

(Sichevich *et al.*, 1985) with the following changes: the 16(*l*) position with mixed Co/Ga occupation is now fully occupied by Al; the 16(*k*) position occupied by Co atoms is now filled with a mixture of Cu and Al atoms. The structure was described in the cited paper as an intergrowth of segments of the $U(Ni_{0.68}Si_{0.32})_{11}$ and Cr_5B_3 structures, maintaining the most typical coordination polyhedra. The list of interatomic distances in $Sr_6Cu_7Al_7$ up to $d/\sum r = 1.05$ is given in Table 5, while that of $Ba_6Cu_7Al_7$ has been deposited. All small atoms, except Al2, are surrounded by more- or less-distorted icosahedra, while Al2 is coordinated with ten alkaline-earth atoms in the form of a bicapped square antiprism.

Comparing the structures of $CaCuAl$, $Sr_6Cu_7Al_7$ and $Ba_6Cu_7Al_7$, one can see that nearly all small atoms are icosahedrally coordinated; around a Cu atom the icosahedron is formed only by Cu or Al atoms; some atomic positions are occupied statistically by Cu and Al atoms. These features are found also in other phases of the system Ca–Cu–Al, namely $Ca_3Cu_2Al_7$ (NbBe₃- or PuNi₃-type ordered derivative), $CaCu_4Al_8$ (ThMn₁₂-type ordered derivative) (Cordier, Czech, Ochmann & Schäfer, 1984) and $CaCu_{6.5}Al_{6.5}$ (NaZn₁₃-type disordered derivative) (Cordier, Czech & Schäfer, 1985). In all compounds the icosahedron is the only or the prevalent coordination polyhedron around the small atoms. In $CaCu_{6.5}Al_{6.5}$, Cu and Al atoms statistically

occupy one position, while Cu fills the other, icosahedrally surrounded only by small atoms.

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Ba₃Al₅, a Simple Atomic Arrangement Also Present in More Complex Structures

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Abstract. $M_r = 546.93$, hexagonal, $hP16$, $P6_3/mmc$, $a = 6.066$ (1), $c = 14.611$ (2) Å, $V = 465.6$ (1) Å³, $Z = 2$, $D_x = 3.90$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 13.3$ mm⁻¹, $F(000) = 466$, room temperature, $R = 0.027$ for 270 reflections with $F_o > 4\sigma(F_o)$. The structure of Ba₃Al₅ belongs to a new type. It shows a sequence of layers similar to that of the MgZn₂ Laves phase, but with a different arrangement of the aluminium tetrahedra: in Ba₃Al₅ isolated pairs of tetrahedra joined by a face are formed, instead of the infinite columns present in the Laves phase. Segments of the Ba₃Al₅ structure are contained also in the structure of the hexagonal Ba₄Al₅, trigonal Ba₇Al₁₃ and rhombohedral Sr₅Al₉ phases.

Introduction. During a study on equiatomic ternary phases formed by alkaline-earth metals, in a Ba–Ni–Al alloy were isolated crystals with hexagonal symmetry. A semi-quantitative electron-microprobe analysis revealed that the crystals did not contain nickel, but only barium and aluminium in the ratio 3:5. The present work reports the structure determination of this new phase in the Ba–Al system.

Experimental. The metals used were Ba 99.5% and Al 99.999% pure. After heating at 1273 K and slowly cooling, the alloy was annealed at 923 K for 8 d. Precession photographs showed $6/mmm$ Laue symmetry and systematic absence of hhl reflections with

$l = 2n + 1$, indicating $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$ as possible space groups. A single crystal with prismatic shape, measuring $0.04 \times 0.09 \times 0.16$ mm, was mounted on an Enraf-Nonius CAD-4 automatic diffractometer equipped with a graphite monochromator and intensities were collected in the ω - θ scan mode. The lattice constants were derived from 25 diffractometer-measured reflections in the θ range 26 – 28° . A semiempirical absorption correction was applied based on the azimuthal scan data of four top reflections with a ratio between max. and min. transmission factors of 2.1. The data collection was made up to $(\sin\theta)/\lambda = 0.7035 \text{ \AA}^{-1}$ with the condition $|h| > |k|$ in the range $-8 \leq h \leq 8$, $0 \leq k \leq 8$, $0 \leq l \leq 20$. The intensity of the check reflections showed no significant variation. The number of measured reflections was 920, of which 301 were independent ($R_{\text{int}} = 0.031$). 31 reflections with $F_o < 4\sigma(F_o)$ were considered unobserved. The structure was solved in the centrosymmetric space group $P6_3/mmc$ by interpreted Patterson methods and refined using F_o^2 's. Anisotropic refinement, 13 parameters varied, $R = 0.027$, $wR = 0.035$, $S = 1.657$, $w = 1/[\sigma^2(F_o) + 0.00057F_o^2]$, max. shift to e.s.d. ratio 0.004, max. and min. electron density in final difference Fourier synthesis 4.2 and -1.2 e \AA^{-3} . * Atomic scattering factors and anomalous-dispersion correction were taken from *International Tables for X-ray Crystallography* (1974). Principal programs used: *SHELXS86* (Sheldrick, 1985) and *SHELXL76* (Sheldrick, 1976).

Table 1 reports the atomic coordinates and thermal parameters, while interatomic distances up to $d/\sum r = 1.13$ ($\sum r$ is the sum of the metallic radii for CN 12) are given in Table 2.

Discussion. The structure of Ba₃Al₅ is represented in the upper left part of Fig. 1 as a projection on the (110) plane. For the layers perpendicular to the c axis, at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, a Kagomé net of Al atoms is symmetrically surrounded by two very close triangular nets of Al and Ba atoms and by a triangular net of Ba atoms. This sequence is found also in the hexagonal MgZn₂ Laves phase, although with a slightly different distribution in the relative distances of the layers. However, the main difference consists in the arrangement of the aluminium tetrahedra. In the Laves phase they form infinite columns along the c axis, by sharing alternatively a vertex and a face, while in Ba₃Al₅ isolated pairs of tetrahedra sharing a face are formed.

In Fig. 1 are drawn also the structures of other phases of the Ba–Al system presenting a close relationship. In all structures aluminium tetrahedra are

Table 1. Atomic coordinates and thermal parameters for Ba₃Al₅

Space group $P6_3/mmc$; $U_{\text{eq}} = \frac{1}{3} \sum_j U_{jj} a_j^* a_j^* a_j^*$
E.s.d.'s are given in parentheses.

		x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Ba1	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.6251 (1)	0.0123 (2)
Ba2	2(a)	0	0	0	0.0259 (3)
Al1	6(h)	0.1547 (3)	2x	$\frac{1}{4}$	0.0202 (8)
Al2	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0.1137 (3)	0.0221 (8)

Table 2. Interatomic distances (\AA) in Ba₃Al₅ up to $d/\sum r = 1.13$

E.s.d.'s are less than 0.01 \AA .

Ba1–Al2	3.49	Al1–2Al2	2.74
–3Al2	3.51	–2Al1	2.82
–6Al1	3.54	–2Al1	3.25
–Ba1	3.65	–4Ba1	3.54
–3Ba2	3.95	–2Ba2	4.00
Ba2–6Al2	3.88	Al2–3Al1	2.74
–6Ba1	3.95	–Ba1	3.49
–6Al1	4.00	–3Ba1	3.51
		–3Ba2	3.88

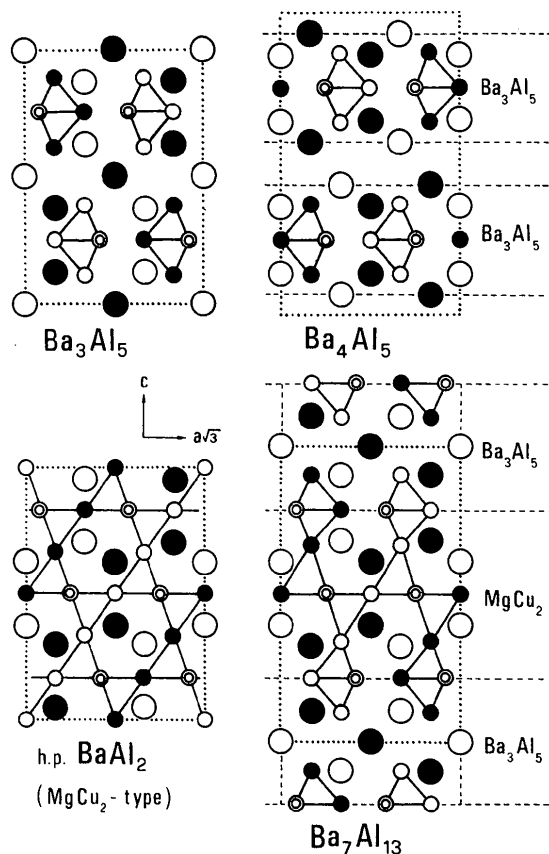


Fig. 1. Projection of the structures of Ba–Al phases in the plane (110) of the hexagonal cell. Open, filled and double circles correspond to heights 0 , $\frac{1}{4}$ and $\frac{3}{4}$, respectively. Large circles: Ba; small circles: Al. The aluminium tetrahedra are shown.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44933 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

present, but arranged in different ways. Isolated pairs of tetrahedra joined by a face are found in Ba_3Al_5 and in Ba_4Al_5 (Fornasini, 1975), while $BaAl_2$, formed only in high-pressure conditions (Cordier, Czech & Schäfer, 1984), shows the infinite framework of tetrahedra joined by vertices typical of the cubic Laves phase $MgCu_2$. The Ba_7Al_{13} structure (Fornasini & Bruzzone, 1975) contains some face-sharing tetrahedra and some of the $MgCu_2$ framework, and can be built up by intergrowth of segments of the Ba_3Al_5 and $MgCu_2$ structures, as outlined in the figure. Alternatively, it can be described as formed by cells of Ba_3Al_5 separated one from the other by insertion of an aluminium Kagomé net. Recognizable segments of the Ba_3Al_5 structure are also found in Ba_4Al_5 , but in the boundary region between two segments of Ba_3Al_5 two Ba layers are inserted instead of one.

Very recently the structure of the rhombohedral Sr_5Al_9 phase has been published (Manyako, Zarechnyuk & Yanson, 1987), described by the authors as an intergrowth of segments of $MgZn_2$ and a hypothetical R_3X_5 structure, while the structure of Ba_7Al_{13} is shown as an intergrowth of the $MgCu_2$ and the same hypothetical R_3X_5 structure. Interestingly, this hypothetical structure corresponds to that of the Ba_3Al_5 phase. So here again is an event common in crystal structure determination: the more complex examples of a structural family are found before the discovery of the simplest parent member!

The coordination polyhedra in Ba_3Al_5 are very similar to those of the related Ba–Al structures. Ba1 is coordinated with 10 Al + 4 Ba in the same manner as

Ba2 in Ba_4Al_5 with a further Al atom; the Ba2 polyhedron, formed by 12 Al + 6 Ba is identical to that of Ba1 in Ba_7Al_{13} . The Al1 atoms forming Kagomé nets are icosahedrally surrounded by 6 Al + 6 Ba. The same coordination is found also around Al in h.p. $BaAl_2$, Al2 in Ba_4Al_5 and Al2, Al3, Al4 in Ba_7Al_{13} . Finally, the environment of Al2, coordinated with 3 Al + 7 Ba, is identical to those of Al1 in Ba_4Al_5 and Al1 in Ba_7Al_{13} . Neither Ba_3Al_5 nor Ba_4Al_5 show Friauf polyhedra around the large atoms, a characteristic feature of the Laves phases; they are present, though, in Ba_7Al_{13} and Sr_5Al_9 structures.

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Structure of $LiCdPO_4$

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Abstract. $M_r = 214.31$, orthorhombic, space group $Pna2_1$, $a = 10.713$ (4), $b = 4.801$ (1), $c = 6.284$ (3) Å,

$V = 323.2$ (1) Å³, $Z = 4$, $D_x = 4.40$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 70.59$ cm⁻¹, $F(000) = 392$, $T = 298$ K, $R = 0.0206$ for 1079 independent reflections with $I > 1.5\sigma(I)$. The structure consists of discrete PO_4 tetrahedra linked by CdO_6 octahedra and distorted LiO_6 octahedra. The Cd–O and Li–O bond lengths

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