



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Physique

www.sciencedirect.com



Quasicrystals / Quasicristaux

Crystal chemistry and chemical order in ternary quasicrystals and approximants

*Cristallochimie et ordre chimique dans les quasicristaux et approximants d'alliages ternaires*Cesar Pay Gómez^{a,*}, An Pang Tsai^b^a Department of Chemistry, Ångström Laboratory, Uppsala University, Box 538, SE-75121 Uppsala, Sweden^b Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan

ARTICLE INFO

Article history:

Available online 8 December 2013

Keywords:

Quasicrystals
Approximants
Cluster
Chemical order
Electron per atom ratio
Cd–Yb type structure

Mots-clés :

Quasicristaux
Approximants
Amas atomique
Ordre chimique
Rapport électron sur atome
Structure de type Cd–Yb

ABSTRACT

In this work we review our current understanding of structure, stability and formation of icosahedral quasicrystals and approximants. The work has special emphasis on Cd–Yb type phases, but several concepts are generalized to other families of icosahedral quasicrystals and approximants. The paper handles topics such as chemical order and site preference at the cluster level for ternary phases, valence electron concentration and its influence on formation and composition, fundamental building blocks and cluster linkages, and the similarities and differences between different families of icosahedral quasicrystals and approximants.

© 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

R É S U M É

Cet article discute notre compréhension actuelle de la formation, de la stabilité et de la structure atomique des quasicristaux icosaédriques et de leurs approximants. Plus particulièrement consacré aux phases de type Cd–Yb, il présente plusieurs concepts qui sont applicables aux autres familles de phases icosaédriques et d'approximants. Ainsi, on discutera ici l'ordre chimique et les sites préférentiels dans les amas atomiques pour les systèmes ternaires, la concentration des électrons de valence et son influence sur la formation et la composition des amas atomiques, blocs constitutifs des structures, et les connexions entre amas, en soulignant les similarités et les différences entre les diverses familles de quasicristaux icosaédriques et leurs approximants.

© 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

Approximants have since the beginning played a crucial role for understanding the structures of quasicrystals. The reason is, as the name implies, the close proximity to the actual quasicrystals, both in terms of composition and structural order. Approximants contain similar building blocks or atomic clusters as do the related quasicrystals. In the approximants, however, these building blocks are arranged periodically, which means that their crystal structures can be solved by conventional

* Corresponding author.

E-mail addresses: cesar.paygomez@kemi.uu.se (C.P. Gómez), aptsai@tagen.tohoku.ac.jp (A.P. Tsai).

methods. The structural knowledge gained can then be used to model the local structure of related quasicrystals and thus help to answer the question “where are the atoms” [1].

Being complex metallic alloys themselves, approximants are interesting in their own right, both in terms of structures and properties. As mentioned, one of their most valuable traits is to serve as points of reference to related quasicrystals [2]. As they are composed of similar building blocks and have similar compositions, they also have similar local crystal chemistry as do the related quasicrystals. In terms of physical properties, we can therefore essentially single out the effects of quasiperiodic long-range order on a number of properties, by comparing the quasicrystals with their related approximants.

There are several kinds of quasicrystals; dihedral quasicrystals contain atomic planes that are quasiperiodic, these planes are then stacked periodically on top of each other. Icosahedral quasicrystals however lack any periodic direction and, in spite of being the most abundant one, their group is also the least understood. Or so it was until the emergence of the binary icosahedral $i\text{-Cd}_{84}\text{Yb}_{16}$ quasicrystal [3], which is due to its high quality, its binary nature, its complete chemical order; the existence of two different approximants resulted in the first complete structure solution of an icosahedral quasicrystal [2].

The impact of $i\text{-Cd}_{84}\text{Yb}_{16}$ echoes far beyond the binary phase alone; it has greatly improved our understanding of icosahedral quasicrystals as a whole. First of all, the binary $i\text{-Cd}_{84}\text{Yb}_{16}$ quasicrystal and the two approximants Cd_6Yb and $\text{Cd}_{76}\text{Yb}_{13}$ are the parent structures for the now largest family of icosahedral quasicrystals and approximants [4–6]. Most members of this family are ternary and they form by substituting Cd by a pair of other elements; typically one late d -block and one p -block element or Mg. Since Cd is replaced by two elements, this results in the introduction of chemical disorder (mixing) in the structures, since these two elements occupy the sites previously only occupied by Cd in the parent structure. Yb can be replaced by other re (Rare Earth) elements, Ca, or Sr [6,7].

2. Chemical disorder

The presence of chemical disorder implies that in addition to answering the question “where are the atoms”, we need to answer a second question: “which atom is where?”

The problem of chemical order/disorder is one that needs to be addressed before claiming that we fully understand the atomic structures of quasicrystals. In the case of $i\text{-Cd}_{84}\text{Yb}_{16}$, the problem was simply not there, but this is no longer so in the ternary phases belonging to the same family. Knowing where the atoms are in the binary phase, however, puts us in an advantageous position in order to investigate the structures of the ternary phases, since, to a large extent, we can foresee where the atoms will be located and where chemical disorder should occur in the ternary structures. In other words, the structure model of the binary $i\text{-Cd}_{84}\text{Yb}_{16}$ quasicrystal can be expanded to related ternary phases of the same family by addressing the problem of chemical order/disorder. In order to do so, we can once again turn to the related approximant structures.

3. Ternary Cd–Yb type approximants

Ternary approximants of the Cd–Yb type family reveal a peculiar kind of partial chemical order at the cluster level; certain atomic sites are quite insensitive to which element inhabits them (resulting in random chemical mixing), while others show absolute selectivity. This trend can be seen for all known ternary approximants of the Cd–Yb family [8–14] and it is also seen in related ternary quasicrystals. The general formula for ternary Cd–Yb type approximants can be written as $(d_{1-x}p_x)_6M$ for 1/1 and $(d_{1-x}p_x)_{76}M_{13}$ for 2/1 where $M = re$, Ca or Sr and $d =$ late d -block element, $p = p$ -block element or Mg. Chemical mixing generally occurs only between the d - and p -block elements; they will occupy the sites that pertain to Cd in the binary parent phase Cd_6Yb . The M atoms (generally re atoms) rarely participate in any chemical mixing with the d - and p -block elements, and thus have well-defined atomic positions in the structures of ternary Yb–Cd type approximants. Other positions, although chemically mixed, can have a strong preference for one element over the other in the d/p element pair; therefore, the term partial chemical order can be preferable to chemical disorder. The actual mixing ratios at each atomic site will vary depending on several parameters specific to the elements that constitute the d/p pair. In fact, it is possible to formulate a general empirical model that applies to ternary Cd–Yb type 1/1 APs, where the distribution of M , d - and p -block elements in each shell of the basic cluster unit of a $(d_{1-x}p_x)_6M$ 1/1 approximant can be predicted quite well.

For this purpose, the ternary Mg–Cd– re system serves as a perfect model system to study chemical order/disorder in Cd–Yb type approximants and quasicrystals due to the large predominance areas of the phases in these systems. The reason is a solid solution between Mg and Cd that allows the Mg content to be increased up to 60% without significantly altering the structures [15]. Furthermore, the X-ray contrast between Cd and Mg is excellent, which allows careful investigation of chemical order at the atomic level to be performed by conventional methods of structure refinement. The results of such refinements are shown in Fig. 1, where three isostructural $(d_{1-x}p_x)_6M$ 1/1 approximants ($M = \text{Y}$, $d = \text{Cd}$ and $p = \text{Mg}$) with different total Mg contents have been investigated. The figure shows the different atomic shells that constitute the basic cluster unit in Cd–Yb type approximants and quasicrystals, and the distribution of chemical species at each atomic site. From the center to the periphery of the Cd–Yb-type cluster, we encounter the following shells in order: the tetrahedron, dodecahedron, icosidodecahedron, and the rhombic triacontahedron (RTH). The only parameter that was changed during the synthesis of these three samples was the total Mg content, but we can clearly see a strong site preference for Mg at specific sites. The three compounds crystallize in the space group $Im\bar{3}$ and three atomic positions that are particularly willing to

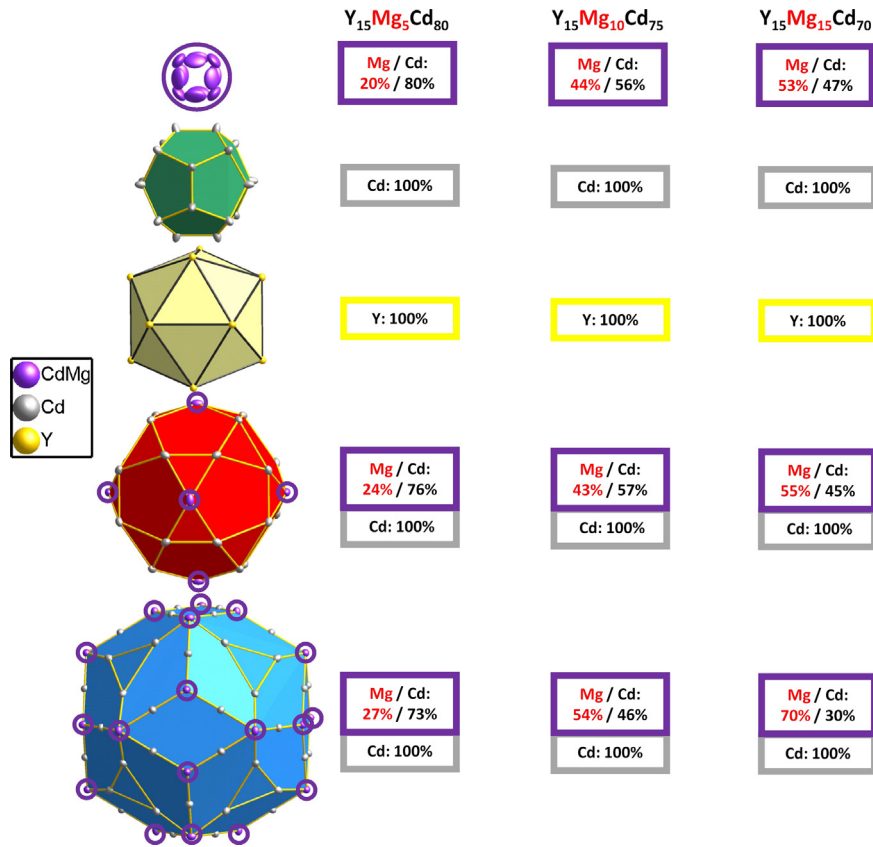


Fig. 1. (Color online.) To the left: the successive sequence of atomic shells of the basic atomic cluster in Cd–Yb type phases. The atomic positions marked by purple circles are those that have the strongest tendency to accept p -block elements according to the empirical model. Remaining sites are pure Cd (grey) or Y (yellow) positions. To the right, we see the refined values of the d/p mixing for three Mg–Cd–Y 1/1 approximants with different Mg content. Their normalized compositions are shown at the top of each corresponding column displaying the mixing at each crystallographic site of the different atomic shells. We should notice that the relative increase of Mg in the encircled sites of the bottom shell, the RTH, shows a steep increase in Mg content (from 27 at.% Mg to 70 at.% Mg) relatively to the total Mg increase in the samples (from 5 at.% Mg to 15 at.% Mg). It is thus clear that Mg concentrates at the vertex positions of the RTH shell. A similar but not so steep increase in the Mg content is seen also in the atomic shell at the cluster center (disordered tetrahedron, top left) and the two-fold vertices of the icosidodecahedron.

accept Mg clearly emerge: the central tetrahedron (24g), the positions on the two-fold axes of the icosidodecahedron (12d) and the vertex positions of the rhombic triacontahedron (12e). The latter, in particular, show a very strong tendency to accept Mg. It should be noted that although Mg mainly concentrates at these positions in the atomic clusters, they will always be mixed with a certain amount of Cd. In the same triacontahedral shell, we find atoms at the mid-edge positions of the rhombic faces (24g), these positions are to 100% composed of Cd atoms, which is a characteristic feature seen in all ternary Cd–Yb type 1/1 APs.

The positions that are mixed are further subject to several conditions which will affect the d/p mixing ratio, as will be further discussed under Section 5. The chemical order in the outer shell of the atomic cluster unit, the rhombic triacontahedron, is particularly well defined: The atomic positions at the mid-edge positions of the rhombic faces of the RTH units are always pure d -block element positions in all known approximants of this family. The vertex positions, although sometimes mixed, are predominantly composed of Mg or p -block elements. This distribution of elements in the different atomic shells of the cluster unit can be generalized to other ternary Cd–Yb type $(d_{1-x}p_x)_6M$ 1/1 approximants with $d = Zn, Cd, Cu, Ag, Au$ or Pd , $p = Mg, Al, Ga, In, Sn, Ge$ or Si and $M = re, Ca$ or Sr . First principles calculations have as of yet not provided a clear cut explanation for this chemical decoration, although it is clearly seen experimentally in numerous ternary phases of this family. The RTH shell shows similar chemical order in ternary 2/1 approximants as well [8,9,11,16], and similar results emerge when investigating ternary Cd–Yb type QCs as seen in the Mg–Cd–Yb system.

4. Ternary Cd–Yb-type quasicrystals

A comparison between the binary i -Cd₈₄Yb₁₆ and the ternary i -Mg₅₂Cd₃₆Yb₁₂ quasicrystals is seen in Fig. 2. The figure shows two planes cutting through the 6-dimensional electron densities of the binary i -Cd₈₄Yb₁₆ and the ternary i -Mg₅₂Cd₃₆Yb₁₂ QCs. We can clearly see three distinct occupation domains (ODs) in both quasicrystals located at the body-center (B), vertex (V) and edge-center (E) positions with the coordinates 1/2(111111), (000000) and 1/2(100000),

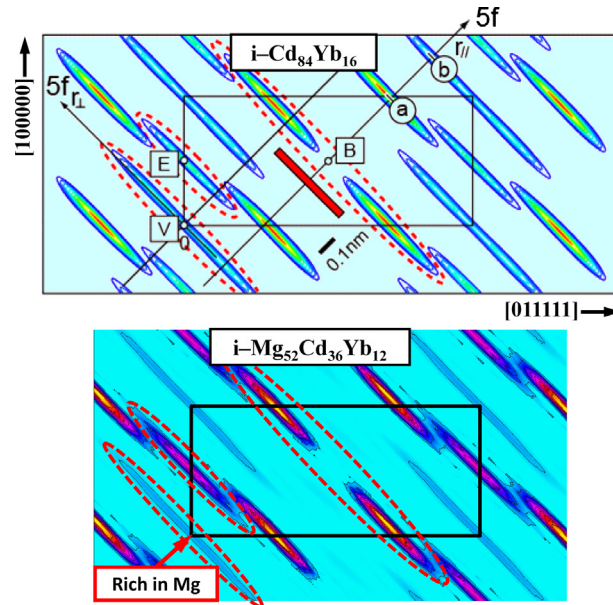


Fig. 2. (Color online.) Equivalent 2D cuts through the 6D electron densities containing five-fold axes in both physical and perpendicular spaces of the binary $i\text{-Cd}_{84}\text{Yb}_{16}$ (top) and the ternary $i\text{-Mg}_{52}\text{Cd}_{36}\text{Yb}_{12}$ (bottom) quasicrystals. The unit cells are marked in black. For the ternary QC, the OD at the corresponding position V has a much lower electron density than that at position E, in contrast to the binary QC where they are equal. This indicates a high content of Mg concentrating at this position in the ternary QC.

respectively, within the 6-dimensional unit cells. In both binary and ternary quasicrystals, the OD at the body-center clearly has the highest electron density compared to the remaining two at the vertex and edge center. This indicates the presence of the heavier element Yb. The difference between the binary $i\text{-Cd}_{84}\text{Yb}_{16}$ and the ternary $i\text{-Mg}_{52}\text{Cd}_{36}\text{Yb}_{12}$ QC is seen when comparing the relative electron densities for the ODs at the vertex and edge-center: while these two ODs have equally high electron densities originating from Cd in the binary QC, we clearly see that the OD at the vertex position has a lower electron density relatively to the edge-center OD in the ternary QC, indicating that it originates mainly from the lighter element Mg. The fact that this contrast is seen is direct evidence of chemical order in the ternary QC.

A different cut containing five-, three- and two-fold axes in the physical space allows us to compare the ternary $i\text{-Mg}_{52}\text{Cd}_{36}\text{Yb}_{12}$ QC with related ternary Mg–Cd–*re* 1/1 approximants, as seen in Fig. 3. The images show cut planes that bisect the RTH clusters perpendicular to two-fold directions. Looking at the contrast between the three atoms that sit in line on the edges of the rhombic faces of the RTH clusters (marked *d*, *b* and *f*), we see a striking resemblance between the ternary $i\text{-Mg}_{52}\text{Cd}_{36}\text{Yb}_{12}$ QC and the related ternary Mg–Cd–*re* 1/1 approximants. First of all, we can confirm that the same polyhedral shells that define the Cd–Yb type cluster in the binary $i\text{-Cd}_{84}\text{Yb}_{16}$ QC are present in both the Mg–Cd–*re* approximants and the $i\text{-Mg}_{52}\text{Cd}_{36}\text{Yb}_{12}$ QC. Furthermore, we can clearly discern that the electron densities at the vertices of the rhombic faces (positions *d* and *b*) of the RTH shells are much lower than those of the mid-edge positions (position *f*). This is a pattern that we recognize from our empirical cluster model, where the heavier *d*-block elements (in this case Cd) are located at the mid-edge positions and the lighter *p*-block elements (in this case, however, the *s*-block element Mg) are located at the vertices of the RTH clusters. In other words, the same chemical order as that observed at the cluster level in numerous ternary Cd–Yb-type approximants can also be seen in ternary QCs of the same family.

5. The e/a criterion in the Cd–Yb family

Since Cd is located in the same column as Zn in the periodic table, it was expected that an icosahedral quasicrystal (*i*-QC) could be produced by replacing Zn with Cd in the Mg–Zn–*re* system. Consequently, a number of new stable *i*-QCs and approximants were discovered in the Cd–*M* ($M = re$ metals or Ca) and Mg–Cd–*M* systems. The binary stable Cd–Yb and Cd–Ca *i*-QCs were found in the same series investigation. In the binary $i\text{-Cd}_{84}\text{Yb}_{16}$ and $i\text{-Cd}_{84}\text{Ca}_{16}$ systems, replacing Cd by equal amounts of In and Ag led to the formation of the stable $\text{In}_{42}\text{Ag}_{42}\text{Yb}_{16}$ and $\text{In}_{42}\text{Ag}_{42}\text{Ca}_{16}$ *i*-QCs compounds. These two stable binaries *i*-QCs have $e/a = 2.0$. In the periodic table, In is trivalent and is located to the right of Cd, while Ag is monovalent and is located to the left of Cd; thus, the two In–Ag *i*-QCs both have $e/a = 2.0$ [17]. In the binary Zn–Sc system, there is no stable binary *i*-QC of high structural quality [18], but the addition of 5 at.% Mg to the 1/1 Zn_6Sc approximant facilitates the formation of a highly-ordered stable *i*-QC [19]. These binary and ternary alloys both have $e/a \approx 2$ [15,20]. Similarly, a stable *i*-QC in the Cu–Mg–Ga–Sc system was discovered by replacing Zn in Mg–Zn–Sc with Ga and Cu [21]. Many more stable *i*-QCs have recently been discovered by substituting Mg with Mn, Fe, Co, Ni, Cu, Pt, Pd, and Ag in the

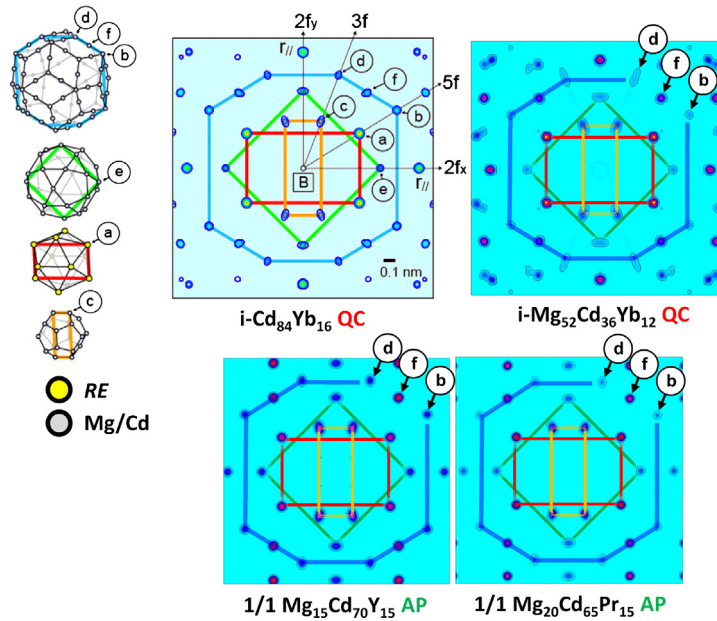


Fig. 3. (Color online.) Electron density maps showing 2D sections of the basic Cd-Yb cluster unit in the quasicrystals $i\text{-Cd}_{84}\text{Yb}_{16}$ and $i\text{-Mg}_{52}\text{Cd}_{36}\text{Yb}_{12}$ (top images), and two related 1/1 Mg-Cd- re approximants ($re = \text{Pr}, \text{Y}$). In the binary $i\text{-Cd}_{84}\text{Yb}_{16}$ quasicrystal, the atoms at the positions d , f , and b all have equal electron densities since they are all Cd atoms. In the ternary quasicrystal and both approximants, however, it is clear that substantial amounts of Mg reside at the d and b positions from the lower electron densities compared to the f position, which corresponds to Cd.

Mg-Zn-Sc system [22,23]. Most stable i -QCs in this group have been summarized in [23]. All these stable i -QCs have the same e/a value, which is the most dominant factor in determining the stability of i -QCs.

As the e/a criterion has its origins in metallurgy, the stable i -QCs are called the Hume-Rothery (H-R) electron compounds. The stability of stable i -QCs has been discussed in terms of H-R conditions [24] and alloy chemistry [23]. The e/a criterion is applicable to approximants as well as stable i -QCs. Starting from Cd_6Yb and Zn_6Sc 1/1 approximants and using the e/a criterion, many 1/1 approximants have been found in Ag-In- M , Au- T - M ($T = \text{Sn}, \text{Si}, \text{Ge}$ and $M = re$ metals or Ca) [14,25], Ga-Cu-Sc, Al-Cu-Sc [10], Al-Pd-Sc [12], Al-Au-Yb [13], Ca-Au-In [11], and Ca-Au-Ga [26] systems. The e/a criterion still applies even for alloys containing tetravalent Sn, Si, and Ge and zero valent Pd. Thus, in terms of the e/a criterion, approximants belong to the same group as H-R electron compounds. The H-R stabilization mechanism is due to the Fermi sphere-Brillouin zone interaction, which is assumed to be responsible for the pseudogap in the density of states at the Fermi level observed in i -QCs and approximants. In the H-R mechanism for i -QCs, the strong interference of electron waves at k and $k + \vec{G}$ induces a pseudogap near the Fermi level, where G is the reciprocal lattice vector that generates strong Bragg diffraction, which satisfies $\vec{G} \approx 2\vec{k}_F$. \vec{G} corresponds to the Brillouin zone of crystals and \vec{k}_F is the wave vector at the Fermi level or the radius of the Fermi sphere, which can be estimated from e/a and the atomic density according to free electron theory [24]. A highly symmetric polyhedron would efficiently interact with the Fermi sphere when $\vec{G} \approx 2\vec{k}_F$, but when $2\vec{k}_F$ deviates from this condition, an i -QC or approximant will no longer appear. Since $2\vec{k}_F$ is derived from e/a , in this case, e/a will be limited to a very narrow range corresponding to sharp compositions. This qualitatively explains why i -QCs and approximants have much narrower composition ranges than conventional intermetallic compounds that have simple structures. In this regard, i -QCs and approximants represent special H-R electron compounds. The phase diagram of the binary Cd-Yb system is seen in Fig. 4, where 1/1 AP, 2/1 AP and i -QC are clearly seen as line compounds with sharp compositions. They should however, belong to the same class of H-R stabilized cluster-based compounds. Interestingly, these three phases are also present in the phase diagram of the In-Ag-Yb system [27].

6. Stability of i -QCs and approximants

Fig. 5a shows three building blocks, an acute rhombohedron (AR), an obtuse rhombohedron (OR) and a rhombic tricontahedron (RTH), while Fig. 5b shows allowed linkages of RTH clusters in the Cd-Yb group. The structure of the 1/1 approximant can be described by an RTH cluster with a b -linkage along the [100] direction and a c -linkage along the [111] direction. Note that a c -linkage is an interpenetration of two RTH clusters sharing an OR. The i -QC and approximants all have a high density of RTH clusters; all the atoms of the 1/1 approximant belong to the RTH cluster and approximately 93.8% of the atoms of the i -QC belong to the RTH cluster [2]. RTH clusters are dominant in the approximants as well as in the i -QC and hence e/a may play a role in stabilizing RTH clusters. On the other hand, the i -QC and the 2/1 approximant are formed only in alloys containing Ca and re with larger atomic radii in several systems, such as Cd- M , Ag-In- M , Au-In- M , and Au-Sn- M , where $M = re$ or Ca. The Ag-In- M , Au-In- M , and Au-Sn- M systems can be regarded as pseudo-

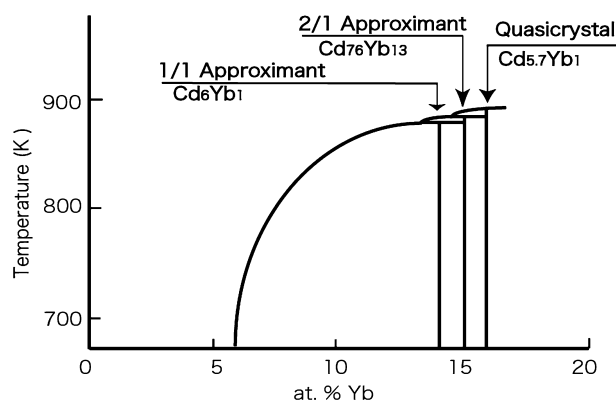


Fig. 4. Part of the Cd–Yb phase diagram showing approximants and quasicrystal as line compounds within a narrow compositional span.

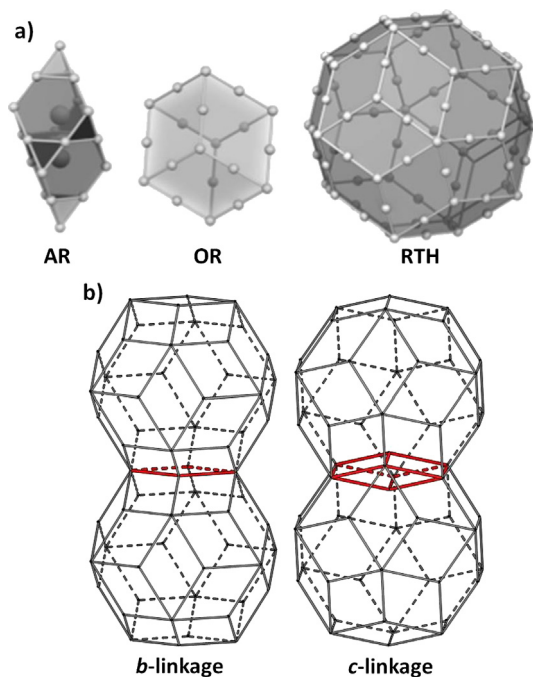


Fig. 5. (Color online.) Fundamental building blocks and cluster linkages in Cd–Yb type approximants and quasicrystals.

binary systems based on the Cd–*M* system. This suggests that the larger *res* or Ca atoms favor the formation of *i*-QCs or 2/1 approximants.

A parameter known as the effective atomic size ratio, $R_{r,e}$, which takes into account both atomic size and concentration, has been introduced to discuss the size effect [25]. It is given by $R_{r,e} = (r_{MC_M}) / (r_{ACA})$, where r and C are respectively the atomic radius and the concentration of each constituent element and the subscript A indicates the major constituent (e.g., Cd, Zn, Ag, and In). Fig. 6 shows the relationship between e/a and $R_{r,e}$ for the three alloy systems and for the Cd–*M* system. It shows that the three phases (i.e. the *i*-QCs and the 2/1 and 1/1 approximants) are distributed in different $R_{r,e}$ regions: $R_{r,e} > 0.22$ for the *i*-QC; $0.21 < R_{r,e} < 0.23$ for the 2/1 approximant; and $R_{r,e} < 0.22$ for the 1/1 approximant. On the other hand, the variation in e/a for the three phases is unclear, but there is a negative correlation between $R_{r,e}$ and e/a for the 1/1 and 2/1 approximants. This negative correlation may be ascribed to most of the *res* being trivalent and having a small atomic size. For the three phases of this class of alloys, e/a generally lies in the range 1.9–2.15. From Fig. 6, it seems that $e/a = 2.0$ is critical for the formation of Cd–(Yb, Ca) and In–Ag–(Yb, Ca) phases. However, this is not the case for the Zn–Sc phases. A $Zn_{80}Mg_5Sc_{15}$ *i*-QC was found by replacing Zn in the Zn_6Sc 1/1 approximant with about 5 at.% Mg. This replacement has a negligible effect on e/a , whereas it increases $R_{r,e}$ from 0.19 for the approximant to 0.21 for the *i*-QC. The e/a criterion applies to both *i*-QCs and approximants, but which phase that forms also depends on the atomic size.

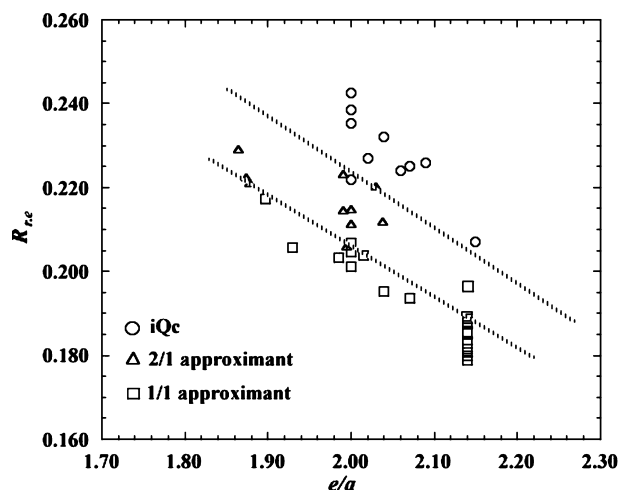


Fig. 6. Relationship between e/a and $R_{r,e}$.

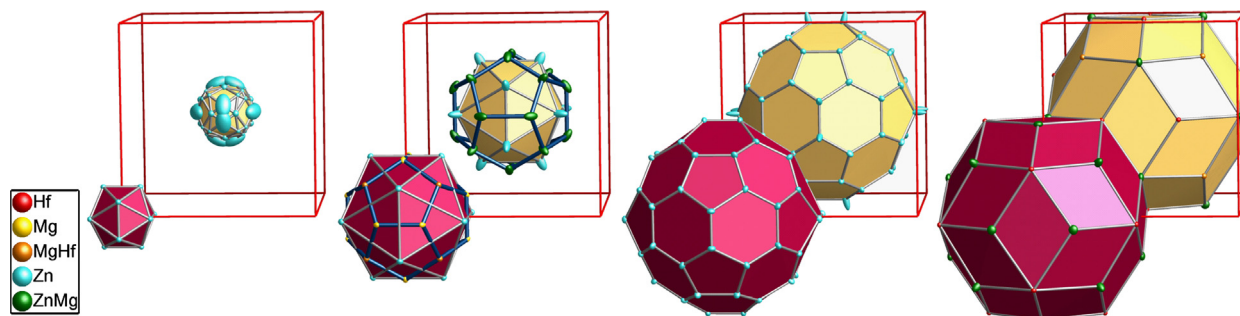


Fig. 7. (Color online.) Polyhedral shells of the 1/1 Zn–Mg– M ($M = \text{Ti, Zr or Hf}$) approximants, showing the existence of two types of Bergman clusters with different positional disorders and chemical decorations.

7. Structure of the icosahedral cluster and e/a

Since the e/a criterion commonly works in both i -QCs and approximants, according to the structural similarity between these two phases, we may presume that the e/a criterion is actually playing a role in stabilizing the icosahedral clusters. Hence, we here focus on the stability of icosahedral cluster in terms of the e/a criterion. Recently, a new group of stable i -QCs and approximants have been reported in Zn–Mg– M ($M = \text{Ti, Zr, Hf}$) system [28,29]. The new alloys were developed from the Zn–Mg–Sc system along the e/a criterion, in which trivalent Sc was replaced by tetravalent elements such as Ti, Zr and Hf, and compositions were designed to have e/a around 2.0–2.15, which is similar to that of the Zn–Mg–Sc system. More recently, three 1/1 approximants in the systems Zn–Mg– M ($M = \text{Ti, Zr or Hf}$) with composition of $\text{Zn}_{77}\text{Mg}_{18}\text{M}_5$ have been synthesized, and their structures have been studied by single-crystal X-ray diffraction [30]. The structure analysis revealed three approximants with the space group $Pm\bar{3}$ containing two different rhombic triacontahedral Bergman clusters which have different chemical decorations, as shown in Fig. 7.

Obviously, the structure of the new approximants containing two distinct icosahedral clusters is different from that of the Zn–Mg–Sc system, which contains the Cd–Yb type cluster, although they have a similar e/a value. Unlike the previously mentioned case where the replacements of Cd or Zn by other elements did not bring change in structure, replacement of Sc by M led to the formation of a new prototype structure. The Sc in the Zn–Mg–Sc system and the M in the Cd– M system are known to occupy the icosahedral shell of the Cd–Yb type cluster, which is also supposed to be the framework of the structure of approximants and i -QCs and the key atomic shell stabilizing Cd–Yb-type clusters. In this aspect, one may easily realize that the icosahedral cluster changes when trivalent Sc is replaced with tetravalent M elements. In terms of the e/a criterion, it can be concluded that the cluster changed its structure in order to preserve the e/a value.

An attractive way of considering the distribution of elements and the chemical order at the cluster level is to say that the clusters strive to achieve an e/a value around 2.0–2.15 locally; this tendency is however inexorably disturbed by other factors such as the effective atomic size ratio and the strict rules of chemical order that apply to certain atomic sites and atomic shells such as the rhombic triacontahedron, where the distribution of d - and p -block elements is fixed to specific positions regardless of their relative valence. In special cases such as in the Mg–Cd– re systems, the Mg/Cd mixing ratio can be varied indefinitely without affecting the total e/a value, since both Mg and Cd are divalent. The atomic site preferences

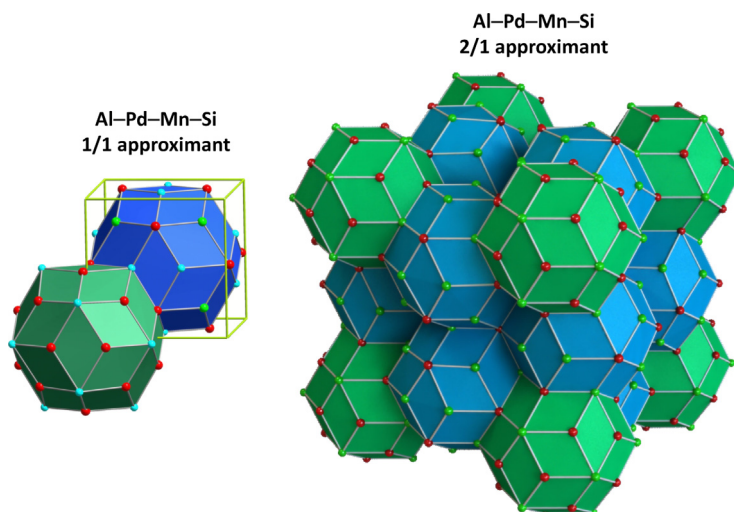


Fig. 8. (Color online.) Approximants of the Mackay-type i -Al-Pd-Mn quasicrystal, visualized with RTH clusters.

can thus be satisfied fully without interfering with the fulfillment of the e/a criterion for these phases. In other systems, however, this is not so. Since the atomic site preference in the RTH shell is so strong, the remaining mixed sites of the cluster must thus compromise and compensate for the induced charge imbalance by adjusting the d/p mixing ratio to yield an appropriate e/a value for the whole cluster, if necessary by sacrificing the site preference and introducing additional chemical mixing. Therefore, we should of course expect different mixing ratios for a Cd-Yb-type approximant containing Au-Si-Gd with monovalent gold, tetravalent silicon and trivalent gadolinium compared to an isostructural phase containing Ag-In-Yb with monovalent silver, trivalent indium and divalent ytterbium. We would, however, also expect only the d -block elements (Au and Ag) to occupy the mid-edge positions of the RTH shells and a higher amount of p -block elements (Si and In) at the vertex positions. The icosahedral shell purely contains the re elements (Gd or Yb), while other mixed sites (the tetrahedron at the center, three-fold vertices of the dodecahedral shell and two-fold vertices of the icosidodecahedral shell) will have a d/p mixing that properly adjusts the total e/a value to 2.0–2.15 for the whole cluster.

One of the reasons that the structure of the binary i -Cd₈₄Yb₁₆ phase could be solved was the redefinition of the basic cluster unit. By defining the basic atomic cluster parting from the approximants as the largest common building block, the rhombic triacontahedron could be uniquely identified. In practice, this meant expanding the original Cd-Yb-type (*a.k.a.* Tsai-type) cluster with yet another external shell. In doing so, a well-known problem in quasicrystal modeling was solved; the glue atom problem [31]. Glue atoms can be seen as atoms that reside outside of the cluster unit and whose whereabouts are undefined in the actual quasicrystal. By effectively expanding the boundary of the cluster, these atoms become part of it and thus the problem is to a large extent eliminated.

An important observation is the fact that the same procedure can also apply to other families of icosahedral quasicrystals and approximants. Based on their constituent atomic clusters, there are three families of icosahedral quasicrystals and approximants: Tsai (or Cd-Yb type), Bergman and Mackay. In approximants of these three families, RTH atomic clusters can be found when using the same principle of cluster expansion. It should be mentioned that this is certainly so for all known Tsai- and Bergman-type approximants [4–6,32,33], but the Mackay family is somewhat different [34]. In several approximants belonging to this family, rhombic triacontahedral cluster units cannot be easily observed, even after expanding the boundaries of the classical Mackay cluster. It is however true that for approximants of the Mackay-type i -Al-Pd-Mn quasicrystal, RTH clusters can be identified in both 1/1 and 2/1 approximants, as seen in Fig. 8 [35,36].

These two approximants have RTH clusters of similar shape and size as those found in Tsai- and Bergman-type QCs and APs. Furthermore, they also have the same inter-cluster connections or linkages. In fact, by observing these linkages along two-fold and three-fold directions in Mackay-type approximants, a parity rule can be identified, which can explain the origin of the superstructure formation that prevails in all known Mackay-type quasicrystals; the icosahedral F-centering. Fig. 9 shows the parity rule applied to the inter-cluster b - and c -linkages along two-fold and three-fold directions respectively in RTH containing approximants and quasicrystals with icosahedral F-centered lattices. Icosahedral F-centering can arise as a form of superlattice ordering caused by differences in chemical decoration among atomic clusters. In approximants of the i -Al-Pd-Mn quasicrystal, we can clearly distinguish two types of RTH clusters (blue and green) that have different decorations of chemical species. Although the linkages between clusters remain the same, we observe that two-fold connections always occur between equal (even parity) clusters and three-fold connections always between unequal clusters (odd parity). The same parity rule is observed for the Bergman-type 1/1 approximants in the systems Zn-Mg- M ($M = \text{Ti, Zr or Hf}$) as seen in Fig. 7. If this parity rule is applied to the subset of 12-fold vertices of the 3-dimensional generalization of the Penrose tiling (3DPT) describing the cluster distribution in a given i -QC, we have automatically generated an F-centered icosahedral lattice.

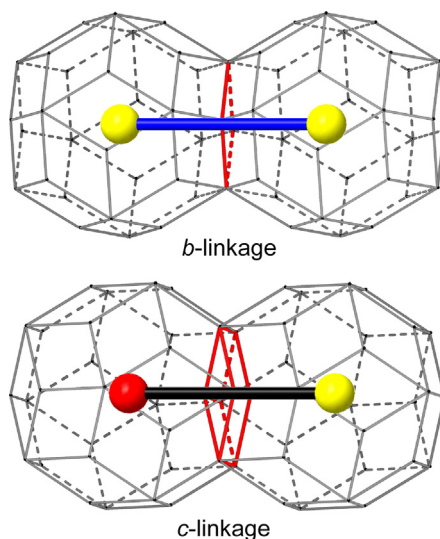


Fig. 9. (Color online.) Parity rule of the *b*- and *c*-linkages in RTH containing F-centered icosahedral quasicrystals and their approximants. Yellow spheres represent even and red spheres represent odd parity vertices of a 3DPT.

Recently, a phase that is structurally related to the 2/1 Al–Pd–Mn–Si approximant was reported in the Al–Pd–Cr–Fe system [37]. This approximant can be classified as a $2 \times 2 \times 2$ ordered superstructure of the 2/1 Al–Pd–Mn–Si approximant reported by Sugiyama et al. [36]. It has been shown that the 2/1 Al–Pd–Mn–Si approximant can be seen as the basic average structure resulting from incomplete superlattice ordering of the type observed in the Al–Pd–Cr–Fe phase. This new approximant provides further insights into the types of ordering that could take place locally in the related *i*-Al–Pd–Mn quasicrystal and fully supports the herein presented linkage and parity rules, although the description using RTH clusters has not previously been used for the Al–Pd–Cr–Fe phase.

8. Concluding remarks

In conclusion, we can say that the expanded rhombic triacontahedron (RTH) has successfully been used to describe the structures of Tsai-type QCs and approximants, and that the same cluster description also applies to other families of icosahedral QCs and approximants, which indicates the kinship between these yet different phases. It is seen that the same chemical order at the cluster level exists in both ternary approximants and quasicrystals of the Cd–Yb-type family. By looking at the distribution of chemical species in ternary approximants, we can then formulate an empirical rule for chemical decoration that locally also applies to ternary Cd–Yb type quasicrystals, which is an important step towards answering the question “which atom is where?” The distribution of chemical species must however still obey the *e/a* criteria, which undoubtedly plays an important role for the stabilization of a particular cluster in quasicrystals and approximants alike. Finally, the origin of icosahedral F-centering can be understood from the parity rule that is observed in related approximants and applies to inter-cluster connections.

References

- [1] P. Bak, *Phys. Rev. Lett.* 56 (1986) 861.
- [2] H. Takakura, C.P. Gómez, A. Yamamoto, M. de Boissieu, A.P. Tsai, *Nat. Mater.* 6 (2007) 58.
- [3] A.P. Tsai, J.Q. Guo, E. Abe, H. Takakura, T. Sato, *J. Nat.* 408 (2000) 537.
- [4] C.P. Gómez, in: *Order and Disorder in the RE–Cd and Related Systems*, Stockholm University, Stockholm, 2003, p. 54.
- [5] C.P. Gómez, S. Lidin, *Angew. Chem., Int. Ed. Engl.* 40 (2001) 4037.
- [6] C.P. Gómez, S. Lidin, *Phys. Rev. B* 68 (2003) 024203(1).
- [7] S.Y. Piao, C.P. Gómez, S. Lidin, *Z. Naturforsch., B* 61 (2006) 644.
- [8] C. Pay Gómez, G.H. Gebresenbut, M. Valldor, in preparation.
- [9] Q. Lin, J.D. Corbett, *J. Am. Chem. Soc.* 128 (2006) 13268.
- [10] T. Honma, T. Ishimasa, *Philos. Mag.* 87 (2007) 2721.
- [11] Q. Lin, J.D. Corbett, *J. Am. Chem. Soc.* 129 (2007) 6789.
- [12] Y.G. So, K. Edagawa, *Mater. Trans.* 50 (2009) 948.
- [13] T. Ishimasa, Y. Tanaka, S. Kashimoto, *Philos. Mag.* 91 (2011) 4218.
- [14] G.H. Gebresenbut, R. Tamura, C. Pay Gómez, *J. Phys. Condens. Matter* 25 (2013) 135402.
- [15] J.Q. Guo, E. Abe, A.P. Tsai, *Jpn. J. Appl. Phys.* 39 (2000) L770.
- [16] Q. Lin, J.D. Corbett, *Inorg. Chem.* 49 (2010) 10436.
- [17] J.Q. Guo, A.P. Tsai, *Philos. Mag. Lett.* 82 (2002) 349.
- [18] P.C. Canfield, M.L. Caudle, C.-S. Ho, A. Kreyssig, S. Nandi, M.G. Kim, X. Lin, A. Kracher, K.W. Dennis, R.W. McCallum, A.I. Goldman, *Phys. Rev. B* 81 (2010) 020201(R).

- [19] T. Ishimasa, Y. Kaneko, H. Kaneko, J. Non-Cryst. Solids 334–335 (2004) 1.
- [20] Y. Kaneko, Y. Arichika, T. Ishimasa, Philos. Mag. Lett. 81 (2001) 777.
- [21] Y. Kaneko, R. Maezawa, H. Kaneko, T. Ishimasa, Philos. Mag. Lett. 82 (2002) 483.
- [22] R. Maezawa, S. Kashimoto, T. Ishimasa, Philos. Mag. Lett. 84 (2004) 215.
- [23] T. Ishimasa, in: T. Fujiwara, Y. Ishii (Eds.), Quasicrystals, Elsevier, 2008, p. 49.
- [24] A.P. Tsai, J. Non-Cryst. Solids 334–335 (2004) 317.
- [25] Y. Morita, A.P. Tsai, Jpn. J. Appl. Phys. 47 (2008) 7975.
- [26] Q. Lin, J.D. Corbett, Inorg. Chem. 47 (2008) 7651.
- [27] S. Ohhashi, J. Hasegawa, S. Takeuchi, A.P. Tsai, Philos. Mag. 87 (2007) 3089.
- [28] J. Hasegawa, S. Takeuchi, A.P. Tsai, Philos. Mag. Lett. 85 (2005) 289.
- [29] S. Ohhashi, E. Abe, M. Tanaka, A.P. Tsai, Acta Mater. 57 (2009) 4727.
- [30] C.P. Gómez, S. Ohhashi, A. Yamamoto, A.P. Tsai, Inorg. Chem. 47 (2008) 8258.
- [31] P. Thiel, Nat. Mater. 6 (2007) 11.
- [32] G. Bergman, J.L.T. Waugh, L. Pauling, Acta Crystallogr. 10 (1957) 254.
- [33] Q. Lin, J.D. Corbett, Proc. Natl. Acad. Sci. USA 103 (2006) 13589.
- [34] F. Puyraimond, M. Quiquandon, D. Gratias, M. Tillard, C. Belin, A. Quivy, Y. Calvayrac, Acta Crystallogr. A 58 (2002) 391.
- [35] K. Sugiyama, N. Kaji, K. Hiraga, Z. Kristallogr. 213 (1998) 168.
- [36] K. Sugiyama, N. Kaji, K. Hiraga, T. Ishimasa, Z. Kristallogr. 213 (1998) 90.
- [37] N. Fujita, H. Takano, A. Yamamoto, A.P. Tsai, Acta Crystallogr. A 69 (2013) 322.