

Problem Solving with Pentagons: Tsai-Type Quasicrystal as a Structural Response to Chemical Pressure

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Supporting Information

ABSTRACT: Even after significant advances in the structural characterization of quasicrystals—phases whose diffraction patterns combine the sharp peaks normally associated with lattice periodicity and rotational symmetries antithetical to such periodicity—this new form of long-range order remains enigmatic. Here, we present DFT–chemical pressure calculations on the Tsai-type quasicrystal approximant CaCd_6 , which reveal how its icosahedral clusters can be traced to simple CaCu_5 -type ($hP6$) intermetallics. The results indicate that the Tsai-type clusters emerge from an atomic-size-driven transformation from planar arrangements to spherical clusters, recalling the relationship between graphene and C_{60} .

Quasicrystals (QCs) are a new form of condensed matter exhibiting the seemingly contradictory properties of long-range atomic order and rotational symmetries incompatible with the translations of crystalline atomic packing.^{1,2} The development of higher-dimensional approaches to quasiperiodic crystals, culminating in the structural determination and refinement of the Tsai-type icosahedral phase $\text{YbCd}_{5.7}$,³ represents a major advance in structural science. As the geometrical details of QCs and their approximants (QCAs) emerge, they inspire still more wonder that such arrangements arise in materials.^{4,5} Understanding and ultimately harnessing the driving forces that shape their long- and short-range order could offer avenues to new atomic arrangements and properties enhanced by aperiodicity.^{4,5}

The formation of icosahedral QCs has been connected to the Hume–Rothery rules for intermetallic compounds, in which valence electron concentration (VEC) and atomic size differences are key factors influencing the stability of a structure.^{6–8} The importance of VEC is supported by theoretical calculations that show the frequent presence of pseudogaps in the electronic density of states at the Fermi energy. This has led to the productive strategy of pseudogap tuning for the discovery of new QCs and QCAs.^{9,10} Atomic size requirements, on the other hand, are difficult to elucidate with theoretical calculations and are mainly inferred from empirical stability ranges.^{8,10,11} Further development is needed to determine how electronic and size factors interact to stabilize icosahedral arrangements in QCs.

Herein, we describe how our recently developed density functional theory (DFT)–chemical pressure (CP) analysis^{12,13} reveals a visual, intuitive picture for the formation of icosahedral clusters in the Tsai family over simple periodic structures. To begin, it is helpful to view metallic QCs and QCAs in their broader context: they are a subset of intermetallic phases, a vast

family of solid-state compounds formed between metallic elements. Intermetallics exhibit a broad structural diversity, with some having unit cells that contain thousands of atoms, such as NaCd_2 ($cF1157$)¹⁴ and $\text{Al}_{55.4}\text{Cu}_{5.4}\text{Ta}_{39.1}$ ($cF23134$).¹⁵ A majority of intermetallics, however, crystallize in simple structures with relatively few atoms per unit cell, such as the CsCl-type phases ($cP2$) and the Laves phases (e.g., MgZn_2 , $hP12$). When these structures are surveyed, a striking observation can be made: complex structures often have compositions similar to those of simple structures in related binary systems. For instance, if we begin with the Tsai-type 1:1 approximant CaCd_6 (Figure 1a)^{16,17} and then look to the corresponding region in the

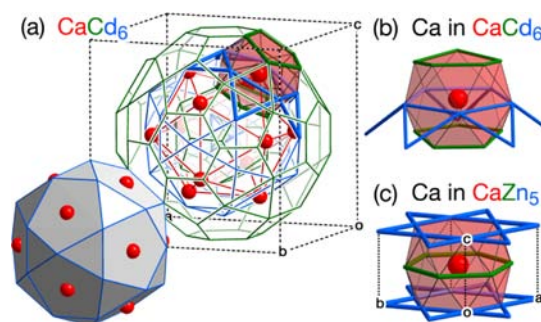


Figure 1. Comparison of the Ca coordination environments in the (a–b) Tsai-type QCA CaCd_6 , and (c) the CaCu_5 -type CaZn_5 .

Ca–Zn system, we find the CaCu_5 -type CaZn_5 phase with only six atoms per unit cell.¹⁸ Comparing the Ca coordination environments in CaCd_6 and CaZn_5 yields a structural relationship in which pentagonal transition metal (TM) rings are replaced with hexagonal ones (Figure 1b,c).¹⁹

The driving forces leading to the CaCd_6 QCA can be seen in the electronic structure of the simpler alternative offered by the CaCu_5 type. To see this, we show in Figure 2 the results of DFT–CP calculations²⁰ on a hypothetical CaCu_5 -type CaCd_5 phase. Large negative CP lobes (black) appear on the central Ca atom, corresponding to a net CP of -559 GPa. The Ca atom contacts are thus longer than their energetically optimal distances. However, contraction along these contacts is prevented by positive CPs (white) within the Cd sublattice. Optimizing the Ca–Cd and Ca–Ca contacts would mean putting increased strain on already overly short Cd–Cd distances.

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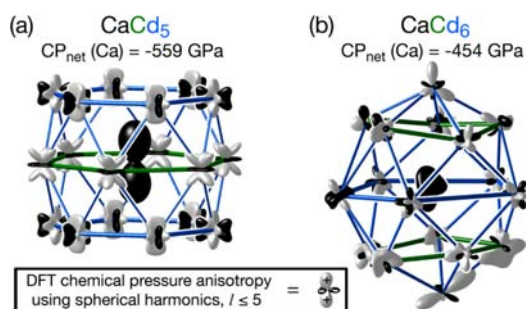


Figure 2. Local CP relief in the Tsai-type QCA CaCd_6 . Comparison of the CP anisotropies around (a) the Ca atoms in the hypothetical CaCd_5 and (b) the most strained Ca atom of CaCd_6 . The size of each lobe is proportional to the CP magnitude calculated for that direction, while the color indicates the sign: black for negative and white for positive.

The pressure–distance paradox²¹ of pressure-induced phase transitions provides a guide to how the structure might respond to this: phases under high external pressure tend to adopt higher coordination numbers. As a consequence, the individual bond lengths increase despite the high pressure. Similarly, under low pressure, atoms in a compound will prefer fewer neighboring atoms but at shorter distances. With the large negative CP on the Ca atoms, we would expect Ca coordination environments adapted for a smaller atom: fewer neighbors with shorter interatomic distances to the central Ca atom.

Earlier, we showed that similar forces were at work in the Ca–Ag system.¹² There, large negative CPs on the Ca atoms are relieved through interfaces between CaCu_5 -type slabs to form the Ca_2Ag_7 structure. The Ca–Cd system exhibits more exotic structural solutions to the same issues: instead of the expected CaCu_5 -type phase, several compounds appear near the 1:5 Ca–Cd ratio,²² including the CaCd_6 QCA.

The CaCd_6 structure has been described previously as a bcc packing of Tsai-type clusters, with the clusters themselves are built from nested polyhedra (Figure 1a). Though the unit cell as a whole initially bears little resemblance to the CaCu_5 type, highlighting the local Ca environment (Figure 1b) yields a pentagonal analog to its familiar hexagonal counterpart in the CaCu_5 type (Figure 1c). Like tightening a too-loose belt, pentagons are expected to provide the tighter coordination needed by the Ca atoms.

DFT–CP analysis of the Tsai-type approximant CaCd_6 supports its comparison with the CaCu_5 type. As in the hypothetical CaCd_5 phase (Figure 2a), the Ca coordination environments of CaCd_6 (Figures 2b,c) exhibit tension between negative CPs along the Ca–Cd contacts and positive CPs along the Cd–Cd ones. However, the transition from hexagonal to pentagonal polyhedra changes the balance of this tension. While in CaCd_5 the Ca CP surfaces are highly anisotropic and large (net CP = –559 GPa), the corresponding surfaces in the Tsai-type QCA are more spherical and smaller (net CPs between –451 and –418 GPa). This is in accord with the CP–distance paradox; moving to fewer, but closer Cd neighbors alleviates negative pressure on the Ca sites.

CaCd_6 's use of pentagons provides a way of locally relieving CP issues but poses a challenge for the long-range atomic arrangements of the structure. Pentagons are more difficult to tile than the original hexagons. The solution taken by CaCd_6 is found in curvature, as is shown in Figure 3, where the CaCu_5 and CaCd_6 structures are dissected layer by layer. The CaCu_5 type is presented as a stacking of a Cu honeycomb net (Figure 3a), a Ca

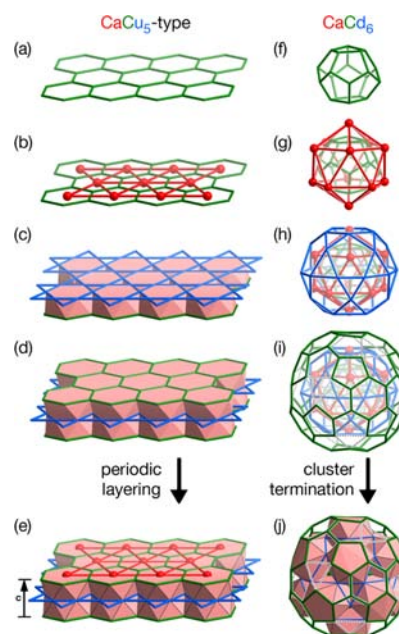


Figure 3. Parallels between the CaCu_5 type and the Tsai-type cluster. The CaCu_5 type is built from a stacking of hexagonally symmetric nets (a–d) and then repeating the sequence periodically to give (e) the full crystal structure. The Tsai-type cluster has corresponding shells based on pentagons shown in parts f–i but ends with (j) cluster termination as the Ca coordination environments are completed. For clarity, the disordered tetrahedron at the center Tsai-type cluster is not shown.

hexagonal net (Figure 3b), and then a Cu kagome net (Figure 3c). These layers stack neatly along the *c* axis, repeating in a periodic fashion. When each hexagon is reduced to a pentagon in the observed CaCd_6 , planar packing is no longer the simplest option. Where the CaCu_5 type exhibits a honeycomb network of TM atoms, the Tsai type curls its pentagonal “net” into a dodecahedron (Figure 3f). Much like a graphene sheet could roll into a C_{60} molecule by reducing some hexagons to pentagons, here a dodecahedron forms when every hexagon contracts to a pentagon. Likewise, the hexagonal net of Ca atoms in the CaCu_5 type becomes an icosahedron in the Tsai cluster (Figure 3g). In the CaCu_5 type, the stacking of layers continues in the creation of a periodic structure, while in CaCd_6 , the corresponding polyhedra nest concentrically until the Ca coordination environments are complete.

In Figure 4, we show the CP anisotropies for the full Tsai-type cluster. Now familiar themes recur: the Ca atoms experience negative pressures, which are counteracted by positive pressures between the Cd atoms as in the original CaCu_5 -type structures. A comparison of the CP anisotropy surfaces throughout this cluster with those of the hypothetical CaCu_5 -type CaCd_5 phase (Figure 4f) shows that the CPs of nearly all of the atoms have been soothed on moving to their corresponding positions in CaCd_6 .

The CP scheme of CaCd_6 also offers insight into another remarkable feature of the Tsai-type clusters that we had set aside until now: the disordered tetrahedra at their cores.^{17,23} As in other places in the structure, some of the Cd–Cd contacts between the central tetrahedron and surrounding dodecahedron experience positive pressure. This would be minimized when the Cd atoms of the tetrahedron lie in the pentagonal hollows of the dodecahedron. However, the symmetry incompatibility²⁴ between the two polyhedra means that when two Cd atoms on the tetrahedron lie in these hollows, the other two directly align

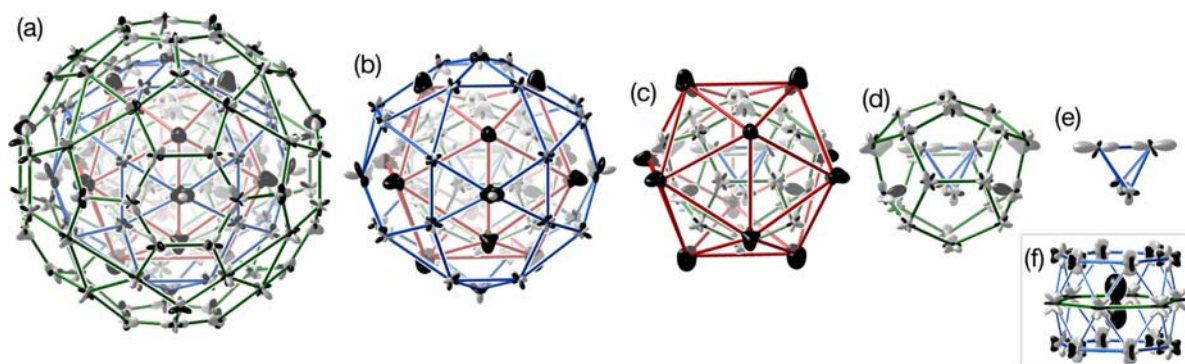


Figure 4. CP analysis of the Tsai-type cluster in CaCd_6 . The entire Tsai-type cluster is shown in part a and then layers are removed to show (b) a Cd icosidodecahedron, (c) a Ca icosahedron, (d) a Cd dodecahedron, and (e) the central Cd tetrahedron (disordered in the experimental structure). For reference, the corresponding results for CaCd_5 are plotted to scale in part f.

with vertices on the dodecahedron (Figure 4d). The resulting interactions exhibit the largest positive pressures in the structure. In our DFT optimization, all tetrahedra were forced to have the same static orientation, allowing systematic strains to build up over the entire crystal. The experimentally observed disorder in the orientation of these tetrahedra may serve to diffuse this strain.

In this Communication, we have traced the formation of QCA CaCd_6 to the severity of CPs in the simple CaCu_5 type. The Ca atoms in the hypothetical CaCu_5 -type CaCd_5 experience strong negative CPs caused by the size of their hexagonal environments. Replacing these hexagons with pentagons, as in the Tsai-type clusters, provides local relief but introduces noncrystallographic 5-fold symmetry. An elegant solution is found in curvature: whereas the CaCu_5 type is composed of flat sheets of neatly periodic hexagonal rings, the introduction of pentagons leads to curved nets and ultimately the spheroidal Tsai-type cluster. The resulting picture illustrates the ability of DFT–CP analysis to integrate the size and electronic components of the Hume–Rothery view of QCs into an intuitive understanding of the origins of icosahedral order. We look forward to exploring the implications of this CP scheme for synthesis: elemental substitutions adjusting atomic sizes should modulate the relative stabilities of simple periodic (CaCu_5 -type) and icosahedral (Tsai-type) arrangements, allowing us to probe the boundaries between these forms of long-range order.

■ ASSOCIATED CONTENT

Supporting Information

Computational procedures, and CP analyses of more CaCu_5 -type phases and of cluster interfaces in CaCd_6 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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