

# Canonical cell model of Cadmium-based icosahedral alloys

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Cadmium-based quasicrystals (Cd-Ca and Cd-Yb) were the first binary alloys discovered to form thermodynamically stable quasicrystals. As a binary alloy, and with a strong size difference between atomic species, they are ideal system for structural and thermodynamic analysis. Observed quasicrystal approximants with crystallographically determined structures can be interpreted as decorations of Henley's canonical cells. We use first-principles total energy calculations to resolve details of the most favorable decorations.

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## I. INTRODUCTION

Thermodynamically stable binary icosahedral quasicrystals occur in the alloy systems  $\text{Cd}_{5.7}\text{Yb}$  and  $\text{Cd}_{5.7}\text{Ca}$  [1–3]. Since their discovery numerous attempts have been made to model their structure. Efforts that rely on “atomic surfaces” and higher dimensional space suffer difficulty since certain atomic positions appear to be displaced far from any simply represented position. Atomic surface representations also average over disorder phenomena in a manner that may hide important details of the structure. More successful models describe the local structural motifs based on cluster models (see Fig. 1). However, these approaches leave unspecified how the clusters arrange to fill space quasiperiodically, and also leave some empty regions that must be filled with “glue” atoms. We simultaneously resolve both these issues within the cluster model by decorating canonical cells [4, 5] with clusters and glue atoms, then filling space using canonical cell tilings. First-principles total energy calculations suggest our proposed structures are plausible.

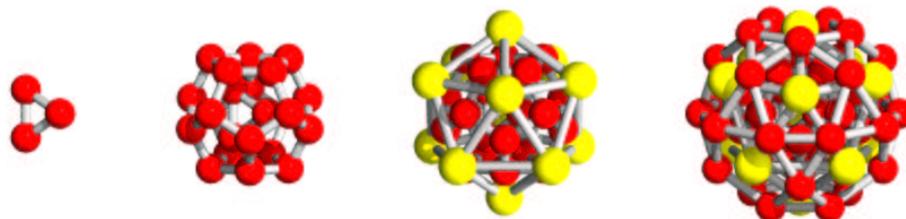


FIG. 1: Adding shells to  $\text{Ca}_{12}\text{Cd}_{54}$  cluster. Left to right: (s1)  $\text{Cd}_4$  tetrahedron (atom at back right hidden from view); (s2)  $\text{Cd}_{20}$  dodecahedron; (s3)  $\text{Ca}_{12}$  icosahedron; (s4)  $\text{Cd}_{30}$  icosidodecahedron.

Cadmium-base quasicrystals created interest both because of their unusual structure and because they occur as binary alloys. Binary alloy systems can be simpler to study, both experiemntally and theoretically, than the ternary alloy systems in which previously known thermodynamically stable quasicrystals occur. One advantage of a binary alloy is the presence of just a single composition variable to control, as opposed to two independent compositions in a ternary. Another advantage, from a theoretical perspective, is the strong size constrast between the large Ca or Yb atoms (nominal diameters 3.95 and 3.88 Å) and the relatively small Cd atoms (nominal diameter 2.98 Å). These elements also exhibit strong differences in electronegativity and other chemical properties. As a result, chemical substitution resulting in mixed site occupancy unlikely. In contrast, at least one pair of elements substitute easily for each other in the stable ternary quasicrystals.

Our approach uses the crystallographically known structures of quasicrystal approximants to validate the basic cluster structure and to identify likely positions of “glue atoms” in the space between clusters. We use first-principles

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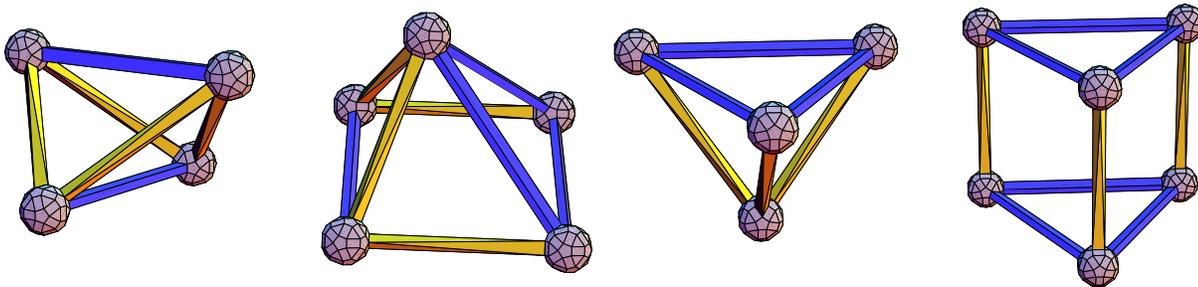


FIG. 2: Canonical Cells [4] illustrated as if constructed from ZomeTools. Icosahedral balls occupy vertices. Blue and yellow edges lie along 2-fold and 3-fold directions.

total energy calculations to optimize our models and resolve details not available from the known approximants, either because of intrinsic structural disorder in the materials or because of the limited number of known structures that can be used as examples.

## II. CANONICAL CELLS

Our Ca-Cd decoration models utilize tilings of “canonical cells” [4]. Space is divided into 4 kinds of cells, denoted  $A, B, C$  and  $D$  (see Fig. 2). Cell vertices are occupied by nonoverlapping icosahedral clusters linked along 2-fold and 3-fold icosahedral directions, which are called  $b$  and  $c$  bonds. The  $A$ -cell is a BCC tetrahedron, the  $B$ -cell is a rectangular pyramid, the  $C$ -cell is triangular tetrahedron and the  $D$ -cell is a trigonal prism. Cell faces are of three types:  $X$  (isosceles triangle with 1  $b$  and 2  $c$  edges);  $Y$  (equilateral triangle with 3  $b$  edges);  $Z$  (rectangle with 2  $b$  and 2  $c$  edges). Packing constraints guarantee that  $B$  and  $C$  cells occur in equal numbers.

Canonical cell tilings can be decomposed into tilings by oblate (OR) and prolate (PR) rhombohedra whose edges run along 5-fold directions. Each cell node becomes a vertex in the rhombohedral tiling with edges in all twelve directions. Each 2-fold  $b$  bond becomes a rhombic dodecahedron (RD, which decomposes into 2 OR and 2 PR). Each 3-fold  $c$  bond becomes a PR. A PR pierces through each  $Y$ -face and also an OR lies on each  $Z$ -face. The  $D$  cell actually contains four interior PR’s, the one piercing its  $Y$ -face, plus three more associated with the three interior (fake)  $c$ -bonds.

Some special positions within the canonical cells are  $\alpha$ ,  $\gamma$  and  $\delta$  sites, and will be used to describe the locations of glue atoms. The  $\alpha$  sites are vertices of the rhombohedron tiling that do not coincide with CCT nodes. The  $\gamma$  sites are located at positions  $1/3$  and  $2/3$  along the long diagonals of the four RD faces that run parallel or perpendicular to the  $b$  bond. The  $\delta$  sites are located at 6D body-center positions, for example they divide the long body diagonal of a PR into segments of length  $\tau^{-2} : \tau^{-3} : \tau^{-2}$ .

In the following we consider the energetics of several canonical cell tilings. Table I lists some of their properties.

TABLE I: Canonical cell tilings considered in this work. Pearson symbol of tiling, name of known compound, numbers of objects per unit cell, first-principles energy

Name.Pearson	Compound	Symmetry	Nodes	A	B	C	D	$\Delta E$
A.cI2	CaCd <sub>6</sub>	$Im\bar{3}$	2	12	0	0	0	stable
BC.hR1		$R\bar{3}m$	1	0	2	2	0	2.8
D.hP1		$P\bar{3}m$	1	0	0	0	1	6.7
ABC.cP8	Ca <sub>13</sub> Cd <sub>76</sub>	$Pa\bar{3}$	8	24	8	8	0	2.9
ABC.mP2		$P2$	2	6	2	2	0	6.4
ABC.mP4		$P2_1/c$	4	12	4	4	0	6.6
ABCD.hR3		$R3m$	3	6	3	3	1	2.6
ABCD.mP4		$P2/m$	4	6	4	4	2	6.9

Two of the tilings correspond to known Ca-Cd structures. The  $\text{CaCd}_6$  structure, also known as the 1/1 cubic approximant, is the pure A-cell tiling A.cI2. The precise structures remain controversial with Pearson type given variously as cI160, cI176, cI184 and cI232 [6–11] as a result of uncertainty regarding the proper orientations of the  $\text{Cd}_4$  cluster center tetrahedra. In fact, there appears to be a low temperature (around  $T=100\text{K}$ ) order-disorder phase transition [10, 12, 13] in which these tetrahedra lock into specific relative orientations. Our calculations [14] confirm that ordering into particular cluster orientations can lower the energy slightly but that at elevated temperatures around  $T=800\text{K}$ , where the quasicrystals form, this degree of freedom should indeed be disordered.

At high temperature all models agree the structure is body-centered cubic, with two basic  $\text{Ca}_{12}\text{Cd}_{54}$  clusters plus 36 Cadmium glue atoms per simple cubic cell. The BCC structure tiles space with canonical A cells, with a cluster center at each A-cell vertex. Each simple cubic cell contains 12 A-cells. The 1/1 approximant structure implies a unique decoration of the A-cell, same for the cluster center tetrahedra. Each A-cell contains 2 Ca atom and 12 Cd atoms.

The canonical cell decoration model implies decorations of prolate- and oblate-rhombahedra that are consistent with an earlier proposal [8] for the 1/1 cubic approximant. An advantage of the canonical cell approach is that it can be systematically extended to model higher approximants and also the icosahedral phase. The other solved approximant structure [15] is the 2/1 cubic approximant,  $\text{Ca}_{13}\text{Cd}_{76}$ . We recognize this as the ABC.cP8 tiling, containing 24A, 8B and 8C cells. The decoration implied for the A-cell agrees precisely with that obtained from the 1/1 approximant.

The structure  $\text{Ca}_2\text{Cd}_7$ .hP68 is based on trigonal prisms, whose triangular faces are Y-faces, but their rectangular faces are not Z-faces, so this structure is not a CCT, and should not be considered a proper approximant. The clusters based at trigonal prism vertices are imperfect basic clusters, and instead of being centered by  $\text{Cd}_4$  tetrahedra, they are centered by  $\text{Cd}_3$  triangles.

### III. TOTAL ENERGY CALCULATIONS

We carry out *ab-initio* calculations using the plane-wave program VASP [16, 17] which yields reasonably accurate total energies. This approach uses ultrasoft pseudopotentials [18, 19] and PAW potentials [20] to represent the effective interaction of valence electrons with ionic cores, and solves the many-body quantum mechanical band structure of these electrons using electronic density functional theory. We choose to model Cd-Ca rather than Cd-Yb because the alkali earth element Ca is easier to treat from first principles than the rare earth element Yb.

First, we use VASP to reproduce the sequence of low-temperature stable phases in the established Ca-Cd binary phase diagram [21]. To do this we calculate the cohesive energy for each known structure, and several hypothetical ones. Each structure is fully relaxed in both unit cell parameters and atomic coordinates. All energies are converged to an accuracy of 1 meV/atom or better by increasing the k-point mesh density. These calculations use PAW potentials in the generalized gradient approximation and a constant plane-wave energy cutoff of 274 eV.

Subtracting each cohesive energy from the tie-line joining the pure elements in their ground states yields enthalpies of formation  $\Delta H_{for}$  (at  $T=0\text{K}$ ). Enthalpies of all known and many hypothetical Ca-Cd structures are plotted in Fig. 3. We label each structure with its name followed by its Pearson symbol.

Agreement between our calculation and the established phase diagram requires that all known low temperature structures lie on the convex hull of enthalpy versus composition. Additionally, all hypothetical structures must lie above the convex hull (we define  $\Delta E$  as a measure of energy above the convex hull), as must all known high temperature, high pressure and metastable phases. Agreement is good but not perfect. We now address the disagreements.

The low and high temperature  $\text{CaCd}_2$  phases are reversed in energy relative to the experimental report that oI12 is stable at high temperatures and hP12 at low. The 11.6 meV/atom energy difference seems too large to be a flaw in our methods. However, the transition between the hP12 and oI12 variants has not been well established experimentally. Most likely, according to our findings, the presumed low temperature hP12 phase is actually a metastable phase, and the nominal high temperature phase is actually stable all the way to low temperatures.

The other disagreement is our finding that  $\text{Cd}_{11}\text{Ce}$ .cP36 touches the convex hull, predicting it should occur as a stable phase. This structure has not been reported in Ca-Cd. We find it to be marginally stable, lying 4.6 meV/atom below the line from  $\text{CaCd}_6$  to pure Cd, so small errors in our calculations could cause us to mis-predict stability. Alternatively, it may be truly stable but difficult to nucleate and grow.

### IV. CCT DECORATION REFINEMENT AND NEW STRUCTURES

Given a specific tiling structure, modelling the atomic structure naturally breaks into two parts: (1) refining the decoration of glue atoms outside the clusters; (2) determining the optimal cluster center tetrahedron orientations.

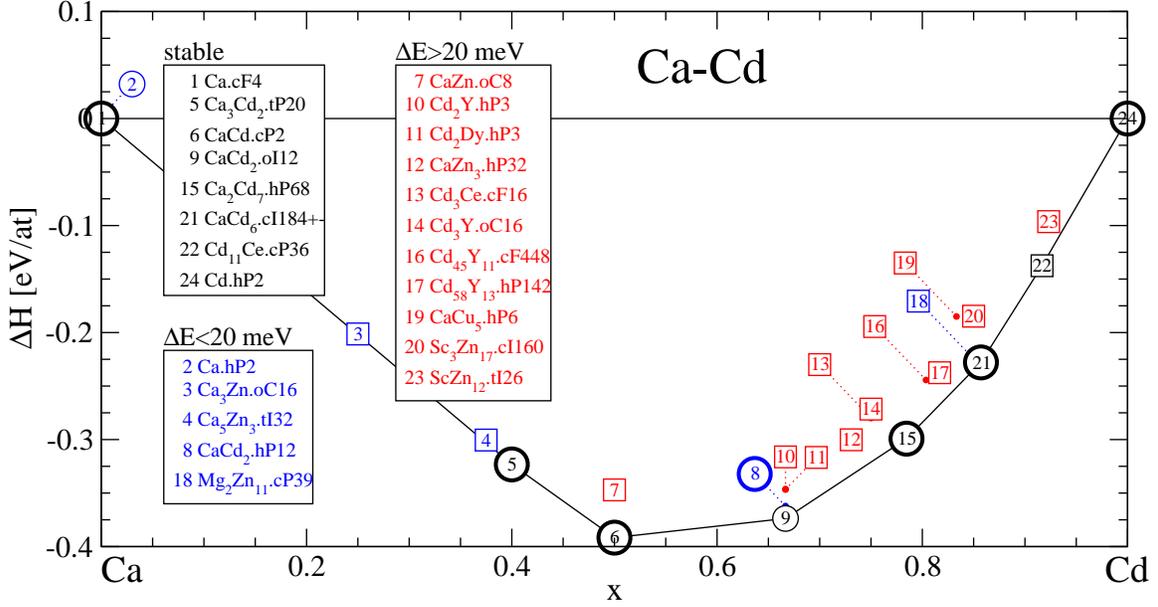


FIG. 3: Enthalpies of formation of Ca-Cd compounds. Notation: heavy circles indicate known low temperature phases; light circles indicate known high temperature phases; squares indicate either structures not reported in Ca-Cd system. Line segments connect vertices of convex hull. Legends list calculated stable structures ( $\Delta E \equiv 0$ ), low but positive energy structures ( $0 < \Delta E < 20$ ), and higher energy structures ( $20 < \Delta E$ ).

We approach task (1) by comparison with known approximant structures (this fixes the decoration of the A cell) and by varying atomic decorations of the BC and D tilings and optimizing their ab-initio energies. The structure of the 1/1 cubic approximant is based on the A.cI2 tiling, and uniquely fixes the glue atom decoration of the A cell. It turns out the Ca-Cd decoration is identical to the  $\alpha$ -AlMnSi decoration [22] with Ca on Mn sites and Cd on Al sites (strangely this interchanges the roles of large and small atoms) except for the following details: (i) Shells  $s_1$  and  $s_2$  of the basic Ca-Cd cluster replace the innermost icosahedron of the Al-Mn Mackay cluster; (ii) restore full SI order (from FCI in  $\alpha$ -AlMnSi) by placing Cd on the  $\delta$  sites in all RD's, not just the even ones. This rule generalizes easily to the other canonical cells. We tested several plausible alternatives and consistently found these rules were optimal. They are also consistent with the experimentally determined structure of the 2/1 cubic approximant based on the ABC.cP8 tiling.

Task 2 remains incomplete at the present time. We made some initial efforts by Monte Carlo annealing using a toy Ca-Cd pair potential to distribute Cd atoms among a list of possible sites based on experimental observations [11]. Unfortunately, this approach does not incorporate interactions of  $s_1$  tetrahedra in neighbouring clusters via distortion of the second shell ( $s_2$ , Cd<sub>20</sub> dodecahedron) of the clusters. Indeed, Cd atoms from the tetrahedra can traverse from one cluster to another by pushing  $s_2$  atoms out of their nominal positions into “cube-center” positions [11] located on the 3-fold linkage between neighbouring clusters. These sites may serve either as a low-energy transient state for a Cd, and indeed such sites have non-zero occupancy in the 2/1 approximant.

$\Delta E$  values of our optimal decorations, listed for the tilings in table I, vary from +2 to +7 meV/atom. We attribute most of the energy variation to the problem of cluster center tetrahedron orientations. However, in the case of larger approximants incomplete  $k$ -point convergence and structural relaxation may also contribute. In cases of very large structures, we carried out some pre-relaxation using EAM potentials [23], because the ab-initio calculations were time- and memory-consuming.

## V. DISCUSSION

We choose to model the Ca-Cd quasicrystal structure using real three-dimensional space rather than the six-dimensional space that is commonly used for quasiperiodic icosahedral structures. One reason for doing so is that many sites cannot be conveniently represented in the six-dimensional space, so the atomic surface structure would have to be quite complicated. Additionally, our calculation of energetics demands a focus on real space structure, especially because the smaller approximants that are in reach of first-principles calculation do not sample perpendicular space

extensively. Yet, they provide all the variety needed to resolve tile decoration rules in real space.

Our final model yields a deterministic assignment of glue atoms within canonical cells. The cluster center tetrahedra are not deterministic, and follow as-yet undiscovered context-dependent rules. We invoked rhombohedron tilings in order to describe certain sites within the canonical cells. However, we cannot give deterministic decoration rules in terms of the rhombohedra because they are on a shorter length scale which requires a great deal of context dependence to achieve low total energy. We could use rhombohedra at a larger length scale, but could then be decomposed back into our canonical cells. Ultimately, the advantage of the CCT model is it focuses on the cluster structure and the linkage rules among clusters.

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