

The Crystal Structure of $(\text{Mg,Na,Al})_2(\text{Al,Zn})_3$

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The structure of $(\text{Mg,Na,Al})_2(\text{Al,Zn})_3$ is determined. It crystallizes in the cubic space group $Im\bar{3}$ with the cell axis $a = 14.2173(7)$ Å, $Z = 2$. A comparison is made with the structure of the quasicrystal approximant $\text{Mg}_{32}(\text{Al,Zn})_{49}$ —the most important difference being the empty icosahedra in the title compound. © 1995 Academic Press, Inc.

INTRODUCTION

The title compound was a by-product of an investigation in the Na–Mg–Zn system. A first inspection by the precession camera showed a possible relationship between this compound and the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase found by Bergman *et al.* in 1957 (1). Both structures are body-centered cubic with almost the same cell axis (14.16 ± 0.03 Å (2) for their compound and $14.2173(7)$ Å for this compound) and crystallize in the space group $Im\bar{3}$, $Z = 2$. Assuming the compounds to be isostructural, an investigation was made using single-crystal X-ray diffraction to find out how the added Na affects the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ structure.

PREPARATION

Pieces of Na were melted together with a mixture of Mg grain and Zn powder in the atomic proportion 1 Na, 2 Mg, and 1 Zn under argon in sealed stainless steel tubes. The initial temperature of 675°C was kept for 2 hr and then slowly decreased (50°C h^{-1}) to room temperature. The tubes were opened under argon in a dry box. Because of difficulties in getting the samples out of the tubes, about 1/4 (by volume) $\alpha\text{-Al}_2\text{O}_3$ powder was added to the tubes before the melting. Apparently the Al_2O_3 reacted in this experiment to form a very stable, silvery, shiny alloy together with Na, Mg, and Zn. The X-ray diffraction powder photograph of the Al_2O_3 used in the experiment revealed that the powder was contaminated—probably with hydroxide and/or hydrate.

CRYSTAL MEASUREMENTS

A single crystal of $0.001 \times 0.075 \times 0.100$ mm³ was selected for the experiment. The X-ray data collection

was made on an Enraf–Nonius CAD4 single-crystal diffractometer using $\text{MoK}\alpha$ radiation ($\lambda(\text{MoK}\alpha) = 0.71069(1)$ Å) and a graphite monochromator. At room temperature, 2995 reflections with $0 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 16$, and $\sin \theta/\lambda \leq 0.5947$ Å⁻¹ were measured. Every reflection was measured for no more than 120 sec. Every hour three standard reflections, (0,5,-3), (6,1,-3), and (0,0,-6), were measured. They showed no decay in intensity. The total X-ray exposure time for the experiment was 48 hr. From 25 reflections with $16^\circ \leq 2\theta \leq 34^\circ$ the cell parameters were determined to be $a = 14.2173(7)$ Å and $V = 2873.7(2)$ Å³. The structure is cubic with the body-centered, centrosymmetric space group $Im\bar{3}$. Other crystal data are $Z = 2$, $M_r = 3305$, $D_x = 3.82$ g cm⁻³, and $\mu = 142$ cm⁻¹.

A correction for Lorentz, polarization, and absorption effects was made using numerical integration. The transmission factor varies from 0.42 to 0.98. The 2995 measured reflections were averaged to 523 independent ones with $R_{\text{int}} = 0.072$. This comparatively large internal R value may be attributed to the rather extreme shape of the crystal. In such a thin plate, even strong reflections may fall under the detection limit because of absorption effects, and that cannot be amended by absorption correction. Of these reflections, 287 had $I > 3\sigma_c(I)$ and were used in the refinement.

The atomic composition of the crystal was studied by scanning electron microscopy (with a JEOL JSM-840A and a Link EDS system). This investigation was made with the actual crystal when all the X-ray data had been collected. The composition in at.% is approximately 21 Na, 27 Mg, 10 Al, and 42 Zn.

REFINEMENT OF THE STRUCTURE

Because of the probable, close relationship between the title compound and the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase, an attempt was made to take the coordinates of the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase as the coordinates of this structure. In the Zn and Al split positions only Zn atoms were placed, and at the Mg positions, Mg atoms were used. When an atom was inserted in position 2(a) ((0,0,0) and (1/2,1/2,1/2)), where the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase has 80%

TABLE 1

Fractional Coordinates, Isotropic Thermal Displacement Parameters, and Occupancy Factors for the Atoms in the $(\text{Mg,Na,Al})_2(\text{Al,Zn})_3$ Phase

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} (\AA^2)	<i>G</i>
Mg/Na(1)	0.1860(3)	0.1860(3)	0.1860(3)	0.010(2)	0.333
Mg/Na(2)	0.0000	0.1173(5)	0.3007(5)	0.013(2)	0.500
Al(4)	0.4031(7)	0.5000	0.0000	0.012(3)	0.250
Mg/Na(3)	0.1968(7)	0.5000	0.0000	0.010(3)	0.250
Zn(1)	0.00000	0.1509(2)	0.0928(2)	0.009(1)	0.434(9)
Al(1)	0.00000	0.1509(2)	0.0928(2)	0.009(1)	0.066
Zn(2)	0.00000	0.3067(2)	0.1799(2)	0.011(1)	0.322(7)
Al(2)	0.00000	0.3067(2)	0.1799(2)	0.011(1)	0.178
Zn(3)	0.1576(2)	0.4033(2)	0.1916(2)	0.014(1)	0.662(12)
Al(3)	0.1576(2)	0.4033(2)	0.1916(2)	0.014(1)	0.338

Al, a very large negative electron density in the Fourier difference map appeared. Removing the atom made the *R* values go down and improved the Fourier difference map.

The structure was refined isotropically on *F*. Anisotropic refinement did not give any noticeable improvement. The function minimized was $\sum w(F_o - F_c)^2$, with $w = [\sigma^2(F_o) + (0.03F_o)^2]^{-1}$. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography" (3). The system of computer programs used in the refinement is described by Lundgren (4).

The refinement was made without the (0, 0, 0) atom. At first the aluminum atoms were not included. The isotropic thermal displacement parameters for Mg and Zn were refined together with the atomic positions, the overall scale factor, and the occupancy factor for the Zn atoms.

After this the aluminum atoms were placed in the Zn atomic positions to get split positions containing both Al and Zn. The occupancy factors for the Al and Zn atoms were calculated to retain the total number of electrons in each position and to give a full occupancy in total. These resulting occupancy factors agree very well with the ones found for the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase. Twenty-three parameters were refined altogether (cf. Table 1)—the overall scale factor, the atomic positions, the Zn/Al ratio in the split positions, and all isotropic thermal displacement parameters. The atomic positions as well as the isotropic thermal displacement parameters for Al and Zn at each split position were set to be identical and coupled to be refined together, since individual refinement either gave no significant change or caused the refinement to diverge. One of the light atoms showed a markedly lower isotropic thermal displacement factor and somewhat shorter overall nearest-neighbor distances than the rest, and in this position Mg was supplanted by Al. No attempt was made to distinguish between Mg and Na in the Mg/Na positions. In the final refinement the agreement factors were $R = 0.055$, $R_w = 0.057$, $S = 1.19$, and $\Delta/\sigma \leq 3 \times 10^{-2}$. The

maximum and the minimum in the last Fourier difference plot were at 1.3 and $-1.7 e \text{\AA}^{-3}$, respectively.

There is some uncertainty about where to place Na, Mg, and Al. These atoms have almost the same number of electrons and are therefore very difficult to distinguish between only by examination of the Fourier difference maps, but fixing the temperature factors to unity for all light atoms and refining the occupancy of the Mg positions indicate that the 16f and 24g positions have a Mg/Na ratio of about 3/1, while the 12e position contains about equal amounts of Mg and Na. The final result for the content of the compound is then $\text{Mg}_{36}\text{Na}_{16}\text{Al}_{40}\text{Zn}_{68}$, but the ratio Mg:Na:Al should be treated with some caution. The refined Mg and Zn content (22.5 and 42.5 at.%, respectively) agree well with these from the electron microscopy determination (27 and 42 at.%, respectively). The Na content (10 at.%), however, is too low (compared to 21 at.%) and the Al content (25 at.%) too large (compared to 10 at.%). This is a combination of the inaccuracy of the chemical analysis and the difficulty in discriminating between the light elements present.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The 24 Zn/Al(1) atoms form two empty, almost regular icosahedra—one around (0,0,0) and the other around (1/2,1/2,1/2) (Fig. 1). The other atoms are located around these icosahedra to form successive shells with increasingly larger diameter. This is very well described by Bergman *et al.* (1). In the second shell Mg/Na(1) and Mg/Na(2) form a pentagonal dodecahedron and Zn/Al(2) a second icosahedron. These two polyhedra together make up a rhombic triacontahedron (Figs. 2 and 3). The fourth and outermost icosahedrally symmetric (fullerene-like) shell is formed from Zn/Al(3) and Al(4) (Figs. 4 and 5). Mg/Na(3) forms a cuboctahedron outside this cluster, breaking the icosahedral arrangement.

The greatest difference between this structure and the $\text{Mg}_{32}(\text{Al,Zn})_{49}$ phase is the Zn/Al(1) icosahedron. In the

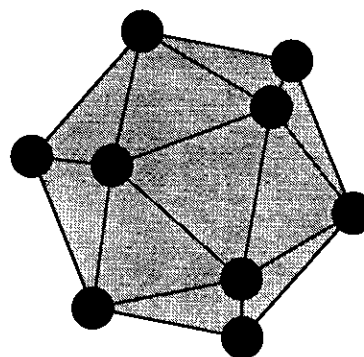


FIG. 1. The innermost, empty icosahedral shell formed by Zn/Al(1).

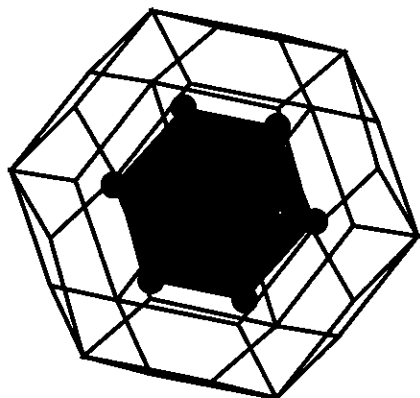


FIG. 2. The second triacontahedral shell formed by Mg/Na(1), Mg/Na(2), and Zn/Al(2) is shown as a net outside the first shell.

$Mg_{32}(Al,Zn)_{49}$ phase this is described as being filled with an Al atom having 80% occupancy in the (0,0,0) position. The electron density peak found was, however, too small for aluminum and did not appear at all when the full reflection material was used. In the title $(Mg,Na,Al)_2(Al,Zn)_3$ structure there is no question that the icosahedron is empty. The last Fourier difference map shows no peak corresponding to an atom in the (0,0,0) position. This is in agreement with Shoemaker and Shoemaker (5), who quote a private communication from Samson.

Cherkashin *et al.* (6) mentions three phases isostructural with the $Mg_{32}(Al,Zn)_{49}$ phase. These are Li_3CuAl_5 , $Li_{35}Zn_{30}Al_{35}$, and the T phase with about 33.7–42.0 at.% Mg, 12.5–6.9 at.% Cu, and 49.8–51.5 at.% Al. The investigations are made by comparison of the experimental and calculated X-ray diffraction powder photographs of the compounds. However, if the $Mg_{32}(Al,Zn)_{49}$ phase is missing the (0,0,0) atom, this might also be the case for these three compounds.

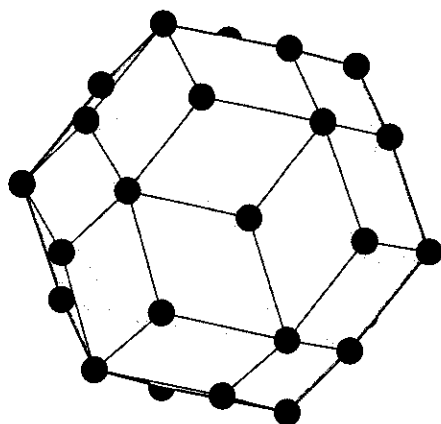


FIG. 3. The completed second shell.

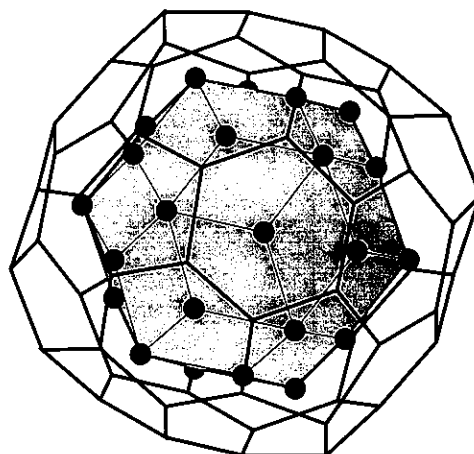


FIG. 4. The third, fullerene-like shell formed from Zn/Al(3) and Al(4) as a net outside the second shell.

The coordination number around Zn/Al(2) and Zn/Al(3) is 12—icosahedrally (cf. Table 2). This is also the case for Zn/Al(1) in the $Mg_{32}(Al,Zn)_{49}$ phase. In the title phase, however, the coordination around Zn/Al(1) is 11 atoms forming an icosahedron with one corner missing. Mg/Na(1) and Mg/Na(2) both have coordination number 16, Al(4) 14, and Mg/Na(3) 15. The center of the hexagons are always Mg/Na sites. There are two hexagons in the polygon around Al(4), three in the one around Mg/Na(3), and four in those around Mg/Na(1) and Mg/Na(2). The shortest distance in the structure is 2.538(4) Å and the longest is 3.564(8) Å. These are for Zn/Al(1)–Zn/Al(2) and Al(4)–Mg/Na(2), respectively. The Zn/Al(1) atoms in the empty icosahedron all have the same distance to the center ((0,0,0) or $(1/2,1/2,1/2)$)—2.518(3) Å. In the $Mg_{32}(Al,Zn)_{49}$ phase this distance is 2.484 Å.

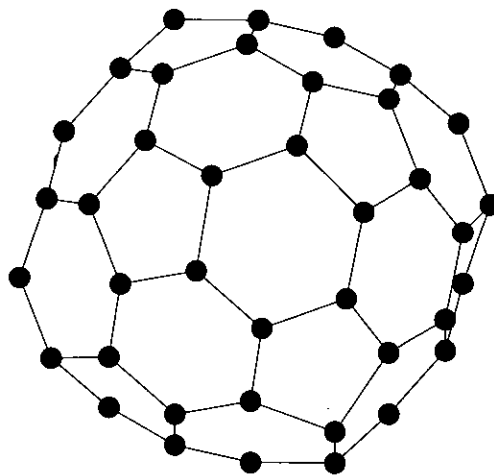


FIG. 5. The completed third shell. Note the deviations from perfect icosahedral symmetry.

TABLE 2
Bonding Distances and Coordination Polyhedra for the Atoms
in the $(Mg,Na,Al)_2(Al,Zn)_3$ Phase

Atom 1	Atom 2	Distance (Å)	Polyhedron
Mg(1)	3Zn/Al(1)	2.999(7)	Friauf polyhedron (tetracapped truncated tetrahedron)
	3Zn/Al(3)	3.096(4)	
	3Zn/Al(3)	3.117(5)	
	Mg/Na(1)	3.153(13)	
	3Zn/Al(2)	3.153(2)	
	3Mg/Na(2)	3.256(5)	
Mg/Na(2)	Zn/Al(1)	2.995(8)	Friauf polyhedron
	2Zn/Al(1)	3.009(7)	
	Mg/Na(3)	3.050(8)	
	2Zn/Al(2)	3.054(5)	
	2Zn/Al(3)	3.102(7)	
	2Zn/Al(3)	3.142(4)	
	Zn/Al(2)	3.194(8)	
	2Mg/Na(1)	3.257(5)	
	Mg/Na(2)	3.336(15)	
	2Al(4)	3.564(8)	
Al(4)	Al(4)	2.755(19)	Bicapped hexagonal antiprism
	Mg/Na(3)	2.933(14)	
	4Zn/Al(3)	2.953(5)	
	2Zn/Al(2)	2.991(5)	
	2Mg/Na(3)	3.118(10)	
	4Mg/Na(2)	3.564(8)	
Mg/Na(3)	Al(4)	2.933(14)	Tricapped truncated prism
	2Mg/Na(2)	3.050(8)	
	4Zn/Al(3)	3.070(6)	
	4Zn/Al(3)	3.101(3)	
	2Al(4)	3.119(10)	
	2Zn/Al(2)	3.260(6)	
Zn/Al(1)	Zn/Al(2)	2.538(4)	Defect icosahedron
	Zn/Al(1)	2.637(5)	
	4Zn/Al(1)	2.650(3)	
	Mg/Na(2)	2.995(8)	
	2Mg/Na(1)	3.000(7)	
	2Mg/Na(2)	3.010(7)	
Zn/Al(2)	Zn/Al(1)	2.538(4)	Icosahedron
	2Zn/Al(3)	2.633(3)	
	2Zn/Al(3)	2.689(4)	
	Al(4)	2.991(5)	
	2Mg/Na(2)	3.054(5)	
	2Mg/Na(1)	3.153(2)	
	Mg/Na(2)	3.194(8)	
	Mg/Na(3)	3.260(6)	
Zn/Al(3)	Zn/Al(2)	2.633(3)	Icosahedron
	2Zn/Al(3)	2.678(2)	
	Zn/Al(2)	2.689(4)	
	Zn/Al(3)	2.749(4)	
	Al(4)	2.953(5)	
	Mg/Na(3)	3.070(6)	
	Mg/Na(1)	3.097(5)	

TABLE 2—Continued

Atom 1	Atom 2	Distance (Å)	Polyhedron
	Mg/Na(3)	3.101(3)	
	Mg/Na(2)	3.102(7)	
	Mg/Na(1)	3.117(5)	
	Mg/Na(2)	3.142(4)	

The description of the structure in terms of successive shells of icosahedral symmetry is succinct—in particular since these ever-increasing polyhedra are quite regular, whereas local coordination in most cases is highly irregular with center-to-vertex distances varying as much as 20%. This certainly suggests a crystallization scheme based on strong interrange interactions leading to the formation of large clusters with high point-group symmetry. The outermost, fullerene-like shell in the polyhedral packing contains half the atoms in the unit cell, and this unit has been analyzed by King (7), who proved the ideal number of valence electrons to be 170. In the title compound this number is 172, leaving the ideal number very much in the range of the experimental inaccuracies.

The $Mg_{32}(Al,Zn)_{49}$ phase is a well-known quasicrystal approximant (8), and the quarternary system, in which the title compound appears, is a strong candidate for quasicrystalline phases, having an additional degree of freedom. Empty icosahedra are interesting but not a new discovery. The structures of empty icosahedra and other large empty polyhedra of, for example, B and Ga, have been studied (9, 10), and the importance of empty icosahedra in icosahedral quasicrystals has been the subject of a previous study (11).

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