described by the general formula A_xMO_2 (Fouassier, Delmas & Hagenmuller, 1975) where A = Na, K and M = Cr, Mn, Co. These materials can be described as covalent MO_2^{n-} layers stacked to give trigonal-prismatic coordination for the A cation which holds the anion sheets together.

References

ANSELL, G. B., LONGO, J. M. & HOROWITZ, H. S. (1978). *Acta Cryst.* A**34**, S157.

CLAVENNA, L. R., LONGO, J. M. & HOROWITZ, H. S. (1977). US patent 4060500.

DELMAS, C., FOUASSIER, C. & HAGENMULLER, P. (1976). *Mater. Res. Bull.* **11**, 1488.

ENRAF–NONIUS (1979). *CAD-4 Structure Determination Package.* Enraf–Nonius, Delft.

FOUASSIER, C., DELMAS, C. & HAGENMULLER, P. (1975). *Mater. Res. Bull.* **10**, 443–450.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

HOROWITZ, H. S. & LONGO, J. M. (1978). *Mater. Res. Bull.* **13**, 1359–1369.

OSWALD, H.R. & WAMPETICH, M. J. (1967). *Helv. Chim. Acta,* **50**, 2023–2034.

RIOU, A. & LECERF, A. (1975). *Acta Cryst.* B**31**, 2487–2490.

SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination.* London, New York: Macmillan.

Sr_9Mg_{38}: Structural Redetermination of 'SrMg$_4$'

BY F. MERLO AND MARIA L. FORNASINI

Istituto di Chimica Fisica, Università di Genova, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy

Abstract. Sr_9Mg_{38}, hexagonal, $P6_3/mmc$, a = 10·500 (2), c = 28·251 (3) Å, Z = 2, D_c = 2·11 Mg m^{-3}, μ(Mo $K\alpha$) = 9·7 mm^{-1}. The final R value is 0·061 for 446 independent reflexions. This study is a structural redetermination of the phase SrMg$_4$, Z = 18, already known in the literature. The presence of four further Mg atoms is detected, changing the stoichiometry to Sr_9Mg_{38}. The atomic coordination of several atoms is increased, and their coordination polyhedra become more regular.

Introduction. During a crystal-chemical analysis of the binary phases formed by the alkaline-earth elements, some anomalous features were observed in the structure of the compound SrMg$_4$, determined by Wang, Kanda, Miskell & King (1965): (a) The measured density, 2·11 Mg m^{-3}, appears greater than the calculated one, 2·03 Mg m^{-3}. (b) The volume contraction, calculated on the basis of the elemental volumes, is negative (ΔV = $-1·1\%$); in other words, an expansion is observed in the compound as regards the elements. This behaviour, which is very unusual for an intermetallic phase, is opposite to that of the other Sr–Mg phases, which show normally positive values of $\Delta V\%$ (8·3 for SrMg$_2$, 4·8 for Sr$_6$Mg$_{23}$ and 1·8 for Sr$_2$Mg$_{17}$). (c) In the unit cell, holes are recognizable corresponding to the 4(f) equipoint of the

space group $P6_3/mmc$ ($\frac{1}{3},\frac{2}{3},z$ with $z \simeq 0·65$) which are large enough to be filled by Mg atoms. The occurrence of these voids, which are infrequent in intermetallic compounds, causes some coordination polyhedra to be incomplete (*e.g.* icosahedra with a missing vertex).

All these circumstances suggested the opportunity of a redetermination of the structure.

A prismatic single crystal of mean dimensions 0·19 × 0·15 × 0·07 mm was isolated from a sample of composition SrMg$_5$, melted in a sealed iron crucible and slowly cooled. Symmetry and extinctions were consistent with the space group $P6_3/mmc$ already found by Wang *et al.* (1965). Data collection was carried out on an Enraf–Nonius CAD-4 four-circle automatic diffractometer in the ω-scan mode using graphite-monochromated Mo $K\alpha$ radiation. 1807 reflexions were measured in the θ range 3–25° and corrected for Lorentz, polarization and absorption effects, applying the semi-empirical correction of North, Phillips & Mathews (1968), by use of ψ-scan data of four top reflexions. Averaging gave 949 independent reflexions. Lattice constants were determined by least-squares refinement of the angular values of 25 reflexions centered on the diffractometer. The positional parameters reported by Wang *et al.* (1965) were assumed as starting values for a full-matrix least-squares refinement in $P6_3/mmc$ with *SHELX* 76

Table 1. *Positional and thermal parameters for* Sr_9Mg_{38}

The e.s.d.'s are given in parentheses. The temperature factor is defined as $T = \exp|-8\pi^2 \times 10^{-2} U(\sin\theta/\lambda)^2|$.

	Equi-point	x	y	z	U (Å^2)
Sr(1)	12(k)	0·1362 (2)	0·2724 (4)	0·0621 (1)	1·6 (1)
Sr(2)	6(h)	0·5312 (3)	0·0624 (6)	0·25	1·5 (1)
Mg(1)	12(k)	0·2337 (5)	0·4674 (10)	0·5547 (3)	1·7 (3)
Mg(2)	12(k)	0·5037 (6)	0·0074 (12)	0·6170 (3)	2·0 (3)
Mg(3)	12(k)	0·1674 (5)	0·3348 (10)	0·6533 (3)	1·8 (2)
Mg(4)	12(k)	0·1743 (5)	0·3486 (10)	0·1898 (3)	2·0 (3)
Mg(5)	6(h)	0·9011 (8)	0·8022 (16)	0·25	1·6 (4)
Mg(6)	6(g)	0·5	0	0	1·9 (4)
Mg(7)	4(f)	0·3333	0·6667	0·0378 (6)	0·6 (5)
Mg(8)	4(f)	0·3333	0·6667	0·1426 (7)	2·0 (5)
Mg(9)	4(f)	0·3333	0·6667	0·6465 (7)	1·3 (5)
Mg(10)	4(e)	0	0	0·1575 (7)	1·8 (5)

Table 2. *Interatomic distances* (Å) *in* Sr_9Mg_{38}

E.s.d.'s are given in parentheses.

Sr(1)	Mg(7)	3·65 (1)	Mg(2)	Mg(8)	3·05 (1)	Mg(5)	2Mg(3)	3·00 (1)
	2Mg(2)	3·66 (1)		Mg(9)	3·21 (1)		2Mg(5)	3·12 (2)
	Mg(10)	3·66 (1)		2Mg(1)	3·22 (1)		2Mg(10)	3·17 (2)
	Mg(4)	3·67 (1)		2Mg(3)	3·23 (1)		4Mg(4)	3·24 (1)
	2Mg(1)	3·70 (1)		Mg(6)	3·31 (1)		2Sr(2)	3·71 (2)
	Mg(1)	3·75 (1)		2Mg(4)	3·58 (1)			
	2Mg(6)	3·78 (1)		Mg(7)	3·71 (1)	Mg(6)	4Mg(1)	3·06 (1)
	2Mg(3)	3·81 (1)		2Sr(1)	3·66 (1)		2Mg(7)	3·21 (1)
	Mg(8)	4·25 (1)		Sr(2)	3·81 (1)		2Mg(2)	3·31 (1)
	2Sr(1)	4·29 (1)					4Sr(1)	3·78 (1)
	2Sr(1)	4·30 (1)	Mg(3)	Mg(5)	3·00 (1)			
				Mg(9)	3·02 (1)	Mg(7)	Mg(8)	2·96 (3)
Sr(2)	4Mg(4)	3·71 (1)		Mg(1)	3·04 (1)		3Mg(1)	3·18 (2)
	2Mg(5)	3·71 (2)		Mg(10)	3·05 (1)		3Mg(6)	3·21 (1)
	2Mg(2)	3·81 (1)		2Mg(2)	3·23 (1)		3Mg(2)	3·71 (1)
	2Mg(9)	3·82 (2)		2Mg(4)	3·28 (1)		3Sr(1)	3·65 (1)
	4Mg(3)	3·90 (1)		2Sr(1)	3·81 (1)			
	2Sr(2)	4·27 (1)		2Sr(2)	3·90 (1)	Mg(8)	Mg(7)	2·96 (3)
							3Mg(2)	3·05 (1)
Mg(1)	Mg(3)	3·04 (1)	Mg(4)	Mg(8)	3·18 (1)		3Mg(4)	3·18 (1)
	2Mg(6)	3·06 (1)		2Mg(5)	3·24 (1)		3Sr(1)	4·25 (1)
	2Mg(1)	3·14 (1)		2Mg(3)	3·28 (1)			
	Mg(9)	3·16 (2)		Mg(10)	3·30 (1)	Mg(9)	3Mg(3)	3·02 (1)
	Mg(7)	3·18 (2)		Mg(4)	3·40 (1)		3Mg(1)	3·16 (2)
	2Mg(2)	3·22 (1)		2Mg(2)	3·58 (1)		3Mg(2)	3·21 (1)
	2Sr(1)	3·70 (1)		Sr(1)	3·67 (1)		3Sr(2)	3·82 (2)
	Sr(1)	3·75 (1)		2Sr(2)	3·71 (1)			
						Mg(10)	3Mg(3)	3·05 (1)
							3Mg(5)	3·17 (2)
							3Mg(4)	3·30 (1)
							3Sr(1)	3·66 (1)

(Sheldrick, 1976), taking atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Three isotropic cycles led to a conventional R value of 0·101. A successive difference synthesis revealed a new peak in the expected position ($\frac{1}{3},\frac{2}{3},0·65$), which could be assigned to an Mg atom. This position introduced, three other cycles of isotropic refinement (29 parameters) lowered the R index to 0·061 for 446 reflexions with $|F_o| > 3\sigma(F_o)$ and weights $w = 1/\sigma^2(F_o)$, while the difference map showed no physically significant deviations from the background values.

The atomic parameters are listed in Table 1, and interatomic distances in Table 2.*

Discussion. The atomic-parameter values obtained in the present work are very close to those determined by Wang *et al.* (1965). Incidentally, two misprints occur in the atomic-parameter table reported in that paper: the x parameter of Sr(h) [corresponding to Sr(2) in the present work] should be $-0·478$ instead of $0·0478$; the z parameter of Mg(f)$_2$ [Mg(8) in the present work] should be $0·1427$ instead of $-0·1427$. Moreover, the x parameter of Mg(k)' [Mg(2) in the present work] is assumed to have the value $\frac{1}{2}$, and apparently it was not refined.

The insertion of four Mg atoms in the new position Mg(9) now allows the calculated density (2·11 Mg m^{-3}) to agree well with that measured by Wang *et al.* (1965). The calculated volume contraction is positive ($\Delta V = +2·9\%$), and lies within the range observed for the other Sr–Mg phases. Interatomic distances present quite normal values as regards the metallic radii of Sr and Mg for the 12-coordination. Mg(1), Mg(3), Mg(5), Mg(6), Mg(9) and Mg(10) are icosahedrally coordinated; Mg(2) and Mg(7) are surrounded by 13 atoms in the form of a distorted pentagonal antiprism capped by one atom on one side and by a couple of atoms on the opposite side; Mg(4) presents the same polyhedron as Mg(2) and Mg(7), but with a missing atom; finally, Mg(8) is surrounded by seven Mg atoms which form a cube with an empty vertex, and by three Sr atoms at 4·25 Å.

The close similarity between Sr_9Mg_{38} and Sr_6Mg_{23} (Th_6Mn_{23} type) was already pointed out by Wang *et al.* (1965), considering the arrangement of the Mg atoms around the octahedral groups of Sr atoms. The geometrical relationship between these structures can also be seen by comparing the unit cell of the 9:38 phase with that of the cubic 6:23 phase, described with hexagonal axes: the half cell is identical in both cases, whilst in the other half cell of the Sr_9Mg_{38} structure the different stacking of the atomic layers and the insertion of other Mg atoms lead to slightly different coordination and stoichiometry.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A24, 351–359.
SHELDRICK, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.
WANG, F. E., KANDA, F. A., MISKELL, C. F. & KING, A. J. (1965). *Acta Cryst.* 18, 24–31.