

if \mathbf{R}_p and \mathbf{R}_q correspond to symmetry operators of order two, E_5 and E_6 are centrosymmetric reflexions. In fact, if \mathbf{R}_m is a rotation matrix for which $\mathbf{R}_p \mathbf{R}_m = \mathbf{R}_q$ (then $\mathbf{R}_q \mathbf{R}_m = \mathbf{R}_p$ also), we have

$$\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)\mathbf{R}_m = \mathbf{h}(\mathbf{R}_q - \mathbf{R}_p) = -\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q),$$

which in terms of phases gives, because of (4),

$$\varphi_{\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)\mathbf{R}_m} = \varphi_{\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)} - 2\pi\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)\mathbf{T}_m = -\varphi_{\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)}. \quad (76)$$

From (76),

$$\varphi_{\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)} = \pi\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)\mathbf{T}_m$$

is easily obtained, and gives the restricted phase values for $\varphi_{\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)}$. If E_5 and E_6 are centrosymmetric reflexions, (60) no longer holds; in fact, the modified Bessel function of zero order involving Z_5 and Z_6 has to be replaced by hyperbolic cosines of suitable arguments and a suitable B' value has to replace B . Furthermore, the problem of generalizing (60) to cases in which more $(\mathbf{R}_p, \mathbf{R}_q)$ pairs exist, which give rise to the crystallographically independent generalized solutions $(\mathbf{h}_1, \mathbf{h}_2)$ of system (5), needs to be solved. All these theoretical aspects are discussed elsewhere (Giacovazzo, 1979b) where a general distribution function is given, which in several cases can be considered a useful approximation of the 'true' distribution of Φ .

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The Elongated Rhombic Dodecahedron in Alloy Structures

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Abstract

With the space-filling elongated dodecahedron or its truncated form as a coordination polyhedron for larger atoms, structures like BaAl_4 , CeMg_2Si_2 , BaHg_{11} and ThMn_{12} can be accurately described.

Introduction

When an alloy contains atoms of very different sizes, it is often useful to describe the structure by a polyhedron

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8. Concluding remarks

A theory has been described which is capable of deriving for any space group the value of a two-phase seminvariant of first rank, $\Phi = \varphi_u + \varphi_v$, given all or some of the magnitudes belonging to the first phasing shell of Φ . The probabilistic formulae are derived both by using the exponential forms of the characteristic functions of the joint probability distributions studied and *via* their Gram–Charlier expansion. A general algebra for two-phase seminvariants of first rank has been developed which makes their estimation easier in the automatic procedures for phase solution.

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of the smaller atoms coordinating the larger atom. An example of this is NaZn_{13} (Shoemaker, Marsh, Ewing & Pauling, 1952). Zn atoms are at the corners of a regular snub cube which is centred by a Na atom, and such snub cubes form the structure by sharing square faces. When dissecting various alloy structures we came across some that could be described by the so-called elongated dodecahedron, one of Federov's five space-filling polyhedra.

The elongated dodecahedron is a polyhedron with 18 corners. It is obtained if the rhombic dodecahedron is elongated along one of its fourfold axes (Fig. 1). The

hexagons formed are not regular as they contain the rhombic polygon angles. There are three different centre–corner distances of $C-(1) = 1.2583d$, $C-(2) = 1.3518d$ and $C-(3) = 1.6546d$, where d is the edge and C the centre and (1), (2) and (3) mark the corners of the polyhedron. Of the structures described below, $BaAl_4$ has this polyhedron, while $CeMg_2Si_2$, $BaHg_{11}$ and $ThMn_{12}$ are better described with a truncated form, obtained by the removal of corner atom (3) (Fig. 2). In fact, the square faces of the truncated dodecahedra in $CeMg_2Si_2$ and $ThMn_{12}$ are capped with the central atoms in two adjacent truncated dodecahedra, which means that complete elongated dodecahedra are interpenetrating. Nevertheless, it is easier to describe these two structure types with the truncated elongated dodecahedron.

$BaAl_4$

The structure type represented by $BaAl_4$ is rather common. The structure is tetragonal with $a = 4.530$, $c = 11.14$ Å. The space group is $I4/mmm$, with two Ba in $2(a)$, four Al in $4(d)$ and four Al in $4(e)$ with $z = 0.380$ (Andress & Alberti, 1935). The structure should be common for ternary systems, which is also the case.

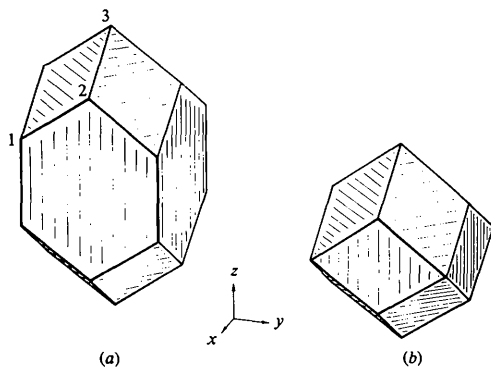


Fig. 1. (a) The elongated rhombic dodecahedron. (b) An ordinary rhombic dodecahedron is shown.

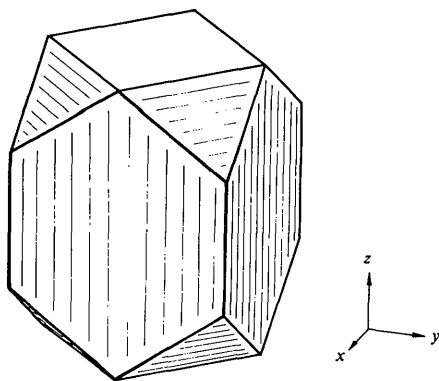


Fig. 2. The truncated form of the elongated rhombic dodecahedron.

Several rare-earth transition-metal silicides have this structure, e.g. $ThCr_2Si_2$ and $ThMn_2Si_2$ (Mn, Cr and Si are similar in size).

The structure is shown in Fig. 3, projected along a , and it can be seen how the elongated dodecahedra have the same orientation and fill space. The polyhedra share hexagons and rhombs and the coordination number for Ba is 22 (18 Al and 4 Ba), the central Ba atoms in four adjacent elongated dodecahedra capping the hexagonal faces.

Calculated cell parameters for a structure built up of ideal elongated dodecahedra are:

$$a = \frac{2d\sqrt{6}}{3} = 1.633d$$

$$c = 2d \left(1 + \frac{2\sqrt{3}}{3} \right) = 4.309d,$$

where d is the edge of the polyhedron. Furthermore:

$$c/a = 2.64$$

and the parameter of position 4(e) is

$$z = \frac{4\sqrt{3} + 3}{12 + 8\sqrt{3}} = 0.384.$$

The observed parameters are given in Table 1.

Table 1. Observed parameters

	c/a	z
$BaAl_4$	2.46	0.380
$ThCr_2Si_2$	2.62	0.374
$ThMn_2Si_2$	2.61	0.386.

$CeMg_2Si_2$

This tetragonal structure, with $a = 4.35$, $c = 5.76$ Å, $P4/mmm$ (Zmii & Gladyshevskii, 1970), is obtained by a

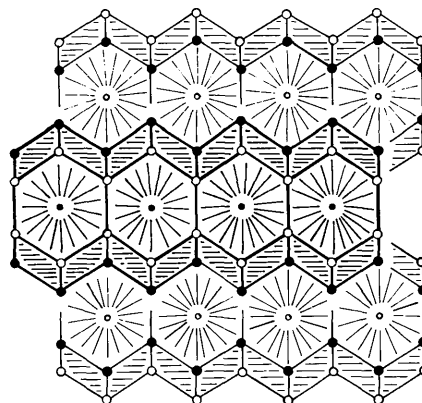


Fig. 3. The structure of $BaAl_4$ seen along a .

slip operation in the BaAl_4 structure, which is appreciated when the two structures are compared (Figs. 3 and 4). The slip operation transforms the original elongated dodecahedra to truncated ones, and makes the latter share hexagonal and square faces. For an ideal truncated elongated dodecahedron:

$$a = 2d \frac{\sqrt{2}}{\sqrt{3}}; \quad c = d + \frac{2d}{\sqrt{3}}; \quad c/a = 1.32;$$

$$z = \frac{a}{2c} = 0.232.$$

Observed parameters, $c/a = 1.356$ and $z = 0.223$, are in good agreement.

BaHg_{11}

This rather common structure type can be constructed from truncated elongated rhombic dodecahedra. In the cubic structure these polyhedra have three different orientations (Fig. 5). The polyhedra share triangular faces (half rhombs) and surround a large cave with square windows (Fig. 6).

The arrangement of these truncated polyhedra also creates empty cubes and if these had been centred by Hg perfect elongated rhombic dodecahedra would have been the building unit. The framework of truncated elongated dodecahedra is interpenetrated by a square-antiprism structure, similar to that present in the Cr_{23}C_6 structure type. A building block consists of six square antiprisms (empty) of Hg-sharing corners around a Hg-centred cubo-octahedron, and such building blocks form the structure with square antiprisms sharing the remaining square faces (Fig. 7).

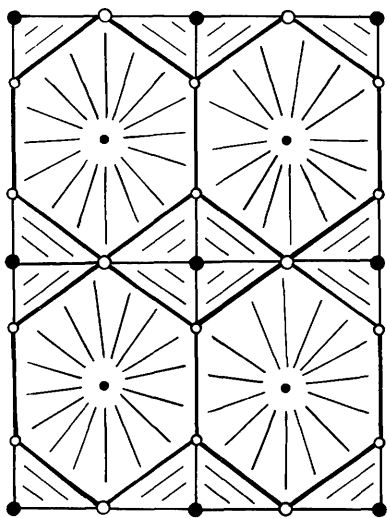


Fig. 4. The structure of CeMg_2Si_2 , seen along a.

These common square faces are identical to the square windows formed by the elongated rhombic dodecahedra. The cubic structure, with $a = 9.62 \text{ \AA}$, has the space group $Pm\bar{3}m$ and there are four different Hg positions. Hg(1) and Hg(2) form the truncated elongated dodecahedron structure, while Hg(2) and Hg(3) form the square-antiprism structure, with Hg(4) at the centre of the cubo-octahedron. Calculated parameters for the structures are given below.

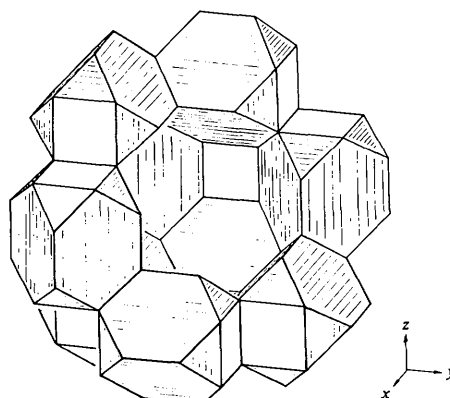


Fig. 5. A clinographic projection of the dodecahedral framework in BaHg_{11} .

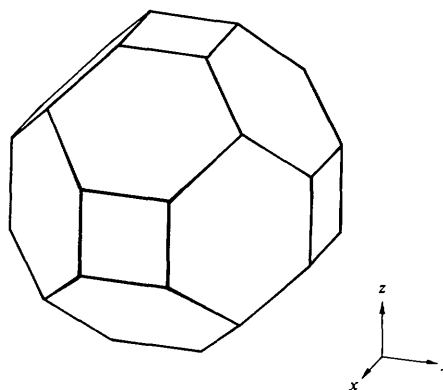


Fig. 6. The cave created by the truncated elongated dodecahedra in BaHg_{11} .

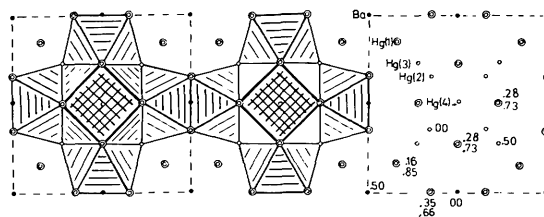


Fig. 7. The interpenetrating framework of square antiprisms in BaHg_{11} .

(1) Elongated dodecahedron structure:

$$a = d \left(\frac{4 + \sqrt{3}}{\sqrt{3}} \right) = 3.31d;$$

$$x_1 = \frac{d}{2a} = 0.151;$$

$$x_2 = \frac{a-d}{2a} = 0.349.$$

(2) Square antiprism structure:

$$a = d \left[\sqrt{2} + 2 \left(\frac{\sqrt{2}}{2} \right)^{1/2} \right] = 3.10d;$$

$$x_2 = \frac{a-d}{2a} = 0.338;$$

$$x_3 = \frac{a-d\sqrt{2}}{2a} = 0.272.$$

The observed parameters are in good agreement with these: Hg(1), $x = 0.155$, Hg(2), $x = 0.345$, and Hg(3), $x = 0.275$ (Peyronel, 1952).

ThMn₁₂

This structure is tetragonal, $a = 8.74$, $c = 4.95$ Å, space group $I4/mmm$, with eight Mn in $8(i)$, $x_i = 0.361$ and eight Mn in $8(j)$, $x_j = 0.277$ (Florio, Rundle & Snow, 1952). The structure has been compared with the CaZn_5 structure, but here we describe a relation with the Cr_3Si structure (Fig. 8). The central tetrahedron in every second *Tetraederstern* is substituted by Th atoms, and every second of the remaining *Tetraedersterns* is rotated 90° . These operations give the structure of ThMn_{12} , the Th atoms

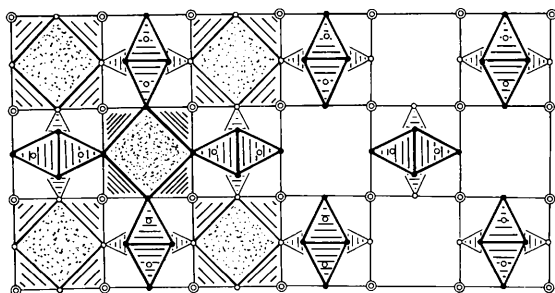


Fig. 8. The structure of ThMn_{12} seen along c . To the right the remaining parts of the Cr_3Si structure are shown. The central *Tetraederstern* is rotated 90° from the Cr_3Si position.

being situated in columns of truncated elongated dodecahedra. The columns are corner-connected to each other and to the remaining *Tetraedersterns*. Calculated parameters are $x_i = 0.375$ and $x_j = 0.250$; c/a calculated from a Cr_3Si structure is 0.50, while it is 0.66 for a structure with ideal elongated rhombic dodecahedra. Exact intergrowth is not possible between the two structures and the observed structure is between the two ideal ones, having $c/a = 0.57$.

Giant unit cells which probably contain elongated rhombic dodecahedra

ThMo_2Si_2 , with $a = 4.01$, $c = 87.5$ Å, was reported to have a pseudo cell of the BaAl_4 structure type (Ban & Sikirica, 1965), with c eight or nine times the c in BaAl_4 . Above we pointed out that a simple slip mechanism transformed the BaAl_4 into the CeMg_2Si_2 structure, and, if such faults occurred regularly, multiples of c would result.

$\text{CeMg}_{12}(\text{I})$ is of the ThMn_{12} type with $a = 10.33$, $c = 5.96$ Å. $\text{CeMg}_{12}(\text{II})$ is also reported to be tetragonal, with $a = 10.33$, $c = 77.5$ Å (Johnson, Smith, Wood & Cramer, 1964). The c axis of $\text{CeMg}_{12}(\text{II})$ is nearly 13 times that of $\text{CeMg}_{12}(\text{I})$. The structure was described as a stacking of 13 tetragonal ThMn_{12} -type cells with a slip of $a/2$ occurring at $z = 4/26, 10/26, 17/26$ and $23/26$. This slip operation can be understood from Fig. 8. At the z values mentioned, the columns of truncated elongated dodecahedra are interrupted, and new columns start to run parallel to the first ones, but in the x, y position of the *Tetraedersterns*. If other slip combinations occur they could be detected by high-resolution electron microscopy; in this case, with Ce—Ce distances of ~ 6 Å, the lattice-image method could be used for direct structure determination. Analogously, ThMo_2Si_2 could be studied with the same technique.

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