exclusively by corner sharing and the pairs are tilted relative to each other.

Large structural similarities between the compounds $K_4Nb_6O_{17}$ and $K_3Nb_7O_{19}$ can be noticed, especially the stacking sequence of the pairs of octahedra along the short axis (6·4 Å). The structure of $K_4Nb_6O_{17}$ projected along this short axis shows that the $Nb_6O_{17}^{4-}$ layers are built of three edge-sharing Nb_2O_{10} units (Fig. 6), while projection of $K_3Nb_7O_{19}$ shows four edge-sharing units together with units which are exclusively corner sharing.

A triclinic phase with a composition very close to that of $K_3Nb_7O_{19}$ has been published by Roth *et al.* (1974). The formula is given as $K_8Nb_{18}O_{49}$ but can also be written as $K_{3·10}Nb_{6·98}O_{19}$. The unit-cell dimensions reported for $K_8Nb_{18}O_{49}$ were used to index our Guinier X-ray powder diffraction film. Refinement of the parameters resulted in a unit cell with $a = 13·356 (9)$, $b = 13·93 (1)$, $c = 15·03 (1)$ Å, $\alpha = 82·24 (5)$, $\beta = 69·54 (6)$ and $\gamma = 89·18 (5)°$; very similar to that given by Roth *et al.*, but the figures of
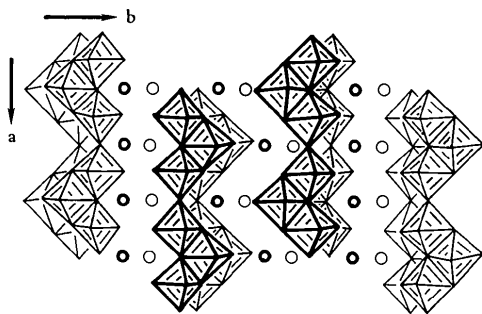

Fig. 6. Projection of the structure of $K_4Nb_6O_{17}$ along the c axis (6·46 Å). The $Nb_6O_{17}^{4-}$ layers contain three pairs of edge-sharing octahedra mutually joined by corner sharing. The layers are interleaved by K^+ ions.

merit were poor, $M(20) = 2$, $F(144) = 5 (0·013, 2461)$. Therefore, it is reasonable to believe that the specimen reported as $K_8Nb_{18}O_{49}$ is essentially the $K_3Nb_7O_{19}$ phase.

This demonstrates the importance of calculating the figures of merit when deriving unit cells with low symmetry from complex powder patterns such as this.

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Strontium and Europium Polynuclear Units in Intermetallic Compounds with Magnesium. Structural Refinements and Relationships

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Abstract

The crystal structures of $(Sr_{0·67}Eu_{0·33})_3Mg_{13}$ [$M_r = 642·61$, hexagonal, $P6_3/mmc$, $a = 10·465 (3)$, $c = 28·166 (5)$ Å, $V = 2671 (2)$ Å^3, $Z = 6$, $D_x = 2·40$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 9·5$ mm^{-1}, $F(000) = 1770$, $T = 294$ K, final R value 0·026 for 567 independent reflections] and $EuMg_{5·2}$ [$M_r = 278·38$, hexagonal, $P6_3/mmc$, $a = 10·395 (3)$, $c = 10·746 (3)$ Å, $V = 1005·6 (9)$ Å^3, $Z = 6$, $D_x = 2·76$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 9·6$ mm^{-1}, $F(000) = 752·4$, $T = 294$ K, final R value 0·026 for

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441 independent reflections] have been refined. The two structure types are known in the literature as 'Sr$_9$Mg$_{38}$' and 'EuMg$_5$' respectively. In the structural redeterminations, additional Mg atoms have been detected. The close resemblance of the two structures to Sr$_6$Mg$_{23}$ (Th$_6$Mn$_{23}$-type) is demonstrated by dividing each of the three structures into suitable stacking units (A_3Mg$_{14}$, A_6Mg$_{20}$; A = Sr, Eu) as well as interstitial volumes filled with Mg atoms. By this process the non-integral stoichiometry of EuMg$_{5.2}$ can be deduced.

Introduction

Europium in its binary compounds with magnesium behaves like the heavier alkaline-earth metals and strontium in particular (Klemm, Kock & Mühlpfordt, 1964). The electronegativities and, due to the electron configuration $4f^7$ of the lanthanide, the metallic radii of europium and strontium have a strong resemblance. Consequently, the phase diagrams of the systems Eu/Mg (Mühlpfordt & Klemm, 1969) and Sr/Mg (Klemm & Dinkelacker, 1947) exhibit similarities. They are mainly characterized by the congruently melting compounds with MgZn$_2$-type structure (Mühlpfordt, 1970) and Th$_2$Ni$_{17}$-type structure (Lueken & Erassme, 1985). Differences in the phase diagrams, however, occur in the range from 75 to 85 at.% Mg. Earlier thermal and structural investigations have shown the occurrence of diverse peritectically melting compounds with clustered heavy atoms, among them 'EuMg$_5$'* [space group $P6_3/mmc$ (Mühlpfordt, 1970)] in the Eu/Mg system. It displays triangles of Eu (see Fig. 1a) with an Eu–Eu distance of 4·3 Å and a much larger distance of 6·1 Å between adjacent triangles. In the Sr/Mg system two compounds with clusters of the larger atoms are known: Sr$_6$Mg$_{23}$ [Th$_6$Mn$_{23}$-type structure, space group $Fm\bar{3}m$ (Wang, Kanda, Miskell & King, 1965)] with characteristic units of Sr octahedra (see Fig. 1b), and 'Sr$_9$Mg$_{38}$' [space group $P6_3/mmc$ (Merlo & Fornasini, 1982)] with Sr triangles and Sr octahedra (see Fig. 1c). Intracluster as well as intercluster distances are nearly identical in all three compounds.

Apart from structural aspects we are interested in magnetic properties of intermetallics with clusters of europium, Compounds of the three above-mentioned structure types are substances suitable for magneto-chemical investigations. In order to correlate the europium content with the strength of magnetic intra-cluster and intercluster exchange interactions between the europium centers, ternary compounds of europium, strontium and magnesium have to be synthesized and the allocation of the heavier atoms has to be determined. To start with, compounds based

on 'EuMg$_5$' and 'Sr$_9$Mg$_{38}$' are investigated. Refinements of crystal structures as well as structural relationships between these compounds and Sr$_6$Mg$_{23}$ are the concern of this work.

Experimental

Preparation

The samples (for compositions see Table 1) were prepared by melting the elements in sealed tantalum crucibles under argon. Magnesium (purity 99·99%; Ventron, Karlsruhe, Federal Republic of Germany) and europium (99·9%, sublimated; Johnson-Matthey, Great Britain) were used without previous treatment. Strontium (99%, Ventron) was purified by fractional sublimation under ultra-high vacuum conditions (Lueken, 1980). In order to receive single-phase products of the incongruently melting compounds, special attention has to be paid to the thermal treatment of the probes: after the samples were heated to ca 1120 K ($i.e.$ ca 200 K above the liquidus area of the ternary system), homogenization procedures were carried out by half turnings of the ampoule around its short middle axis at 30 min intervals. Subsequently the probes were cooled down to 890 K (just above the liquidus curve) at a rate of 1 K min^{-1}, after that more slowly to 840 K ($i.e.$ ca 40 K below the peritectic point) at a rate of 0·01 K min^{-1}. In the last step of the thermal treatment the samples were held at 840 K for three weeks in order to complete the peritectic reaction.
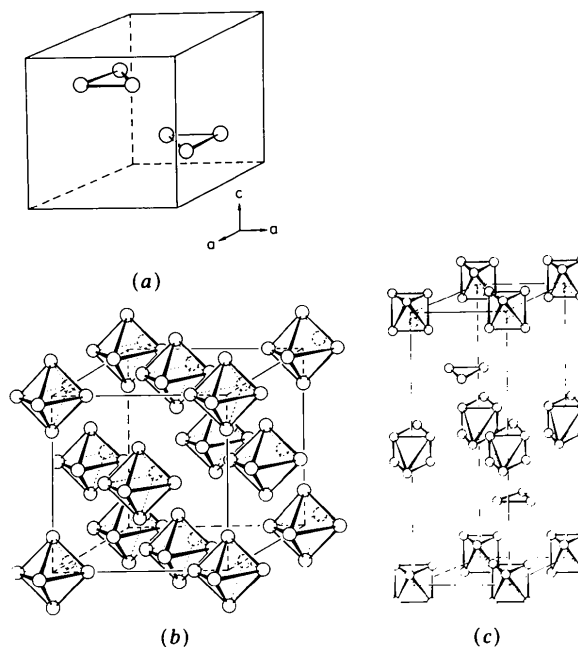

(a)

(b)   (c)

Fig. 1. (a) Arrangement of Eu$_3$ groups in the unit cell of EuMg$_{5.2}$. (b) Arrangement of Sr$_6$ groups in the unit cell of Sr$_6$Mg$_{23}$. (c) Arrangement of Sr$_3$ and Sr$_6$ groups in the unit cell of Sr$_3$Mg$_{13}$.

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* Substance formulae given in quotation marks are corrected in this work.

Table 1. *Details of preparation and structural investigations*

	(I)	(Ia)	(II)	(IIa)
Sample composition (Sr:Eu:Mg)	6:3:38	7:2:39	0:1:5	6:3:47
Radiation ($K\alpha$)	Mo	Ag	Mo	Ag
Wavelength (Å)	0·71069	0·56083	0·71069	0·56083
Lattice parameters				
a (Å)	10·465 (3)	10·488 (7)	10·395 (3)	10·463 (2)
c (Å)	28·166 (5)	28·225 (5)	10·746 (3)	10·833 (5)
V (Å^3)	2671 (2)	2689 (3)	1005·6 (9)	1027·0 (9)
Substance formula*	$(Sr_{0·67}Eu_{0·33})_3Mg_{13}$	$(Sr_{0·78}Eu_{0·22})_3Mg_{13}$	$EuMg_{5·2}$	$Eu_{0·33}Sr_{0·67}Mg_{5·2}$
Formula weight	642·61	621·38	278·38	202·27
Crystal size (mm)	0·25 × 0·23 × 0·20	0·28 × 0·25 × 0·18	0·20 × 0·15 × 0·18	0·30 × 0·15 × 0·10
μ (mm^{-1})	9·5	5·9	9·6	4·8
Max. $(\sin\theta)/\lambda$ (Å^{-1})	0·69	0·89	0·70	1·08
$F(000)$	1770·0	1720·0	752·4	651·9
Range of h	0–12	0–15	0–14	0–22
k	0–12	0–15	0–14	0–22
l	0–33	0–41	0–15	0–23
Number of reflections measured	3794	4927	674	4081
Number of unique reflections	1008	2287	674	1558
Number of reflections in refinements [$I > 3\sigma(I)$]	567	882	441	778
Number of refined parameters	57	57	26	26
Values of R	0·026	0·036	0·026	0·023
wR†	0·032	0·044	0·033	0·026

* Obtained from single-crystal investigation.
† Unit weights.

Table 2. *Results of structural refinements of* $(Sr_{0·67}Eu_{0·33})_3Mg_{13}$

The e.s.d.'s are given in parentheses. $U_{eq} = B_{eq}/8\pi^2$; $B_{eq} = \frac{4}{3}\sum_i \sum_j T_{ij}B_{ij}$ (Hamilton, 1959).

	Site	x	y	z	U_{eq} (Å^2)
Eu/Sr(1)*	12(k)	0·13680 (4)	0·27360 (8)	0·06229 (2)	0·0158
Eu/Sr(2)†	6(h)	0·53062 (6)	0·0612 (1)	0·25	0·0155
Mg(1)	12(k)$_1$	0·2323 (2)	0·4646 (4)	0·5545 (1)	0·012
Mg(2)	12(k)$_2$	0·5034 (2)	0·0068 (4)	0·6179 (1)	0·0175
Mg(3)	12(k)$_3$	0·1669 (2)	0·3338 (4)	0·6536 (1)	0·0157
Mg(4)	12(k)$_4$	0·1757 (2)	0·3514 (4)	0·1902 (1)	0·0167
Mg(5)	6(h)	0·9012 (3)	0·8024 (6)	0·25	0·014
Mg(6)	6(g)	0·5	0·0	0·0	0·0137
Mg(7)	4(f)$_1$	0·3333	0·6667	0·0375 (2)	0·0193
Mg(8)	4(f)$_2$	0·3333	0·6667	0·1438 (2)	0·0175
Mg(9)	4(f)$_3$	0·3333	0·6667	0·6491 (2)	0·011
Mg(10)	4(e)	0·0	0·0	0·1582 (2)	0·012
Mg(11)	2(c)	0·3333	0·6667	0·25	0·015

$R = 0·026$; $wR = 0·032$ (unit weights); $S = 5·258$; $(\Delta/\sigma)_{max} = 0·01$; $(\Delta\rho)_{max} = 0·9$; $(\Delta\rho)_{min} = -1·1$ e Å^{-3}.

* Amount of Eu: 31 (1)%.
† Amount of Eu: 37 (2)%.

Structural investigations

Single crystals were examined by Weissenberg and precession methods to determine crystal quality, cell constants and systematic absences. Data collection for structure refinements was carried out on an Enraf-Nonius CAD-4 four-circle automatic diffractometer (ω–2θ scan) using graphite-monochromated Ag $K\alpha$ and Mo $K\alpha$ radiation. Lattice parameters were determined by least-squares refinement of the setting angles of 25 computer-centered reflections in the range $6 < \theta < 14°$. Three standard reflections were monitored every 150 reflections to check crystal stability. No decrease of intensity during data collection was observed. Specific details concerning sample

Table 3. *Results of structural refinements of* $EuMg_{5·2}$

The e.s.d.'s are given in parentheses. $U_{eq} = B_{eq}/8\pi^2$; $B_{eq} = \frac{4}{3}\sum_i \sum_j T_{ij}B_{ij}$ (Hamilton, 1959).

		Occupancy				
	Site	(%)	x	y	z	U_{eq}(Å^2)
Eu	6(h)	100	0·19510 (3)	0·39021 (6)	0·25	0·0163
Mg(1)	12(k)	100	0·8401 (1)	0·6802 (2)	0·0888 (2)	0·0210
Mg(2)	6(h)	100	0·5680 (4)	0·1360 (8)	0·25	0·0167
Mg(3)	6(g)	100	0·5	0·0	0·0	0·0196
Mg(4)	4(f)	100	0·3333	0·6667	0·9981 (5)	0·0184
Mg(5)	4(e)	26 (1)	0·0	0·0	0·0883 (2)	0·034
Mg(6)	2(b)	77 (2)	0·0	0·0	0·25	0·10
Mg(7)	2(a)	40 (1)	0·0	0·0	0·0	0·041

$R = 0·026$; $wR = 0·033$ (unit weights); $S = 3·118$; $(\Delta/\sigma)_{max} = 0·02$; $(\Delta\rho)_{max} = 0·7$; $(\Delta\rho)_{min} = -1·0$ e Å^{-3}.

composition, crystal size, unit cell, number of reflections, absorption coefficient *etc.* of the compounds are presented in Table 1. Full-matrix least-squares refinements on F were performed on a VAX 11/730 computer (Digital Equipment Corporation) using the CAD-4 *SDP* program system (Frenz, 1978). Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). An empirical absorption correction was applied to the crystal of sample (I) [(Sr, Eu)$_3$Mg$_{13}$]. Specific results of structural refinements [R, wR, S, $(\Delta/\sigma)_{max}$, $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$] are presented in Tables 2 [for (I)] and 3 [for (II) (EuMg$_{5·2}$)].

Results of structural refinements

Sr$_3$Mg$_{13}$-*type structure*

Single crystals of (I) investigated with photographic methods showed cell parameters resembling

those of 'Sr$_9$Mg$_{38}$'; systematic absences were consistent with space group $P6_3/mmc$. With positional parameters given by Merlo & Fornasini (1982), full-matrix least-squares refinements with isotropic temperature factors and random distribution of Eu and Sr led to a conventional R factor of 0·063. In a successive difference Fourier synthesis, remaining electron density was observed at position 2(c). Calculation of the distances from this position to the nearest atoms confirmed that the interstices could be occupied by Mg atoms. The inclusion of this position in the refinements pushed the R factor down to 0·036 (isotropic thermal parameters) and 0·0271* (anisotropic thermal parameters) and changed the substance formula to $(Sr_{0.67}Eu_{0.33})_3Mg_{13} \equiv$ $(Sr_{0.67}Eu_{0.33})_9Mg_{39}$. Apart from the new site set, the positional parameters are very close to those determined by Merlo & Fornasini (1982).

In order to evaluate the accuracy in the determination of the Eu/Sr allocation, a series of refinements with fixed deviations from random distribution was carried out keeping the overall stoichiometry constant (*i.e.* an average of 33 at.% Eu and 67 at.% Sr for the two heavy-atom positions). The optimum with $R = 0.0263$* was obtained for a model with 37 (2)% Eu on site 6(h) and consequently 31 (1)% on 12(k). Standard deviations have been estimated using Hamilton's significance test (Hamilton, 1965) with $\Delta R = 0.0002$. Apparently the two heavy atoms differ a little in their preference for the two sites.

The positional parameters, isotropic thermal parameters and interatomic distances are presented in Tables 2 and 4.† In the preparation of sample (Ia), the new stoichiometry was taken into account. The results of refinements are consistent with those obtained in the case of (I) (final R factor: 0·036) apart from the allocation of the heavy atoms which are randomly distributed in (Ia).

The structural consequences of inserting Mg(11) into 'Sr$_9$Mg$_{38}$' are illustrated in Fig. 2. Mg(11) is surrounded by eleven atoms (eight Mg and three Sr; see also Table 4) forming a pentacapped trigonal prism (see Fig. 2a). Mg(11) contributes to the coordination polyhedra of Mg(8), Mg(4) and Sr/Eu(2): (i) Mg(8) is now surrounded by eight Mg atoms (mean distance to the central atom: 3·07 Å) forming a nearly regular cube and by three Sr atoms at 4·24 Å (see Fig. 2b); (ii) the coordination number (CN) of Mg(4) is now thirteen (see Fig. 2c) equaling that of Mg(2)

* In order to apply Hamilton's significance test, R factors of this accuracy are required.

† Lists of structure factors and anisotropic temperature factors for (I) and (II), and the results of refinements concerning (Ia) and (IIa) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43587 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Interatomic distances (Å) in $(Sr_{0.67}Eu_{0.33})_3Mg_{13}$

Atom	Neighbour	Distance	Atom	Neighbour	Distance
Eu/Sr(1)–Eu/Sr(1)		4·295(1)(×2)	Mg(4)	–Eu/Sr(1)	3·671(3)
		4·297(1)(×2)		–Eu/Sr(2)	3·684(2)(×2)
	–Mg(1)	3·673(1)(×2)		–Mg(2)	3·551(3)(×2)
		3·718(3)		–Mg(3)	3·275(2)(×2)
	–Mg(2)	3·655(2)(×2)		–Mg(4)	3·369(5)
	–Mg(3)	3·797(2)(×2)		–Mg(5)	3·239(3)(×2)
	–Mg(4)	3·671(3)		–Mg(8)	3·142(6)
	–Mg(6)	3·759(3)(×2)		–Mg(10)	3·311(2)
	–Mg(7)	3·630(1)		–Mg(11)	3·316(1)
	–Mg(8)	4·237(3)	Mg(5)	–Eu/Sr(2)	3·697(2)(×2)
	–Mg(10)	3·666(4)		–Mg(3)	2·982(3)(×2)
Eu/Sr(2)–Eu/Sr(2)		4·271(1)(×2)		–Mg(4)	3·239(3)(×4)
	–Mg(2)	3·772(3)(×2)		–Mg(5)	3·102(2)(×2)
	–Mg(3)	3·887(2)(×4)		–Mg(10)	3·145(5)(×2)
	–Mg(4)	3·684(2)(×4)	Mg(6)	–Eu/Sr(1)	3·759(3)(×4)
	–Mg(5)	3·697(2)(×2)		–Mg(1)	3·051(2)(×4)
	–Mg(9)	3·764(4)(×2)		–Mg(2)	3·321(3)(×2)
	–Mg(11)	3·576(1)		–Mg(7)	3·200(2)(×2)
Mg(1)	–Eu/Sr(1)	3·673(1)(×2)	Mg(7)	–Eu/Sr(1)	3·630(1)(×3)
		3·718(3)		–Mg(1)	3·173(5)(×3)
	–Mg(1)	3·171(1)(×2)		–Mg(2)	3·727(4)(×3)
	–Mg(2)	3·224(3)(×2)		–Mg(6)	3·200(2)(×3)
	–Mg(3)	3·032(3)		–Mg(8)	2·994(8)
	–Mg(6)	3·051(2)(×2)	Mg(8)	–Eu/Sr(1)	4·237(3)(×3)
	–Mg(7)	3·173(5)		–Mg(2)	3·048(2)(×3)
	–Mg(9)	3·231(5)		–Mg(4)	3·142(6)(×3)
Mg(2)	–Eu/Sr(1)	3·655(2)(×2)		–Mg(7)	2·994(8)
	–Eu/Sr(2)	3·772(3)		–Mg(11)	2·993(6)
	–Mg(1)	3·224(3)(×2)	Mg(9)	–Eu/Sr(2)	3·764(4)(×3)
	–Mg(3)	3·211(3)(×2)		–Mg(1)	3·231(5)(×3)
	–Mg(4)	3·551(3)(×2)		–Mg(2)	3·215(5)(×3)
	–Mg(6)	3·321(3)		–Mg(3)	3·019(1)(×3)
	–Mg(7)	3·727(4)	Mg(10)	–Eu/Sr(1)	3·666(4)(×3)
	–Mg(8)	3·048(2)		–Mg(3)	3·029(1)(×3)
	–Mg(9)	3·205(2)		–Mg(4)	3·311(2)(×3)
Mg(3)	–Eu/Sr(1)	3·797(2)(×2)		–Mg(5)	3·145(5)(×3)
	–Eu/Sr(2)	3·887(2)(×2)	Mg(11)	–Eu/Sr(2)	3·576(1)(×3)
	–Mg(1)	3·032(3)		–Mg(4)	3·316(1)(×6)
	–Mg(2)	3·211(3)(×2)		–Mg(8)	2·993(6)(×2)
	–Mg(4)	3·275(2)(×2)			
	–Mg(5)	2·982(3)			
	–Mg(9)	3·019(1)			
	–Mg(10)	3·029(1)			

and Mg(7); (iii) the CN of the heavy atoms at 6(h) increases to seventeen (see Fig. 2d), the same as that of the heavy atoms at 12(k).

EuMg$_{5.2}$-type structure

Examinations by rotation, Weissenberg and precession photographs of a single crystal isolated from sample (II) revealed systematic absences consistent with space group $P6_3/mmc$ and unit-cell dimensions to match those of 'EuMg$_5$'. Initial full-matrix least-squares refinements based on the 'EuMg$_5$'-type structure with isotropic temperature factors ($R = 0.054$) led to positional and thermal parameters similar to those found by Mühlpfordt (1970); in particular, the high temperature factor of Mg at 2(a) was confirmed, indicating a partial filling of this site. Furthermore, a difference Fourier synthesis showed residual electron density along the c axis with maxima at positions 4(e) with $z \simeq 0.1$ and 2(b). Therefore in successive refinements additional Mg atoms were positioned on these sites. The corresponding occupancies including Mg on 2(a) were estimated with fixed isotropic temperature factors for these sites. These temperature factors were set at the mean value of the thermal parameters obtained for the Mg sites 12(k), 6(h),

6(g) and 4(f) in the preceeding calculations. The refinements converged to $R = 0.041$ (isotropic temperature factors).

The results of the concluding refinements carried out with alternating fixed anisotropic temperature factors and occupancies of Mg at 2(a), 2(b) and 4(e)
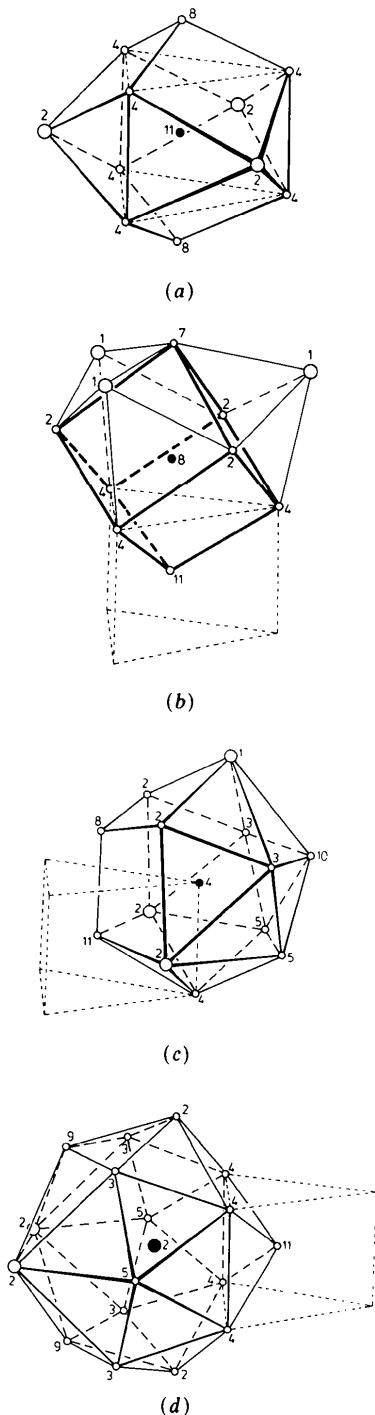
(a)

(b)

(c)

(d)

Fig. 2. Coordination polyhedra of (a) Mg(11), (b) Mg(8), (c) Mg(4) and (d) Sr(2) in the Sr_3Mg_{13}-type structure.

are listed in Table 3 ($R = 0.026$). Interatomic distances are presented in Table 5. The unit cell is illustrated in Fig. 3.

The three partially filled positions are occupied by 3·3 (1) Mg atoms. The additional Mg atoms compared to 'EuMg$_5$' change the substance formula to $EuMg_{5.2}$ (to be more precise: $EuMg_{5.22(2)}$). This result is confirmed by X-ray structure investigation of the isotypic compound $SrMg_{5.2}$; furthermore, a comparison of the volume of '$SrMg_5$' with the volumes of Sr_6Mg_{23} and Sr_3Mg_{13} suggests a similar increase of the Mg content [volume increment method of Biltz (1934) (Erassme & Lueken, 1986)]. The reason for the disordered arrangement of Mg atoms along the c axis in $EuMg_{5.2}$ will become obvious through a comparison of the three intermetallic cluster compounds (see below).

In the preparation of the ternary sample (IIa), the new stoichiometry was taken into account. Single-crystal investigations showed that lattice parameters and space group were consistent with those of (II). Photographs did not exhibit additional reflections pointing to lower symmetry or multiplication of the axes. Therefore, random distribution of Eu and Sr on site 6(h) can be assumed. Full-matrix least-squares refinements with random distribution of the heavy atoms were carried out by the same procedure as described above. The results were consistent with those obtained from (II).*

Structural relationships between Sr_6Mg_{23}, Sr_3Mg_{13} and $EuMg_{5.2}$

The three structures Sr_6Mg_{23}, Sr_3Mg_{13} and $EuMg_{5.2}$ show remarkable similarities. This can be demonstrated by dividing each of the three structures into (i) stacking units consisting of the heavy-atom clusters and their Mg coordination polyhedra (CP) and (ii) interstitial volumes filled with Mg atoms.
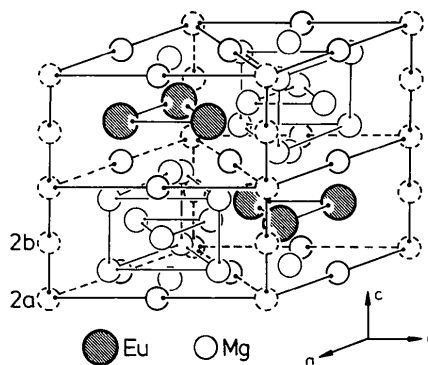
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* See deposition footnote.

Fig. 3. Unit cell of $EuMg_{5.2}$; circles with broken lines correspond to partially filled positions 2(a) and 2(b).

Table 5. *Interatomic distances* (Å) *in* $EuMg_{5.2}$

Eu–Eu	4·311 (1) (×2)	Mg(2)–Eu	3·679 (2) (×2)
–Mg(1)	3·673 (2) (×4)	–Mg(1)	3·218 (3) (×4)
	3·694 (2) (×2)	–Mg(2)	3·076 (4) (×2)
–Mg(2)	3·679 (2) (×2)	–Mg(3)	2·952 (1) (×2)
–Mg(3)	3·866 (1) (×4)	–Mg(4)	3·203 (4) (×2)
–Mg(4)	3·677 (4) (×2)	Mg(3)–Eu	3·866 (1) (×4)
–Mg(5)	3·919 (11) (×2)	–Mg(1)	3·209 (3) (×4)
–Mg(6)	3·513 (1)	–Mg(2)	2·952 (1) (×2)
–Mg(7)	4·422 (1) (×2)	–Mg(4)	3·001 (1) (×2)
Mg(1)–Eu	3·673 (2) (×2)	Mg(4)–Eu	3·677 (4) (×3)
	3·694 (2)	–Mg(1)	3·259 (3) (×3)
–Mg(1)	3·454 (3) (×2)	–Mg(2)	3·203 (4) (×3)
	3·464 (3)	–Mg(3)	3·001 (1) (×3)
–Mg(2)	3·218 (3) (×2)		
–Mg(3)	3·209 (3) (×2)		
–Mg(4)	3·259 (3) (×2)		
–Mg(5)	2·879 (3)		
	3·451 (14)		
–Mg(6)	3·360 (3)		
–Mg(7)	3·033 (3)		

Firstly, suitable CP have to be chosen as stacking units. In Sr_6Mg_{23} and Sr_3Mg_{13}, octahedra of Sr occur which, apart from differences in symmetry and slightly varying distances, have an identical environment with regard to their nearest Mg neighbours. The CP around the Sr_6 cluster (see Fig. 4*b*) consists of 38 Mg atoms. In view of the fact that some of these Mg atoms belong to several adjacent polyhedra, the stoichiometry of that unit is Sr_6Mg_{20} ($\equiv Sr_6Mg_8Mg_{12/2}Mg_{18/3}$). Compared to the species Sr_6Mg_{23} ($\equiv Sr_6Mg_8Mg_{12/2}Mg_{24/3}Mg_{6/6}$) presented by Wang *et al.* (1965) (see Fig. 4*a*), the CP in question is truncated: Mg atoms on 4(*b*) and one fourth of the Mg atoms on 32(f)$_1$ are omitted. Here, however, Sr_6Mg_{20} lends itself to stacking because of the close resemblance to the corresponding CP around the trinuclear heavy-atom clusters in $EuMg_{5.2}$ and
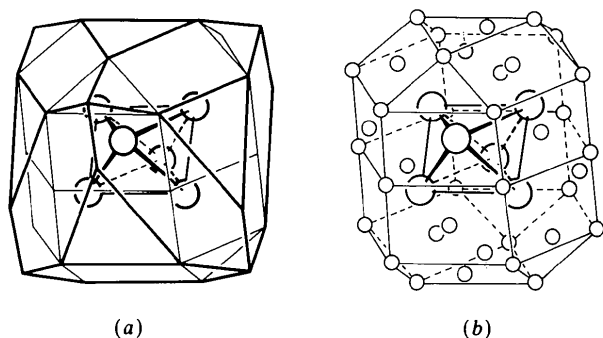
Sr_3Mg_{13}. In both structures these equilateral triangles are surrounded in an identical fashion by 29 Mg atoms (see Fig. 5). Again, since some Mg atoms are shared by several adjacent CP, the suitable stacking unit can be represented by $A_3Mg_5Mg_{6/2}Mg_{18/3} \equiv A_3Mg_{14}$ ($A = $ Sr, Eu). On comparison of Figs. 4(*b*) and 5, the relationship between the two CP is obvious: the two parts of the A_6Mg_{20} unit, each containing triangles of A, are identical to the A_3Mg_{14} unit with one missing cap.

The second step in building up the three structures consists of combining the CP and filling the interstitial volumes with Mg atoms as shown in Fig. 6 where CP are delineated by connecting lines between Mg surface atoms.

The structure of Sr_6Mg_{23} can be traced by stacking Sr_6Mg_{20} units in terms of closest packing (stacking sequence: *ABC*). The occurring interstitial volumes – their center positions correspond to the octahedral interstitial sites of cubic closest-packed spheres – consist of three parts: one central compressed octahedron flanked in face-shared fashion by two trigonal prisms. (This sequence of three interstices running in

(*a*)

(*b*)

Fig. 4. (*a*) Sr_6Mg_{23} unit; the truncated unit Sr_6Mg_{20} is represented by thin lines. (*b*) Sr_6Mg_{20} unit.
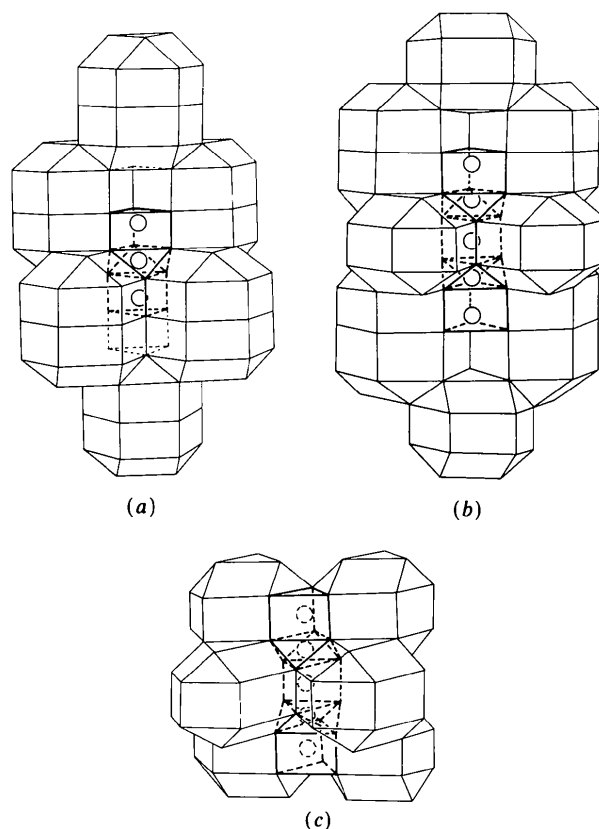

Fig. 5. A_3Mg_{14} unit ($A = $ Eu, Sr).

(*a*)

(*b*)

(*c*)

Fig. 6. (*a*) Stacking of Sr_6Mg_{20} units in Sr_6Mg_{23}; interstitial volumes marked by bold lines are occupied by three Mg atoms. (*b*) Stacking of Sr_3Mg_{14} and Sr_6Mg_{20} units in Sr_3Mg_{13}; interstitial volumes marked by bold lines are occupied by five Mg atoms with central atom Mg(11). (*c*) Stacking of Eu_3Mg_{14} units in $EuMg_{5.2}$; interstitial volumes marked by bold lines are occupied on average by 3·3 Mg atoms per unit cell.

the [001] direction of the trigonal setting is displayed in Fig. 6a.) The three spaces are occupied by Mg atoms forming a three-linked chain and leading to the overall stoichiometry 6:23. (For reasons of expediency the unit octahedron plus three-linked chain is here preferred to the otherwise more appropriate one of a body-centered cube.) Owing to the size of the Mg atoms (metallic radius ~ 1·6 Å) and the distances between the interstitial sites of ~2·7 Å, it is impossible to have the centers of all three interstices occupied by Mg atoms: one Mg atom is situated in the center of the distorted octahedron [4(b)], therefore the two Mg atoms [$32(f)_1$] in the contiguous trigonal prisms are displaced from the centers by ~0·5 Å resulting in an Mg–Mg distance of ~3·2 Å throughout the chain.

The Sr_3Mg_{13}-type structure consists of an equal number of Sr_6Mg_{20} and Sr_3Mg_{14} units and can be formed by stacking closest-packed layers alternately consisting of either species (stacking sequence: $CaC'b$; the small letters are used for the trinuclear species, the prime indicates a reflected image). Compared to the structure of Sr_6Mg_{23}, the occurring interstitial volumes are more extended: they are each formed by three trigonal prisms and two distorted octahedra. Their linkage follows the same principle as in Sr_6Mg_{23} (see Fig. 6b) with center-to-center distances of ~2·7 Å. The interstitial volume is filled in symmetrical order around the central site 2(c) by a chain of five nearly equidistant (~3·0 Å) Mg atoms [Mg(11), Mg(8), Mg(7) with Mg(11) occupying the central site 2(c) (see Fig. 2)], resulting in the overall stoichiometry of $Sr_6Mg_{20} + Sr_3Mg_{14} + 5Mg = Sr_9Mg_{39} \equiv Sr_3Mg_{13}$.

$EuMg_{5·2}$ is composed of Eu_3Mg_{14} units (stacking sequence: ab). The occurring interstitial volumes are now extended to infinity in the [001] direction (see Fig. 6c), i.e. face-shared distorted octahedra alternate with trigonal prisms forming an infinite channel. From geometrical arguments it follows that it is impossible to fill all interstitial sites [2(a) and 2(b); distance: ~2·7 Å] with Mg. On average only 3·3–3·6 Mg atoms per unit cell (instead of 4) can be arranged in the channel with the suitable Mg–Mg distance range of 3·0–3·2 Å. The X-ray structure investigation, confirming this estimate, yields 3·3 atoms spread along the c axis with maximum occupancies at positions 2(a) and 2(b).

Concluding remarks

In spite of the close resemblance of europium and strontium with regard to their structural chemistry they form different binary polynuclear compounds with magnesium. Obviously there is no formation of

europium octahedra in a magnesium matrix (up to now it has not been possible to synthesize Eu_6Mg_{23} and Eu_3Mg_{13}); the synthesis of $SrMg_{5·2}$ in single crystals on the other hand is more complicated than the preparation of $EuMg_{5·2}$ (Erassme & Lueken, 1986). For a more detailed analysis of such factors as radius ratios [metallic radii for CN 12: $r_{Eu} \simeq$ 2·04 Å, $r_{Sr} \simeq$ 2·15 (Teatum, Gschneidner & Waber, 1960; Pearson, 1972)], the outlined descriptive approach might serve as a starting point. Subsequent investigations as to symmetry and distances (Lueken, Elsenhans & Stamm, 1987) will have to scrutinize the environment of Mg atoms (i) at the surface of stacking units and (ii) in the interstitial volumes. On the other hand, the non-existence of europium hexanuclear units might be related essentially to pure electrostatic effects: the higher effective positive charge of the europium core compared to that of strontium destabilizes polynuclear units exceeding a critical number of europium atoms. In this case mixed crystals $(Sr_{1-x}Eu_x)_3Mg_{13}$ with $x > 0·5$ should exhibit a distinct depletion of europium in the octahedral position compared to the triangular position. Further investigations of those structure-determining factors are in progress.

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