

Atomic model of decagonal quasicrystal approximants and phasons

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We investigate the atomic structure of model decagonal quasicrystals. Periodic crystalline structures which share the local structure of the decagonal phase model may represent equilibrium phases to which the quasicrystal transforms at low temperatures. Rearrangements of atoms within the unit cells constitute a ‘phason flip’ and result in only modest alterations of the local structure. Reconstructed electron densities reveal double peaks which appear to correspond to these phason displacements.

1. Introduction

Electron densities reconstructed from five- and six-dimensional Patterson analysis of electron diffraction data [1,2] suggest plausible models for atomic positions in icosahedral and decagonal quasicrystal phases. These models, which represent the structure in terms of ‘atomic surfaces’, have the virtue of explicitly placing atoms in an exactly quasiperiodic pattern over arbitrarily large distances. It is of interest to ask how well these models behave over short lengths. Do they correspond to reasonable atomic locations? How are we to interpret unphysically short interatomic distances and fractional occupation probabilities?

In an effort to answer these questions we wish to study the simplest crystalline structures which share the local atomic structure of the quasicrystal models. We can ask whether the model is mechanically stable for reasonable interatomic potentials and we can ask what alterations would lower the energy. Ultimately one hopes to find a set of atomic environments compatible with decagonal symmetry, and a set of potentials for which these structures are at least close to the

ground state. Given such a model, one interesting problem is to understand the atomic displacements involved in phason excitations and the corresponding energetics. In particular we look for evidence of Penrose-like matching rules which could force a quasiperiodic ground state, or else for a near degeneracy so that entropy could explain the quasiperiodicity.

2. Structural models and phasons

Models compatible with experimental diffraction data are available for both icosahedral and decagonal phases [3,4]. Decagonal phases possess an average periodicity along the z axis, which we can exploit for simplifying our analysis of structures and for simply drawing pictures. The most specific and detailed decagonal phase model available is that of Burkov [4,5], who presents atomic surfaces as well as an attractive analysis of the resulting structure in terms of atomic clusters. Figure 1 shows the large (50 atom) and small (11-atom) clusters. These clusters lie at the vertices of 36° and 72° rhombi as shown. Then space is filled by tiling the plane with rhombi obeying the ‘binary tiling’ condition, which simply requires that where tiles share a vertex consistency must be maintained in cluster type.

White atoms are claimed to represent aluminum, and black ones transition metals. Copper

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is treated as a transition metal in this model. The evidence for choice of atomic species comes from the intensity of electron density peaks [2], coupled with a requirement that atomic surfaces contain only single species [4]. Thus the assignment of atomic species is rather uncertain. But we stick with Burkov's assignments for the purposes of this paper.

Within each decagonal layer the Burkov model reproduces a two-dimensional two species atomic model [6] which was the first hypothetical model to display a quasicrystal equilibrium state. The large and small Burkov clusters replace the large and small atoms of the two-dimensional model. We hypothesize that, at least for Lennard–Jones interactions the ground state of this two-dimensional model phase separates into two small unit cell crystals which are quasicrystal approximants. In fig. 2 we illustrate these crystalline states layered with the Burkov atomic decoration of the clusters. In both cases the crystal space group is centered orthorhombic (Cc2m). It proves convenient to select rhombic prisms with horizontal edge length 20 \AA and height 4 \AA as the unit cells. The first (fig. 2(a)) has a 36° acute angle, and stoichiometry $\text{Al}_{40}(\text{Co}, \text{Cu})_{28}$. The other (fig. 2(b)) has a 72° acute angle and stoichiometry $\text{Al}_{66}(\text{Co}, \text{Cu})_{44}$. The decagonal quasicrystal mixes these

two unit cells for overall stoichiometry $\text{Al}_{0.597}(\text{Co}, \text{Cu})_{0.403}$.

These postulated structures might actually occur in nature. Low temperature Monte Carlo annealing, as well as dynamical growth studies, of the two-dimensional Lennard–Jones alloy result in microstructures resembling random mixtures of the two crystal phases, each single phase domain containing just a few unit cells [7]. Thus we examine HREM studies of the low temperature transformation products which result when decagonal quasicrystals are annealed below about 600°C . The idea is to look for repeated patterns and match cell size and shape. HREM pictures of the low temperature annealed state of decagonal quasicrystals reveal ‘ring contrasts’ of about the right size to correspond to large clusters. Cells reminiscent of our 72° crystal (fig. 2(b)) appear in AlCuCo [9]. Motifs similar to both our 36° and 72° crystals appear in AlMnPd [8] with edge lengths $r \times 20 \text{ \AA}$ implying larger fundamental clusters for this material. We expect our model crystal phases should describe these real crystalline structures to the same degree as Burkov's model describes the real decagonal phase.

Depending on precise details of stoichiometry and sample preparation other microstructures may be found instead [10]. To our knowledge the

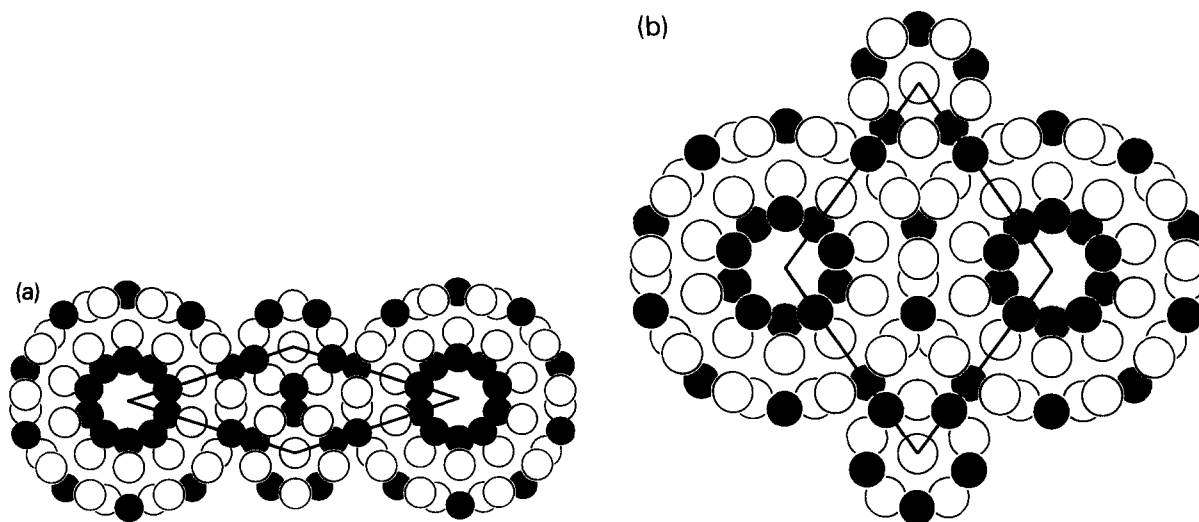


Fig. 1. (a) Thin (36°) and (b) fat (72°) binary tiling rhombi decorated with large and small Burkov clusters.

crystalline structures shown here are the smallest found in quasicrystal transformation products, suggesting that the Burkov clusters may be funda-

mental building units. However, we note that known decagonal phase approximants $\text{Al}_{13}\text{Co}_4$ and Al_5Co_2 , which share some structural charac-

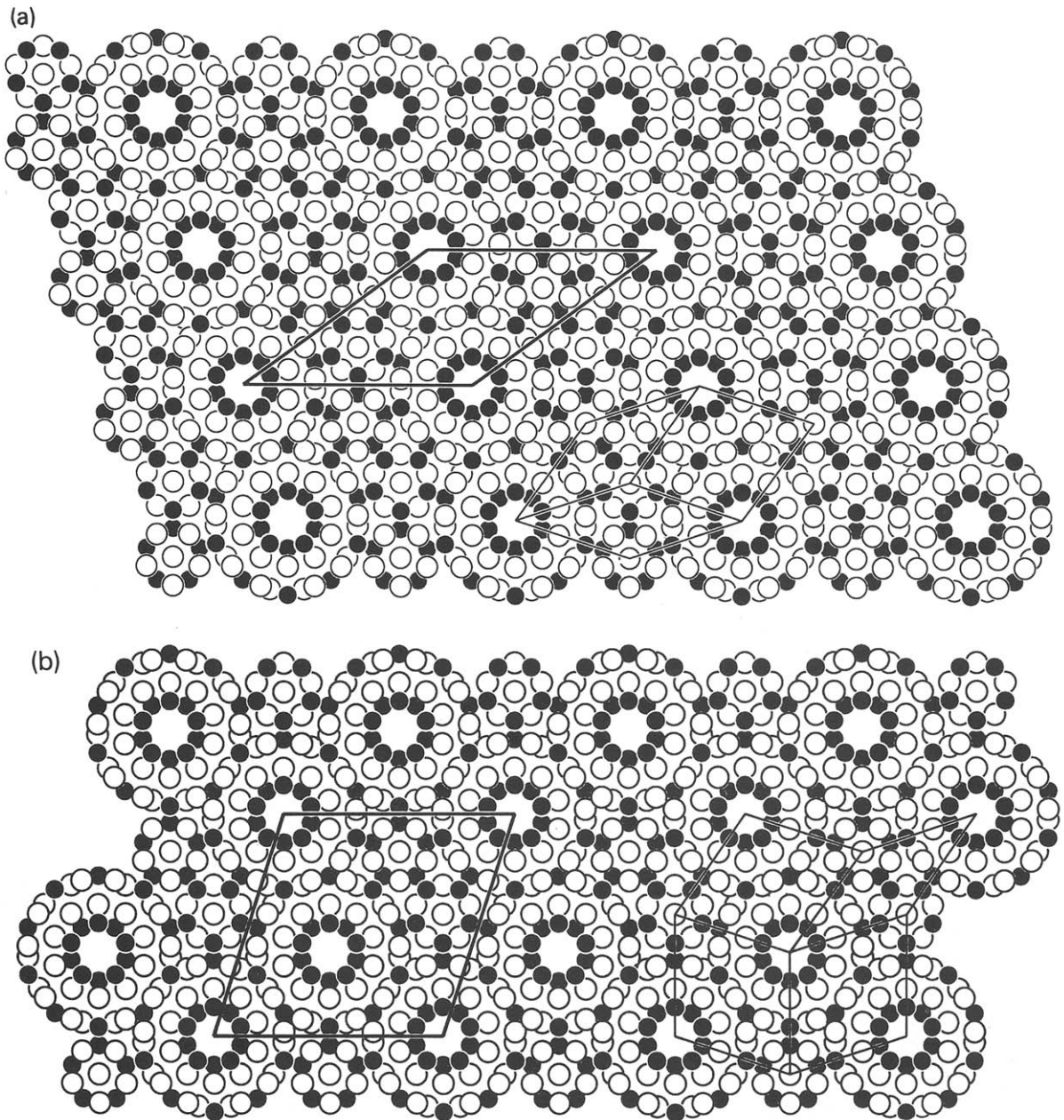


Fig. 2. Hypothetical crystal structure with (a) 68 atoms per unit cell and (b) 110 atoms per cell. Heavy lines denote primitive cell, while thin lines reproduce binary tiles which comprise a unit cell.

teristics with Burkov, lack complete, undistorted, large clusters. So there may be some smaller, more fundamental, structural units than Burkov's clusters. In this case agreement between our proposed crystalline states and HREM may be just a lucky coincidence. In fact, if Burkov clusters are indeed fundamental structural units then their numbers should be conserved in the low temperature annealing. One would expect to find both crystal types (figs. 2(a) and (b)) in coexistence at low temperatures.

Accepting Burkov's model for the remainder of this paper we may investigate the atomic motions corresponding to phasons. The simplest phason flip in a binary tiling model is the octagon flip [11]. A complete octagon is shown in fig. 3(a). The flip is a reflection through the shortest diagonal. Note that the atomic structure around the outer edge is symmetric under this reflection. Now consider the energy cost of introducing a phason flip into a structure containing an octagon

(note that the crystal in fig. 2(b) contains almost a complete octagon). We have a choice of flipping an entire column of octagons simultaneously, maintaining translational invariance along the z axis, or only a partial column, so that a reflected layer sits on top of an unreflected layer (see fig. 3(b)).

By flipping an entire column of octagons we maintain all vertical bonds intact. Thus, to compute the energy cost of such a flip we must look within a layer across the boundary of the octagon. But, because of the symmetry of the octagon edge under the phason flip, the affected bonds must reach from the interior of one cell into the interior of a neighboring cell – a distance of at least 6 \AA . When realistic interatomic potentials are considered [12], it is seen that there can be no significant energy cost associated with such a flip because the potentials essentially vanish by about 6 \AA .

If the entropy of the phasons is to contribute

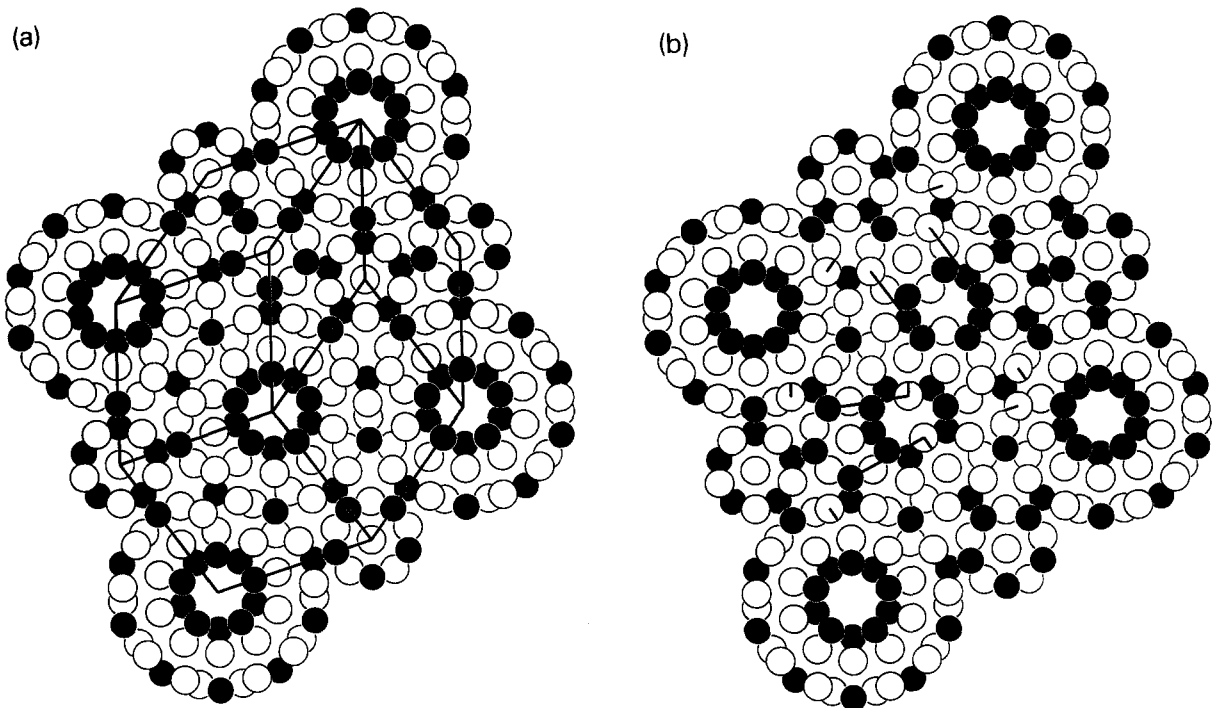


Fig. 3. (a) Octagon with 1.77 \AA bonds relaxed (see ref. [11]) and binary tiling rhombi superimposed. Note that the interior of the octagon (i.e. omitting the outer two thin rhombi) reproduces the unit cell of the 72° crystal (fig. 2(b)). (B) Octagon with top layer flipped. Line segments denote atomic displacements or interchanges from unflipped state (a).

to quasicrystal stability it must be extensive – proportional to the product of sample dimensions. Flipping an entire column provides an entropy proportional to the area of the decagonal layers (i.e. the number of octagonal columns). Thus we investigate the effects of flipping a partial column of unit cells in order to pick up a three-dimensional entropy [13]. Figure 3(b) illustrates the result of flipping the upper layer of the octagon while leaving the lower layer in place. Structural changes fall into two simple categories. First, there are small displacements of six aluminum atoms to nearby sites illustrated by short line segments drawn from initial to final locations. In addition there are four interchanges of aluminum atoms with a transition metal located about 5.3 Å away, preceded or followed by a small (about 0.93 Å) displacement of the aluminum. In all cases, the aluminum atoms involved in the phasons motion belong to the outer rings of large clusters, and hence are in any case subject to displacement by relaxation [12].

We may ask about the energy cost of each component of the phason flip. First consider the six displacements of aluminum atoms. Counting the number of nearest neighbor bonds of each type, we find that three atoms acquire an extra Al–Al bond, while the other three drop one. Thus there is no net energy cost or benefit from this portion of the phason, at least at the level of nearest neighbor bonding and neglecting relaxation from the ‘ideal’ positions shown. Now consider the atoms which switch atomic identity. Counting the numbers of nearest neighbor bonds reveals a net conversion of one Al–Al bond and one Cu–Cu bond into two Al–Cu bonds. From the interatomic potentials shown in ref. [12], we estimate a net decrease in energy of about -0.3 eV following the phason flip. However, each interchange separately raises or lowers the energy by amounts of up to 0.4 eV. Our ultimate conclusion is that our starting configuration (i.e. the Burkov model) is not optimal and therefore the phason energy is not reliable.

We may still extract more general conclusions. First, the phason flip may take place through modest displacements of a small number of atoms. In fact, the principal mechanism appears to be

displacement of an atom in one layer by a distance of about 0.93 Å across a 2.44 Å bond in the adjoining layer. This generally agrees with other suggestions for the phason [12]. Remarkably, the electron density [2] reveals split peaks across such bonds corresponding to initial and final atomic locations. Thus, the electron density appears to confirm our interpretation of the phason motion. Given the uncertainty in assignment of chemical identity in the Burkov model, and the fact that it is a pseudo-binary model, the role of chemical interchange in real phason motion remains uncertain.

3. Conclusion

In conclusion, we use the Burkov model decagonal phase to address two questions: What are the structures into which quasicrystals transform at low temperatures, and what are the atomic motions involved in a phason? We propose two simple crystal structures consistent with the Burkov model and point out agreement of unit cell parameters with experimentally observed microstructures. Experimental determination of the actual structures of these crystalline phases would be of great importance in constructing improved models of the quasicrystal phase. Then we show the phason flip consists of only modest atomic rearrangements, and modest energy cost. Double peaks in the electron densities support our picture of the atomic displacements involved in phason rearrangements.

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