The Crystal Structure of SrAl

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The phase SrAl has cubic symmetry with $a = 12.753$ Å, space group $P2_13$, $Z = 32$ and $\varrho_{obs} = 2.93$ g cm^{-3}. The structure has been solved by direct methods and refined to a final R index of 0.127 for the observed reflexions. The structure of SrAl is closely related to that of the cubic phase InCl. A survey of the 1:1 intermetallic compounds formed by the Group III*b* elements is given and structural relationships are discussed. The compound SrGa was confirmed to have the same structure as SrAl, with $a = 12.484$ Å.

Introduction

This work is a part of a structural study of the intermediate phases formed by alkaline earth metals with the Group III*b* elements.

The Sr–Al system contains three intermetallic compounds, namely SrAl$_4$ (BaAl$_4$-type), SrAl$_2$ (CeCu$_2$-type) and 'Sr$_3$Al$_2$', whose powder pattern was indexed on the basis of a primitive cubic lattice with $a = 12.753$ Å (Bruzzone & Merlo, 1974).

The purpose of the present work was to define the crystal structure and the exact stoichiometry of this phase.

Experimental and structure determination

Since the exact stoichiometry of this phase, which forms by peritectic reaction, was unknown, a careful examination was necessary to define better its composition. A series of samples of compositions in the range 60 to 50 at.% Sr were prepared with the procedure described elsewhere (Bruzzone & Merlo, 1974) and annealed for one month at 600°C.

The micrographic analysis supported the formula SrAl instead of Sr$_3$Al$_2$, while powder patterns confirmed the known value of the cell constant and absence of a solid solubility range. The pyknometric density, 2.93 g cm^{-3}, was in good agreement with the value of 2.936 g cm^{-3}, calculated on the basis of 32 SrAl formulae per cell.

A single crystal with approximate dimensions 0.23 ×0.14×0.05 mm was chosen for the X-ray examination. Intensity data were obtained from integrated precession photographs, taken with Mo *K*α radiation and measured by a microdensitometer. Lorentz, polarization and absorption corrections were applied describing the crystal as an eight-faced polyhedron ($\mu_{Mo} = 216$ cm^{-1}).

After a survey of the collected reflexions, the Laue symmetry *m*3 could be established and the systematic absence of *h*00 reflexions with $h = 2n + 1$ indicated the cubic non-centrosymmetric $P2_13$ space group.

From 156 observed independent reflexions a group of 78 with normalized structure factors $E \geq 1.50$ was selected for the symbolic addition procedure (Karle & Karle, 1966). The origin and the enantiomorph were specified by assigning respectively a phase angle of 0° to the 10,7,0 reflexion and 90° to 5,12,0; phase angles of ten other *hk*0 reflexions were obtained through the $\sum_1$ formula (Hauptman, 1972) and, in addition, the reflexions 540; 15,4,0; 4,15,0; 574; 862 and 8,10,2 were assigned symbols. In the course of applying the $\sum_2$ relationships all the symbols could be determined and this starting set was used to generate new phases. Finally, all the 78 phases could be obtained and their values, refined by the tangent formula, were employed as input for a three-dimensional E map.

Taking into account the highest peaks, 32 Sr atoms were recognizable. A subsequent difference electron density could be interpreted also on the basis of dimensional considerations and allowed 32 Al atoms to be located.

Using a modified version of the program by Busing, Martin & Levy (1962), full-matrix least-squares refinement of 16 positional parameters, overall temperature and scale factors was carried out on the 156 observed reflexions and after three cycles an R value of 0.127 was obtained. Since the number of observed reflexions was low, no attempt was made to refine further by using single atomic temperature factors as variables. The final atomic parameters of SrAl are given in Table 1. The observed and calculated structure factors

Table 1. *Atomic parameters of* SrAl

Space group $P2_13$; $a = 12.753$ Å; $B = 0.0$ (2) Å^2.

	Position	x	y	z
Sr(1)	12(*b*)	0.196 (2)	0.436 (1)	0.995 (1)
Sr(2)	12(*b*)	0.477 (1)	0.294 (2)	0.063 (1)
Sr(3)	4(*a*)	0.186 (1)	x	x
Sr(4)	4(*a*)	0.819 (1)	x	x
Al(1)	12(*b*)	0.241 (4)	0.811 (5)	0.426 (5)
Al(2)	12(*b*)	0.252 (4)	0.321 (5)	0.416 (5)
Al(3)	4(*a*)	0.576 (5)	x	x
Al(4)	4(*a*)	0.962 (4)	x	x

are reported in Table 2; owing to the large number of unobserved reflexions, they were omitted in the list.*

The phase 'Sr$_3$Al$_2$' had been found to be isostructural with the 'Sr$_3$Ga$_2$' phase occurring in the Sr–Ga system (Bruzzone, 1966). A sample with stoichiometry SrGa was prepared and annealed at 500°C and gave a powder pattern quite similar to that of SrAl. Evidence of the isomorphism between SrGa and SrAl is thus confirmed and the lattice constant of SrGa, $a = 12 \cdot 484$ Å, is in good agreement with the value already reported (Bruzzone, 1966).

Discussion

Table 3 shows the interatomic distances in SrAl. With few exceptions these values show appreciable contractions as regards the distances calculated on the basis of the elemental metallic radii of Sr and Al for the coordination number 12. Moreover, a comparison of the Al–Al distances shows that these values in SrAl (2·55–2·67 Å) are the shortest among those of all the compounds formed by alkaline earths with Al.

On account of the evident gap occurring in the distance distribution (Bruzzone, Fornasini & Merlo, 1970), it is quite simple to evaluate the number of neighbours around each type of atom. So, Sr(1), Sr(2), Sr(3) and Sr(4) are coordinated with nine Sr atoms at distances 4·02 to 4·54 Å; Sr(1) and Sr(3) are surrounded also by six Al at distances 3·33 to 3·68 Å with a total coordination of 15, whilst Sr(2) and Sr(4) are surrounded by seven Al at distances 3·13 to 3·68 Å with a

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* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31371 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
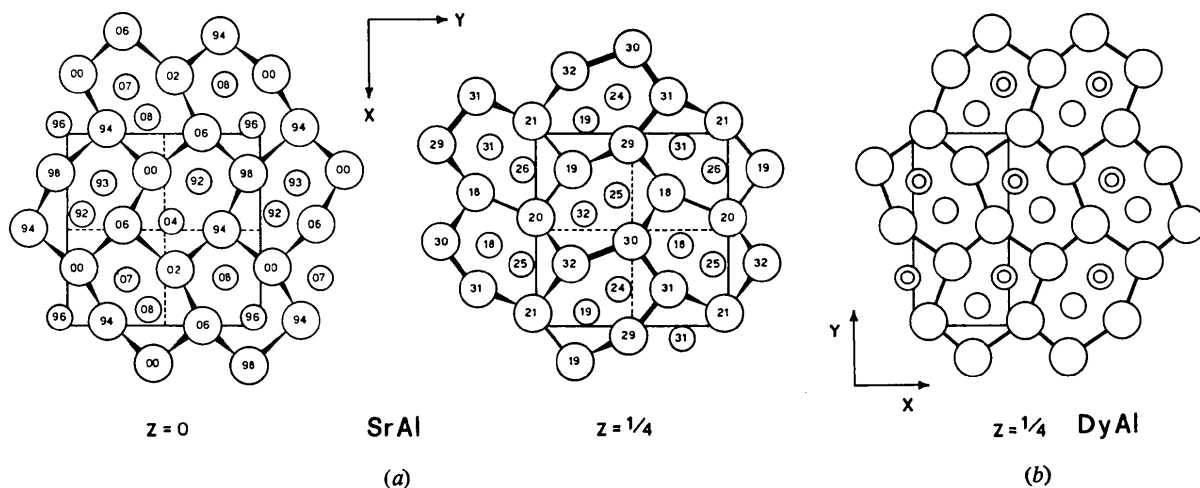
total coordination of 16. Al(1) and Al(3) are both coordinated with six Sr and three Al atoms (2·55–2·67 Å) and together form distorted tetrahedra; Al(2) and

Table 3. *Interatomic distances in* SrAl (Å)

Sr(1)–2Sr(1)	4·21	Sr(4)–3Sr(1)	4·23
–1Sr(2)	4·11	–3Sr(1)	4·28
–1Sr(2)	4·12	–3Sr(2)	4·42
–1Sr(2)	4·15	–3Al(1)	3·68
–1Sr(2)	4·21	–3Al(2)	3·50
–1Sr(3)	4·02	–1Al(4)	3·16
–1Sr(4)	4·23		
–1Sr(4)	4·28	Al(1)–1Sr(1)	3·37
–1Al(1)	3·37	–1Sr(2)	3·35
–1Al(2)	3·33	–1Sr(2)	3·55
–1Al(2)	3·64	–1Sr(2)	3·61
–1Al(2)	3·65	–1Sr(3)	3·45
–1Al(3)	3·62	–1Sr(4)	3·68
–1Al(4)	3·68	–2Al(1)	2·67
		–1Al(3)	2·55
Sr(2)–1Sr(1)	4·11		
–1Sr(1)	4·12	Al(2)–1Sr(1)	3·33
–1Sr(1)	4·15	–1Sr(1)	3·64
–1Sr(1)	4·21	–1Sr(1)	3·65
–2Sr(2)	4·54	–1Sr(2)	3·42
–1Sr(3)	4·15	–1Sr(2)	3·49
–1Sr(3)	4·26	–1Sr(3)	3·50
–1Sr(4)	4·42	–1Sr(4)	3·50
–1Al(1)	3·35	–2Al(2)	2·57
–1Al(1)	3·55		
–1Al(1)	3·61	Al(3)–3Sr(1)	3·62
–1Al(2)	3·42	–3Sr(2)	3·37
–1Al(2)	3·49	–3Al(1)	2·55
–1Al(3)	3·37		
–1Al(4)	3·13	Al(4)–3Sr(1)	3·68
		–3Sr(2)	3·13
Sr(3)–3Sr(1)	4·02	–1Sr(4)	3·16
–3Sr(2)	4·15		
–3Sr(2)	4·26		
–3Al(1)	3·45		
–3Al(2)	3·50		

Fig. 1. Atomic arrangement in the (*xy*) layers of the SrAl and DyAl structures. Large circles Sr or Dy; small circles Al. The cell edges are drawn with full lines. (*a*) Two sections of SrAl are represented with the atoms brought together on the ideal levels $z = 0$ and $z = \frac{1}{4}$, the numbers indicating the actual z values ($\times 10^2$). The edges of hypothetic NaCl cells are outlined with dashed lines. (*b*) The section at $z = \frac{1}{4}$ of DyAl is drawn. Doubled circles correspond to couples of Al atoms which lie at $z = 0$ and $z = \frac{1}{2}$

Al(4) are both coordinated with seven Sr, but Al(2) with two other Al(2) atoms form equilateral triangles, whilst for Al(4) no bond distances Al–Al are observed. The mean coordination numbers for Sr and Al are then 15·5 and 8·8, respectively.

The crystal structure of SrAl exhibits a close resemblance to that of the cubic phase InCl (van den Berg, 1966). They have comparable lattice constant values, the same space group and the same atomic position occupied (Sr in place of Cl and Al in place of In). InCl was described by the author to have a deformed rocksalt structure with the length of its cell axis doubled. SrAl can again be regarded as derivable from the NaCl type, but with a more pronounced distortion.

In Fig. 1(a) two sections of the structure of SrAl are represented with the atoms brought together on the ideal levels $z=0$ and $z=\frac{1}{4}$, the maximum displacement being 1·0 Å, and the edges of hypothetic NaCl cells are outlined with dashed lines.

From a purely crystallographic point of view, the two structures of InCl and SrAl differ slightly, but the variation of the atomic parameters leads to a quite different chemical behaviour. Indeed, through the sequence NaCl–InCl–SrAl, a gradual increase of the coordination numbers is observed, so that the progressive distortion from the basic structure of NaCl is related to a progressive increase in the number of neighbours. This fact is supported by the corresponding decrease of the electronegativity difference between the partner atoms (2·1 for NaCl, 1·4 for InCl and 0·5 for SrAl) which leads to a sharp diminution of the ionic character.

A survey of the known equiatomic MX compounds formed by the Group IIIb elements (X = Al, Ga, In, Tl) with the metallic elements shows that four structure types occur more frequently, namely CsCl (47 compounds), CrB (19 compounds), DyAl (8 compounds), NaTl (5 compounds) and CeAl (3 compounds).

It is difficult to give a general interpretation about the occurrence of these structure types, since the M partner elements vary through a large range of dimensions, electronegativity, valence, etc., and then different factors can influence the choice of a particular structure. Nevertheless, the examination of structural relationships, dimensional ratios and volume contractions suggests that there are two groups: CsCl and NaTl types on the one hand and CrB, DyAl and CeAl on the other.

Fig. 2 reports the distribution of the MX compounds with the cited structures, as a function of radius ratios r_M/r_X (using the metallic radii for coordination number 12) and volume percent contractions ΔV (calculated on the basis of the elemental atomic volumes). As can be seen, the CsCl- and NaTl-type compounds, based on the same b.c.c. packing, occur in a range of $r_M/r_X = 0.80$ to 1·25 and generally show high values of ΔV, from 5 to 28 % (save ScAl with minor contraction).

The CrB, DyAl and CeAl types exhibit a different packing of analogous trigonal prisms formed by six M

atoms; moreover, as already noted by Bècle & Lemaire (1967), CeAl and DyAl are closely related. The phases with CrB or DyAl or CeAl structure occur in a range of radius ratios $r_M/r_X = 1.23$ to 1·42 (save HfAl, ZrAl and ScGa at 1·10–1·15) and show lower ΔV from 1 to 10 % (save CaGa). The two compounds SrAl and SrGa are found at some higher dimensional ratios, 1·51 and 1·55, with volume contractions of 11 and 20 %, respectively, and their crystal structure can be related to the DyAl type.

In Fig. 1(b) the (xy) layer at $z=\frac{1}{4}$ of DyAl is given. By comparing Fig. 1(a) (SrAl) and Fig. 1(b) (DyAl), it can be seen that in both structures the M atoms form a common two-dimensional motif (outlined by solid lines in the drawing), which is planar in DyAl and slightly waved in SrAl. On the other hand, the tridimensional stacking of the layers is different in both structures and results in a certain difference of the coordination numbers.

Concerning the X–X bonds, some differences can be pointed out in the CrB, DyAl and SrAl types. It is known that in the CrB structure the X atoms form independent zigzag chains; in DyAl the X atoms form non-planar chains of triangles joined by one vertex. On the other hand, no infinite chains exist in SrAl, but only three different motifs, namely tetrahedra, triangles and 'isolated' atoms, all of these included in cages of M atoms.
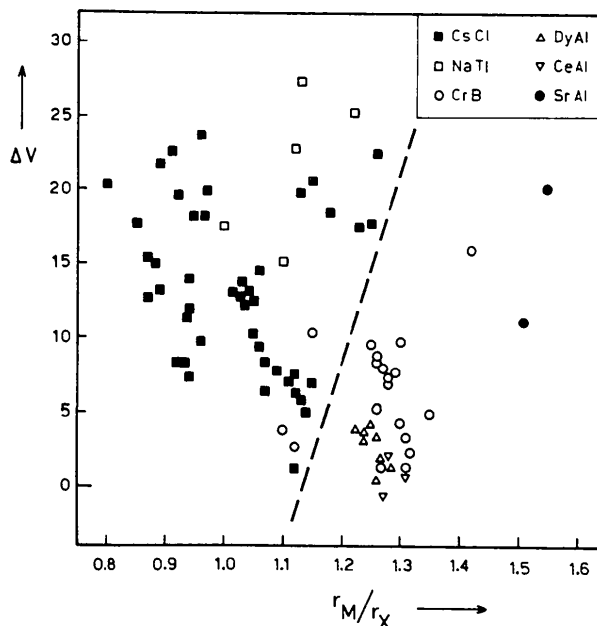
Fig. 2. Distribution of the equiatomic MX compounds formed by the metallic elements (M) with the Group IIIb elements (X = Al, Ga, In, Tl), as a function of radius ratio r_M/r_X and volume percent contraction ΔV.

References

BÈCLE, C. & LEMAIRE, R. (1967). *Acta Cryst.* **23**, 840–845.

BERG, J. M. VAN DEN (1966). *Acta Cryst.* **20**, 905–910.

BRUZZONE, G. (1966). *Boll. Sci. Fac. Chim. Ind.* **24**, 113–132.

BRUZZONE, G., FORNASINI, M. L. & MERLO, F. (1970). *J. Less-Common Met.* **22**, 253–264.

BRUZZONE, G. & MERLO, F. (1974). *J. Less-Common Met.* **39**, 1–6.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Oak Ridge National Laboratory Report ORNL-TM-305.

HAUPTMAN, H. A. (1972). *Crystal Structure Determination.* New York: Plenum.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

The Crystal and Molecular Structure of *cis*-2,2,4,4-Tetramethyl-1,3-cyclobutanediol

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$C_8H_{16}O_2$; orthorhombic, $Pna2_1$; $Z = 8$; $a = 10.395$ (2), $b = 16.556$ (1), $c = 10.166$ (1) Å; $D_o = 1.09$, $D_c = 1.09$ g cm^{-3}. The structure has two molecules in the asymmetric unit. The cyclobutane rings are non-planar, with dihedral angles of 19.0 (7) and 16.0 (7)°.

A 1:1 mixture of *cis*- and *trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (Matheson, Coleman & Bell Laboratories, Cincinnati, Ohio) was dissolved in ethyl acetate and the solution was allowed to evaporate slowly. This resulted in the formation of two morphologically distinct crystal types (Soltzberg, 1969). One set of crystals, hexagonally shaped, was found to be the *trans* isomer (Margulis, 1969). The other set has been postulated to be the *cis* isomer (Soltzberg, 1969).

After several recrystallizations from ethyl acetate of the postulated *cis* isomer, NMR and the melting point (Hasek, Elam, Martin & Nations, 1961) verified that it was indeed a pure sample of *cis*-2,2,4,4-tetramethyl-1,3-cyclobutanediol. A small crystal, $0.50 \times 0.40 \times 0.35$ mm, was mounted in a thin-walled Lindemann capillary tube. The 0.50 mm axis (*b*) was parallel to the walls of the capillary tube.

Approximate cell dimensions, systematic absences (0*kl*: $k + l$ odd; *hk*0: *h* odd), and orthorhombic symmetry were noted from photographic and preliminary diffractometer data. The photographic data were taken with nickel-filtered Cu *K*α radiation. The possible space groups were *Pnma* and *Pna2₁*. This information is consistent with the results of Soltzberg (1969).

With vanadium-filtered Cr *K*α radiation ($\lambda = 2.2916$ Å), 13 reflection angles with high 2θ values were accurately measured. The lattice constants were determined by a least-squares fit (Williams, 1964) using the extrapolation function of Nelson & Riley (1945). The values obtained for room temperature (23°C) were $a = 10.395$ (2), $b = 16.556$ (1) and $c = 10.166$ (1) Å. The volume of the unit cell is 1749.56 Å³, and the calculated density for eight molecules of $C_8H_{16}O_2$ (F.W. 144.22) is 1.09 g cm^{-3}.

The intensities of 1196 independent reflections, up to $2\theta = 45°$, were measured using zirconium-filtered Mo *K*α radiation ($\lambda = 0.7107$ Å). Intensities were measured with a Siemens manual diffractometer using the θ–2θ scan technique with a scan rate of 2° min^{-1}. The background was measured graphically. The take-off angle was 3.0° and the receiving slit was 4×4 mm. A check of the intensities of several reflections selected as standards showed them to remain constant within statistical and instrumental fluctuations during the data collection. The Lorentz and polarization corrections were made in the usual manner. For Mo *K*α X-rays, the linear absorption coefficient of this compound is 0.81 cm^{-1}. No absorption correction was made. The standard deviation of each intensity measurement was estimated by the formula:

$$\sigma^2(I) = CT + CB + (0.05CT)^2 + (0.05CB)^2,$$

where CT is the total counts and CB is the background counts. The error in the structure factor, $\sigma(F_o)$, was calculated from $\sigma(I)$ by the finite difference method (Williams & Rundle, 1964). If $CT \leq CB$, then F_o was set to zero. In the least-squares refinement the weight of a reflection was $1/[\sigma(F_o)]^2$.

The observed systematic absences do not lead to a positive identification of the space group; *Pnma* and *Pna2₁* are both possibilities. Soltzberg (1969) attempted structural solution in the centric space group, *Pnma*, but was unsuccessful and he suggests *Pna2₁* as the correct space group.

The structure factors were scaled by Wilson's method (Wilson, 1942) and were converted to normalized structure factors by *FAME* (Dewar, 1970) for use in the phase determination. The statistical distribution of the