in the range which encompasses these two compounds, should be re-examined.

So far, A_6B_{23}-type compounds have been observed in the following intermetallic binary systems*; Th–Mn, Sr–Li, Sr–Mg and Ba–Mg†. One wonders why Ba_6Li_{23} does not exist. In order to determine whether the A_6B_{23}-type compound is primarily atomic-size dependent, a table of atomic radius ratios (r_A/r_B) for the elements which form A_6B_{23}-type compounds was made (Table 6(a)). It was immediately noted from this table that in the systems in which the A_6B_{23}-type compound has been found, the atomic radius ratio (r_A/r_B) falls in the range, 1·32 to 1·38; whereas the Ba/Li atomic radius ratio, 1·43, is outside this range. This supports the view that the A_6B_{23}-type compound is atomic-size-factor dominated and consequently serves to explain the non-existence of Ba_6Li_{23}. Table 6(b) shows all compounds formed in each binary system comprised of elements which form A_6B_{23}-type compounds. It is noted from this table that the systems in which the A_6B_{23}-type compound is found are the ones which have three or more intermediate phases.

Another interesting observation, in this series of intermetallic compounds, is the close similarity of the atomic arrangement of Mg(Li) atoms around the triangularly and octahedrally arranged Sr(Ba) atoms. This is seen in Fig. 1(b), (c) and (d). The observed interatomic distances between Sr atoms seem to be fairly constant both in Sr_6Mg_{23} and $SrMg_4$. The Mg interatomic distances, on the other hand, appear to vary more, ranging from the shortest distances of

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* The A_6B_{23}-type compounds have also been found in ternary systems; e.g. $Mg_6Si_7Cu_{16}$ (Nagorsen & Witte, 1953; Bergman & Waugh, 1953, 1956), $Ti_6Si_7Ni_{16}$ (Beattie & Snyder, 1956; Beattie & Hagel, 1957). The compounds of $A_6Si_7Ni_{16}$, where A = Mn, V, Nb, Ta, Zr, Hf and the compound $Mn_6Ge_7Ni_{16}$ were reported by Gladyshevskii et al. (1962). Several additional isotypic ternary phases (so called 'G phases') were reported in a paper by Spiegel, Bardos & Beck (1963).

† After the present paper had been written and accepted for publication, one of the authors (Wang, 1964) in his continuing investigation at the U.S. Naval Ordnance Laboratory, has confirmed that the A_6B_{23}-type compound also exists in the following binary systems; Y–Mn, Nd–Mn, Sm–Mn, Gd–Mn, Tb–Mn, Dy–Mn, Ho–Mn, Er–Mn and Tm–Mn (see also Wang, Gilfrich, Ernst & Hubbard (1964) for a report on the crystal structure of Gd_6Mn_{23}).

Table 6

(a) Atomic radius ratios (r_A/r_B) for elements which form A_6B_{23}-type compounds.*

(b) Compounds formed by elements which form A_6B_{23}-type compounds. Diagonal lines indicate systems which have not been investigated.

r_B \ r_A	Sr(2·10)	Ba(2·17)	Th(1·79)
Li(1·52)	1·38	1·43	1·18
Mg(1·59)	1·32	1·35	1·13
Mn(1·36)	1·54	1·59	1·32

(a)

B \ A	Sr	Ba	Th
Li	Sr_6Li_{23} Sr_3Li_2 Sr_8Li	$BaLi_4$	
Mg	$SrMg_2$ Sr_6Mg_{23} $SrMg_4$ Sr_2Mg_{17}	$BaMg_2$ Ba_6Mg_{23} Ba_2Mg_{17}	$ThMg_9$
Mn			$ThMn_2$ Th_6Mn_{23} $ThMn_{12}$

(b)

* Atomic radii are from *Interatomic Distances* (1958).

3·056 Å between Mg$(f)_2$–Mg(d) in Sr_6Mg_{23}, and 3·055 Å between Mg(e)–Mg$(k)_2$ in $SrMg_4$ to the longest distances, 3·464 Å, between Mg$(f)_1$–Mg$(f)_2$ in Sr_6Mg_{23} and 3·338 Å between Mg(g)–Mg$(k)'$ in $SrMg_4$. However, the minimum Mg$(f)_2$–Mg(d) distance in Sr_6Mg_{23} and the minimum Mg(e)–Mg$(k)_2$ distance in $SrMg_4$ are between Mg atoms with the same relationship to the octahedrally clustered Sr atoms. In $BaLi_4$, both the intra- and inter-triangular Ba–Ba distances have a constant value of 4·58 Å. This indicates an atomic radius of 2·29 Å for the Ba atom.

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Layer Structure Polytypism Among Niobium and Tantalum Selenides

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Single crystals of several varieties of tantalum and niobium selenide layer structures have been grown by vapor transport methods. Two two-layer forms have the NbS_2 structure, a three-layer form is like rhombohedral MoS_2, and two four-layer forms are new structures with a selenium stacking sequence of $AABBAACC...$, and $AABABBAB...$, respectively. These have been refined by least-squares methods. Refinement adjusts the c coordinates of the selenium atoms 0·1 Å away from positions in which each atom sheet is spaced at equal intervals along z. This adjustment moves the selenium atoms away from the interleaving metal atoms.

The trigonal prism coordination units in the niobium and tantalum compounds tend to be slightly shorter in the z direction and longer in the x direction than similar molybdenum coordination units.

Introduction

The disulfides of molybdenum, tungsten and niobium (Jellinek, 1963) and the diselenides of molybdenum (James & Lavik, 1963) and tungsten (Glemser, Sauer & König, 1948) are layer structures in which each cation* has as nearest neighbors six anions arranged

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* It is recognized that there is probably a high degree of covalency in these compounds; nevertheless, the terms cation and anion will be used to designate the two species involved.

at the apices of a trigonal prism. Disulfides of tantalum have been reported in which cations have trigonal prismatic and/or octahedral anion coordination (Jellinek, 1963). All of these structures can be considered as two-dimensionally infinite 'layer molecules' within which the bonding is quite strong. These 'layer molecules' are stacked in a close-packed manner and the bonding between them is weak.

The common notation used in the description of close packed structures, *i.e.* a hexagonal close