

protonated. The idealized symmetry of the borate molecule, ignoring the hydrogen atoms, is  $mm2$  ( $C_{2v}$ ) and, including the hydrogen atoms, the symmetry is  $m$  ( $C_s$ ). The site symmetry in the space group is also  $m$ , which is a remarkable feature for a larger borate molecule, as has been pointed out by Zobetz (1982).

The Pt borate complexes are held together by a network of hydrogen bonds and the potassium–oxygen polyhedra. All hydrogen atoms in the structure, the hydrogen atoms of the hydroxyl groups as well as those of the water, participate in the hydrogen-bond network. The individual distances and angles have been deposited. Between the Pt borate complexes the potassium cations are located in such a way that all oxygen atoms in the structure, except that bonded between the two tetrahedral boron atoms and the oxygen O(6), build up the oxygen coordination polyhedra around the potassium cations. K(1) has a tenfold coordination which can be considered as a strongly distorted bicapped square antiprism. K(2) has a ninefold coordination which may best be described as a distorted tricapped trigonal prism. Both cation polyhedra are strongly connected in two dimensions by sharing several corners and edges; they build up double layers in the  $bc$  plane.

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## Structures of Nearly 1:1:1 Phases in $M$ –Cu–Al ( $M$ =Ca, Sr, Ba) Systems

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**Abstract.**  $\text{Ca}_{30}\text{Cu}_{29.5}\text{Al}_{33.7}$ ,  $M_r = 3986.1$ , hexagonal,  $hP93.2$ ,  $P6/mmm$ ,  $a = 15.256$  (2),  $c = 9.252$  (1) Å,  $V = 1864.9$  (4) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 3.55$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 10.9$  mm<sup>-1</sup>,  $F(000) = 1894$ , room temperature,  $R = 0.038$  for 723 reflections with  $F_o > 3\sigma(F_o)$ .  $\text{Sr}_6\text{Cu}_{6.6}\text{Al}_{7.4}$  ( $\text{Ba}_6\text{Cu}_{6.8}\text{Al}_{7.2}$ ),  $M_r = 1144.7$  (1450.4), tetragonal,  $I180$ ,  $I4/mcm$ ,  $a = 8.427$  (2),  $c = 25.995$  (7) [ $a = 8.533$  (1),  $c = 27.249$  (4)] Å,  $V = 1846.0$  (8) [1984.1 (4)] Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 4.12$  (4.86) Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 26.0$  (19.7) mm<sup>-1</sup>,  $F(000) = 2062$  (2507), room temperature,  $R = 0.055$  (0.051) for 481 (658) reflec-

tions with  $F_o > 3\sigma(F_o)$ . The CaCuAl structure presents in part features of a Frank–Kasper layer structure and is closely related to the cubic  $\text{Mg}_{32}(\text{Zn},\text{Al})_{49}$  phase. Several atomic sites have occupational disorder, especially those occupied by small atoms. All Cu and/or Al atoms but one are icosahedrally coordinated.  $\text{Sr}_6\text{Cu}_7\text{Al}_7$  and  $\text{Ba}_6\text{Cu}_7\text{Al}_7$  are isotypic, with a slight difference in the mixed filling of a site by Cu and Al atoms. Their structure is a site-occupation variant of the  $\text{La}_6\text{Co}_{11}\text{Ga}_3$  structure. All small atoms are surrounded by icosahedra, save an Al atom coordinated with ten alkaline earths in the form of a bicapped square antiprism.

**Introduction.** In ternary systems containing rare-earth or alkaline-earth metals, the most populous classes of compounds occur with 1:1:1 and 1:2:2 composition. As regards the equiatomic 1:1:1 composition, while for rare-earth-containing phases a large number of crystallographic data are available, only a few alkaline-earth compounds have been investigated, several of them presenting substitutional disorder.

This work deals with the study of the nearly equiatomic phases formed by Ca, Sr and Ba with Cu and Al indicated in the following by the approximate formulas CaCuAl, Sr<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub> and Ba<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub>.

**Experimental.** Alloys with equiatomic 1:1:1 composition were prepared from metals of commercial purity (Ca and Ba 99.5%, Sr 99%, Cu and Al 99.999%) by thermal treatment at 1373 K and slow cooling. In all samples large tabular crystals were formed; however, metallographic examination showed only the alloy of CaCuAl to be homogeneous, while the others were biphasic with prevalence of a less oxidizable phase (60%). Single crystals were isolated in each sample. Precession photographs showed for CaCuAl *6/mmm* Laue symmetry and no extinctions, indicating the possible space groups *P622*, *P6mm*, *P6m2*, *P62m* and *P6/mmm*; for Sr<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub> and Ba<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub> *4/mmm* Laue symmetry, systematic absences of *hkl* reflections with  $h+k+l=2n+1$  and of *0kl* with  $l=2n+1$ , indicating the possible space groups *I4cm*, *I4c2* and *I4/mcm*.

In the following, the experimental details are referred to the Ca, Sr and Ba crystals, in order. The data collections were made on crystals measuring  $0.04 \times 0.08 \times 0.12$ ,  $0.02 \times 0.08 \times 0.20$  and  $0.02 \times 0.14 \times 0.15$  mm by means of an Enraf-Nonius CAD-4 automatic diffractometer with graphite monochromator, in the  $\omega$ - $\theta$ ,  $\omega$  and  $\omega$ - $\theta$  scan modes. Lattice parameters were obtained from 25 diffractometer-measured reflections in the  $\theta$  range 18–22, 24–31 and 25–30°. A semiempirical absorption correction based on the azimuthal scan data of top reflections was applied with a ratio between max. and min. transmission factors of 1.2, 2.7 and 7.4. Intensities were collected up to  $(\sin\theta)/\lambda = 0.7035 \text{ \AA}^{-1}$  with the condition  $|h| > |k|$  in the range  $-21 \leq h \leq 21$ ,  $0 \leq k \leq 21$ ,  $0 \leq l \leq 13$ ;  $-11 \leq h \leq 11$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 36$ ;  $-12 \leq h \leq 12$ ,  $0 \leq k \leq 12$ ,  $0 \leq l \leq 38$ . No intensity variation was observed in check reflections. The number of measured reflections was 3205, 1479 and 1578, of which 1113 ( $R_{\text{int}} = 0.057$ ), 749 ( $R_{\text{int}} = 0.094$ ) and 798 ( $R_{\text{int}} = 0.059$ ) were independent. Reflections with  $F_o < 3\sigma(F_o)$ , 390, 268 and 140, were considered unobserved.

The structure of CaCuAl was solved by direct methods in the centrosymmetric space group *P6/mmm*, given by statistical tests as the most probable. From the very beginning of the refinement, it was apparent that

Table 1. Atomic coordinates and thermal parameters for CaCuAl

Space group *P6/mmm*;  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

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

	x	y	z	Occ.(%)	$U_{\text{eq}}(\text{\AA}^2)$
Ca1	12(o) 0.2099 (1)	2x	0.2029 (2)	100	0.0106 (5)
Ca2	6(m) 0.1322 (1)	2x	$\frac{1}{2}$	100	0.0158 (8)
Ca3	6(j) 0.3808 (2)	0	0	100	0.0131 (7)
Ca4	4(h) $\frac{1}{2}$	$\frac{1}{2}$	0.3068 (3)	100	0.0100 (7)
Ca5	2(e) 0	0	0.2231 (6)	80.1 (6)	0.0183 (15)
Ca6	2(e) 0	0	0.3673 (22)	19.9 (6)	0.010 (4)†
X1	12(q) 0.1628 (1)	0.4930 (1)	$\frac{1}{2}$	{Cu 48.2 (5) {Al 51.8 (5)	0.0102 (6)
X2	12(o) 0.4494 (1)	2x	0.2526 (1)	{Cu 63.6 (6) {Al 36.4 (6)	0.0117 (4)
X3	12(n) 0.3557 (1)	0	0.3524 (2)	{Cu 22.0 (5) {Al 78.0 (5)	0.0115 (6)
X4	12(n) 0.2109 (1)	0	0.2134 (1)	{Cu 71.9 (6) {Al 28.1 (6)	0.0188 (4)
X5	6(l) 0.1101 (1)	2x	0	{Cu 18.2 (6) {Al 81.8 (6)	0.0173 (12)
X6	6(l) 0.3953 (1)	2x	0	{Cu 10.5 (6) {Al 89.5 (6)	0.0123 (9)
Cu	3(g) $\frac{1}{2}$	0	$\frac{1}{2}$	100	0.0103 (7)
X7	1(a) 0	0	0	{Cu 5.0 (2) {Al 14.9 (5)	0.012 (6)†

† Isotropically refined.

Table 2. Atomic coordinates and thermal parameters for Sr<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub>

Space group *I4/mcm*;  $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ .

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

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Sr1	16(f) 0.1677 (1)	$\frac{1}{2} + x$	0.1858 (1)	0.0141 (3)
Sr2	8(f) 0	0	0.3946 (1)	0.0103 (4)
Cu1	16(f) 0.1771 (2)	$\frac{1}{2} + x$	0.0548 (1)	0.0112 (4)
Cu2	4(d) 0	$\frac{1}{2}$	0	0.0125 (7)
Al1	16(f) 0.3837 (4)	$\frac{1}{2} + x$	0.0875 (2)	0.0092 (9)
Al2	4(a) 0	0	$\frac{1}{2}$	0.0134 (19)
X*	16(k) 0.0644 (4)	0.2056 (4)	0	0.0106 (8)

\* Cu 40(1)% + Al 60(1)%.

Table 3. Atomic coordinates and thermal parameters for Ba<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub>

Space group *I4/mcm*;  $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ .

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

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Ba1	16(f) 0.1675 (1)	$\frac{1}{2} + x$	0.1836 (1)	0.0153 (2)
Ba2	8(f) 0	0	0.3935 (1)	0.0091 (2)
Cu1	16(f) 0.1774 (2)	$\frac{1}{2} + x$	0.0510 (1)	0.0112 (5)
Cu2	4(d) 0	$\frac{1}{2}$	0	0.0103 (9)
Al1	16(f) 0.3856 (4)	$\frac{1}{2} + x$	0.0826 (2)	0.0096 (11)
Al2	4(a) 0	0	$\frac{1}{2}$	0.0198 (25)
X*	16(k) 0.0638 (4)	0.2064 (4)	0	0.0134 (10)

\* Cu 45(1)% + Al 55(1)%.

several sites had mixed occupation by the Cu and Al atoms. For each of these sites a variable occupation factor was introduced, with the constraint that the sum of Cu and Al occupancies should be unity on each site.

As the refinement proceeded, a new detail became evident. Two other peaks on the difference Fourier map could be attributed to a Ca atom and a mixed Cu/Al atom, on the basis of geometrical considerations. They are indicated as Ca6 and X7 in the atomic-positions table. Since these new atoms are incompatible with the Ca5 position, they were given the same occupancy factor and refined with the constraint that the sum of occupancies of Ca5 and Ca6 (or X7) should be unity. The relative occupancies of the X7 position by Cu and Al atoms were tentatively adjusted till the isotropic thermal factor associated with this position refined to a reasonable value. In several anisotropic cycles based on  $F_o$ 's the site-occupation factors and thermal parameters were alternately fixed and varied, with the final results: 59 parameters varied,  $R = 0.038$ ,  $wR = 0.043$ ,  $S = 1.139$ ,  $w = 1/[\sigma^2(F_o) + 0.00105 F_o^2]$ ; max. shift to e.s.d. ratio 0.02; max. and min. electron density in final difference Fourier synthesis 2.3 and  $-1.6 \text{ e } \text{\AA}^{-3}$ . The final composition was  $\text{Ca}_{30}\text{Cu}_{29.5(1)}\text{Al}_{33.7(1)}$ .

For  $\text{Sr}_6\text{Cu}_7\text{Al}_7$  and  $\text{Ba}_6\text{Cu}_7\text{Al}_7$  the structure of the phase  $\text{La}_6\text{Co}_{11}\text{Ga}_3$  (Sichevich, Lapunova, Sobolev, Grin' & Yarmolyuk, 1985) with space group  $I4/mcm$  and very similar lattice constants was chosen as starting model. Unlike the model, both structures showed different occupations of two atomic positions leading to different compositions:  $\text{Sr}_6\text{Cu}_{6.60(4)}\text{Al}_{7.40(4)}$  and  $\text{Ba}_6\text{Cu}_{6.80(4)}\text{Al}_{7.20(4)}$ . Anisotropic refinement, 33 parameters varied,  $R = 0.055$  ( $R = 0.051$  for the Ba-containing crystal),  $wR = 0.067$  (0.046),  $S = 0.919$  (8.721),  $w = 1/[\sigma^2(F_o) + 0.0035 F_o^2]$  [ $w = 1/\sigma^2(F_o)$ ]; max. shift to e.s.d. ratio 0.02 (0.008); max. and min. electron density in final difference Fourier synthesis 3.0 and  $-2.4$  (3.8 and  $-4.1$ )  $\text{e } \text{\AA}^{-3}$ .

Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Principal programs used: *MULTAN80* (Main *et al.*, 1980) and *SHELX76* (Sheldrick, 1976).

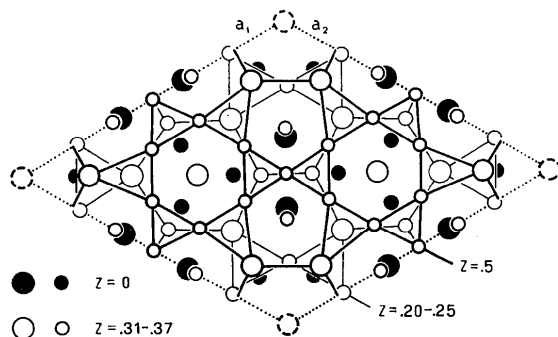


Fig. 1. Projection of half the cell of  $\text{CaCuAl}$  on the (001) plane. Large circles: Ca; small circles: Cu or Al. The dashed circle at the cell origin indicates a column formed by atoms Ca5, Ca6 and X7 with partial occupation.

A semi-quantitative electron-microprobe analysis was carried out on bulk  $\text{CaCuAl}$  alloy and on the  $\text{Sr}_6\text{Cu}_7\text{Al}_7$  single crystal. In both cases the composition obtained from the crystallographic refinement was confirmed.

The atomic coordinates and thermal parameters of  $\text{CaCuAl}$ ,  $\text{Sr}_6\text{Cu}_7\text{Al}_7$  and  $\text{Ba}_6\text{Cu}_7\text{Al}_7$  are reported in Tables 1, 2 and 3 respectively.\*

## Discussion.

### The $\text{CaCuAl}$ structure

The structure of  $\text{CaCuAl}$  is represented in Fig. 1. The block between  $z = 0.20$  and  $z = 0.80$  is very similar to a Frank-Kasper layer structure. Two rumped primary nets occur at  $z = 0.20-0.25$  (atoms connected by thin lines) and symmetrically at  $z = 0.75-0.80$ , and another primary net at  $z = 0.5$  (atoms connected by thick lines), all of these forming hexagons, pentagons and triangles. Two secondary rumped nets (not connected open circles) at  $z = 0.31-0.37$  and symmetrically at  $z = 0.63-0.69$ , forming triangles, are alternated with the primary nets. The atoms indicated by full circles give rise to a subsidiary primary layer at  $z = 0$  and their insertion between two other primary nets interrupts the typical sequence of a Frank-Kasper structure.

$\text{CaCuAl}$  shows a noticeable resemblance to the cubic phase  $\text{Mg}_{32}(\text{Zn},\text{Al})_{49}$  (Bergman, Waugh & Pauling, 1957) discussed by Pearson (1972). A drawing of part of this structure between  $z \approx 0.2$  and  $z = 0.5$  is shown in Fig. 2, where the slab common to both structures is enclosed by dashed lines. If a sixfold axis perpendicular to the plane of the drawing through the point  $0, \frac{1}{2}, 0$  is

\* Lists of structure factors and anisotropic thermal parameters for all three compounds and interatomic distances for  $\text{Ba}_6\text{Cu}_7\text{Al}_7$  have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44932 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

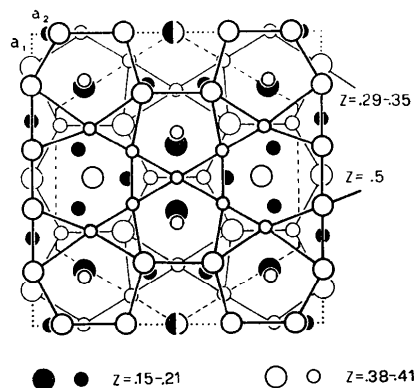


Fig. 2. Projection of the structure of  $\text{Mg}_{32}(\text{Zn},\text{Al})_{49}$  along the edge of the cubic cell between  $z \approx 0.2$  and  $z = 0.5$ . Large circles: Mg; small circles: Zn or Al. The slab common to the  $\text{CaCuAl}$  structure is enclosed by dashed lines.

Table 4. *Interatomic distances (Å) in CaCuAl up to  $d/\sum r = 1.22$* 

E.s.d.'s are less than 0.01 Å, save for Ca6–Ca5 and Ca6–X7 distances where they are 0.02 Å. The multiplicity of bonds marked by an asterisk is dependent on the degree of occupancy of the position.

Ca1–2X3	3.16	Ca2–4X4	3.18
–2X1	3.18	–4X3	3.27
–2X4	3.20	–2X1	3.28
–2X2	3.20	–2Ca1	3.43
–X5	3.24	–2Ca2	3.49
–2X6	3.39	–2Ca6	3.70*
–Ca4	3.40	–2Ca5	4.33*
–Ca2	3.43		
–2Ca3	3.50	Ca3–4X2	3.25
–Ca1	3.75	–2X4	3.26
		–2X3	3.28
Ca4–3X2	3.11	–2X6	3.31
–6X1	3.18	–4Ca1	3.50
–3X6	3.28	–2X5	3.60
–3Ca1	3.40	–Ca3	3.64
–Ca4	3.58		
		Ca6–X7	3.40*
Ca5–6X4	3.22	–6X4	3.52
–6X5	3.57	–6Ca2	3.70
–Ca6	3.79*	–Ca5	3.79*
–Ca5	4.13*		
–6Ca2	4.33		
X1–Cu	2.54	X2–Cu	2.65
–X1	2.55	–X2	2.67
–2X3	2.69	–2X3	2.74
–X1	2.70	–X6	2.74
–2X2	2.78	–2X1	2.79
–2Ca4	3.18	–Ca4	3.11
–2Ca1	3.18	–2Ca1	3.20
–Ca2	3.28	–2Ca3	3.25
X3–X4	2.56	X4–2X5	2.55
–Cu	2.59	–X3	2.56
–2X1	2.69	–2Ca2	3.18
–X3	2.73	–2Ca1	3.20
–2X2	2.74	–2X4	3.22
–2Ca1	3.16	–Ca5	3.22*
–2Ca2	3.27	–Ca3	3.26
–Ca3	3.28	–Ca6	3.52*
X5–4X4	2.55	X6–2X2	2.74
–2X5	2.91	–2X6	2.84
–X7	2.91*	–2Ca4	3.28
–2Ca1	3.24	–2Ca3	3.31
–2Ca5	3.57*	–4Ca1	3.39
–2Ca3	3.60		
X7–6X5	2.91	Cu–4X1	2.54
–2Ca6	3.40*	–4X3	2.59
		–4X2	2.65

applied to the common slab, the whole atomic arrangement of CaCuAl is obtained, disregarding some minor discrepancies, such as the site occupation of the small atoms and the occupational disorder along the sixfold axis in the CaCuAl cell.

The similarity between the two structures can also be seen in terms of the 13-icosahedron unit given by Cenzual, Chabot & Parthé (1985) for the Mg<sub>32</sub>(Zn,Al)<sub>49</sub> structure, and composed of '13 centred icosahedra where 12 outer icosahedra share vertices with a central one, the centres of the surrounding

Table 5. *Interatomic distances (Å) in Sr<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub> up to  $d/\sum r = 1.05$* 

E.s.d.'s are less than 0.01 Å.

Sr1–Cu1	3.41	Sr2–4X	3.29
–2Al1	3.53	–4Cu1	3.37
–2Al2	3.55	–4Al1	3.41
–Al1	3.63	–Al2	3.76
–2Sr2	3.77	–4Sr1	3.77
–Sr1	3.87		
–Sr1	4.00	Cu2–4X	2.54
–2Sr1	4.37	–4Cu1	2.55
–4Sr1	4.44	–4Al1	2.66
Cu1–Cu2	2.55		
–Al1	2.60	Al1–Cu1	2.60
–2X	2.61	–2Cu1	2.66
–2Al1	2.66	–Cu2	2.66
–2X	2.67	–2X	2.76
–Cu1	2.85	–Al1	2.77
–2Sr2	3.37	–2Sr2	3.41
–Sr1	3.41	–2Sr1	3.53
		–Sr1	3.63
X–Cu2	2.54		
–2X	2.57	Al2–8Sr1	3.55
–2Cu1	2.61	–2Sr2	3.76
–2Cu1	2.67		
–X	2.74		
–2Al1	2.76		
–2Sr2	3.29		

icosahedra being themselves icosahedrally arranged'. Such a unit is present also in the CaCuAl structure and, repeated by the hexagonal symmetry, gives rise to a framework of interpenetrating polyhedra. The central icosahedron contains a Cu atom [it is an Al atom in Mg<sub>32</sub>(Zn,Al)<sub>49</sub>], while the surrounding icosahedra are centred by X1, X4 and X6 atoms, the icosahedra centred by X4 having a missing vertex. A similar mixed occupation of the two small atoms in several atomic sites was also found in the Mg<sub>32</sub>(Zn,Al)<sub>49</sub> phase.

In Table 4 are reported the interatomic distances in CaCuAl up to  $d/\sum r = 1.22$  ( $\sum r$  is the sum of the elemental radii for CN 12). Around Ca1, Ca2 and Ca4 there are Frank–Kasper polyhedra, with some distortion in the case of Ca2. Ca3 is surrounded by a pentagonal prism with all capped faces (CN 17), Ca5 by a hexagonal prism with all capped faces (CN 20) and Ca6 by a hexagonal antiprism capped on the hexagonal faces (CN 14). The atoms X1, X2, X3, X6 and Cu are icosahedrally coordinated, the Cu atom being surrounded only by small atoms. The X4 polyhedron is a defective icosahedron with a missing vertex, the X5 polyhedron can be described as an icosahedron or as a distorted defective icosahedron, depending on the site occupation of the partially filled positions, while X7 with the lowest number of contacts presents hexagonal bipyramidal coordination.

#### *The Sr<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub> and Ba<sub>6</sub>Cu<sub>7</sub>Al<sub>7</sub> structures*

The structure of these two compounds is a site-occupation variant of the La<sub>6</sub>Co<sub>11</sub>Ga<sub>3</sub> structure

(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  $Ca_3Cu_2Al_7$  (NbBe<sub>3</sub>- or PuNi<sub>3</sub>-type ordered derivative),  $CaCu_4Al_8$  (ThMn<sub>12</sub>-type ordered derivative) (Cordier, Czech, Ochmann & Schäfer, 1984) and  $CaCu_{6.5}Al_{6.5}$  (NaZn<sub>13</sub>-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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## Ba<sub>3</sub>Al<sub>5</sub>, 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) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 3.90$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 13.3$  mm<sup>-1</sup>,  $F(000) = 466$ , room temperature,  $R = 0.027$  for 270 reflections with  $F_o > 4\sigma(F_o)$ . The structure of Ba<sub>3</sub>Al<sub>5</sub> belongs to a new type. It shows a sequence of layers similar to that of the MgZn<sub>2</sub> Laves phase, but with a different arrangement of the aluminium tetrahedra: in Ba<sub>3</sub>Al<sub>5</sub> isolated pairs of tetrahedra joined by a face are formed, instead of the infinite columns present in the Laves phase. Segments of the Ba<sub>3</sub>Al<sub>5</sub> structure are contained also in the structure of the hexagonal Ba<sub>4</sub>Al<sub>5</sub>, trigonal Ba<sub>7</sub>Al<sub>13</sub> and rhombohedral Sr<sub>5</sub>Al<sub>9</sub> 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