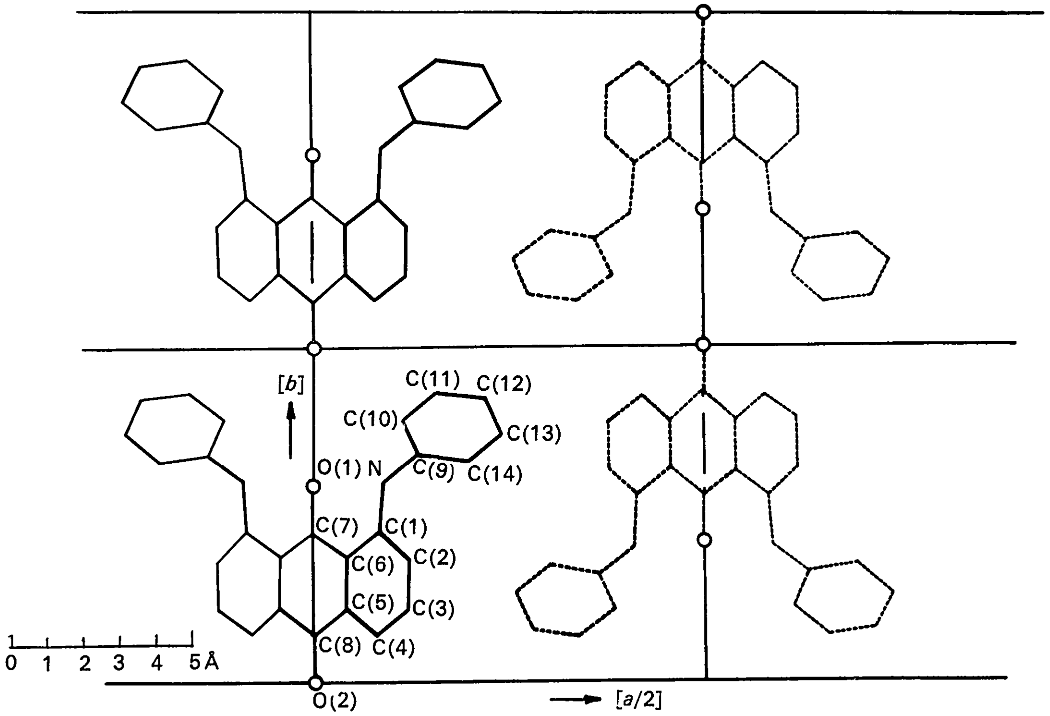

Fig. 3. Projection of structure along c.

not be treated as a rigid body, and computer programs for dealing fully with more complex vibrations are not yet ready.

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The Crystal Structure of So-Called α-$LaAl_4$ (La_3Al_{11})

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An analysis of the structure of what is known in the literature as α-$LaAl_4$ revealed that the correct formula is La_3Al_{11}. Analogous formulae seem to apply to 'α-$CeAl_4$', 'α-$PrAl_4$' and 'α-$NdAl_4$'. La_3Al_{11} crystallizes in the space group *Immm*; $a=4{\cdot}431$, $b=13{\cdot}142$, $c=10{\cdot}132$ Å. There are two formula units in the unit cell. The structure was refined by least-squares methods to a weighted R index of 7·9%. Details of the structure are presented and its relation to 'β-$LaAl_4$' is discussed.

Introduction

Hitherto $LaAl_4$ has been known to occur in two different modifications, but the various investigators disagree about the transition temperature. According to Gschneidner's (1961) review the phase transition takes place at 813° ± 3°C, whereas Buschow (1965*a*) found experimental evidence for a phase change at 915°C.

There has been considerable confusion about the structure of $LaAl_4$. The oldest publication (Rossi, 1933) mentions a tetragonal lattice with $a=13{\cdot}2$ and $c=5{\cdot}1$ Å. Nowotny (1942) indexed his powder diagrams of $LaAl_4$ quenched from 600°C (this must have been the low-temperature or α modification) on the basis of a body-centered tetragonal unit cell with $a=4{\cdot}431$ and $c=10{\cdot}23$ Å. According to Nowotny the structure is isomorphous with $BaAl_4$. Iandelli (1958) obtained essentially identical results, although his lattice constants are slightly different: $a=4{\cdot}405$, $c=10{\cdot}140$ Å. Buschow (1965*a*), however, attributed this same structure to the high-temperature or β phase, but for the α modification he found a body-centered, orthorhombic lattice with $a=4{\cdot}431$, $b=13{\cdot}142$, $c=10{\cdot}132$ Å. And this, finally, bears some resemblance to the hexagonal lattice with $a=13{\cdot}2$ and $c=10{\cdot}2$ Å proposed by Gaume-Mahn & Cohen (1957).

The present work is an attempt to elucidate the structure of so-called α-$LaAl_4$ on the basis of single-crystal X-ray diffraction data.

Experimental

Alloy buttons, prepared as described earlier by Buschow (1965*a*), were remelted in a high purity alumina crucible under purified argon in an induction furnace. The molten material was allowed to cool to room temperature inside a silica tube, so that a solid rod (length 10 cm) was obtained. This rod was transferred into an alumina tube, which was then passed slowly through a Bridgman furnace, again under purified argon. During the recrystallization process large single-crystalline regions were formed, which – according to the cleavage properties of the rod – occurred in a preferred orientation.

The X-ray diagram of a powdered sample of this material proved to be essentially identical with the orthorhombic diffraction pattern previously obtained by Buschow.

For single-crystal work a small piece of the rod was chopped off. It was irregularly shaped with cross sections in various directions between 0·2 and 0·4 mm. A rotation diagram made by means of a Weissenberg camera confirmed the correctness of Buschow's indexing. The lattice parameters were not redetermined.

The crystal was then mounted on the automatic diffractometer 'PAILRED' and oriented along the **a** direction. Preliminary measurements showed that – apart from the influence of trivial factors – all even layer lines are identical, as well as all odd ones. Therefore, the data collection was confined to the $0kl$ and $1kl$ reflexions. Actually, two half-planes in index space ($l\ge 0$, k positive and negative) were measured out to $\Upsilon=90°$ ($\sin\theta/\lambda\simeq 1{\cdot}13$) and the average values of $I(hkl)$ and $I(h\bar{k}l)$ were taken afterwards.

The number of independent reflexions amounted to 558, of which 202 were given zero weight, because their relative counting-statistical error, $\sigma(I)/I$, was greater than 0·3. For all other reflexions the weight factors of the structure factors were computed by the formula $w=4I^2/\{\sigma(I)\,.\,F_o\}^2$, a lower boundary of 0·02 being set for $\sigma(I)/I$.

The integrated intensities were measured with crystal-monochromatized Mo $K\beta$ radiation ($\lambda=0{\cdot}6323$ Å) utilizing the ω-scan technique and equi-inclination geometry. After subtraction of the background, the intensity data were corrected for Lorentz and polarization effects. Absorption corrections were not applied, although they must have been appreciable ($\mu=84$ cm^{-1}); this probably accounts for the rather high final R value.

The atomic scattering factors listed in *International Tables for X-ray Crystallography* (1962) were used throughout this work.

Determination and refinement of the structure

The only observed systematic absences were those corresponding to a body-centered lattice. Therefore, at first sight, four space groups would be possible: $I222$, $I2_12_12_1$, $Imm2$ and $Immm$. It is easily concluded from the foregoing information, however, that all atoms lie in the planes $x=0$ and $x=\frac{1}{2}$, so that these planes are true mirror planes. This excludes the first two space groups. It was tentatively assumed that $Immm$ would be the correct one, and this choice was eventually confirmed by the success of the structure analysis.

Since, presumably, the present structure would be very similar to that of $BaAl_4$, it was decided to begin immediately with a full-matrix least-squares refinement on the basis of a threefold unit cell of $BaAl_4$ [Fig. 1(*a*)]. The expression for the atomic scattering factors was taken as $f=f_0\exp(-B\sin^2\theta/\lambda^2)$, individual B parameters being attributed to all independent atoms. Since absorption corrections were not applied, the computed values of these B parameters have no simple physical meaning. The quantity to be minimized was

$$\Sigma\, w(|F_o|-|F_c|)^2.$$

In a few cycles the weighted R-index, defined as

$$R_w=\Sigma\, w\big||F_o|-|F_c|\big|/\Sigma\, w|F_o|\,,$$

was down to 11·9%. At this stage the parameters of Al(1) constituted the most remarkable feature of the structure. The Al(1)–Al(1) distance was found to be 1·9 Å (2·86 Å in pure aluminum); the computed value of B[Al(1)] was 25 Å^2, *i.e.* about 50 times as large as the B parameter of any other atom. This strongly suggested that one Al(1) atom ought to be removed, so that the chemical formula of this alloy would be La_3Al_{11}. The corresponding structure is shown in Fig. 1(*b*).

On removal of one Al(1), R_w immediately dropped to 8·5%, $\Sigma\, w(|F_o|-|F_c|)^2$ decreased to 56% of its previous value, and an acceptable value was found for B[Al(1)]. After a few more refinement cycles the calculated shifts of the atomic coordinates were less than 10^{-6} times the unit-cell edge and the refinement was discontinued; R_w had reached the final value of 7·9%.

Table 1. *Observed and calculated structure factors*

h = 0

k	l	F_o	F_c
2	0	-13.8	-12.1
4	0	10.0	9.3
6	0	171.7	168.4
8	0	-4.5	-4.6
10	0	55.1	49.6
12	0	64.2	69.1
14	0	-8.3	-1.0
16	0	71.9	67.4
18	0	25.3	18.8
20	0	8.5	5.1
22	0	54.0	54.1
24	0	3.9	2.6
26	0	15.8	12.8
28	0	31.2	29.9
1	1	5.7	4.6
3	1	103.4	97.8
5	1	-32.5	-28.1
7	1	53.4	47.1
9	1	52.5	45.7
11	1	-30.3	-25.3
13	1	69.6	63.3
15	1	13.4	7.2
17	1	-13.3	-8.9
19	1	59.6	56.4
21	1	-11.1	-10.4
23	1	0.0	8.2
25	1	38.6	37.0
27	1	-2.4	-13.6
29	1	7.2	18.6
0	2	70.7	91.1
2	2	-15.9	-15.7
4	2	61.7	56.7
6	2	84.2	77.0
8	2	-61.3	-55.6
10	2	78.3	70.4
12	2	54.8	48.3
14	2	-39.4	-36.0
16	2	59.9	54.3
18	2	15.9	14.6
20	2	-6.8	-2.4
22	2	40.8	37.9
24	2	0.0	-7.5
26	2	15.9	16.9
28	2	26.0	23.4
1	3	7.6	4.8
3	3	125.0	135.2
5	3	-44.4	-42.1
7	3	52.5	49.1

k	l	F_o	F_c
9	3	99.3	88.4
11	3	-45.8	-41.6
13	3	61.6	57.1
15	3	46.3	41.4
17	3	-16.7	-15.4
19	3	49.2	47.5
21	3	10.1	8.7
23	3	7.9	7.9
25	3	32.6	32.3
27	3	0.0	-4.5
0	4	104.9	135.6
2	4	13.9	16.5
4	4	37.3	38.6
6	4	94.8	90.6
8	4	11.4	11.6
10	4	73.0	67.5
12	4	34.7	27.1
14	4	7.8	8.2
16	4	78.3	75.5
18	4	-5.1	-3.7
20	4	9.4	9.5
22	4	59.1	58.2
24	4	-6.6	-10.8
26	4	16.4	16.8
28	4	32.4	33.1
1	5	-29.9	-32.6
3	5	103.5	117.3
5	5	-41.5	-42.5
7	5	1.9	6.6
9	5	63.9	59.9
11	5	-31.7	-30.7
13	5	42.5	40.7
15	5	17.6	15.8
17	5	-16.4	-15.5
19	5	45.1	46.8
21	5	0.0	-5.2
23	5	6.2	0.7
25	5	31.2	32.5
27	5	-5.8	-6.4
0	6	79.8	95.9
2	6	-9.0	-10.2
4	6	37.2	39.4
6	6	80.1	81.7
8	6	-39.2	-38.6
10	6	61.6	58.9
12	6	52.6	50.1
14	6	-28.1	-26.0
16	6	56.8	52.2

k	l	F_o	F_c
18	6	19.3	16.6
20	6	-8.9	-0.8
22	6	42.2	38.4
24	6	0.0	-3.8
26	6	9.8	15.6
28	6	23.0	23.5
1	7	33.8	36.7
3	7	54.4	59.6
5	7	-11.1	-12.5
7	7	70.3	70.9
9	7	48.9	46.9
11	7	-25.0	-24.4
13	7	68.4	67.7
15	7	24.7	22.5
17	7	-8.3	-5.3
19	7	50.8	51.4
21	7	-7.7	-0.9
23	7	8.5	14.5
25	7	34.2	34.8
27	7	-8.6	-10.9
0	8	105.3	125.0
2	8	-17.1	-16.3
4	8	4.5	9.3
6	8	91.8	98.5
8	8	-22.2	-22.5
10	8	34.2	38.2
12	8	53.6	49.7
14	8	-16.2	-14.8
16	8	46.9	49.3
18	8	13.3	14.9
20	8	-7.9	-1.4
22	8	38.0	40.5
24	8	-10.4	-0.5
26	8	10.3	11.1
1	9	-13.5	-17.2
3	9	67.9	72.1
5	9	-20.5	-22.0
7	9	12.5	10.9
9	9	34.2	33.1
11	9	-17.1	-15.8
13	9	41.5	40.6
15	9	-8.9	0.0
17	9	-8.8	-8.2
19	9	45.3	46.6
21	9	-12.6	-12.0
23	9	8.5	2.6
25	9	29.3	32.8

k	l	F_o	F_c
0	10	68.1	75.9
2	10	6.9	4.1
4	10	29.0	33.2
6	10	58.8	62.6
8	10	-11.9	-12.6
10	10	50.3	52.3
12	10	33.2	34.1
14	10	-5.0	-9.0
16	10	51.0	52.9
18	10	5.6	8.3
20	10	0.0	4.4
22	10	36.6	41.1
24	10	-8.6	-5.3
26	10	3.8	15.6
1	11	9.4	10.1
3	11	68.5	74.0
5	11	-24.4	-25.1
7	11	37.5	39.4
9	11	57.7	61.2
11	11	-27.9	-31.2
13	11	41.3	44.1
15	11	34.0	35.4
17	11	-11.5	-12.0
19	11	36.4	36.3
21	11	9.7	10.1
23	11	8.3	8.2
25	11	22.4	25.6
0	12	46.0	49.7
2	12	-4.2	-2.3
4	12	22.5	23.3
6	12	39.4	40.6
8	12	-19.6	-16.3
10	12	36.7	42.0
12	12	22.8	20.0
14	12	-13.2	-11.8
16	12	41.7	45.0
18	12	4.1	0.6
20	12	0.0	1.5
22	12	32.6	36.0
24	12	-13.7	-9.6
1	13	-12.9	-10.3
3	13	64.7	65.6
5	13	-15.1	-16.8
7	13	11.7	11.2
9	13	37.0	37.4
11	13	-11.6	-13.7
13	13	31.6	33.3

k	l	F_o	F_c
15	13	13.0	9.3
17	13	0.0	-6.9
19	13	34.4	38.4
21	13	-8.0	-4.4
23	13	1.5	2.7
0	14	72.3	76.6
2	14	-9.2	-1.4
4	14	16.5	15.9
6	14	58.0	63.0
8	14	-11.3	-8.5
10	14	31.4	34.6
12	14	32.4	34.9
14	14	-3.1	-5.7
16	14	40.7	42.0
18	14	12.4	11.6
20	14	0.0	2.9
22	14	34.4	35.4
1	15	12.7	12.5
3	15	33.3	4.4
5	15	-14.2	-10.6
7	15	33.0	33.6
9	15	27.4	26.6
11	15	-18.0	-16.5
13	15	38.6	39.9
15	15	10.7	11.7
17	15	-8.9	-5.3
19	15	32.9	34.9
21	15	0.0	-2.8
0	16	45.6	49.1
2	16	-8.9	-9.9
4	16	14.4	11.9
6	16	41.4	43.6
8	16	-19.6	-22.2
10	16	25.9	27.0
12	16	28.2	28.5
14	16	-13.0	-16.9
16	16	27.5	29.8
18	16	15.0	10.4
20	16	-5.7	-2.6
1	17	0.0	0.9
3	17	46.1	47.3
5	17	-9.2	-8.4
7	17	15.8	17.3
9	17	30.3	30.3
11	17	-7.5	-8.9
13	17	27.3	30.9

k	l	F_o	F_c
15	17	11.9	10.4
17	17	0.0	-3.2
19	17	30.6	33.0
0	18	52.9	48.2
2	18	0.0	2.5
4	18	11.0	14.3
6	18	38.9	38.6
8	18	-4.7	-1.9
10	18	24.5	29.0
12	18	18.8	18.6
14	18	-8.3	-0.6
16	18	34.1	36.5
1	19	-3.3	-1.5
3	19	38.4	40.2
5	19	-12.4	-14.8
7	19	15.2	14.3
9	19	27.1	30.2
11	19	-9.5	-16.7
13	19	20.9	23.5
15	19	18.1	15.2
0	20	29.7	28.8
2	20	-5.1	-1.4
4	20	15.9	15.2
6	20	26.8	25.7
8	20	-8.1	-11.9
10	20	25.7	26.1
12	20	16.9	16.4
1	21	11.4	4.7
3	21	36.4	35.0
5	21	-4.2	-5.0
7	21	14.4	17.4
9	21	25.7	24.9
11	21	-10.0	-6.8
0	22	41.9	41.0
2	22	0.0	-3.1
4	22	5.4	5.8
6	22	32.2	34.0

h = 1

k	l	F_o	F_c
1	0	4.6	4.3
3	0	129.3	121.1
5	0	-70.3	-62.2
7	0	60.7	54.3
9	0	100.2	66.5
11	0	-68.7	-62.6
13	0	57.6	52.3
15	0	52.1	47.1
17	0	-26.2	-25.1
19	0	42.1	38.6
21	0	7.8	10.3
23	0	3.0	5.8
25	0	30.1	26.4
27	0	-6.1	-6.4
29	0	18.3	18.5
0	1	70.7	99.7
2	1	-8.5	-7.1
4	1	49.1	42.5
6	1	81.7	71.6
8	1	-33.8	-29.3
10	1	74.3	66.1
12	1	35.3	30.1
14	1	-22.1	-12.1
16	1	68.3	63.0
18	1	0.0	1.5
20	1	7.5	2.0
22	1	47.6	47.0
24	1	-13.0	-11.3
26	1	13.1	16.5
28	1	27.0	28.0
1	2	11.8	12.7
3	2	153.6	166.3
5	2	8.1	5.2
7	2	48.4	43.8
9	2	91.2	81.3
11	2	9.1	6.7
13	2	76.1	70.4
15	2	28.7	20.9
17	2	4.4	5.2
19	2	69.5	67.3
21	2	-8.7	-1.5
23	2	11.7	10.8
25	2	42.5	44.4
27	2	-6.6	-5.2
29	2	13.1	18.7
0	3	108.9	145.9
2	3	-41.9	-44.7
4	3	-13.1	-9.4
6	3	108.8	104.2
8	3	-48.2	-43.8
10	3	33.1	30.8
12	3	49.7	43.8
14	3	-30.5	-27.0
16	3	49.8	47.9

k	l	F_o	F_c
18	3	5.0	7.9
20	3	-5.1	-7.4
22	3	38.9	40.5
24	3	0.0	-5.4
26	3	6.4	8.8
28	3	21.6	23.2
1	4	31.1	35.2
3	4	51.6	56.1
5	4	-22.9	-23.2
7	4	78.2	74.3
9	4	45.1	41.2
11	4	-36.3	-34.1
13	4	74.8	68.8
15	4	19.1	17.0
17	4	-12.7	-10.3
19	4	54.8	50.6
21	4	0.0	-5.8
23	4	11.6	12.2
25	4	35.1	33.8
27	4	-7.4	-14.8
29	4	16.3	21.7
0	5	89.9	110.9
2	5	-10.3	-11.2
4	5	38.4	40.4
6	5	93.6	94.3
8	5	-40.6	-40.1
10	5	60.6	60.3
12	5	64.4	59.0
14	5	-25.4	-26.1
16	5	55.3	53.4
18	5	24.2	22.2
20	5	6.4	0.0
22	5	40.5	39.4
24	5	-9.1	-0.4
26	5	17.3	16.7
28	5	20.3	24.4
1	6	3.0	3.6
3	6	109.0	125.6
5	6	-11.0	-9.5
7	6	31.3	34.0
9	6	74.7	71.4
11	6	-9.0	-8.3
13	6	57.9	57.2
15	6	26.1	23.2
17	6	-8.1	-2.2
19	6	55.1	55.7
21	6	0.0	0.7
23	6	8.3	8.1
25	6	35.4	37.8
27	6	-3.6	-5.0
0	7	66.8	75.2
2	7	-16.9	-20.1
4	7	-6.6	-0.8

k	l	F_o	F_c
6	7	48.0	48.7
8	7	-16.3	-16.3
10	7	35.9	34.6
12	7	9.4	7.1
14	7	-13.9	-11.6
16	7	53.1	52.5
18	7	-10.9	-13.3
20	7	-5.7	-1.9
22	7	42.3	44.5
24	7	-13.9	-16.2
26	7	6.0	9.5
28	7	21.9	25.6
1	8	6.8	6.4
3	8	89.6	101.3
5	8	-21.3	-26.4
7	8	35.7	39.0
9	8	71.1	73.7
11	8	-28.3	-29.9
13	8	49.7	48.9
15	8	37.1	36.8
17	8	-6.8	-11.7
19	8	43.4	42.5
21	8	7.2	8.9
23	8	6.6	7.3
25	8	28.2	29.3
27	8	-5.6	-3.2
0	9	53.7	60.9
2	9	4.2	3.4
4	9	44.2	45.8
6	9	54.0	56.5
8	9	-25.0	-25.8
10	9	59.3	60.3
12	9	40.8	39.1
14	9	-18.1	-18.1
16	9	51.6	51.7
18	9	14.9	13.5
20	9	7.1	3.7
22	9	38.6	37.9
24	9	-3.5	-4.4
26	9	8.2	18.2
1	10	3.8	7.7
3	10	61.6	67.2
5	10	-14.1	-12.4
7	10	29.0	34.1
9	10	42.6	42.1
11	10	-16.5	-15.2
13	10	44.0	48.5
15	10	15.8	13.7
17	10	-9.4	-5.2
19	10	42.1	45.5
21	10	-6.4	-3.8
23	10	5.6	7.7
25	10	30.5	31.7

k	l	F_o	F_c
27	10	-14.1	-9.0
0	11	85.1	90.5
2	11	-23.6	-26.8
4	11	-11.3	-11.9
6	11	66.2	68.6
8	11	-20.6	-23.8
10	11	19.2	18.3
12	11	33.0	29.1
14	11	-17.5	-16.0
16	11	35.5	37.4
18	11	7.8	3.7
20	11	-7.1	-5.7
22	11	32.1	34.4
24	11	0.0	-4.7
26	11	7.2	5.7
1	12	15.0	18.1
3	12	57.2	60.6
5	12	-3.4	-0.1
7	12	39.7	39.9
9	12	35.6	39.1
11	12	-8.7	-5.1
13	12	47.9	51.2
15	12	11.9	13.7
17	12	0.0	1.1
19	12	44.0	47.1
21	12	-10.7	-2.6
23	12	9.4	11.1
25	12	33.0	33.2
0	13	50.7	54.1
2	13	-4.9	-5.0
4	13	22.6	25.1
6	13	46.5	49.7
8	13	-21.8	-24.2
10	13	38.4	40.3
12	13	34.4	34.4
14	13	-14.4	-17.7
16	13	35.0	38.8
18	13	15.3	13.3
20	13	0.0	0.4
22	13	28.6	30.1
24	13	0.0	-2.1
1	14	0.0	0.8
3	14	49.9	54.1
5	14	-20.3	-19.5
7	14	21.1	23.2
9	14	39.7	40.1
11	14	-23.6	-22.3
13	14	31.0	33.7
15	14	19.8	19.2
17	14	-13.6	-10.1
19	14	29.4	31.8
21	14	0.0	2.0
23	14	6.6	4.5

k	l	F_o	F_c
0	15	50.5	47.8
2	15	-6.3	-3.9
4	15	13.0	9.9
6	15	39.5	36.0
8	15	-5.9	-7.7
10	15	26.8	29.1
12	15	17.0	13.0
14	15	-7.3	-5.1
16	15	37.5	39.2
18	15	0.0	-3.6
20	15	5.5	1.7
22	15	30.3	34.3
1	16	3.0	3.6
3	16	61.4	64.4
5	16	0.0	-5.9
7	16	18.1	20.4
9	16	39.9	43.8
11	16	-10.9	-6.7
13	16	31.9	34.3
15	16	20.4	19.6
17	16	0.0	-1.6
19	16	32.9	35.8
21	16	5.3	4.4
0	17	38.7	39.0
2	17	0.0	-5.6
4	17	13.4	14.1
6	17	34.4	34.2
8	17	-14.1	-17.0
10	17	26.2	27.9
12	17	25.0	21.4
14	17	-12.3	-12.9
16	17	31.0	30.6
18	17	0.0	6.1
20	17	0.0	-0.4
1	18	9.6	7.1
3	18	29.1	30.6
5	18	-8.7	-10.2
7	18	22.8	24.1
9	18	24.6	23.4
11	18	-12.9	-14.5
13	18	28.3	30.7
15	18	15.2	10.5
17	18	-12.1	-5.6
0	19	50.1	49.0
2	19	-59	-5.7
4	19	5.0	7.1
6	19	40.6	41.3
8	19	-8.4	-10.8
10	19	21.2	21.1
12	19	24.2	24.2
14	19	0.0	-7.8
16	19	24.9	27.8

k	l	F_o	F_c
1	20	0.0	5.4
3	20	39.0	38.5
5	20	-7.9	-1.5
7	20	16.8	17.9
9	20	23.0	24.5
11	20	-4.2	-2.3
13	20	27.9	29.0
15	20	3.3	8.0
0	21	30.6	30.7
2	21	-11.6	-5.4
4	21	10.3	7.3
6	21	25.8	25.9
8	21	0.0	-11.8
10	21	18.2	18.9
12	21	14.1	14.4
1	22	4.9	3.4
3	22	32.3	31.8
5	22	-6.8	-9.0
7	22	18.6	16.2
9	22	25.6	25.6

Table 2. *Final atomic parameters*

	x	y	z	B	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
La(1)	0	0	0	0·22 Å^2	0	0	0·06 Å^2
La(2)	0	0·31688	0	0·31	0·00015	0	0·04
Al(1)	0	0	$\frac{1}{2}$	0·8	0	0	0·3
Al(2)	0	0·3338	0·3683	0·4	0·0006	0·0008	0·1
Al(3)	0	0·1378	0·2729	0·7	0·0006	0·0010	0·2
Al(4)	0	$\frac{1}{2}$	0·2181	0·4	0	0·0013	0·2

Table 3. *List of short interatomic distances*

	Coordination		Distance
La(1)	4	Al(3)	3·31 Å
	8	Al(2)	3·39
	4	Al(4)	3·61
	2	La(2)	4·16
	2	La(1)	4·43
La(2)	4	Al(3)	3·25
	4	Al(2)	3·26
	2	Al(4)	3·27
	2	Al(1)	3·27
	2	Al(3)	3·63
	2	Al(2)	3·74
	1	La(1)	4·16
	2	La(2)	4·43
	1	La(2)	4·81
Al(1)	4	Al(3)	2·93
	4	Al(4)	3·13
	4	La(2)	3·27
Al(2)	2	Al(3)	2·66
	1	Al(4)	2·66
	1	Al(2)	2·67
	1	Al(3)	2·75
	2	La(2)	3·26
	2	La(1)	3·39
	1	La(2)	3·74
Al(3)	2	Al(2)	2·66
	1	Al(2)	2·75
	2	Al(4)	2·86
	1	Al(1)	2·93
	2	La(2)	3·25
	1	La(1)	3·31
	1	Al(3)	3·62
	1	La(2)	3·63
Al(4)	2	Al(2)	2·66
	4	Al(3)	2·86
	2	Al(1)	3·13
	2	La(2)	3·27
	2	La(1)	3·61

The corresponding structure factors are listed in Table 1 and the atomic parameters in Table 2. Table 3 contains a list of all short interatomic distances with estimated standard deviations computed from the inverse of the normal-equations matrix.

A Fourier synthesis and a difference Fourier synthesis in the section $x=0$ showed features of anisotropic thermal vibration of La(1), La(2) and Al(1) preferentially directed along the z axis; the correctness of the structure was substantially confirmed.

Discussion

La$_3$Al$_{11}$ constitutes, to the best of the authors' knowledge, a new structure type in intermetallic compounds. 'α-CeAl$_4$', 'α-PrAl$_4$' and 'α-NdAl$_4$', which all have essentially the same X-ray powder pattern (Buschow, 1965*b*), are doubtless isostructural and should be represented therefore by the formulae Ce$_3$Al$_{11}$, Pr$_3$Al$_{11}$ and Nd$_3$Al$_{11}$.

There are noticeable discrepancies between the various reported values of the 'LaAl$_4$' lattice constants, even after transformation to the same tetragonal unit cell. These discrepancies were tentatively interpreted

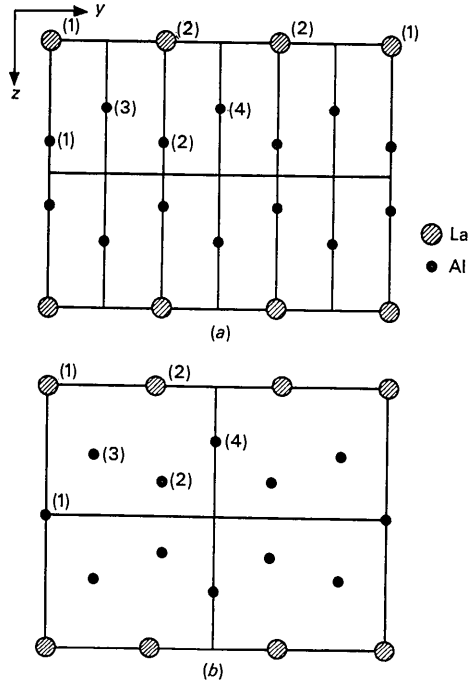

Fig. 1. (*a*) Threefold unit cell of BaAl$_4$-type structure; section $x=0$. (*b*) Unit cell of La$_3$Al$_{11}$. Section $x=0$.

Table 4. *Comparison of X-ray powder diagrams corresponding to* La–Al *samples of different composition*

Composition of sample	Excess	Spurious lines	a	b	c
20·0 at. % La	Al	Al	4·431 (5) Å	13·142 (10) Å	10·132 (7) Å
21·4	—	none			
22·2	La	LaAl$_3$	4·435	13·149	10·125

by Gschneidner in terms of a considerable homogeneity region. In order to check this interpretation the X-ray powder diagrams of three arc-cast samples annealed at 800°C and containing slightly different relative amounts of La and Al were compared (Table 4). The first (20·0 at.% La) was Buschow's original diagram, which had served for his determination of the 'α-$LaAl_4$' lattice constants; besides the La_3Al_{11} lines, there are also weak lines of Al. The second, corresponding to the exact stoichiometric composition (21·4 at.% La) shows no other lines than those of pure La_3Al_{11}, whereas the third (22.2 at.% La) also contains $LaAl_3$ lines. This proves not only that the homogeneity region is rather small but also that La_3Al_{11} is indeed the correct chemical formula. The invariance of the lattice constants tends to corroborate the former conclusion.

Since the high-temperature modification cannot be quenched (Buschow), one would think that all previous investigations, which were carried out at room temperature, would refer to the low-temperature phase. The question then arises why the orthorhombic structure had not earlier been recognized. Poor resolution of the X-ray diagrams might be held responsible, but such an explanation seems particularly unsatisfactory in the case of Rossi's work, which involves tetragonal Laue photographs of single-crystalline samples. We are inclined to believe, therefore, that the $BaAl_4$-type structure is stabilized by chemical impurities. Although this idea needs experimental verification, it should be noted that purer starting materials were available to us (La 99·9%, Al 99·99%) than to any of the previous investigators, and also that our method of sample preparation was probably less apt to introduce contamination.

Since it is impossible to quench the high-temperature modification, the α and the β phases are likely to have the same chemical composition, in which case they should be designated as α-La_3Al_{11} and β-La_3Al_{11}. If so, and if Buschow's statement is correct that 'β-$LaAl_4$' has the $BaAl_4$-type structure, the phase transition entails the ordering of vacancies by diffusion. This conclusion is not necessarily at variance with the reported sharpness (Buschow, 1965*a*) of the transition.

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Crystal and Molecular Structure of *S*,*S*-Dimethyl-*N*-methylsulphonylsulphilimine, $(CH_3)_2SNSO_2CH_3$

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The crystal structure of *S*,*S*-dimethyl-*N*-methylsulphonylsulphilimine has been solved by three-dimensional Patterson and Fourier calculations. The parameters have been refined by the aid of Booth's differential syntheses, with a final $R=0·106$. The S–N distances [$1·58_1$(10) and $1·63_3$(9) Å] indicate a delocalized S–N–S d_π bond system. The S–N–S bond angle is 116·2 (6)°, the average S–O distance, $1·44_6$ Å. The C(1)–S(VI) bond distance, $1·74_9$ (12) is similar to other C(sp^3)–S(VI) bonds. The C(sp^3)–S(IV) bond distances [1·74 (7) and 1·74 (3) Å] are rather short, which can be explained only with the supposition of strong hyperconjugation. The large e.s.d.'s of the C(2)–S(IV) and C(3)–S(IV) bonds are due to the intensive thermal motion of the C(2) and C(3) atoms.

Introduction

The structure and the stereochemistry of the *N*-acrylsulphilimines have been investigated by Kucsman and his collaborators (Kucsman, 1953, 1958; Kucsman & Kapovits, 1964). These investigations gave interesting results concerning the bond system and the configuration of these compounds. Among others the presence of a strong S(IV)–N d_π bond in the *N*-sulphonylsulphilimines ($RR'SNSO_2Q$) has been proved by infrared