

Ca₂₈Ga₁₁, a Structure with Three Types of Coordination Polyhedra around the Gallium Atoms

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Abstract. $M_r = 1889.2$, orthorhombic, $oI78$, $Imm2$, $a = 5.324$ (1), $b = 61.445$ (7), $c = 7.488$ (1) Å, $V = 2449.6$ (6) Å³, $Z = 2$, $D_x = 2.56$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 9.03$ mm⁻¹, $F(000) = 1802$, room temperature, $R = 0.051$ for 900 reflections with $F_o > 2\sigma(F_o)$. The Ca₂₈Ga₁₁ structure is characterized by three types of calcium polyhedra surrounding the gallium atoms: tricapped trigonal prisms, distorted cubes and distorted cubicosahedra (ten-vertex polyhedra similar to those found around Si in Co₂Si). The linkage of these polyhedra gives rise to columns or slabs which alternate along the greatest axis of the cell. No Ga–Ga contacts are present.

Introduction. A systematic study of the crystal chemistry of intermetallic phases formed by alkaline earths with Al and Ga led to the structure resolution of Ba₇Al₁₃ (Fornasini & Bruzzone, 1975), Ba₄Al₅ (Fornasini, 1975), Ba₁₀Ga (Fornasini & Merlo, 1979), Ba₈Ga₇, Sr₈Ga₇ and Sr₈Al₇ (Fornasini, 1983). In the Ca–Ga phase diagram (Bruzzone, 1966) seven compounds exist, three of which are on the Ca-rich side: Ca₂Ga, Ca₅Ga₂ and Ca₃Ga. The phase 'Ca₂Ga' was identified as Ca₂Ga₃ with Cr₅B₃ structure (Bruzzone, Franceschi & Merlo, 1978). This paper deals with the structure determination of Ca₂₈Ga₁₁, reported as 'Ca₃Ga₂' in the corresponding system.

Experimental. Ca₂₈Ga₁₁ prepared from Ca (99.9 wt%, Fluka, Switzerland) and Ga (99.999 wt%, Koch-Light, England) by melting in sealed Fe crucible and slowly cooling. Parallelepipedal single crystal 0.03 × 0.10 × 0.10 mm mounted on Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice constants determined by least squares over 25 diffractometer-measured reflections in the range $20 < \theta < 24^\circ$; data collection in ω - θ scan mode up to $\sin\theta/\lambda = 0.65$ Å⁻¹ with $0 \leq h \leq 6$, $0 \leq k \leq 78$, $-9 \leq l \leq 9$. Spherical and semiempirical absorption correction by azimuthal scan data of two top reflections, ratio between max. and min. transmission factors 1.76. No significant variation in intensity of standard reflections during data collection. 3101 measured reflections, 1667 independent with $R_{int} = 0.091$, 900 with $F_o > 2\sigma(F_o)$ used in refinement. Orthorhombic

symmetry, presence of hkl only if $h + k + l = 2n$, possible space groups $I222$, $I2_12_12_1$, $Imm2$ and $Immm$. Although statistical tests gave indications of hypercentric distribution, structure resolution was made in $Imm2$, taking into account both geometrical considerations and observed intensity values of the 00l reflections. Structure solved using direct methods; 11 peaks identified, six corresponding to Ga and five to Ca atoms; remaining ten Ca atoms localized by difference Fourier synthesis. Anisotropic refinement to 120 parameters based on F 's, with $R = 0.051$, $wR = 0.056$, $S = 1.1$, $w = 1/[\sigma^2(F_o) + 0.00107F_o^2]$; max. shift to e.s.d. 0.4, max. and min. heights in final difference Fourier synthesis 1.0 and -1.3 e Å⁻³, respectively. Since changing the sign of the positional parameters gave no improvement in the final R value, the original configuration was retained. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); programs used: *MULTAN80* (Main *et al.*, 1980) and *SHELX76* (Sheldrick, 1976). A powder pattern of Ca₂₈Ga₁₁ taken with Cu $K\alpha$ radiation was indexed with the aid of *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977) and confirmed the crystal and the bulk material to have the same composition and structure.

Atomic coordinates and thermal parameters are given in Table 1.*

Discussion. A drawing of Ca₂₈Ga₁₁ projected along [100] is shown in Fig. 1. It is a two-layered structure characterized by three types of calcium polyhedra surrounding the gallium atoms: tricapped trigonal prisms, distorted cubes (shaded) and ten-vertex polyhedra (stippled). A complicated linkage among these polyhedra occurs, forming columns or slabs which alternate along the greatest axis of the cell. Columns of trigonal prisms around Ga(1) and Ga(5) running in the [100] direction and sharing a triangular face are

* Lists of structure factors, anisotropic thermal parameters and distances involving the calcium atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42645 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

connected together, as $2/3$ of the atoms at the vertices of each prism form waist contacts with Ga centering the nearest prism. These trigonal prisms are further joined to cubes through the sharing of vertices. Two distinct kinds of distorted cubes exist in the structure. One of these, centered by Ga(3), forms slabs where each cube shares edges with six other cubes. The other kind, centered by Ga(2) and connected *via* edges with two cubes along the short axis, forms columns that are not linked together, where each cube shares edges with four ten-vertex polyhedra. Finally, pairs of ten-vertex polyhedra around Ga(4) joined by a face give rise to columns along [100] by sharing faces, and leave room in between for trigonal prisms filled by Ga(6).

These coordinations of the gallium atoms are not unusual, as they occur in several Ga-containing intermetallic phases (Pearson, 1967). A ten-vertex polyhedron very similar to that around Ga(4) is recognizable in Yb_2Ga (Palenzona & Cirafici, 1979) and Pr_2Ga (Cirafici & Franceschi, 1979), both belonging to the Co_2Si type, a branch of the PbCl_2 structure. It is present with other Ga-centered polyhedra in Pd_5Ga_3 (Rh_5Ge_3 type) with cubes and in Pd_4Ga_2 (Khalaff & Schubert, 1974) with icosahedra. This polyhedron, which is often not well identified in the literature, can be considered as intermediate between a tricapped trigonal prism (nine-vertex polyhedron) and a cubicosahedron (ten-vertex polyhedron consisting of one half of a cube and one half of an icosahedron), and we proposed to call it 'distorted cubicosahedron'. On the other hand, in Mg_2Ga (Frank & Schubert, 1970) the Ga atoms are all surrounded by nine Mg atoms forming tricapped trigonal prisms, while Mg_5Ga_2 and Ta_5Ga_3 (W_5Si_3 type) give examples of structures containing Ga-centered cubicosahedra.

In Table 2, for the sake of brevity, only the interatomic distances involving gallium atoms are reported, while those around calcium atoms have been deposited. Distances up to $d/\sum r = 1.20$, where d is the observed distance and $\sum r$ the appropriate sum of the metallic radii after Teatum, Gschneidner & Waber (1968), were taken into account, as this value represents a common limit suitable to define the coordination polyhedron around each atom. Since the distances are spread over a large range, from 3.02 to

3.89 Å for Ga—Ca and from 3.44 to 4.62 Å for Ca—Ca contacts, the coordination polyhedra are often distorted.

Table 1. Atomic coordinates and thermal parameters for $\text{Ca}_{28}\text{Ga}_{11}$

$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. E.s.d.'s are given in parentheses.

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} (Å ²) |
|----------------------|----------|------------|-----------|-----------------------------------|
| Ca(1) 4(<i>d</i>) | 0 | 0.3626 (2) | 0.535 (2) | 0.021 (4) |
| Ca(2) 4(<i>d</i>) | 0 | 0.4564 (2) | 0.126 (2) | 0.018 (4) |
| Ca(3) 4(<i>d</i>) | 0 | 0.1825 (2) | 0.094 (2) | 0.018 (3) |
| Ca(4) 4(<i>d</i>) | 0 | 0.2759 (2) | 0.528 (2) | 0.016 (3) |
| Ca(5) 4(<i>d</i>) | 0 | 0.0829 (2) | 0.611 (2) | 0.030 (4) |
| Ca(6) 4(<i>d</i>) | 0 | 0.1467 (2) | 0.716 (2) | 0.029 (4) |
| Ca(7) 4(<i>d</i>) | 0 | 0.4401 (2) | 0.680 (2) | 0.018 (3) |
| Ca(8) 4(<i>d</i>) | 0 | 0.3832 (3) | 0.986 (2) | 0.032 (4) |
| Ca(9) 4(<i>d</i>) | 0 | 0.2620 (2) | 0.0* | 0.020 (3) |
| Ca(10) 4(<i>d</i>) | 0 | 0.0300 (3) | 0.958 (2) | 0.022 (3) |
| Ca(11) 4(<i>d</i>) | 0 | 0.2058 (3) | 0.676 (2) | 0.028 (4) |
| Ca(12) 4(<i>d</i>) | 0 | 0.0966 (3) | 0.083 (2) | 0.027 (4) |
| Ca(13) 4(<i>d</i>) | 0 | 0.3240 (3) | 0.921 (2) | 0.030 (4) |
| Ca(14) 2(<i>b</i>) | 0 | 0.5 | 0.746 (2) | 0.022 (5) |
| Ca(15) 2(<i>a</i>) | 0 | 0 | 0.550 (3) | 0.023 (5) |
| Ga(1) 4(<i>d</i>) | 0 | 0.1395 (1) | 0.307 (2) | 0.016 (2) |
| Ga(2) 4(<i>d</i>) | 0 | 0.4092 (2) | 0.338 (2) | 0.021 (1) |
| Ga(3) 4(<i>d</i>) | 0 | 0.2271 (1) | 0.293 (2) | 0.025 (2) |
| Ga(4) 4(<i>d</i>) | 0 | 0.0440 (1) | 0.358 (2) | 0.017 (2) |
| Ga(5) 4(<i>d</i>) | 0 | 0.3196 (1) | 0.323 (2) | 0.027 (3) |
| Ga(6) 2(<i>b</i>) | 0 | 0.5 | 0.332 (2) | 0.008 (3) |

* Arbitrarily fixed.

Table 2. Interatomic distances (Å) in $\text{Ca}_{28}\text{Ga}_{11}$ involving the Ga atoms

| | | | |
|--------------|-----------|--------------|-----------|
| Ga(1)—Ca(3) | 3.09 (2) | Ga(2)—Ca(8) | 3.08 (2) |
| —Ca(6) | 3.09 (2) | —Ca(7) | 3.19 (2) |
| —Ca(12) | 3.12 (2) | —2Ca(5) | 3.20 (1) |
| —2Ca(8) | 3.29 (1)* | —Ca(1) | 3.22 (2) |
| —2Ca(1) | 3.35 (1)* | —2Ca(12) | 3.25 (1) |
| —2Ca(13) | 3.58 (1)* | —Ca(2) | 3.31 (2) |
| Ga(3)—Ca(9) | 3.07 (1) | Ga(4)—Ca(5) | 3.05 (2) |
| —Ca(3) | 3.12 (2) | —Ca(15) | 3.06 (1) |
| —2Ca(9) | 3.15 (1) | —Ca(10) | 3.12 (2) |
| —Ca(11) | 3.15 (2) | —2Ca(7) | 3.13 (1) |
| —2Ca(4) | 3.33 (1) | —2Ca(2) | 3.33 (1) |
| —Ca(4) | 3.48 (2) | —Ca(12) | 3.83 (2) |
| | | —2Ca(14) | 3.89 (1) |
| Ga(5)—Ca(13) | 3.02 (2) | Ga(6)—2Ca(2) | 3.09 (1) |
| —Ca(1) | 3.08 (2) | —Ca(14) | 3.10 (2) |
| —Ca(4) | 3.09 (2) | —4Ca(10) | 3.37 (1)* |
| —2Ca(11) | 3.28 (1)* | —2Ca(15) | 3.40 (2)* |
| —2Ca(3) | 3.35 (1)* | | |
| —2Ca(6) | 3.47 (1)* | | |

* Trigonal prism.

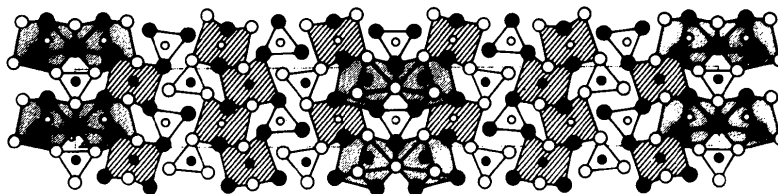


Fig. 1. Projection of the $\text{Ca}_{28}\text{Ga}_{11}$ structure along [100]. Large circles: Ca; small circles: Ga. Open circles represent atoms at $x = 0$ and full circles atoms at $x = \frac{1}{2}$. The polyhedra around gallium, namely trigonal prisms, distorted cubes (shaded) and ten-vertex polyhedra ('distorted cubicosahedra', stippled) are outlined.

The ratios of the height to base in the trigonal prisms around Ga(1), Ga(5) and Ga(6) show values much higher than unity (elongated prisms), so that the distances of Ga to Ca at the vertices of the prism are larger than the waist contacts.

The calcium atoms, distributed over fifteen site sets, have polyhedra that are identical or closely related to each other, with coordination numbers from 11 to 15. For example, Ca(1) and Ca(3) are surrounded by 4Ga + 9Ca in the same manner, while Ca(15) is lacking a Ca atom; an identical polyhedron formed by 4Ga + 10Ca is found around Ca(2), Ca(4) and Ca(12); the same applies to Ca(6), Ca(10) and Ca(13) coordinated with 3Ga + 10Ca, and to Ca(8) and Ca(11) coordinated with 3Ga + 11Ca.

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Structure of Hexakis(1-methylimidazole)cadmium(II) Nitrate and its ¹¹³Cd Solution and Solid-State NMR Spectrum

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Abstract. [Cd(C₄H₆N₂)₆](NO₃)₂, *M_r* = 729.04, monoclinic, *P*2₁/*n*, *a* = 11.335 (3), *b* = 7.726 (1), *c* = 19.059 (3) Å, β = 95.60 (2)°, *V* = 1661 (1) Å³, *Z* = 2, *D_m* = 1.47 (2), *D_x* = 1.46 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 7.18 cm⁻¹, *F*(000) = 748, *T* ~ 293 K, *R* = 0.051 for 3060 observed reflections. The structure may be described as isolated hexakis(1-methylimidazole)Cd^{II} ions and disordered nitrate ions separated by ordinary van der Waals distances. The coordination polyhedron of Cd^{II} may be described as a slightly tetragonally compressed octahedron of N atoms from the non-methylated N atoms of the imidazoles. The Cd atom is on a center of symmetry

with Cd–N distances of 2.366 (6), 2.362 (6) and 2.331 (5) Å. The solid-state cross-polarization/magic-angle spinning, CP/MAS, ¹¹³Cd NMR signal is observed at 230 p.p.m. and the methanol solution signal is observed at 177 p.p.m., both deshielded relative to the 0.1 mol dm⁻³ Cd(ClO₄)₂ in D₂O standard.

Introduction. ¹¹³Cd NMR has been shown to be a versatile probe of the metal-ion site in compounds ranging from Cd-containing organometallics to Zn, Ca enzymes in which the naturally occurring metal has been replaced by Cd. In some of these enzymes the chemical shifts are such that few, if any, model compounds are known. For example, the values found for calmodulin and troponin C are at ~–100 p.p.m. relative to the 0.1 *M* Cd(ClO₄)₂ in D₂O standard. A

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