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Stefan Brühne, Eckhard Uhrig, Guido Kreiner, Wolf Assmus. Local atomic 3D real space structural analysis of icosahedral Mg-Zn-RE (RE = Y and Ho) alloys: Strategy, method and models. *Philosophical Magazine*, 2005, 86 (03-05), pp.463-468. 10.1080/14786430500333331 . hal-00513618

HAL Id: hal-00513618

<https://hal.science/hal-00513618>

Submitted on 1 Sep 2010

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Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-05-May-0141.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	16-Aug-2005
Complete List of Authors:	Brühne, Stefan; Universität Frankfurt, Physikalisches Institut Uhrig, Eckhard; Universität Frankfurt, Physikalisches Institut Kreiner, Guido; Max-Planck-Institut für Chemische Physik fester Stoffe Assmus, Wolf; Universität Frankfurt, Physikalisches Institut
Keywords:	X-ray diffraction, structure analysis, radial distribution functions, quasicrystals
Keywords (user supplied):	



Local atomic 3D real space structural analysis of icosahedral Mg-Zn-RE (RE = Y and Ho) alloys: Strategy, method and models

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The local structure of any condensed matter is accessible *via* an atomic pair distribution function (PDF) analysis. Here, the local atomic structure of the well-ordered quasicrystals *fcc*-Mg₂₅Y₁₁Zn₆₄, *fcc*-Ho₉Mg₂₆Zn₆₅ and *si*-Ho₁₁Mg₁₅Zn₇₄ have been investigated by PDFs obtained from in-house X-ray and synchrotron powder data. Least-squares refinements using periodic 1/1- and 2/1-approximants as models for the local atomic structure have been performed. They reveal predominantly Frank-Kasper-type coordination polyhedra. The basic building block is a Bergman cluster of about 100 atoms with 14 Å diameter. RE₈ cubes of edge length 5.4 Å are part of the cluster occupying pentagon dodecahedral positions. The cluster connection scheme follows in general that of Henley's Canonical Cell Tiling (CCT). However, according to our results, overlapping clusters are likely to be present in the quasicrystalline structure. Thus interpenetration seems to be a general feature for clusters in quasicrystals which complicates the ongoing discussion on their nature.

1. Introduction

Among the known icosahedral (*i*) quasicrystals there exist well-ordered phases in the system Mg-Zn-RE (RE = Y, Dy, Er, Gd, Ho, Tb) [1, 2]. A strategy to circumvent the problems which are posed to their X-ray structure analysis by the absence of 3D periodicity is to use periodic approximants as models representing the *local* atomic structure. Due the lack of suitable approximants in the systems with rare earth metals the Fibonacci approximants of icosahedral phases of the Mg-Zn-X (X = Al, Ga) systems as listed in table 1 are promising candidates to describe the local atomic structure. In case of the cubic *p/q*-approximants the unit cell parameters *a*(3D) are related to the 6D primitive hypercubic unit cell parameter *a*(6D) by the following equation with $\tau = (\sqrt{5} + 1)/2$:

$$a(3D) = 2 a(6D) (p\tau + q) / \sqrt{2 + \tau} \quad (1).$$

Their periodic structures can be understood in terms of the Canonical Cell Tiling (CCT) [3] with only two kinds of edges and four different types of Canonical Cells. The edges are called *b*-bond ($b \approx 14$ Å) and *c*-bond ($c = \sqrt{3}/2 b \approx 12$ Å) and the cells A, B, C and D, respectively. Here, the Bergman cluster of approx. 14 Å (*b*) diameter occupy the nodes of the CCT. In many cases measurements of physical properties have shown that quasicrystals and higher approximants behave similarly. Therefore, the crystal structure of a 2/1-approximant

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should be an adequate starting point to describe the local structure up to 30 Å of the respective quasicrystal.

Table 1 Fibonacci approximants of icosahedral phases in the Mg-Zn-*X* (*X* = Al, Ga) systems as models for the local atomic structure of quasicrystals in the Mg-Zn-*RE* (*RE* = Y, Dy, Er, Gd, Ho, Tb) systems.

<i>p/q</i>	space group	$\sim a(3D)/\text{Å}$	Pearson symbol	example	CCT cell content	ref.
1/0	<i>Pm-3</i>	9	cP39	Mg-Zn	–	[4]
1/1	<i>Im-3</i>	14	cI160	Al-Mg-Zn	12A	[5]
2/1	<i>Pa-3</i>	23	cP680	Al-Mg-Zn	24A 8B 8C	[6]
3/2-2/1-2/1	<i>Cmc2₁</i>	37-23-23	oC1108	Ga-Mg-Zn	24A 12B 12C 4D	[7]
3/2	<i>Pa-3</i>	37	cP2888	Ga-Mg-Zn	72A 32B 32C 8D	[7]

2. Method

The local structure of materials is accessible from powder diffraction data using the normalized scattering intensity $S(Q)$ with $Q = 4\pi \sin(\theta)/\lambda$ [8]. The atomic pair distribution function (PDF) in form of the reduced pair distribution function $G(r)$ is given by the following sine Fourier transform of $S(Q)$:

$$G_{\text{exp}}(r) = 2/\pi \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ \quad (2).$$

A function $G_{\text{calc}}(r)$ can be calculated from suitable models with the atomic scattering factors f for all pairs of atoms (*i, j*), $\langle f \rangle$ as the average scattering factor and ρ_0 as the average electron density:

$$G_{\text{calc}}(r) = 1/r \sum_i \sum_j [f_i f_j / \langle f \rangle^2 \delta(r - r_{ij})] - 4\pi r \rho_0 \quad (3)$$

Least-squares refinement of the model using PDFFIT [9] minimizes the residual R for N data points of the PDF:

$$R = \sqrt{\left\{ \sum_{i=1}^N [G_{\text{obs}}(r_i) - G_{\text{calc}}(r_i)]^2 / \sum_{i=1}^N G_{\text{obs}}^2(r_i) \right\}} \quad (4).$$

Here, we report on results of investigations on *fci*-Mg₂₅Y₁₁Zn₆₄, *fci*-Ho₉Mg₂₆Zn₆₅ and *si*-Ho₁₁Mg₁₅Zn₇₄ using in-house diffractometer ($Q_{\text{max}} = 13.5 \text{ Å}^{-1}$) and synchrotron diffractometer data ($Q_{\text{max}} = 30 \text{ Å}^{-1}$) [10-13]. The starting models have been obtained by taking crystal-chemical considerations into account. In the crystal structures of the Mg-Zn-*X* approximants of 1/1 and 2/1 type Al or Ga have been replaced by Zn and the Mg atoms partially by *RE* atoms. The $G(r)$ have been refined by the least-squares method optimizing the scale factor, the positional parameters and the atomic displacement factors.

3. Results

The experimental and the calculated PDF's are in good agreement up to 17 Å or 27 Å, respectively [10-13]. The data fitting using a 2/1-approximant as a model for the local structure is as expected much better than that of the 1/1-approximant. Due to its large cell

1
2
3 volume the 2/1-approximant allows the characterization of the medium range icosahedral
4 bond-orientation order (cluster to cluster packing) whereas the 1/1-approximant is restricted to
5 describe the short range order inside of the clusters.
6

7 The coordination type polyhedra of the atoms are predominant of Frank-Kasper-type. Zn
8 atoms are surrounded by 11, 12, 13 or 14 nearest neighbours. The coordination numbers (CN)
9 of Mg are 14, 15 or 16 and that of the *RE* atoms always 16. The fundamental structural unit is
10 a Bergman cluster of 104 or 105 atoms. Its concentric shell architecture is conveniently [7]
11 described by the following sequence with details are given in table 2. Centre: α^0 (1 atom or
12 vacancy, CN 12); 1st shell: α^1 (12 atoms: inner icosahedron, CN 11 or 12); 2nd shell: β (20
13 atoms: pentagon dodecahedron, CN 16) and α^2 (12 atoms: outer icosahedron, CN 12), 3rd
14 shell: α^3 and γ (60 atoms: soccer ball, CN 12 and 14). The 32 atoms of the 2nd shell together
15 with the inner icosahedron combine to a cluster which is known as the Pauling
16 triacontahedron. The remaining atoms are glue atoms at certain δ positions with CN = 13, 15
17 and 16. RE_8 cubes of edge length 5.4 Å are inscribed in the pentagon dodecahedral shell (8
18 out of 20 β atoms). All atoms are arranged to achieve an almost tetrahedrally close packing
19 (tcp). In the crystal structure of higher approximants the RE_8 cubes of different pentagon
20 dodecahedra are tilted with respect to each other in adjacent clusters. In the respective
21 quasicrystalline structure a weighted number of cube orientations would allow for the overall
22 icosahedral symmetry *m*-3-5. A pentagon dodecahedral shell with an inscribed RE_8 cube and a
23 decoration of a C-cell by RE_8 cubes is shown in figure 1.
24

25 In case of the *fci* phases with about 65 at-% Zn the centre of the Bergman clusters are
26 empty, *i.e.* there is a constitutional vacancy [11, 12]. However, in the quasicrystal structure of
27 *si*-Ho₁₁Mg₁₅Zn₇₄ [10] with its higher zinc content the centre is occupied by Zn atoms. So far,
28 no further discussion of the difference between 6D *F* or *P* type quasicrystals based on the
29 present results is possible. The Bergman clusters occupy the nodes of a CCT and share
30 common edges (two shared γ -atoms define a perpendicular *b*-bond) and hexagonal faces (*c*-
31 bond normal to six shared α^3 atoms). This is depicted in figure 2. For details on the cluster
32 packing and the labelling scheme refer to [7, 11].
33

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38 **Table 2.** The distribution of the elements among special positions for *i*-Mg-Zn-*RE* phases; the special positions
39 are labelled by small greek letters; if applicable the residual *R* (PDF real space refinement) is given for the 1/1-
40 and the 2/1-approximants used as models for the local atomic structure; □ denotes a vacancy.
41

<i>i</i> -phase	<i>fci</i> -Ho ₉ Mg ₂₆ Zn ₆₅		<i>fci</i> -Mg ₂₅ Y ₁₁ Zn ₆₄	<i>si</i> -Ho ₁₁ Mg ₁₅ Zn ₇₄
a(6D)/Å	2 × 5.18(3)		2 × 5.19(2)	5.144(3)
reference	[11]		[12]	[10]
$Q_{\max}/\text{Å}^{-1}$	13.5		30.0	13.5
approximant	1/1	2/1	2/1	1/1
<i>R</i> / %	21.8	12.9	13.7	20.4
site label			chemical decoration	
α^0	□	□	□	Zn
α^1	Zn	Zn	Zn	Zn
β	Mg, Ho	Mg, Ho	Mg, Y	Mg, Ho
α^2	Zn	Zn	Zn	Zn
α^3	Zn	Zn	Zn	Zn
γ	Mg, Zn	Mg, Zn	Zn	Zn
δ	Mg, Ho	Mg, Ho, Zn	Mg, Y, Zn	Zn

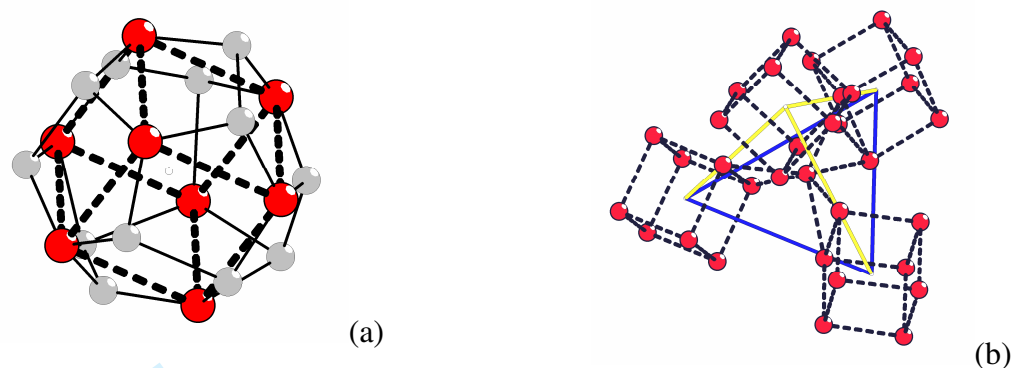


Figure 1. a) 20 β atoms of the 2nd shell form a pentagon dodecahedron consisting of 12 Mg (grey) and 8 RE (dark) atoms. The latter form an inscribed cube, thus the local symmetry of this shell is $m-3$. (b) Partial structure of RE_8 cubes surrounding the CCT nodes of a C-cell showing four out of five possible different orientations in the respective quasicrystal structure; the cubes are interconnected via a RE atom at a central δ position; dotted lines represent $RE-RE$ distances of approx. 5.4 Å.

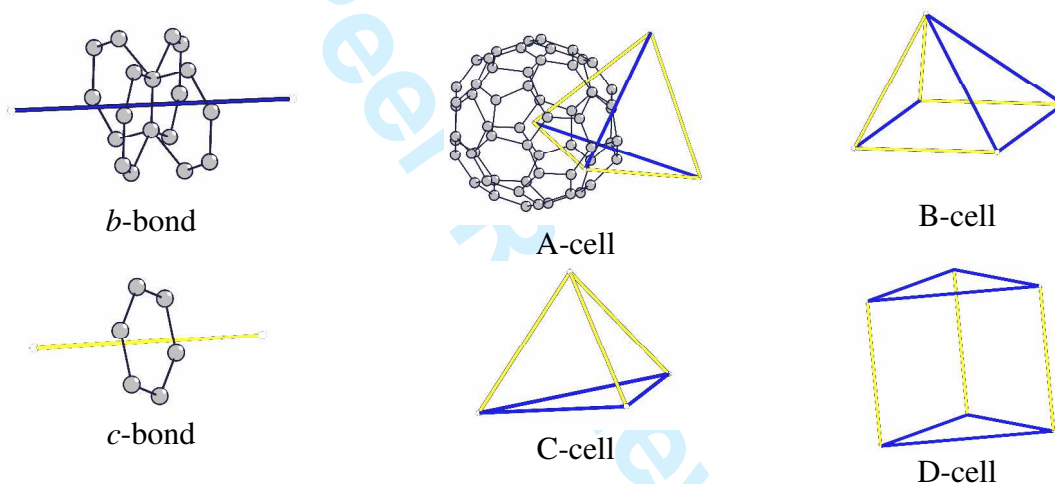


Figure 2. The canonical cells A, B, C and D and the two kinds of bonds b and c as used in the CCT [3] model; selected atoms of the 3rd shells of the Bergman cluster are displayed to show the decoration of the b -bond, the c -bond and the A cell; b -bond: the atoms correspond to γ and α^3 positions; c -bond: six atoms at α^3 positions; A-cell: 60 atoms of γ and α^3 positions surrounding one node.

4. Discussion

The present investigation of the local atomic structure of icosahedral phases in the Mg-Zn-RE systems supports the Bergman cluster as a fundamental structural unit and their packing according to the CCT model. Moreover, the technique of the real space local structure refinement of the PDF of quasicrystals in conjunction with the tiling approach using approximant structures has proven to be a powerful method in the structure analysis of quasiperiodic materials, *e.g.* the assignment of the RE atom positions in the cluster. The next step is now the modelling of even higher approximants as a basis of the local atomic structure in combination with high resolution total and partial PDF's. Using such an approach it should be possible to shed light on the still open question about the decoration of the D-cell. In this study, short and medium range order as introduced by the D-cells has been disregarded since 1/1- and 2/1-approximants do not contain such cells. However, D-cells are present in the

crystal structure of large approximants like $3/2-2/1-2/1-(\text{Ga,Zn})_{197}\text{Mg}_{95}$ [7]. In this structure, Pauling triacontahedra at the nodes and in the interior of the D-cell are fused sharing two β and two α^2 atoms of their 2nd shells. These atoms define a rhombus normal to a common two-fold direction of the clusters as shown in figure 3. The distance between the centres of the Pauling triacontahedra is $\tau^{-1} \times b$, which is equal to the unit cell parameter of the cubic $1/0$ approximant $\text{Mg}_2\text{Zn}_{11}$ [4]. By introducing this new type of ‘bond’ of length $\tau^{-1} \times b$ it is possible to decompose a D-cell and the three adjacent B-cells into A-, C- and new types of cells as shown in figure 3. So far only a ‘brute force’ algorithm [3] is known to generate very large CCT-approximants. There is hope, that the new ‘ $\tau^{-1}b$ -bond’ will enable to find a sophisticated algorithm to generate a *quasiperiodic* CCT [3, 14].

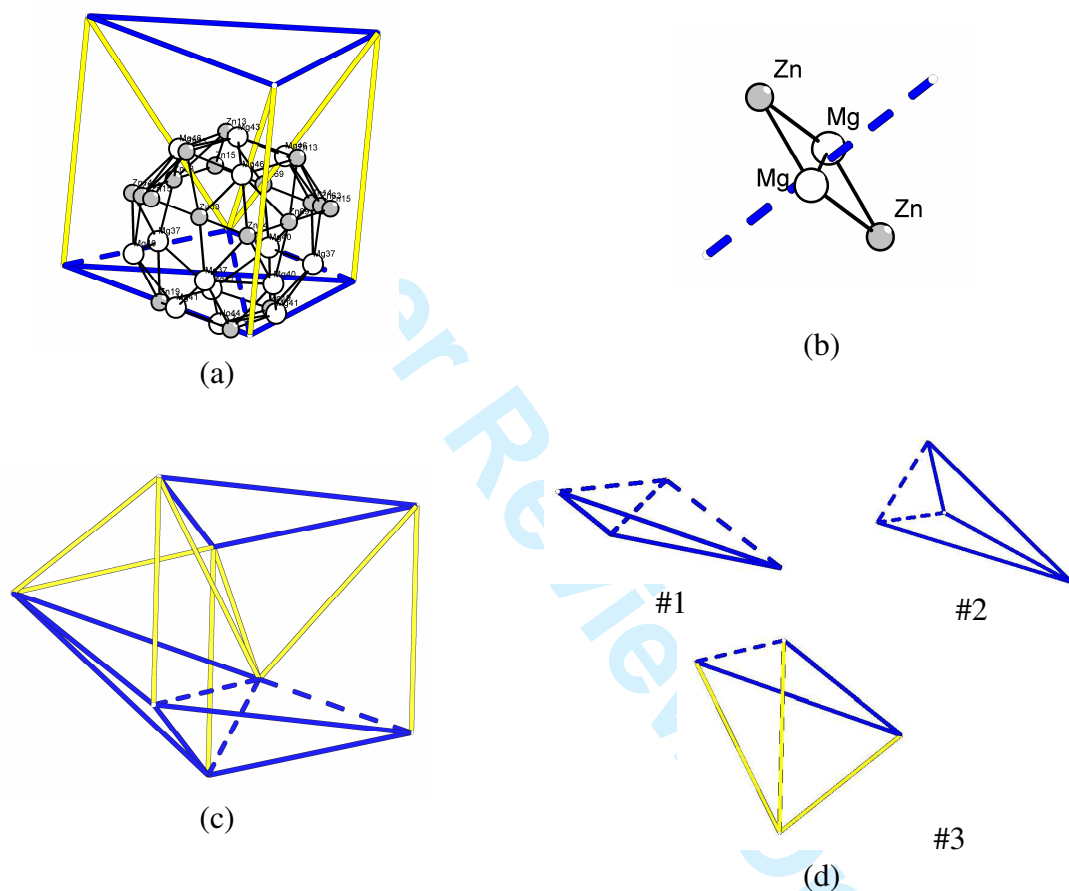


Figure 3. a) Part of the D-cell decoration with a Pauling triacontahedron inside as found in the $3/2-2/1-2/1$ approximant of the Ga-Mg-Zn system; the new ‘bond’ has length $\tau^{-1}b$ (dotted dark line). b) Part of a) on a larger scale; the dotted line is the $\tau^{-1}b$ bond with Zn and Mg atoms corresponding to α^2 and β positions. c) The D-cell and adjacent B-cells are partitioned into A- and C-cells and other new cell types (d).

The variety of new types of cells anticipates a complicated construction scheme for the long range icosahedral structure. On the other hand, the already fair agreement with the local quasicrystal structure PDF data points to only a few changes in order to describe the ‘‘true’’ situation. As a main conclusion, overlapping or interpenetration of the basic Bergman cluster occurs along the $\tau^{-1}b$ -bond. *Interpenetration* also may be an important general aspect in the ongoing discussion on ‘‘clusters’’ in quasicrystals [15].

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