

The physical space model of the Tsai-type quasicrystal

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The binary $\text{Cd}_{5.7}\text{Yb}$ phase representing the Tsai-type category of the icosahedral quasicrystals is solved by the assignment of a unique atomic decoration to rhombohedral units in the Ammann–Kramer–Neri tiling. The unique decoration is found for units with an edge length of 24.1 Å and $\bar{3}m$ internal point symmetry. The structural refinement was carried out for two underlying tilings generated by the projection method for 6D space. The difference lies in the location of the origin point which for one tiling is in the vertex and for the second one in the center of the 6D unit cell. The two tilings exhibit mutual duality. The choice of the tiling has a minor effect on the final structural model as both converge to an R factor of $\sim 11.5\%$. The main difference is related to the treatment of the Cd_4 tetrahedral motif which is either orientationally ordered and aligned with the threefold axis or disordered and modeled as a partially occupied icosahedron. Both models can be presented as a covering by rhombic triacontahedral clusters with identical positions of clusters within rhombohedral units. The shell structure is Tsai-type in the case of the first tiling and Bergman-type for the other.

1. Introduction

The discovery of the $\text{Al}_{86}\text{Mn}_{14}$ metallic phase with symmetry compatible with the icosahedral point group revolutionized the understanding of solids (Shechtman *et al.*, 1984). The newly discovered material was called a quasicrystal (QC; a full list of abbreviations used in this paper is given in Table 1), as proposed by Levine & Steinhardt (1984). At first, it was speculated that a quasicrystalline phase is merely a form of metallic glass (Bancel *et al.*, 1985; Stephens & Goldman, 1986*a,b*; Steinhardt *et al.*, 1983) or a twinned crystal (Field & Fraser, 1984; Yang, 1979). The first confirmation that a QC could be a stable phase of matter came with the discovery of the first stable icosahedral quasicrystal (iQC) in the AlCuLi system (Dubost *et al.*, 1986). However, only after the discovery of the stable $\text{i-Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ QC (the ‘i’ before the phase composition indicates it is a phase with icosahedral symmetry) that extensive research on the stability of QCs started (Tsai *et al.*, 1987*a,b*).

Higher-dimensional ($n\text{D}$) analysis of aperiodic crystals is the most frequently used in the literature (Katz & Duneau, 1986; Kalugin *et al.*, 1985; Elser, 1985; Bak, 1985) for modeling quasicrystalline structures. The idea behind it is that the 3D structure can be generated upon projecting the $n\text{D}$ lattice decorated with so-called occupation domains (ODs) onto physical space. The $n\text{D}$ approach provides necessary mathematical tools for the calculation of the structure factor. The alternative approach is the average unit cell (AUC) based on the periodic reference lattice concept (Wolny, 1998, 2018).

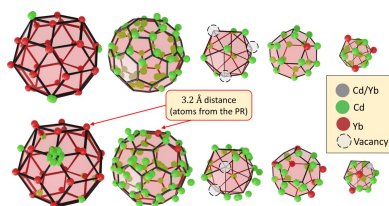


Table 1
List of abbreviations.

ADP	Atomic displacement parameter	OD	Occupation domain	QC	Quasicrystal
AKNt	Ammann–Kramer–Neri tiling	OR	Oblate rhombohedron	RD	Rhombic dodecahedron
AUC	Average unit cell	PAC	Periodic approximant crystal	RE	Rare earth
i	Icosahedral	PR	Prolate rhombohedron	RTH	Rhombic triacontahedron
nD	Higher-dimensional				

The great breakthrough in understanding the atomic structure of iQCs came with the model of the binary $\text{Cd}_{5.7}\text{Yb}(\text{Cd}_{85.1}\text{Yb}_{14.9})$ phase (Takakura *et al.*, 2007; Takakura, 2008; Takakura & Strzałka, 2017) which provided a template for other structures of QCs in the Tsai-type family (Yamada *et al.*, 2016*a,b*, 2017). It was the first binary iQC to be discovered along with $\text{Cd}_{85}\text{Ca}_{15}$ (Guo *et al.*, 2000; Tsai *et al.*, 2000; Palenzona, 1971). Two periodic approximant crystals (PACs) with cubic symmetry, $1/1 \text{ Cd}_6\text{Yb}$ and $2/1 \text{ Cd}_{5.8}\text{Yb}$, were known for i- CdYb and provided information on the local atomic arrangement that was adapted for the QC (Gómez & Lidin, 2001). The novelty of the model was that the structure was understood as interpenetrating rhombic triacontahedral (RTH) clusters with a concentric Tsai-type shell structure.

The RTH clusters in the model by Takakura *et al.* (2007) are connected only along two- and threefold axes (*b* and *c* linkages, respectively). The interstitial part between RTH clusters is filled with the prolate rhombohedron (PR) and the oblate rhombohedron (OR) decorated in the manner of the $2/1$ PAC. What is worth mentioning is 20 PRs in the interstitial part of the structure form a stellate polyhedron that conforms to a Bergman cluster (Bergman *et al.*, 1952). The existence of the Bergman cluster in a Tsai-type QC is particularly interesting because the markers of Tsai clusters in the 2D section of the electron density map in i- ZnMgTm QC, which is a Bergman-type QC with rare earth (RE) elements (Luo *et al.*, 1993; Niikura *et al.*, 1994*a,b*), could be found also (Buganski *et al.*, 2020*a*). There is a mutual relationship between the Tsai and Bergman clusters in quasicrystalline structures, which is explored in this article.

This paper has two main objectives. Initially, the intention was to test whether it was possible to construct a real-space model of a Tsai QC with rhombohedral units. The atomic structure of i- ZnMgTm has already been solved using rhombohedral units of the Ammann–Kramer–Neri tiling (AKNt) (Buganski *et al.*, 2020*a*; Kramer & Neri, 1984), by exploiting a τ^3 inflation rule for primitive icosahedral QCs (Ogawa, 1985; Guyot & Audier, 2014). As a natural progression, in our first objective we aimed to explore whether the same methodology can be applied to QCs with different cluster shell structures. To this end, we selected the i- CdYb phase, a well-studied QC structure, as our focus. Upon examining the real-space electron density map, we observed numerous Bergman clusters exhibiting mutual linkages, like those found in the Bergman i- ZnMgTm QC.

Next, we conducted a full structural refinement, assuming that the Bergman clusters occupy positions within rhombohedral units typically occupied by Tsai clusters. Our secondary objective was to assess the feasibility of this alternative cluster

choice without compromising the model’s agreement with experimental data.

2. The *ab initio* structure solution

The iterative self-consistent algorithm that we used to obtain the phases of the diffraction peaks is implemented in the *SUPERFLIP* software (Palatinus, 2004). It is based on a combination of a charge-flipping algorithm (Oszlányi & Sütő, 2004) and a low-density elimination method (Takakura *et al.*, 2001). The final evaluation function, which in crystallography is represented by the *R* factor, is frequently <20% for QCs (Kuczera *et al.*, 2012, 2014) and this is low enough for the preparation of a starting model for the structural refinement. Phasing with *SUPERFLIP* gave the final *R* factor as 16.7%.

The set of 5197 symmetry-independent X-ray diffraction peaks was chosen for the structural solution with $|F| > 2\sigma(|F|)$. The same dataset was used by Takakura *et al.* (2007), where 5024 diffraction reflections were used with an accuracy of 3σ . This model involves more parameters because the size of rhombohedral units is large and, therefore, the higher number of diffraction peaks is beneficial. The original X-ray diffraction data was collected by Takakura *et al.* (2007) using synchrotron radiation with a single-crystal sample.

2.1. The *nD* analysis

2D sections in planes parallel to high-symmetry directions through a 6D electron density were calculated. Sections include fivefold axes (5f): $[011111]$ and $[100000]$, threefold axes (3f): $[101100]$ and $[010011]$ and twofold axes (2f): $[110000]$ and $[001001]$. The sections are presented in Fig. 1. All three ODs, already reported by Takakura *et al.* (2007) in this system, are visible in the 5f section. The red rectangle gives a frame for the 6D unit cell with a lattice constant $a_{6D} = a_r(2^{1/2}) = 8.045 \text{ Å}$, where a_r is the edge length of the basic rhombohedron. Although perpendicular space can be arbitrarily scaled, it is assumed here that the length of the unit vector in physical space is the same as the length in perpendicular space, and the use of Ångström as a unit in perpendicular space is justified.

OD_B is a high electron density domain, which means that Yb positions are generated by the domain. The center of the domain, marked with an ‘a’ circle, is empty. It corresponds to the nodes of the 12-fold subset of AKNt. With a circle ‘b’, an overlap between OD_B and OD_E is marked, which created an ambiguity in the atomic position. Since two close-distance positions cannot be simultaneously occupied, that is, a split-atom position or otherwise a phason flip site. The electron

density is reconstructed based on the reverse Fourier transform; therefore, the smearing of the OD is also caused by the truncation effect akin to the limited resolution of the diffraction data (de Boissieu *et al.*, 1988). The splitting of the electron density marked 'c' in the $3f$ section corresponds to the dodecahedral shell with atoms splitting along the $3f$ axis. The same was reported in i-CdMgYb (Yamada *et al.*, 2017). The breathing effect can be attributed to the existence of the central atom in the cluster that causes the atoms of the closest shell to relocate [the effect known in the 1/1 approximant of the Bergman QC (Gómez *et al.*, 2008) or face-centered iQC (Buganski *et al.*, 2020c)] or the relaxation due to the disorder in the tetrahedron (Gómez & Lidin, 2003).

The distance between OD_B and OD_V in parallel space is equal to 9.205 Å in the $5f$ direction and 8.382 Å in the $3f$ direction. Both numbers are important for understanding the relationship between Tsai and Bergman clusters in the structure, which is explained in Section 2.2.

2.2. Physical space analysis

In this section, the local atomic arrangement reflected by the electron densities calculated in physical space is discussed. The 2D electron density map was calculated in a plane perpendicular to a $2f$ axis. The matrix (60) from the review paper by Yamamoto (1996) was used. From that map, two regions where the clusters were located were selected. One for

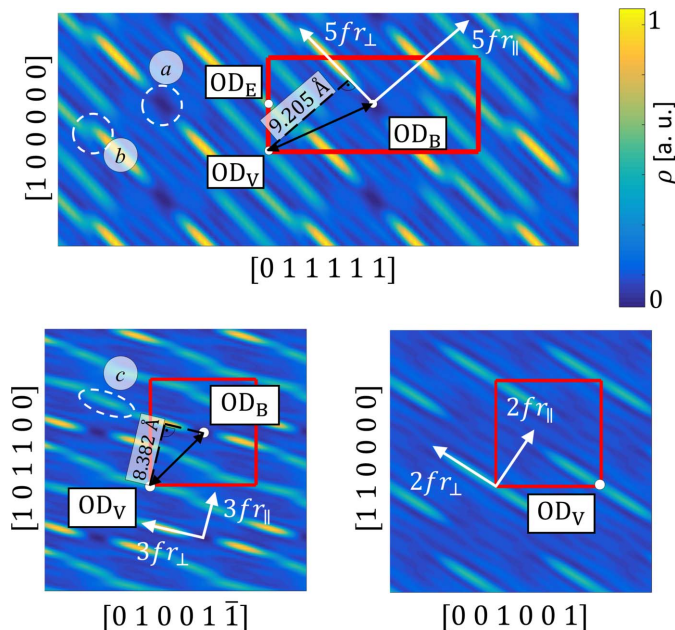


Figure 1

High-symmetry sections through the 6D electron density map involving perpendicular space. Three 2D sections are presented, which involve the $5f$, $3f$ and $2f$ directions. The ODs are marked and labeled in each section. The frame of the 6D unit cell is drawn as a red rectangle. The empty space in the OD_B, corresponding to unoccupied positions in the 12-fold subset of the AKNt is marked with a circle *a* on the $5f$ section. Two other regions of interest are marked 'b' – the overlap between OD_B and the OD_E forming a phason flip site and 'c' – the splitting of atoms along the threefold axis. The distances in parallel space between the OD_B and the OD_V are given.

the Tsai cluster and the other for the Bergman cluster (Fig. 2). Within each region, a full 3D electron density was calculated to obtain isosurfaces corresponding to atoms in the structure. The level of the isosurface plot was set at $\rho_{\text{iso}} = (1/30)\rho_{\text{max}}$, where ρ_{max} is the maximal electron density. That was also the level for later determination of the starting structural model for refinement. In Fig. 2, all shells of both clusters are presented. For both clusters, the center is occupied by an atom. Many clusters with a central atom in the i-CdYb electron density map were found and, therefore, they might be more prevalent than originally expected for the i-CdYb phase. Two clusters presented here are linked to each other along the $5f$ axis, which is known as the *a*-linkage. This linkage is not the same as reported in i-ZnMgTm between Bergman clusters (Buganski *et al.*, 2020a). The length of this linkage is equal to 9.205 Å and is longer than the latter by τ . The longer *a*-linkage will be denoted as *a*_l-linkage. The common part between the Tsai cluster and Bergman cluster has the shape similar to the rhombic icosahedron but the rhombic faces are truncated and form irregular pentagons. The atomic decoration of this unit is asymmetric along the linkage axis.

The linkage between Tsai and Bergman clusters in the structure is not rare. In fact, the Tsai cluster can be completely surrounded by Bergman clusters, as shown in Fig. 2 in the bottom right-hand corner. The vertex of the RTH shell of the

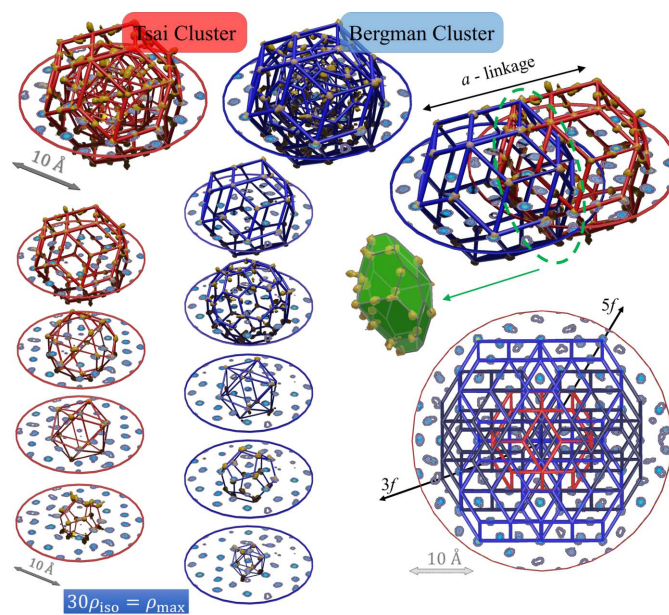


Figure 2

Analysis of the local atomic structure in the i-CdYb QC. Two types of clusters are identified, *i.e.* the Tsai (red) and Bergman (blue) clusters. The shell structure of each cluster is presented as a wireframe skeleton with isosurfaces of the electron density. The isosurface is calculated at the level of $\rho_{\text{iso}} = 1/30\rho_{\text{max}}$. The Tsai and Bergman clusters are linked along the *a*_l-linkage with a length of 9.205 Å which corresponds to the real space distance between the centers of OD_V and OD_B. The common part between the overlapping RTH outer shell is a rhombic icosahedron with truncated vertices. A Tsai cluster can be pictured as a central cluster surrounded by Bergman clusters with one vertex in the center of the Tsai cluster for each Bergman cluster. Clusters with the $3f$ symmetry vertex centered are darker blue compared to clusters with the $5f$ vertex centered.

Bergman cluster is located in the center of the Tsai group. Clusters with the $3f$ vertex in the center of the Tsai cluster are plotted in a darker color. Various linkages are realized by Bergman clusters around the Tsai cluster. The b -linkage [length $b = a_r[4 + 8/(5^{1/2})]^{1/2} = 15.661 \text{ \AA}$] is realized by clusters lying on opposite sides of the Tsai cluster with the $5f$ vertex located in the center of the Tsai cluster. The adjacent $5f$ vertex-connected clusters form a short b -linkage (length $b_s = a_r\tau = 9.205 \text{ \AA}$). The adjacent $3f$ and $5f$ vertex-connected clusters form the a -linkage (length $a = a_r = 5.689 \text{ \AA}$). The c -linkage [length $c = b(3^{1/2})/2 = 13.562 \text{ \AA}$] connects $3f$ with the second neighboring cluster of $5f$. Finally, there is also the shortest b -linkage [length $b_{ss} = a(3 - \tau)^{1/2} = 6.688 \text{ \AA}$] between $3f$ -bound clusters.

The length of the a_r -linkage corresponds to the physical space distance between the center of the OD_V and the OD_B in the $5f$ -axis direction already given in Section 2.1. If the 6D electron density was shifted along $[1\ 1\ 1\ 1\ 1\ 1]/2$, both ODs would be interchanged. The relationship between Tsai and Bergman clusters is analogous to the shift in 6D space along the diagonal of the 6D unit cell that changes the places of the ODs. Therefore, cluster centers of one type are generated by the vertex-bound OD, and cluster centers of the other type are generated by the center-bound OD. Tsai clusters are associated with the 12-fold subset of the AKNt, but the Bergman clusters are associated with the 12-fold subset of the dual AKNt. Dual AKNt is generated by the RTH OD located not at the origin of the 6D unit cell, but at its center. This is directly related to the definition of a dual tessellation but in 6D space (Mihalkovič *et al.*, 1996; Gailiunas & Sharp, 2005). Both tilings correspond to the uniform shift of 6D space; therefore, the choice of the tiling should not affect the final result of the structural modeling.

3. Structure refinement

Structural refinement was carried out in MATLAB software with the *fmincon* optimization function against 5197 symmetry-independent diffraction peaks. The trust region algorithm was chosen. The condition of convergence was either the size of the step in parametric space ($<10^{-7}$) or the first-order optimality ($<10^{-3}$). The function that was optimized was the crystallographic R factor. The structure factor was calculated based on the AUC approach (Wolny, 1998; Wolny *et al.*, 2018) with the separation of the geometric part of the structure factor and the atomic decoration term (Buczek & Wolny, 2006; Strzalka *et al.*, 2015). The same atomic decoration was assumed for all orientations of each type of rhombohedron. It is a typical application of the tiling-and-decoration routine (Elser & Henley, 1985), previously applied to both decagonal (Kuczera *et al.*, 2011, 2012; Buganski *et al.*, 2019) and icosahedral QCs (Buganski *et al.*, 2020a). Atomic decoration was applied to τ^3 inflated rhombohedra with an edge length of $24.1 \text{ \AA}$. The asymmetric part of each rhombohedron was identified as $1/12$ th of the volume (the point symmetry of the rhombohedral units is $3m$). Only atoms in the asymmetric part were refined.

The starting model was obtained based on the procedure described by Buganski *et al.* (2020a). The main idea was to find the maxima of electron density calculated within randomly selected rhombohedra of the AKNt. The atomic species were assigned in the positions of maxima taking into account the peak value. For maxima with electron density $(0.35\rho_{\max} - 0.65\rho_{\max})$ mixed occupancy was assumed. Atoms were considered to be Yb above this limit and Cd below it. If the electron density was $<0.1\rho_{\max}$, the position had an occupancy set to 0.5. The boundaries were chosen with the restriction of experimental composition and density.

Various structural parameters were refined; most importantly, the atomic positions. If atoms lie in special positions (vertex, edges, faces), the positions were constrained. The atomic displacement parameters (ADPs) were refined by assuming an isotropic distribution of phonons. The partial occupancy probability for mixed sites was allowed, maintaining that all must sum up to one. If during refinement the probability of one type of atom reached >0.9 , the probability of that type of atom was set to 1 and not refined further. The phasonic ADP in the form of a single parameter in the general Debye–Waller factor was used (Lubensky *et al.*, 1986; Bancel, 1989, 1990; Jarić & Nelson, 1988). The fractional occupancy of atomic sites was allowed. If the site had an occupancy of >0.9 then it was set to 1 and not refined further. A single extinction parameter was considered (Chandrasekhar, 1960; Darwin, 1914; Ewald, 1917). The extinction correction was simpler than that used in the *qcdiff* software (Yamamoto, 2008), which is based on the formalism described by Kato (1976a,b) and was utilized by the Takakura *et al.* (2007) model. A single scale factor between the experimental and calculated diffraction amplitudes was also refined. The form factors for X-ray diffraction scattering were used with the correction for the anomalous dispersion (Karle, 1980; Guss *et al.*, 1988).

Two models were prepared: one for the AKNt and the other for its dual counterpart. Since the dual tiling is generated by the projection method with the OD placed in the 6D unit-cell center rather than its vertex the same tiling can be used for the production of both models. The model for the dual tiling has the electron density calculated with the additional phase factor equal to the translation from the vertex position to the center of the 6D unit cell.

3.1. Refinement of Tsai clusters

The refinement converged with $R = 11.48\%$ against 424 parameters. This makes the peak-to-parameter ratio equal to ~ 12.3 . The number of parameters used here is larger than used by Takakura *et al.* (2007) and is directly related to the number of independent atoms in the asymmetric part of the rhombohedra. In the OD modeling with the nD approach, the number of independent atoms is a hyperparameter that can be arbitrarily chosen. In total, there are 85 refinable atoms in the PR and 60 atoms in the OR. The final composition is $Cd_{84.9}Yb_{15.1}$ with a density of 8.99 g cm^{-3} . Regarding the atomic composition, the model reproduces the experimental value ($Cd_{85.07}Yb_{14.93}$). The calculated density is a little larger

than reported (8.88 g cm^{-3}); however, it was estimated for 1/1 PAC, which is Cd rich with respect to the QC. The density of the QC can be higher. The residual electron density is $<1.6\%$ of the electron density calculated with experimental diffraction amplitudes.

The final model is depicted in Fig. 3. Orientations of units are given by three vectors of the icosahedral lattice, *i.e.* vectors spanning the PR along the $5f$ axes. Each shell of the Tsai cluster is plotted separately. The first feature is the presence of the *a*-linkage at the edge of both rhombohedra with Yb atoms occupying the center of the cluster. Along the same edge, there is a short interatomic distance ($\sim 2 \text{ \AA}$) between two Cd atoms, one of which belongs to the outer shell of the RTH and the other to the icosahedral shell of the second cluster in the linkage. It is caused by the existence of the phason flip site exactly in the positions of those atoms. The RTH cluster covering is also possible in the case of i-CdYb, and no division between cluster-belonging atoms and interstitial atoms agglomerated in PR units is necessary, as discussed by Buganski *et al.* (2020a). All atoms are found to be part of the subsequent shells of Tsai clusters if the *a*-linkage is allowed. Interestingly, the centers of the Tsai clusters are occupied by Yb atoms, except one cluster which lies on the longer body diagonal with $3f$ symmetry. The central part of this cluster is occupied by one atom on the body diagonal axis,

and one atom slightly shifted from this axis, but is located on the mirror plane. When all symmetries of the asymmetric unit are applied, four atoms with 100% occupancy each are recovered. Later, when the large RD unit is analyzed, it will be evident that this is a tetrahedron. The orientation is the same as in 1/1 PAC of i-ScZn measured at 92 K (Ishimasa *et al.*, 2007).

To better understand the local atomic configurations in the model, we have drawn the RD with two PRs and two ORs with all atomic positions restored by using symmetry operations. The RD with all Yb atoms and Cd atoms contained within six icosahedra is given in Fig. 4(a). The six icosahedra together with two others located along the $2f$ axis and connected via a short *b*-linkage form a hexagonal bipyramid marked with blue. The edge length of the hexagonal bipyramid aligned with the threefold direction is equal to the length of the *c*-linkage. The edge-bound icosahedra provide a grid for the remaining Yb atoms but are shaded with a light color; otherwise, the image would be incomprehensible. We have not plotted all Cd atoms either for the sake of clarity.

The tetrahedron can be found in four icosahedra that were generated by clusters in PR units only. Tetrahedra along the $3f$ axis (body diagonal) of the PR point toward each other like arrows. The icosahedra within the OR have centers occupied by Yb with a significant disorder of Cd atoms in the dodecahedral shell. The magnified picture of both icosahedron types with and without a tetrahedron inside is presented in Fig. 4(b). The face of the tetrahedron is perpendicular to the $3f$ axis of the PR with the apex atom on the axis. The tetrahedron is not centered within the dodecahedron. However, no distortion was created to the dodecahedron, as reported in i-ScZn (Yamada *et al.*, 2016a). The distortion in the dodecahedron occurs in a pseudo-Tsai cluster (Gebresenbut *et al.*, 2020) with an Yb atom inside. With the label 'e', the split atomic position is marked at the $3f$ vertex of the dodecahedron. There is also a Cd atom that protrudes through the icosahedral shell.

The inner clusters in the RD form a short *b*-linkage presented by a 'd' motif in Fig. 4(a) and magnified in Fig. 4(c). What is most clearly visible here is a disorder within the outer shell of the RTH. Atoms that seem to float above the RTH shells are Cd atoms linked to the $3f$ vertices of the RTH. Split atoms along the $3f$ direction were mentioned in Section 2.1. Here, it was not modeled as a split atom, but the residue of that disorder is a shift from the original position.

The common part of RTH clusters here forms a double-capped RD which is τ^3 deflated with respect to the one in Fig. 4(a). This is a manifestation of the self-similarity (Takakura *et al.*, 2007) of QCs. The inner structure of the small RD is complex but fully explained in Fig. 4(d). Two Yb atoms (labelled c) occupying the apex positions of the octahedron are shared by two overlapping icosahedra visible in a motif 'd'. Within the square basis of an octahedron, there are four atoms which belong to the dodecahedral (b) and icosidodecahedral (a) shells. Atoms that belong to dodecahedra are split with half-occupancy between dodecahedral shells of linked clusters. Atoms 'a' are all generated by an icosidodecahedron, also in a hexagonal prism.

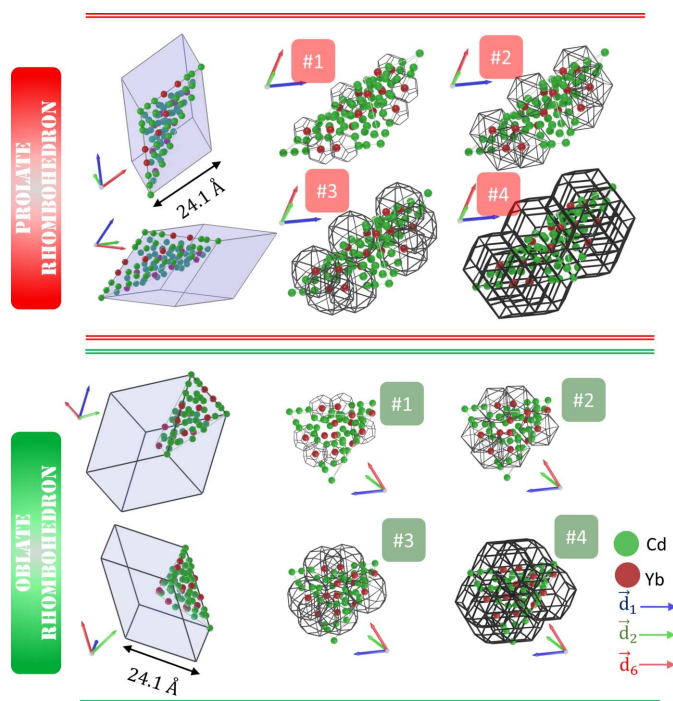


Figure 3

Atomic decoration of rhombohedral units in the i-CdYb refined model with Tsai clusters. The orientation of each unit is given by three vectors of icosahedral setting, directed toward the vertices by a common face of the icosahedron. All shells of the Tsai cluster are given individually for clarity. The shells are dodecahedron (#1), icosahedron (#2), icosidodecahedron (#3) and rhombic triacontahedron (#4). In most cases, there is a Yb atom at the center of the clusters.

The correlation plot between the calculated and observed diffraction amplitudes is given in Fig. 4(e). High-intensity peaks are aligned along the center-of-mass line (red); however, single peaks deviate from it even above 10^{-2} . Apart from that, there is a natural broadening, mostly symmetrical, for small peaks. For QCs, small-amplitude diffraction peaks very often deviate toward smaller F_{calc} values appearing as a tail, which is attributed to a multiple-scattering effect (Fan *et al.*, 2011) or phasonic disorder (Buganski *et al.*, 2016, 2019). The phasonic ADP was estimated as $1.54a_f^2$. To compare this value with the results given by Yamada *et al.* (2016a) for i-ScZn or Yamada *et al.* (2017) for i-Cd-Mg-Yb we need to recalculate the values in those papers. The conversion constant is $8\pi^2$. The general Debye–Waller formula for phasons used in those papers is $\exp[-(b_{\text{ph}}k_{\perp}^2)/2]$, where b_{ph} is a phasonic ADP parameter and $k_{\perp}$ is the length of the vector of perpendicular subspace of reciprocal space. The formula used here is $\exp[-(b_{\text{ph}}k_{\perp}^2)/(16\pi^2)]$. After conversion, the result for i-ScZn is $4.98a_f^2$ and for i-Cd-Mg-Yb it ranges from $2.91a_f^2$ to $4.57a_f^2$ depending on the Mg concentration (Yamada

et al., 2017). Our result is two to three times smaller, indicating a very small phasonic disorder.

3.2. Refinement of Bergman clusters

The refinement converged with $R = 11.69\%$ against 432 parameters. It makes the peak-to-parameter ratio equal to ~ 12 . In total, there are 81 refinable atoms in PR and 57 atoms in OR. These are atoms that are not affined to the tetrahedron. Because the tetrahedron is now located in the vertices of rhombohedral units, we needed to treat the tetrahedron as a partially occupied icosahedron. In the asymmetric part of rhombohedron there are three vertices, which convert to 36 additional atoms each with one-third occupation probability. The refinement of each atom independently would be inefficient; therefore, for all the icosahedra, we assumed two parameters: the scale parameter and the phasonic ADP, the

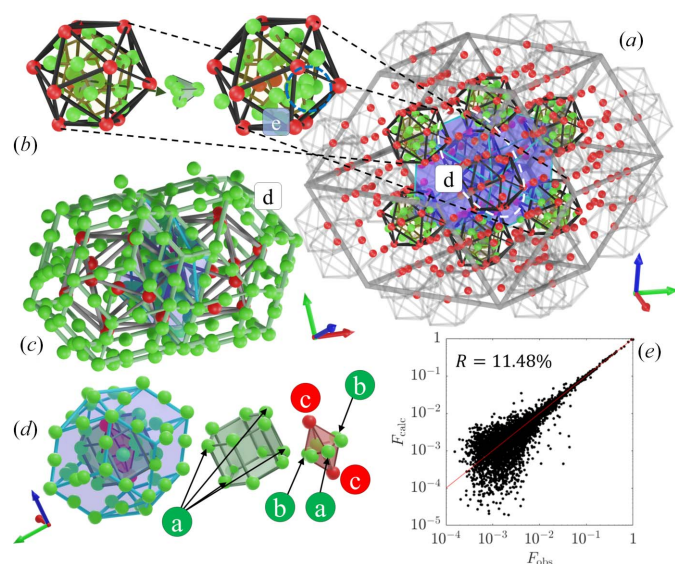


Figure 4

The local atomic arrangement in i-CdYb is based on the agglomeration of PR and OR in the RD unit (colors of the atoms as in Fig. 3). In (a), the RD with Yb atoms is plotted with a hexagonal bipyramid (blue) formed by eight icosahedral shells. Atoms of Cd, located on the dodecahedral shells within marked icosahedra, are plotted. With light shading, all edge-bound icosahedra are plotted to form a grid for the remaining Yb atoms. In (b), the magnified picture of the two hexagonal types of icosahedra is presented. The tetrahedron-centered one is generated by the PR unit, while the other is part of the OR. The tetrahedron has one of its faces perpendicular to the $3f$ axis, directed along the longer body diagonal of the PR. In (c), the magnified image of short b -linked triacontahedra is presented. The common part has the shape of a double-capped RD presented in (d). The inner structure is formed by a hexagonal prism of Cd and an octahedron with two Yb atoms in apices. Sites 'a' are generated by an icosidodecahedral shell, while sites 'b' are formed by dodecahedra. The sites 'b' are split. The correlation plot (e) between calculated F_{calc} and observed F_{obs} . The diffraction amplitudes show good agreement; however, a classical broadening for low-intensity peaks is observed. The orientations of each unit in space are given by three perpendicular vectors directed along the $2f$ axes.

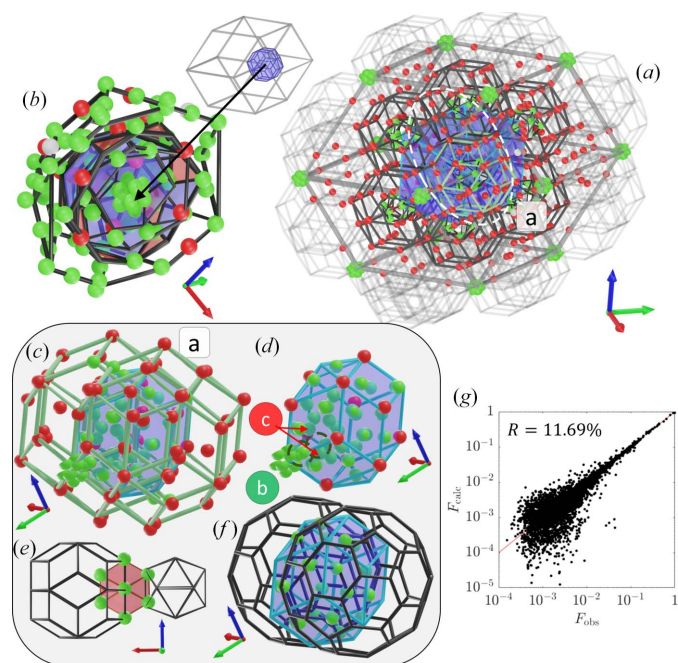


Figure 5

Local atomic arrangement in i-CdYb based on the agglomeration of PR and OR in the RD unit (colors of the atoms as in Fig. 5). In (a), the RD with Yb atoms is plotted with hexagonal bipyramid (blue) formed by eight RTH shells. Atoms of Cd, located in the vertices of icosahedral #1 shells, are marked with the addition of partially occupied sites associated with the tetrahedron. With light shading, all edge-bound RTH units are plotted to form a grid for the remaining Yb atoms. In (b), the magnified image of half of the Tsai cluster with a tetrahedron is depicted. The tetrahedron is assumed to be a partially occupied icosahedron with 0.3 occupancy probability. In (c), the magnified image of short b -linked triacontahedra is presented. The common part has the shape of a double-capped RD (d). The internal structure is made up of a hexagonal bipyramid and Cd atoms belonging to polyhedra (e) and (f). Atoms 'b' and 'c' create short distances. Atom 'b' comes from an icosahedral shell that forms the b -linkage and is located at the phason flip site. Atom 'c' is generated by an external icosahedral shell. We believe that this is not a consistent feature because the symmetry-related side from the RD is free of this atom. The orientations of each unit in space are given by three perpendicular vectors directed along the $2f$ axes. In (g), the correlation plot between calculated F_{calc} and observed F_{obs} diffraction amplitudes are shown.

same for all atoms in the icosahedra. The scale parameter is responsible for increasing/decreasing the size of the icosahedron as a whole object. Initially, the icosahedron was oriented with one of the faces being perpendicular to the $3f$ axis and centered in the vertex. Only the size of the icosahedron changes during refinement, not its orientation. The final composition is $\text{Cd}_{84.97}\text{Yb}_{15.03}$ with a density of 8.89 g cm^{-3} . Also, in this model, both calculated atomic composition and the density reproduce the experimental values very well. The residual electron density was also $<1.6\%$. The number of atoms in the model is larger than that for the Tsai cluster refinement, which is akin to the treatment of the tetrahedron in the structure.

In contrast to the model with Tsai clusters, one site in the OR is treated as a mixed-occupied site. It is 70/30% occupied by Cd/Yb. The atom can be seen in Fig. 5(b), located at the mid-edge position on the RTH outer shell

In Fig. 6 the atomic decoration of the asymmetric rhombohedral units with Bergman clusters is depicted. Analogously to the previous structural model, all atomic positions can be described as packings of RTH clusters. The positions of RTH clusters are the same as in the previous refinement (see Fig. 3 for comparison), but this time the shell structure is Bergman type.

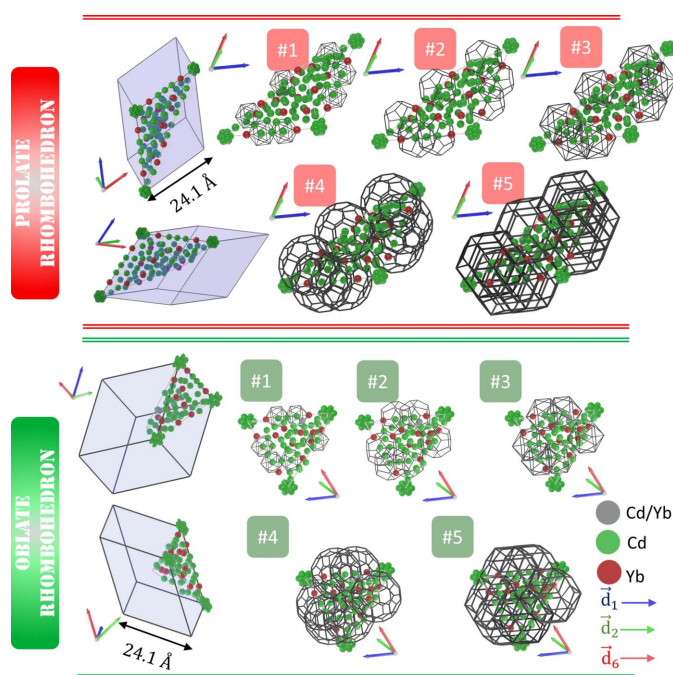


Figure 6

Atomic decoration of rhombohedral units in the i-CdYb refined model with the dual AKNt and Bergman clusters. The orientation of each unit is given by three vectors of icosahedral setting, directed toward the vertices a common face of the icosahedron. All shells of the Bergman cluster are given individually for clarity. The shells are icosahedron (#1), dodecahedron (#2), icosahedron (#3) (shells #2 and #3 form a rhombic triacontahedron), soccerball polyhedron (#4) and rhombic triacontahedron (#5). In most cases, there is a Cd atom in the center of the cluster. The disordered tetrahedron treated as a partially occupied icosahedron can be seen in the vertices of PR and OR.

The atoms in the vertices of the RTH outer shell are Yb, with an occasional Cd atom or a disordered tetrahedron. The density of RE elements within this shell is higher than in i-ZnMgTm, which is a natural consequence of the crystal composition. i-ZnMgTm has a concentration of RE elements almost twice lower than that of i-CdYb. There is a Cd atom on the edge of the asymmetric unit of the PR, very close to the vertex-bound tetrahedron. It is generated by the vertex of the dodecahedral shell. This atom is very close to an empty site next to the Yb atom lying on the edge of the PR. The empty site belongs to the #3 icosahedron and is empty due to the vicinity of the Yb atom, exactly like in the AgInYb PAC structure described by Li *et al.* (2008). The centers of Bergman clusters are occupied by Cd atoms.

By analogy to the refinement with Tsai clusters, the local atomic arrangement is considered within the RD. The visualization of the most interesting features is presented in Fig. 5. The RD unit is plotted in Fig. 5(a), where Yb atoms are presented with specially selected Cd atoms. Cd atoms are only plotted within eight icosahedral #1 shells centered within RTH clusters and for the disordered tetrahedron. Eight RTH clusters form a hexagonal bipyramid of the same size and orientation as in the Tsai cluster refinement. The grid for Yb atoms is formed by the RTH outer shell.

The short b -linkage formed by the apex positions in the hexagonal bipyramid is depicted in Fig. 5(c) with the analysis of the internal motifs in Figs. 5(d)–5(f). Once again, a double-capped small RD unit is formed, but with Yb atoms in the vertices. One disordered tetrahedron, generated by the internal vertex of the RD, replaces the Yb atom. Most Cd atoms belong to the intersection of two soccerball polyhedra and occupy sites at rhombic faces of the small RD. It is the local structural feature reported in the Bergman type i-ZnMgHo QC by Takakura *et al.* (2006). Eight Cd atoms inside the RD form a small hexagonal bipyramid that is rotated by 90° with respect to the large hexagonal bipyramid. The rotation is along the $2f$ axis, going through the vertices in the caps of RD. The hexagonal bipyramid is a motif found in the Bergman QC related and used to constitute a model of QC in i-AlZnMg (Henley & Elser, 1986) or i-AlCuLi (Yamamoto, 1992). In these structures, the bipyramid had a non-rotated orientation. Atoms in the hexagonal bipyramid are generated by a small icosahedron and a small RTH shell that is a combination of shells #2 and #3 [Fig. 6(e)]. In the double-capped RD, there are two sites that create small distances. The first one, 'b', is generated by the icosahedral #3 shell. This atom belongs to the phason flip site. Therefore, it can occupy two positions with the same probability marked with a dotted line circle. The position 'c' is close to the atoms in the soccerball polyhedron, making those atoms split. These atoms are generated by an icosahedral shell #3 that is outside the short b -linkage. On the opposite, symmetry-related side of RD the atom does not appear.

The tetrahedron is located at the vertices of rhombohedral units. This was expected since the tetrahedron in non-shifted electron density was found along the $3f$ axis of PR in positions corresponding to body-centered positions of the 6D unit cell.

After the shift, the body-centered positions become vertex-centered sites. All shells surrounding the tetrahedron are plotted in Fig. 6(b) and constitute a Tsai cluster. The Tsai cluster was found at the central node vertex of the large RD.

The correlation plot between the calculated and observed diffraction amplitudes is given in Fig. 6(g). High-intensity peaks are aligned along the center-of-mass line (red) with an occasional deviation above 10^{-2} in amplitude. A similar effect was observed in the refinement of the Tsai cluster. The broadening effect is also present here, being mostly symmetric. The value of the phasonic ADP is $1.96a_f^2$. It is larger than in the previous refinement, but still smaller than reported for other Tsai-type quasicrystals or even CdYb modeled by Takakura *et al.* (2007).

4. Discussion

The structure of i-CdYb is the second iQC structure solved by the real space method with the structural units being two rhombohedral of the AKNT. The exploitation of the τ^3 inflation rule of P-type iQCs (Ogawa, 1985) helps to overcome the problem of finding a unique atomic decoration for the PR and the OR. It was speculated whether the model used for i-ZnMgTm Bergman QC (Buganski *et al.*, 2020a) can be extended to other types of iQCs. The results provided in this paper prove the model can be made for Tsai-type QC but at this point the crystallographic *R* factor is higher than for the model by Takakura *et al.* (2007). Although the *R* factor is here higher (11.48% and 11.69% against 9.4%), the refined chemical composition agrees better with the experimental value [the composition reported by Takakura *et al.* (2007) is $\text{Cd}_{83.7}\text{Yb}_{16.3}$, whereas in this refinement it is $\text{Cd}_{84.9}\text{Yb}_{15.1}$ (Tsai clusters) and $\text{Cd}_{84.97}\text{Yb}_{15.03}$ (Bergman clusters)]. The calculated mass densities (8.89 g cm^{-3} for Tsai and 8.98 g cm^{-3} for Bergman) reproduce the experimental value (8.88 g cm^{-3}).

The phasonic ADPs obtained here are 2–3 times smaller than in the case of the *nD* approach. It is not a trivial difference as the formula in both methods is the same and is given by an exponentially decaying function. This amount of difference in a decay parameter drastically changes the shape of the curve, therefore, there must be another function that compensates for it. From other refinements of QCs, it is evident that the value of the extinction parameter is coupled with the phasonic ADP (Buganski *et al.*, 2019; Buganski *et al.*, 2020b). Both are global parameters affecting the model in its entirety. The formula for the extinction effect is different in Takakura *et al.* (2007). It is more complex and possibly allows the *R* factor to be lower. On the other hand, the lower phasonic ADP correlates better with the sample of i-CdYb being an excellent quality crystal.

The calculations were carried for two structural models. The difference between models comes from the displacement of the 6D electron density by a half body-diagonal vector. Since such a translation does not change the structure, both models should be complementary, and they are. Both converge to similar *R* factors and the same local motifs can be found. It

could be deduced that Bergman-type QCs are the same as Tsai type. They are in fact not identical. One, maybe the most important, difference is RE elements for i-CdYb are agglomerated in the OD_v, resembling the RTH OD of the simple decoration model with a hole in the stellate-polyhedron-type OD (Takakura *et al.*, 2007). RE elements in i-ZnMgTm belong to the stellate polyhedron OD, and the hole is in the RTH OD (Buganski *et al.*, 2020a). A simple uniform shift cannot interchange the location of atomic species between ODs. For this reason, those two structures are not isostructural even though both can be represented by either Tsai or Bergman clusters alone.

Both types of clusters can be regarded as structure building units in both 1/1 and 2/1 PACs. In the paper by Li *et al.* (2008) it was proposed that the i-AgInYb 2/1 Tsai-type PAC can be modeled as a packing of 102-atom pseudo-Bergman cluster. The term ‘pseudo’ come from the observation that shells of the cluster are deformed with additional vacancies at the #3 icosahedral shell where vacancies are created by the short distance to Yb atoms located at the #1 icosahedral shell. In the paper by Buganski & Wolny (2023), the deformations of subsequent shells were characterized. It was additionally proven that the same structure representation with Bergman clusters holds in 1/1 PACs. The fact is that the characteristic shell deformation, described by Li *et al.* (2008) and Buganski & Wolny (2023) especially for the soccerball shell, pertains to Bergman clusters in Tsai-type structures regardless of whether they are periodic or quasiperiodic. To confirm it is present in the model of i-CdYb, the shell structure of exemplary Bergman clusters is plotted in Fig. 7. Cd atoms are significantly displaced from the vertices of the soccerball polyhedron even creating split atoms on the join between the PR and the OR (Fig. 7, bottom). Vacancies in the #3 icosahedral shell have the same origin as in PACs. The number of vacancies depends on

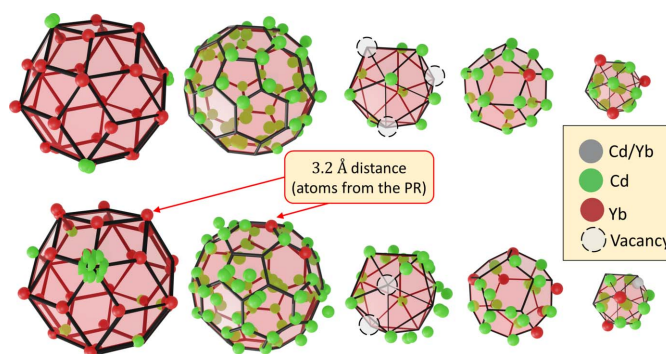


Figure 7

Bergman clusters in two positions within the RD. The upper shell structure is produced on the body diagonal position, whereas the lower one is produced on the edge shared by the PR and the OR. The positional disorder on the soccerball shell and vacancies at the icosahedral shell are consistent with features observed in the PACs. Two Yb atoms located on the soccerball polyhedron form a short distance with Yb atoms at the RTH shell known to occur within the interstitial part (PR units) of the Takakura *et al.* (2007) model.

the position of the cluster. For instance, the cluster on the body diagonal of the PR has three vacancies related to three Yb atoms in the #1 shell, whereas the cluster formed by the face-sharing PR and OR has only two vacancies. The site dependence of the number of vacancies is consistent with what was observed for PACs by Buganski & Wolny (2023). The novelty of the QC is Yb atoms occupy vertices of the soccerball that was not recognized in PACs. Those atoms form a short 3.2 Å bond with Yb atoms at the RTH shell. A bond of that length is in fact present in the model by Takakura *et al.* (2007) and is related to Yb atoms on the longer body diagonal of PR units. Since here the whole structure is interpreted solely as the covering by RTH clusters, the short RE–RE bond must have been accommodated within RTH clusters. The bond found its place between the vertices of the RTH and the soccerball shells.

The tetrahedron is found in both considered models. In the Tsai-cluster refinement, tetrahedra occupy two high-symmetry positions, *i.e.* the $3f$ sites dividing the longer body diagonal in a 1:τ:1 ratio. Both are oriented in such a way that one of the faces is perpendicular to the diagonal axis. Because the symmetry of the tetrahedron matches the symmetry of the site where it is located, there is no observable disorder of this tetrahedron. The orientational order can be useful for QCs where the order in the orientation of the tetrahedron is reported, such as the superstructure in 2/1 PAC of i-CdMgYb (Yamada, 2021). On the other hand, in the Bergman cluster refinement, the tetrahedron is found in the vertices of both the PR and the OR. It is compatible with the Tsai-cluster refinement because the sites mentioned at the longer body diagonal become vertices of rhombohedra upon the shift in 6D space discussed earlier. The tetrahedron in the Bergman cluster-based refinement cannot be treated as ordered in one orientation. It was modeled as an icosahedron with one-third site occupancy. It can be seen here how the choice of the tiling influences the structural solution. The point density of the tetrahedral sites in the Tsai-cluster refinement is $2[\tau/(\tau V_{\text{PR}} + V_{\text{OR}})]$ because the ratio of PR to OR is τ:1. Quantities V_{PR} and V_{OR} are the volume of the PR and OR, respectively. The point density in the Bergman-cluster refinement is $(\tau + 1)/(\tau V_{\text{PR}} + V_{\text{OR}}) = \tau[\tau/(\tau V_{\text{PR}} + V_{\text{OR}})]$. The point density is obviously different. Probably not all of the sites in the Tsai-cluster model are occupied by tetrahedra, and the partial occupancy with the Cd or Yb atom should be assumed. This solves the problem, but within the current experimental resolution it cannot be confirmed.

Models presented here do not provide more details about the atomic structure of i-CdYb. The lower value of the R factor in the Takakura *et al.* (2007) model undoubtedly indicates that model as the better one. However, it was proven that the real-space modeling with the AKNt can be applicable to more than just Bergman-type iQCs with R factors within the range that is contemporarily possible including the nD approach. At this stage it is impossible to state whether higher values of R factors are akin to too strict restrictions imposed on both the atomic composition and phasonic ADPs. The method must be further tested.

5. Summary

The atomic structure of the icosahedral Cd_{5.7}Yb binary quasicrystal was solved using the Ammann–Kramer–Neri tiling and its dual tiling as a quasilattice. The unique decoration of two rhombohedra that make up the Ammann–Kramer–Neri tiling was found when the inflation rule for primitive icosahedral lattices was used. The uniqueness of our study is to compare two structural models based on two types of dual tiling with Tsai- or Bergman-type clusters, whereas only the Tsai-type model is reported in the literature (the CdYb icosahedral quasicrystal is considered a reference model of the Tsai-type quasicrystal). Crystallographic R factors are estimated to be 11.48% and 11.69%, and the respective final refined compositions (densities) are Cd_{84.9}Yb_{15.1} (8.99 g cm^{−3}) and Cd_{84.97}Yb_{15.03} (8.89 g cm^{−3}) for the Tsai and Bergman models, respectively. The 6D approach was used only for the analysis of the interatomic correlations, but the refinement was carried out in real space, based on the average-unit-cell method. It was shown that the structure can be represented as a covering by either Tsai clusters or Bergman clusters with the existence of a short a -linkage along the fivefold axis. Bergman clusters exhibit the same local deformations that are known to be present in Tsai-type periodic approximant crystals. Locations of cluster centers of either Tsai or Bergman type in the quasicrystal are mutually related to the shift of the electron density along the body diagonal of the 6D unit cell. The treatment of the tetrahedron inside the Tsai cluster can be either an orientationally ordered unit or a partially occupied icosahedron without icosahedral symmetry breaking.

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