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A five-dimensional model of dodecagonal Ta–Te quasicrystals with fractal occupation domains

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The consideration of two approximants of the first stable dodecagonal Ta–Te quasicrystal shows that the five-dimensional (5D) space group of the dodecagonal phase is $P\overline{1}2m2(12^5mm)$ and the structure consists of five layers within a 10 Å period. A 5D quasicrystal model leading to the two approximant structures by the introduction of appropriate linear phason strains is derived by the section method. The model shows 20 Å dodecagonal clusters (DDC) arranged at each vertex of the square-triangle dodecagonal pattern and has fractal occupation domains, suggesting that the quasicrystal has either a deterministic or a random square-triangle packing of the DDC.

1. Introduction

A Ta–Te dodecagonal (DD) phase is known to be the first stable DD phase and the only example of quasicrystals in chalcogenides (Krumeich *et al.*, 1994). Other DD quasicrystals found so far are all metastable and only obtainable as powders, so that it was impossible to determine their detailed structure (Ishimasa *et al.*, 1985; Chen *et al.*, 1988). On the other hand, a crystal available for the X-ray single-crystal method has been grown in the Ta–Te DD phase (Conrad, 1997). Therefore, this is a key material for the DD quasicrystals. There exist two crystal approximants, $Ta_{97}Te_{60}$ and $Ta_{181}Te_{112}$, which have chemical compositions similar to that of the DD phase, $Ta_{63}Te_{37}$ (Conrad, 1997; Conrad & Harbrecht, 1998). They are pseudo-tetragonal with $a = 27.62$, $c = 20.61$ Å and $a = 37.58$, $c = 20.66$ Å. The DD phase has a period along the 12-fold axis (the c axis) with $c = 20.79$ Å. In all cases, the diffraction intensity in odd layers normal to the c^* axis is very weak, suggesting that these are weakly modulated structures along the c axis. The space group of the average structure of both approximants with $c_0 = c/2$ is $P\overline{4}2_1m$. In this paper, we neglect such a weak modulation and only consider their average structures with the lattice constants a and c_0.

2. Crystal approximants

The crystal approximants are important for understanding DD quasicrystal structures. In this paper, we construct a five-dimensional (5D) model, which is consistent with the approximants, by applying the section method. It is shown that the 5D model can reproduce the $Ta_{181}Te_{112}$ structure by introducing an appropriate linear phason strain and $Ta_{97}Te_{60}$ can be interpreted as a superstructure of a fictitious structure with a smaller lattice constant, which is also obtained from the 5D model. Finally, the stabilization mechanism of the DD phase is discussed based on this model. The structure analyses clarified that both approximants can be considered as layer structures with the layers normal to the c axis or as column structures consisting of two DD columns parallel to the c axis, the diameter of which is about 20 Å (Conrad, 1997). Fig. 1 shows an approximant structure obtained from a 5D model of the quasicrystal given later by introducing the linear phason strain. It is not difficult to recognize that this is isostructural to $Ta_{181}Te_{112}$, although this is an ideal structure and slight deviation of atom positions from the real structure is seen. The 20 Å clusters are located at vertices of a pattern drawn by thick lines. The symmetry of the DD clusters is hexagonal. The approximant includes five puckered layers within the period along the c axis. The Ta layer at $z = 0$ sandwiched by two additional Ta layers and two Te layers gives a framework of the structure. The atoms of the other layers decorate this framework in a unified way. The two kinds of dodecagons seen in the framework differ only in orientation: one is obtained from the other by 30° rotation around the sixfold axis. A characteristic feature of the arrangement of the dodecagons is that the different dodecagons are connected to each other by sharing an edge and forming squares. In the triangle, two dodecagons have the same orientation.

It is reasonable to consider that the atom arrangement of the DD phase is locally similar to that of the two approximants. The high-resolution transmission-electron-microscopy images suggest that in the DD phase the DD clusters are arranged so as to make a DD pattern composed of squares and triangles with the edge length of 20 Å (Conrad, 1997). Examples of such patterns are the Stampfli pattern (SP) (Stampfli, 1986) and its modifications. They are obtained by the section method (Baake *et al.*, 1992). The SP includes many skinny rhombi other than the squares and triangles but they

can be eliminated by a sophisticated method using a recursive generation of the occupation domain (OD) as discussed later. Such a 2D DD pattern is obtained from a 2D section of a 4D periodic structure (crystal), although a real 3D structure needs a 5D crystal.

The framework with a few distorted hexagons (Fig. 2) can be generated by the OD shown in Fig. 3(*c*), which includes the 'pinwheel' (Figs. 3*a*, *b*) (Smith, 1993). We call this pattern the modified Stampfli pattern (MSP) of the first generation. The MSP of the zeroth generation is given by the central dodecagon of Fig. 3(*c*) (Niizeki & Mitani, 1987), which agrees with the SP. This includes many distorted hexagons compared with the first generation shown by thin lines.

The MSP of the second generation further reduces the number of the hexagons, where each small dodecagon in Fig. 3(*c*) is replaced by the new small occupation domain with the shape of Fig. 3(*c*) but with size smaller by a factor λ^{-2} and the pinwheel with the new pinwheel obtained from the new small OD by cutting six triangular parts as in the pinwheel of the first generation. [The scaling factor $\lambda = (1 + 3^{1/2})/2^{1/2}$ is the similarity ratio of the DD lattice.] This procedure leads to a fractal OD and is equivalent to that based on the 'pinwheel theorem' (Baake *et al.*, 1992; Smith, 1993; Cockayne, 1994).

It is known that a fractal OD is necessary in order to obtain a DD pattern consisting of squares and triangles but has no hexagons (Cockayne, 1994). For simplicity, we show a model based on the first generation MSP since this pattern includes only a few hexagons and it is enough to derive the approximant structures. Following the same procedure, the model based on the fractal OD can be obtained.

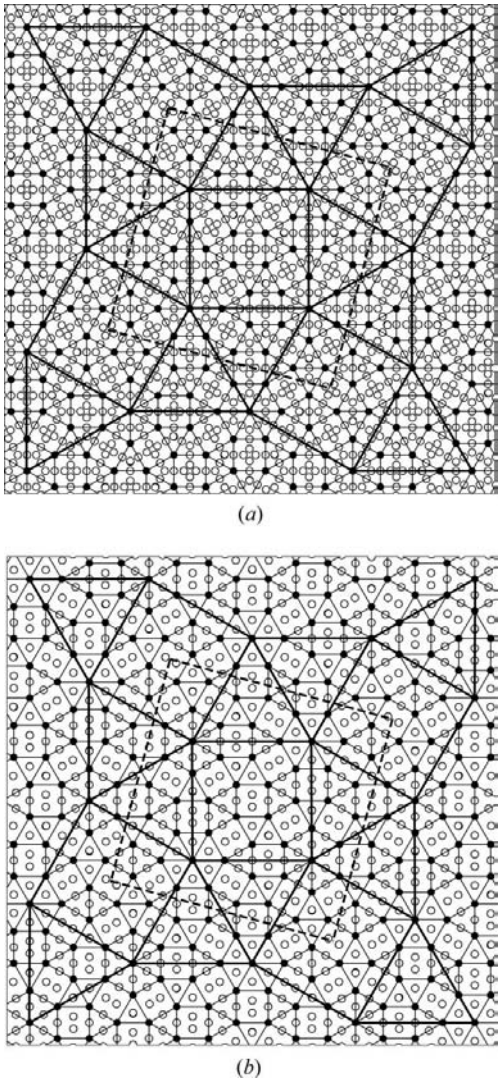

Figure 1
The crystal approximant of the DD Ta–Te quasicrystal derived from the 5D quasicrystal model by the introduction of the phason strain. (*a*) The projection of three Ta layers of the approximant along the *c* axis. (*b*) Its lower two layers ($z \leq 0$). Te atoms (not shown) are above and below the solid circles and the centers of each square and triangle. Solid lines represent the framework consisting of Ta atoms at $z = 0$. The centers of DD clusters are joined by thick lines. The dashed lines show the unit cell.

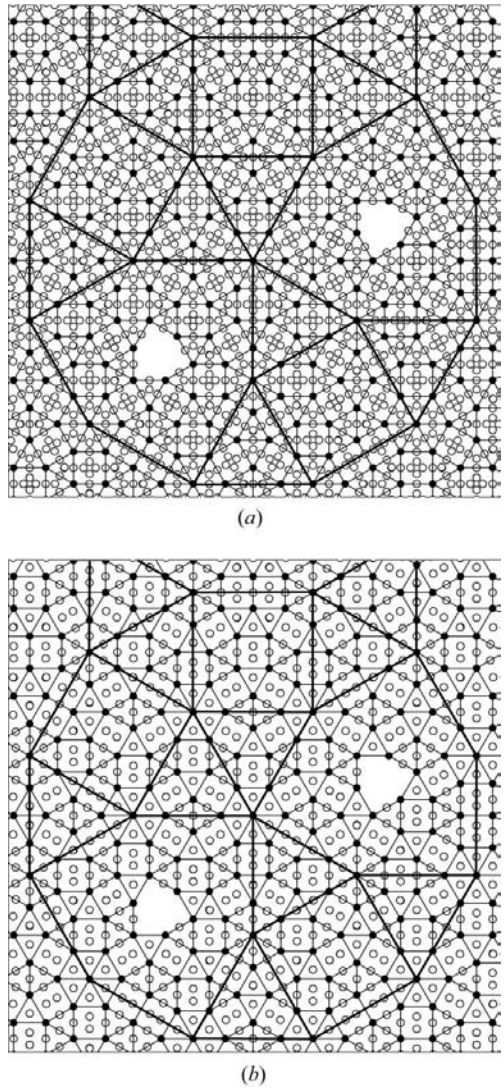

Figure 2
Model structure of the Ta–Te quasicrystal. (*a*) Three Ta layers projected along the d_5 (periodic) axis. (*b*) Its lower two layers. Solid lines joining Ta atoms at $u = 0$ show the framework of the quasicrystal. Te atoms are at the center of each square or triangle similar to those of the approximant. For the hexagonal holes, see the text.

3. Quasicrystal models

In order to obtain a 5D crystal model for the real DD phase, we remark that Ta atoms decorating the framework of the approximant are located at the edge center of each edge, the face center of each triangle and four positions in each square. Furthermore, the edges are classified into two groups, one of which is parallel to the six directions related by the sixfold rotations, and the other makes an angle of 30° from them. The edge center atoms of the first group are above the framework, while those of the second are below it. Accordingly, the triangles are classified into two groups according to their orientations. The face-center atoms of the first and second groups are situated above and below the framework, respectively. Similarly, the squares form three groups related by 30° rotations. Each square has two pairs of atoms in its interior. A given pair is located above (below) the framework if it is parallel to an edge belonging to the first (second) edge group. The same decoration of the MSP gives a model of the DD phase.[1] The decoration breaks a mirror plane normal to the 12-fold axis, leading to the space group $P\overline{1}2m2(12^5mm)$. The atom positions of the DD phase are obtained from the OD's at the special positions listed in Table 1.

The method to obtain such decorations is known (Yamamoto & Hiraga, 1988; Yamamoto, 1996). The vertices of the framework come from the OD at the origin [1*a* in Table 1, where the coordinate system in Yamamoto (1996) is used]. There are six sites for the edge center atoms. The edge center positions are obtained from the OD's at $(0, 1/2, 0, 0, u)$ and positions equivalent to them (6*a*). Similarly, the face-center positions are obtained from the OD's at four sites (4*a*) and the four sites in the square come from the occupation domains at 12 positions (12*a*). All these sites are occupied by Ta atoms, while Te atoms are above and below the vertices of the framework (2*a*) and the face center of each square and triangle (4*a*, 6*b*).

The shape of the OD's for these atoms can be calculated by the intersections of the OD's. For example, the OD for the edge center atoms at $(0, 1/2, 0, 0, u)$ (Fig. 3*d*) are the intersection of the OD's for the framework at $(0, 0, 0, 0, u)$ and $(0, 1, 0, 0, u)$ in the internal (perpendicular) space.[2] This procedure gives rise to a 5D model that provides a 3D structure consistent with the approximants. All independent OD's are shown in Figs. 3(*c*)–(*f*).

The hexagonal holes in the MSP of the first generation (Fig. 2) can be removed by adding one point in each hexagon that divides the hexagon into a square, two triangles and a skinny rhombus. This point is obtained from a small (open) OD at the position shown by the arrow in Fig. 3(*c*) and 11 domains equivalent to it under the DD symmetry. The same decorations for the new squares and triangles also need to add corresponding small domains in Figs. 3(*d*)–(*f*).

The MSP of the first generation includes many DD clusters (but with hexagonal symmetry) in two orientations, which are related by 30° rotation to each other, as in the crystal approximant. However, the arrangement of the DD clusters is different from that of the crystal approximant. In the approximant, the two adjacent clusters forming the square have different orientations and the two clusters facing along the diagonal have the same orientation (Fig. 1). In contrast, there is no such cluster arrangement in the MSP (Fig. 2). Nevertheless, we can show that the approximant structure can be obtained from the 5D model as shown below.

4. Derivation of the crystal approximants

The $Ta_{181}Te_{112}$ structure is obtained from the 5D model by introducing a tetragonal phason represented by the 2×2 phason matrix $\mathbf{U}$ with $U_{11} = U_{22} = \lambda^{-2(n+1)}/2$, $-U_{12} = U_{21} = \lambda^{-2(n+1)}3^{1/2}/2$ and cutting at the 3D space passing through $(0, 1/2, 1/2, 0, 0)$, the site symmetry of which is $\overline{4}m2(4^3mm)$. [The phason matrix in Yamamoto (1996) is used.] A series of tetragonal approximant structures with the lattice constant $a = \lambda^{2n}a_0$ is obtained for any even integer starting from $n = 2$, where a_0 is the edge length of the square

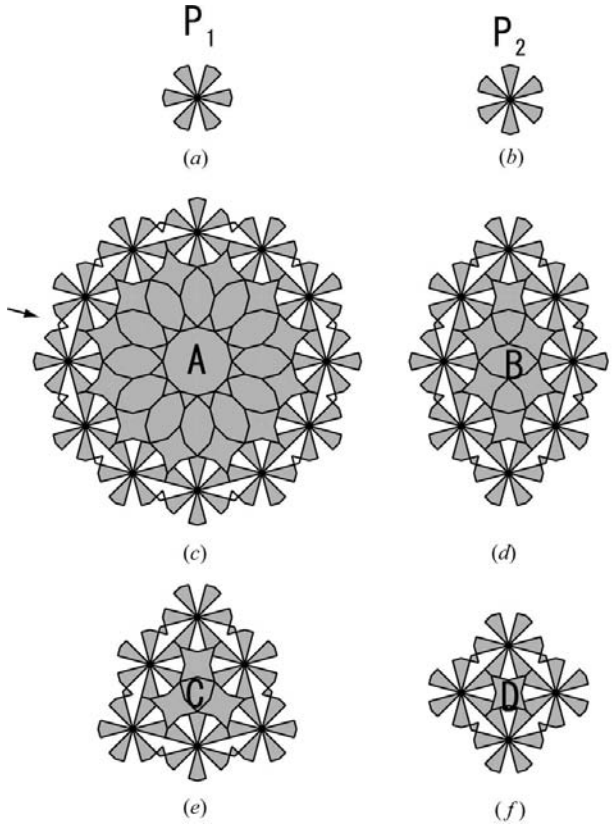

Figure 3
OD's of the 5D model of the Ta–Te quasicrystal. (*a*), (*b*) Two pinwheel patterns appearing in the model, (*c*) the OD at the origin, (*d*) at $(0, 1/2, 0, 0, u)$, (*e*) at $(0, 2/3, 0, 1/3, u)$ and (*f*) at $(0, 1/2, 1/2, 0, u)$ and $(0, 1/2, z, 0, u)$. The coordinates show the center of the occupation domain except for the last, while $(0, 1/2, z, 0, u)$ show a point on the vertical line through the center in (*f*). A corner vector of the central dodecagon of (*c*) is $\lambda^{-2}(1, 0, 0, 0, 0)$. These polygonal OD's are of the first generation of the model. They become truly fractal as the generation N becomes infinity.

[1] A similar decoration for a different dodecagonal tiling has been given (Gähler, 1988).
[2] In Yamamoto (1996), 'union' in §15 should be read as 'intersection'.

Table 1
Atom positions of the 5D model with the space group $P\overline{1}\overline{2}m2(12^5mm)$.

The first and third columns show the Wyckoff symbol and a representative of several equivalent positions. The number in the Wyckoff symbol means the order of the special position. The atom and the OD in Fig. 3 are listed in the fourth and fifth columns.

W. S.	Site symmetry	Rep. position	Atom	OD
1*a*	$\overline{1}\overline{2}m2(12^5mm)$	0, 0, 0, 0, 0	Ta	(*c*)
2*a*	$6mm(6^5mm)$	0, 0, 0, 0, *u*	Te	(*c*)
4*a*	$3m(3^2m)$	0, 2/3, 0, 1/3, *u*	Ta, Te	(*e*)
6*a*	$mm2(mm1)$	0, 1/2, 0, 0, *u*	Ta	(*d*)
6*b*	$mm2(mm1)$	0, 1/2, 1/2, 0, *u*	Te	(*f*)
12*a*	$m11(m11)$	0, 1/2, *z*, 0, *u*	Ta	(*f*)

and/or triangle of the framework. This is related to the lattice constant of the DD lattice a_d by $2a_d/6^{1/2}$. $Ta_{181}Te_{112}$ corresponds to the smallest n in this series. $Ta_{97}Te_{60}$ belongs to another series given by $U_{11} = U_{22} = \lambda^{-2(n+1)}$, $U_{12} = U_{21} = 0$ with odd n. For $n = 1$, we have an approximant with $a' = \lambda^2 a_0 \simeq 20$ Å, which is smaller than the lattice constant a of $Ta_{97}Te_{60}$ by the factor $1/2^{1/2}$. If the 5D lattice were primitive, the orientations of the two clusters in $Ta_{97}Te_{60}$ would be the same. Because the two clusters have different orientation, a doubled superstructure of the 5D lattice is required. This means that $Ta_{181}Te_{112}$ can be derived directly from the present 5D model, while a 5D superstructure model is necessary for $Ta_{97}Te_{60}$. However, the diffraction pattern of the quasicrystal does not suggest such a superstructure. In this respect, $Ta_{181}Te_{112}$ is better as an approximant of the DD phase than $Ta_{97}Te_{60}$.

5. Discussion

The approximant structure implies that the DD clusters are energetically favored constituents in the quasicrystal. Then the most stable structure will take the DD pattern with the maximum cluster density. In the model given above, the cluster centers are at the vertices of the zeroth-generation MSP, which has many distorted hexagons leading to the small cluster density (Cockayne, 1994). The packing fraction of the cluster can be improved by the use of the MSP of a higher generation. When we use the fractal OD giving the maximum packing fraction, the OD of the cluster center is the same in shape as, but smaller by a factor λ^{-2} than, that of the Ta atoms constructing the framework. This is due to the self-similarity of the DD lattice and the fractal nature of the OD.

The fractal OD giving close-packed cluster arrangements is, however, not unique but an infinite number of such patterns exists (Cockayne, 1994). Even in the MSP of the first generation shown in Fig. 3, the model with the domains *A*–*D* in which the pinwheels P_1 and P_2 are interchanged is equally probable. This leads to the 3D structure where the two kinds of dodecagons are interchanged in Fig. 2. This model also gives the same approximant by the introduction of the phason strain. Another possible model is obtained from the mixture of these two, where the location of the cluster center is the same as in the two models mentioned above but the orientation of the clusters is random. This is given by the 5D model in which each pinwheel is replaced by the envelope of the pinwheel (small dodecagon like the central decagon in Fig. 3*c*). The OD given by the envelope should be occupied by an occupation probability of 1/2. This model is deterministic for the arrangement of the DD clusters but random in their orientation. Such a consideration concludes that, if some deterministic structure is more stable than the others, additional conditions are necessary. One of them will be the linkage of the cluster appearing in the approximant, where the adjacent clusters have different orientations. However, the dodecagonal pattern with the maximum cluster density includes many triangles, which prevent such a cluster arrangement. This may suggest that the dodecagonal quasicrystal is essentially non-deterministic at least in orientation and favors the random tiling stabilized by the entropy.

6. Summary and concluding remarks

We proposed 5D models of the DD phase of a Ta–Te quasicrystal with pinwheel and fractal OD's. The latter gives the quasicrystal structure in which two DD clusters with the hexagonal symmetry are arranged on each vertex of a deterministic square–triangle pattern with the densest packing fraction.

The former can reproduce the $Ta_{181}Te_{112}$ structure *via* the introduction of the phason strain. There exist two 5D models leading to the approximant structures. Another model gives the same DD cluster distribution but they are orientationally randomly oriented.

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