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## Structural sub-units of the Al–Mn–Pd decagonal quasicrystal derived from the structure of the $T_3$ Al–Mn–Zn phase

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**Abstract.** Structural sub-units of the Al–Mn–Pd decagonal quasicrystal are derived from the structure of the  $T_3$  Al–Mn–Zn crystalline approximant and both atom positions and species are defined. The structure of the Al–Mn–Pd decagonal quasicrystal can be constructed by these sub-units. The atom decoration of these structural sub-units is comparable to the single-crystal x-ray structure analysis. Meanwhile the high-resolution electron microscopy image of the Al–Mn–Pd decagonal quasicrystal can be explained as an aperiodic aggregation of these sub-units.

### 1. Introduction

Recently, some stable decagonal quasicrystals (DQCs) have been shown to form in conventionally solidified Al–Ni–Co [1], Al–Cu–Co [2] and Al–Mn–Pd [3] alloys. The Al–Mn–Pd DQC is the first stable one with a period of about 1.24 nm while the two others have periods of about 0.4 nm. These stable DQCs usually show sharply defined spots in the diffraction pattern compared with those of the metastable ones. Millimeter-sized single crystals may be grown, which is a prerequisite for structural determination by x-ray diffraction [4–6] as well as for measurement of physical properties [7]. Because of these promising properties, the stable DQCs have attracted the most attention.

Structural determination is still one of the most interesting aspects in the research on the DQCs. Two methods are successfully used in the structural study of the DQCs, one is the high-dimensional analysis of the x-ray diffraction data obtained from a single crystal of the DQCs and this method has suggested that the DQC is an irrational section of a five-dimensional (5D) periodic structure with a three-dimensional (3D) hyper-plane [4–6]. The other is grounded on the hypothesis that the crystalline approximants and the DQCs possess the same or similar atom clusters, packed periodically in the former and aperiodically in the latter [8].

Recently a structure of the Al–Mn–Pd DQC has been determined by Steurer *et al* [6], in which a 5D x-ray analysis is applied on a single crystal of the Al–Mn–Pd DQC. A 3D structural model is obtained by projecting the high-dimensional structure into a physical space. Atomic arrangements of the Al–Mn–Pd DQC [9] are also proposed based on the combination of the high-resolution electron microscopy (HREM) image of the Al–Mn–Pd DQC [10] and a single-crystal x-ray diffraction analysis of the Al–Mn DQC [5].

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In this paper, structural sub-units for the Al–Mn–Pd DQC are derived from the structure of the  $T_3$  Al–Mn–Zn crystalline approximant. Firstly several crystalline approximants of the DQCs are reviewed in section 2 and the icosahedral atom cluster is derived from the  $T_3$  Al–Mn–Zn crystalline approximant in section 3. Secondly the initial aggregation of the icosahedral atom clusters is discussed in section 4 and sub-units of the Al–Mn–Pd DQC are proposed in section 5. Finally we show that the existence of the structural sub-units is supported by the x-ray and HREM experiments in section 6.

## 2. Crystalline approximants of decagonal quasicrystals

It has been reported that the Al–Mn–Pd DQC coexists with the high-temperature orthorhombic  $Al_{11}(Mn, Pd)_4$  phase [3], which is isostructural with the  $Al_3Mn$  phase [11]. The resemblance of the electron diffraction patterns indicates that both phases are composed by the same or similar structural sub-units [3].

As a crystalline approximant of the Al–Mn DQC, the structure of the  $Al_3Mn$  phase was studied by several groups [12–15] and has now been well determined by x-ray analysis of the single crystal [13–15]. We can decipher the structural sub-units of the Al–Mn–Pd DQC directly from the  $Al_3Mn$  structure, as it had been done for the Al–Mn DQC [8, 16]. However, there is still uncertainty about the positions of Pd atoms, since the Pd atoms are believed to partially occupy the Mn or Al atom sites in the high-temperature  $Al_{11}(Mn, Pd)_4$  (or  $Al_3(Mn, Pd)$ ) phase [3].

Li and Kuo have worked out the structural relationship between the  $\pi$ -AlMn and the  $Al_3Mn$  [12, 17]. Both of these phases are crystalline approximants of the Al–Mn DQC. It was confirmed that they are composed of the same structural sub-units packed periodically in different ways. The  $\pi$ -AlMn phase also has isostructural phases in ternary alloy systems, for example  $Al_{20}Mn_3Cu_2$  [18],  $Al_{60}Mn_{11}Ni_4$  [19] and  $T_3$  Al–Mn–Zn [20]. The structures of the latter two phases were determined by the x-ray analysis of the single crystals. The crystalline approximants of the Al–Mn(–Pd) DQC are listed in table 1.

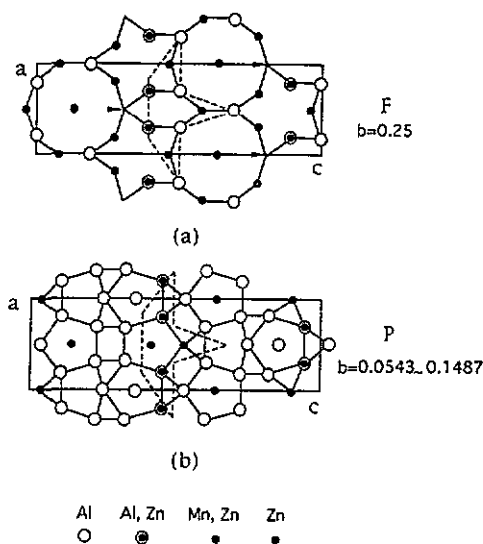
Table 1. The crystalline approximants of the Al–Mn(–Pd) decagonal quasicrystal.

Phase	Composition (at.%)	Lattice parameters (nm)	Space group	References
Al–Mn DQC	$Al_{78}Mn_{22}$	1.24 (periodicity)	$10_5/mmc$	[4]
Al–Mn–Pd DQC	$Al_{70}Mn_{17}Pd_{13}$	1.24 (periodicity)	$10_5/mmc$	[3]
$\pi$ -AlMn	$Al_{80}Mn_{20}$	$a = 0.77$ $b = 1.24$ $c = 2.36$	—	[8]
$Al_3Mn$	$Al_{72}Mn_{28}$	$a = 1.484$ $b = 1.246$ $c = 1.251$	$Pn2_1a$ , $Pnma^a$	[11, 13]
$Al_{60}Mn_{11}Ni_4$	$Al_{80}Mn_{14.7}Ni_{5.3}$	$a = 0.755$ $b = 1.25$ $c = 2.38^b$	$Bbmm$	[16]
$T_3AlMnZn$	$Al_{68.8}Mn_{17.5}Zn_{13.7}$	$a = 0.778$ $b = 1.26$ $c = 2.38^b$	$Bbmm$	[17]
$Al_{20}Mn_3Cu_2$	$Al_{80}Mn_{12}Cu_8$	$a = 0.772$ $b = 1.25$ $c = 24.2^b$	—	[15]

<sup>a</sup> The structure of the  $Al_3Mn$  phase was determined by Higara *et al* [13] and Shi *et al* [11], independently. The space group of the  $Al_3Mn$  phase is suggested to be  $Pnma$  in [13] and  $Pn2_1a$  in [11].

<sup>b</sup> The  $b$  and  $c$  lattice parameters of the crystalline phases reported in the literature are exchanged and given in the table in order to make the  $b$  axis comparable to the tenfold axis of the decagonal quasicrystal.

We notice that the composition of the  $T_3$  Al–Mn–Zn phase is comparable to that of the Al–Mn–Pd DQC (see table 1). In addition, the atom radii of Zn (0.138 nm) and Pd (0.137 nm) are almost equal. Thus, it is possible that the Pd atoms may occupy the same



**Figure 1.** The plan views of (a) flat layer F and (b) puckered layer P in the structure of the  $T_3$  Al-Mn-Zn crystal phase. The atom positions are connected with short bars to illustrate the characteristics of the structure. The positions indicated with arrow heads are also connected although no atoms are in these positions in the structure of the  $T_3$  Al-Mn-Zn phase, but Al are atoms in these positions in the isotopic structure of the  $Al_{60}Mn_{11}Ni_4$  phase.

position in a local structure of the Al-Mn-Pd DQC as the Zn atoms do in the  $T_3$  Al-Mn-Zn ternary phase.

The structure of the  $T_3$  Al-Mn-Zn crystalline phase was determined by Damjanovic in 1961 [20]. Table 1 gives the crystalline data for the  $T_3$  Al-Mn-Zn phase. Its structure can be described as an alternate packing of flat (F, f) and puckered (P, p) layers perpendicular to its  $b$  axis with a sequence of PFP' pfp' . . . ; the p, f layers correspond to P, F layers by a  $180^\circ$  rotation along the  $b$  axis and P', p' correspond to P, p through a mirror perpendicular to the  $b$  axis. The plan views of the flat layer and the puckered layer are shown in figure 1. An algorithm able to reproduce both decagonal and approximant crystals of all types known so far was deciphered from this approach [21].

### 3. Atom cluster in the $T_3$ Al-Mn-Zn crystalline approximant

The structure of the  $T_3$  Al-Mn-Zn phase can be also described by a network of pentagonal prisms formed by Al atoms and atom clusters in them. These atom clusters are four interpenetrating icosahedral chains connected by a pentagonal prism and they form a periodicity of about 12.4 nm along the  $b$  axis. Figure 2 shows (a) the positions of the icosahedral chains and (b) a single column of the icosahedral chain. For simplicity and clarity, we shall use two pentagons superposed in opposite orientations to represent the projection of the chains and a large pentagon to represent the projection of the Al atom pentagonal prism in the following. In fact, this method has already been used to describe the structure of the  $Al_3Mn$  phase, as given by Shi *et al* [13].

We supposed that the interpenetrating icosahedral chain is the basic common atom cluster in both the structures of DQCs and several crystalline approximants. Since the

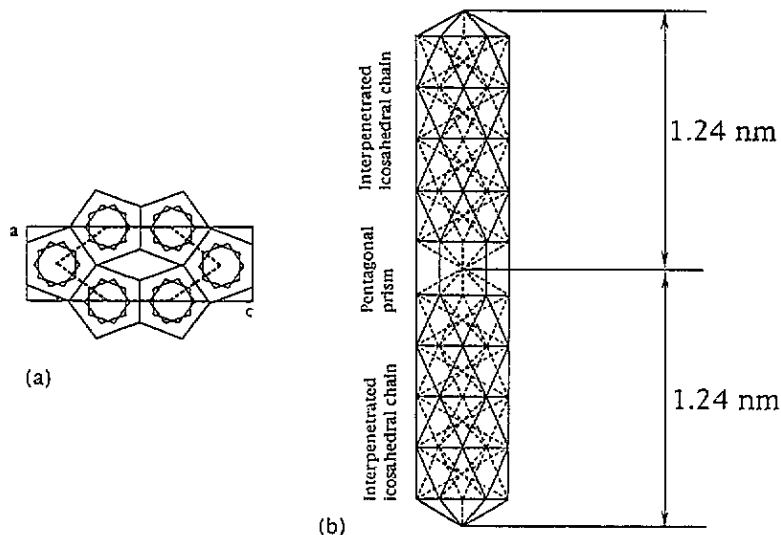


Figure 2. (a) The structural description of the  $T_3$  Al-Mn-Zn phase as a network of pentagonal prisms formed by Al atoms and atom clusters in them and (b) a single column of the interpenetrating icosahedral chains connected by a pentagonal prism.

interpenetrating icosahedral chain is always in a large pentagonal prism formed by Al atoms, the atom cluster can be considered as a pentagonal prism.

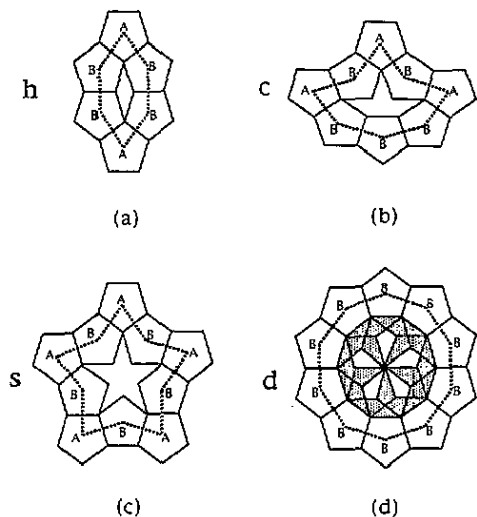
#### 4. Initial aggregation of the atom clusters

The  $T_3$  Al-Mn-Zn structure can be further described by its hexagonal sub-units, which are formed by six adjacent pentagonal prisms†. Figure 2(a) shows the aggregation of the atom clusters in the  $T_3$  Al-Mn-Zn structure. Only two types of cluster linkage are found in the sub-unit: type A is a cluster with two other clusters connected to its two adjacent edges and type B is a cluster with two other clusters connected to its two distinct edges. Thus both the atom clusters and the way they link up can be found in the  $T_3$  Al-Mn-Zn structure.

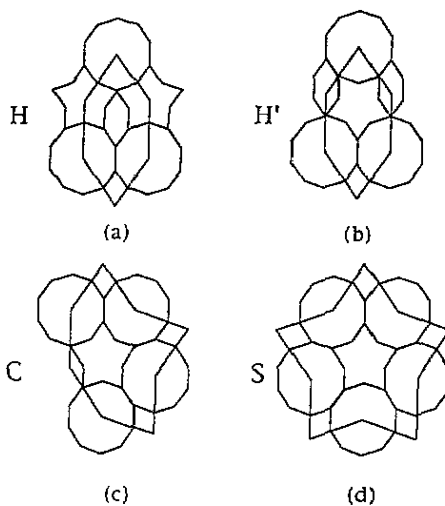
In order to obtain the structural sub-units of DQCs, we consider the initial aggregation of the atom clusters with fivefold (or tenfold) rotational symmetry. It is obvious that only two ways of aggregation can be obtained, which are shown in figure 3(c) and (d). Meanwhile, two shrunken states of the perfect fivefold (or tenfold) symmetry can possibly occur. One is the hexagonal aggregation, which appears in the  $T_3$  Al-Mn-Zn structure, and the other one is an aggregation with a crown shape, which is shown in figure 3(b).

The four kinds of initial aggregation of the atom clusters can be referred to as the basic structural sub-units in DQCs and crystalline approximants. They are labelled as h (hexagon), c (crown), s (star) and d (decagon), according to the shapes of these sub-units (figure 3). The structure of the Al-Mn DQC is composed of three sub-units, h, c and s [16], whereas the structure of the Al-Mn-Pd DQC is mainly composed of h, s and d sub-units, and scarcely includes the c sub-unit.

† Only part of the pentagonal prisms contribute to the new hexagonal prism.



**Figure 3.** The initial aggregation of the atom clusters: (a) flattened hexagon *h*; (b) crown *c*; (c) star *s* and (d) decagon *d*.



**Figure 4.** The four large sub-units in the Al-Mn-Pd decagonal quasicrystal, which are composed of the basic ones in figure 3: (a), (b), large hexagons *H* and *H'*; (c) large crown *C* and (d) large star *S*.

## 5. Structural sub-units of the Al-Mn-Pd decagonal quasicrystal

### 5.1. Formation of the sub-units

We propose that the structural sub-units of the Al-Mn-Pd DQC are much larger than those of the Al-Mn DQC by considering the experimental results (see section 6). The sub-units in the Al-Mn-Pd case again have the shapes of the flattened hexagon, crown and star; however, they are  $\tau^2$  ( $\tau$  is the gold mean) times larger than those in the Al-Mn case. These large sub-units in figure 4 are denoted as *H*, *H'*, *C* and *S* to distinguish them from *h*, *c*, *s* and *d* sub-units, in which *H* and *H'* are two large sub-units possessing the same flattened hexagon shape.

### 5.2. Atom distribution

Like the structural description of the  $T_3$  Al-Mn-Zn phase, the atom arrangements in the structural sub-units of the Al-Mn-Pd DQC are also shown in flat and puckered layers. The atom arrangements in the sub-units *h*, *c*, *s* have already been given for the Al-Mn DQC [16] and those in the Al-Mn-Pd DQC can be obtained by replacing some Al and Mn atoms with Pd atoms partially or totally (as we will do for the sub-unit *d* in the following). Therefore, we will now only focus on the atom arrangement in the sub-unit *d*, which is the specific unit for the Al-Mn-Pd DQC.

Figure 5 shows the atom arrangement in the sub-unit *d* of the Al-Mn-Pd DQC: (a) the flat layer and (b) the puckered layer. The local correspondence between the flat and puckered layers in the *d* sub-unit is similar to that in the  $T_3$  Al-Mn-Zn phase since they are constructed from identical 3D atom clusters. The atom arrangements surrounding the *d* sub-unit can be deduced from the interpenetrating icosahedral cluster. In addition, those near the centre of the *d* sub-unit can also be obtained from the local structure of the  $T_3$

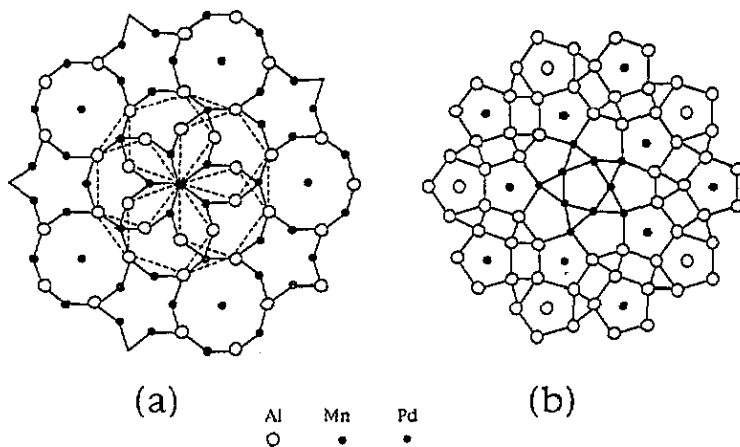


Figure 5. The atom arrangement in the *d* sub-unit of the Al-Mn-Pd decagonal quasicrystal: (a) the flat layer and (b) the puckered layer. A boat-like area (marked in dotted lines) corresponds to that in figure 1 and to the shaded area in figure 3(d).

Al-Mn-Zn phase. In order to make this point clear, a boat-like area is marked with dotted lines in figure 1. This area corresponds to the overlapping shaded area shown in figure 3(d).

The atom decoration of the sub-units in the Al-Mn-Pd DQC obviously leads to the correct local environment with (a) no atom pairs being too short and (b) appropriate chemical order. This arrangement is also reasonable in the edge area when two sub-units are packed together.

### 5.3. Aperiodic packing of the structural sub-units

The structural sub-units of the Al-Mn-Pd DQC can be packed together in general aperiodic ways or special ones with quasiperiodicity. A two-colour Penrose tiling was proposed by Li *et al* [22], in which the original Penrose tiling can be transformed to a quasiperiodic tiling composed of three tiles in flattened hexagonal, crown and star shapes. Figure 6 shows the relationship between the two-colour Penrose tiling and the original Penrose tiling. It is easy to see that the structural sub-units can be packed according to the two-colour Penrose tiling but are not forced to it. Therefore, a genuine decagonal quasiperiodic structure can be constructed. However, this does not mean that the structure of the Al-Mn-Pd decagonal quasicrystal must be necessarily quasiperiodic since a random packing may enforce aperiodicity as well.

## 6. Discussion

### 6.1. Comparison with x-ray diffraction results

Recently, the structure of the Al-Mn-Pd DQC was determined by a high-dimensional analysis of single-crystal x-ray diffraction data [6]. Figure 7 shows the characteristic cross sections of the 30 Å diameter column of the Al-Mn-Pd DQC in (a) the flat layer and (b) the puckered layer [6]. In the flat layer, the two configurations of figure 5(a) and 7(a) are almost the same except for the ten excess Al atoms in the middle of the *d* sub-unit. In the puckered layer, the two configurations of figure 5(b) and 7(b) are almost the same except for some divergences in local atomic arrangement, which are indicated with arrow heads in figure 7(b).

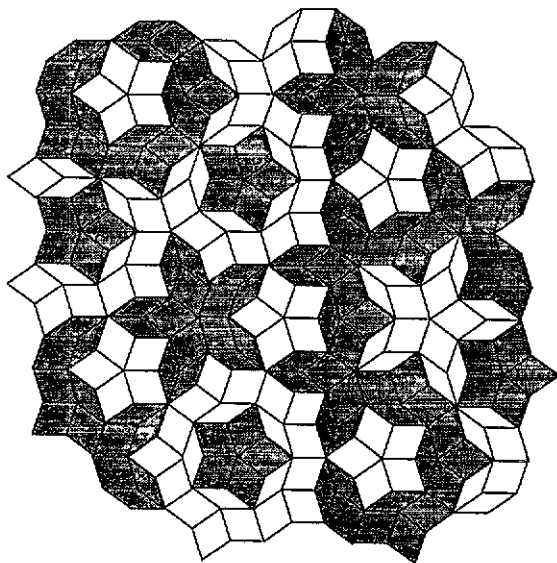


Figure 6. The two-colour Penrose tiling composed of three basic sub-units with flattened hexagonal, crown and star shapes.

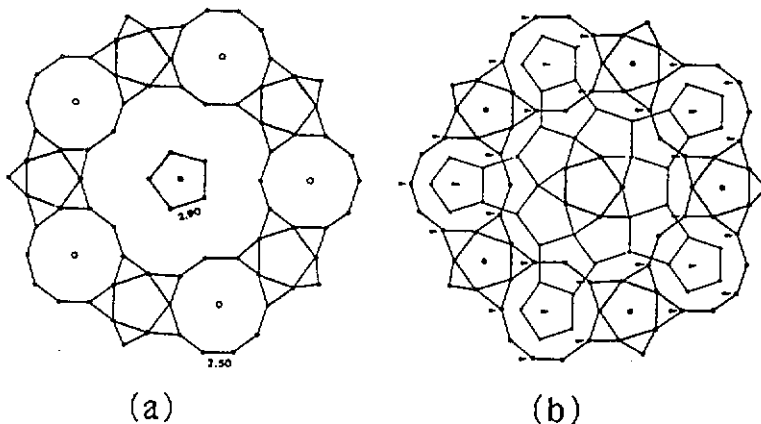


Figure 7. The characteristic cross sections of the 30 Å diameter column of the Al-Mn-Pd decagonal quasicrystal in (a) the flat layer and (b) the puckered layers. (Figure 4(b) and (c) from [6 (Steurer 1993)]).

The electron density maps of the Al-Mn-Pd DQC obtained by Steurer *et al* (figure 8(a)-(c) in [6 (Steurer *et al* 1993)]) are reproduced in figure 8: (a) in the flat layer and (b) and (c) in the puckered layer. As indicated by arrow heads in figure 8(a), there are quite strong peaks corresponding to the positions of the excess Al atoms in our model (with a little shift). In the meantime, the atoms marked by arrow heads in figure 7(b) correspond to some quite weak peaks in figure 8(b) and (c).

It is shown that the d sub-units derived from the  $T_3$  Al-Mn-Zn structure is comparable



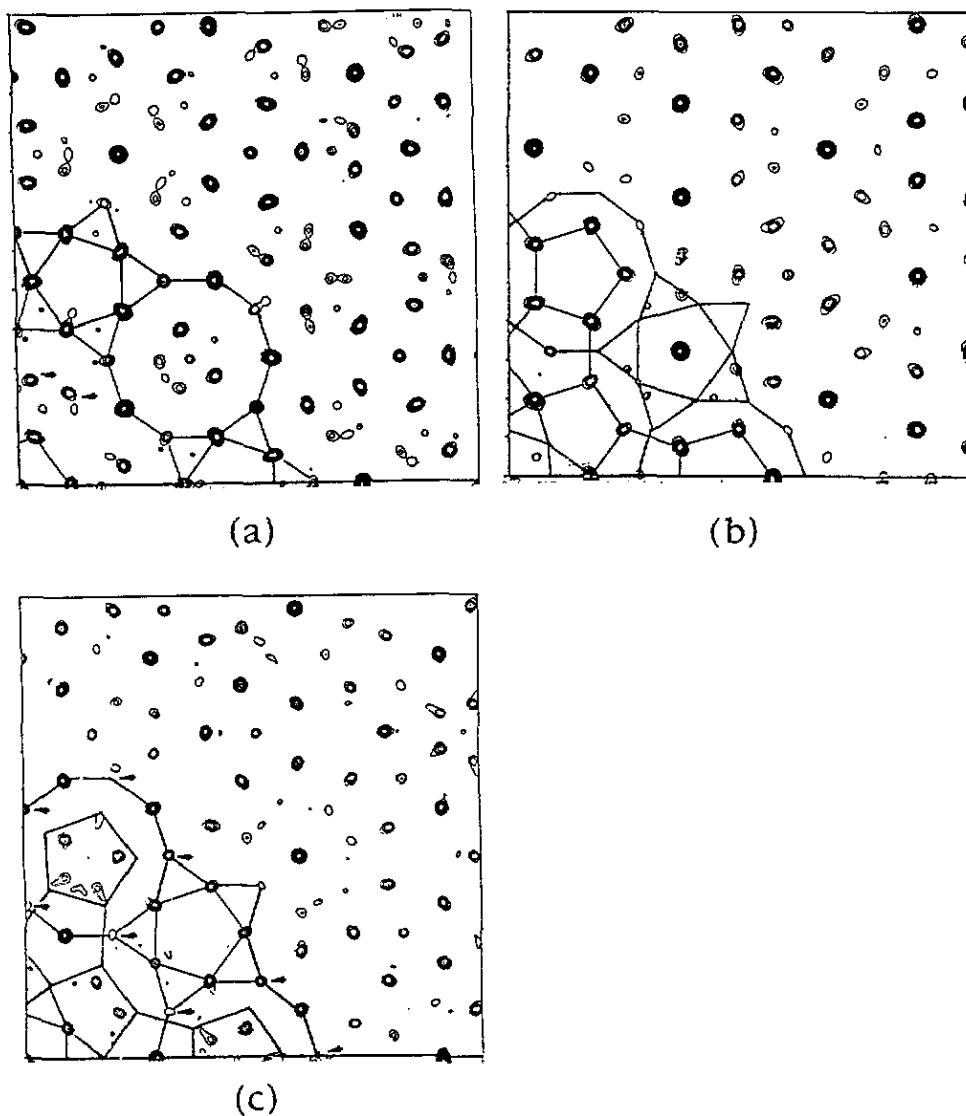


Figure 8. The electron density maps of the Al-Mn-Pd DQC obtained by Steurer *et al* : (a) in the flat layer and (b) and (c) in the pucker layer (figure 8(a)-(c) in [6 (Steurer *et al* 1993)]).

to the experimental result for the DQC although they are not totally identical.

### 6.2. Comparison with high-resolution electron microscopy results

An atomic arrangement of the Al-Mn-Pd DQC has been also independently presented by Hiraga and Sun [9]. This work is based on the combination of the HREM image [10] and a local atomic arrangement of the Al-Mn DQC [5]. It is worth pointing out that the atom positions in their work are identical to those we obtain from the crystalline approximant. However, they declared that their structural model has a composition of about  $\text{Al}_4(\text{Mn}, \text{Pd})$ , which is in conflict with the composition  $\text{Al}_{70}\text{Mn}_{17}\text{Pd}_{13}$  of the DQC phase. In contrast, the composition of our model is quite close to  $\text{Al}_{70}\text{Mn}_{17}\text{Pd}_{13}$  since an aperiodic structure of the

sub-units has only a slight change from the experimental value for the composition of the  $T_3$  Al-Mn-Zn approximant and we assume that the Zn atoms are replaced by the Pd atoms (see section 2).

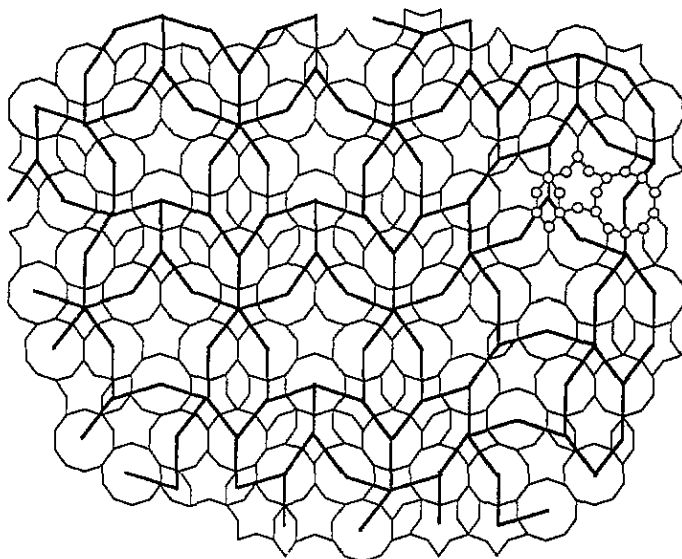


Figure 9. An aperiodic lattice composed of three kinds of sub-unit, in which the icosahedral cluster chains locate on the vertices of the h, s, d sub-units, is illustrated. This aperiodic lattice can explain the HREM image of the Al-Mn-Pd decagonal quasicrystal (figure 1 of [10]).

The HREM image of the Al-Mn-Pd DQC (figure 1 of [10]) can be completely described by our structural sub-units. Figure 9 shows a quasilattice composed by the three kinds of large sub-unit (H, H', C and S); the positions of icosahedral cluster chains are located at the vertices of the three small sub-units (h, s and d). As shown by Hiraga *et al* [15], the interpenetrating icosahedral clusters can be recorded as image spots in HREM experiments. Thus, it is found that the HREM image of the Al-Mn-Pd DQC (figure 1 of [10]) can be described by the aperiodic lattice composed of our structural sub-units. This kind of explanation is very successful since the vertices of the three small sub-units (h, s and d) in figure 9 overlap exactly on the image spots in the HREM image of the Al-Mn-Pd DQC.

### 6.3. Relationship between Al-Mn-Pd and Al-Mn decagonal quasicrystals

The Al-Mn-Pd and Al-Mn DQCs are closely related in structure. Due to the addition of the Pd element, a stable DQC was found in the Al-Mn-Pd alloy system, in contrast to the metastable DQC in the Al-Mn alloy system. This fundamental difference is naturally reflected in their structures and it is shown that the former is of higher structural quality than the latter by comparing their diffraction patterns. This means that the Al-Mn-Pd DQC shows lattice correlation of longer range than the Al-Mn DQC [3].

The Pd atoms in our model, e.g. the d sub-unit, occupy special positions in both the flat layer and the puckered layer. This is perhaps the reason why the d sub-unit only occurs in the Al-Mn-Pd DQC and not in the Al-Mn DQC. It is interesting to note that the sub-units of Al-Mn-Pd and Al-Mn DQCs are related by a hierarchical inflation/deflation rule. Considering the larger size of the sub-units, this explains why the Al-Mn-Pd DQC

has a much larger correlation length than the Al-Mn DQC does. Thus, the structures of the Al-Mn-Pd and Al-Mn DQCs can be unified.

We suggest that the individual sub-units h, c and s could possibly appear in the structure of the Al-Mn-Pd DQC with minor frequencies. The appearance of individual sub-units h, c and s does not change the atom near-neighbour coordination; however, it reduces the long-range correlation in the structure of the Al-Mn-Pd DQC. In our view, the less frequently the individual small sub-units (h, c and s) occur, the more perfect the Al-Mn-Pd DQC will be.

### Acknowledgments

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### References

- [1] Tsai A P, Inoue A and Masumoto T 1989 *Mater. Trans. Japan Inst. Met.* **30** 463
- [2] He L X, Wu Y K, Meng X M and Kuo K H 1990 *Phil. Mag. Lett.* **61** 15
- [3] Beeli C, Nissen H-U and Robadey J 1991 *Phil. Mag. Lett.* **63** 87
- [4] Steurer W and Kuo K H 1990 *Phil. Mag. Lett.* **62** 185; 1990 *Acta Crystallogr. B* **46** 703
- [5] Steurer W 1991 *J. Phys.: Condens. Matter* **3** 3397
- [6] Steurer W 1993 *J. Non-Cryst. Solids* **153-154** 92  
Steurer W, Haibach T, Zhang B, Beeli C and Nissen H-U 1993 *J. Phys.: Condens. Matter* **6** 613
- [7] Wang Y P, Lu L and Zhang L 1993 *J. Non-Cryst. Solids* **153-154** 361
- [8] Li X Z and Kuo K H 1993 *Phil. Mag. B* **65** 525
- [9] Hiraga K and Sun W 1993 *Phil. Mag. Lett.* **67** 117
- [10] Hiraga K 1993 *J. Non-Cryst. Solids* **153-154** 28
- [11] Taylor M A 1960 *Acta Metall.* **8** 256
- [12] Li X Z, Shi D and Kuo K H 1993 *Phil. Mag. B* **66** 331
- [13] Shi N C, Li X Z, Ma J S and Kuo K H 1993 *Acta Crystallogr.* at press
- [14] Kang S S, Malaman B, Venturini G and Dubois J M 1992 *Acta Crystallogr. B* **48** 770
- [15] Hiraga K, Kaneko M, Matsuo Y and Hashimoto S 1993 *Phil. Mag. B* **67** 193
- [16] Li X Z 1994 *J. Non-Cryst. Solids* submitted
- [17] Li X Z and Kuo K H 1992 *Phil. Mag. B* **66** 117
- [18] Robinson K 1952 *Phil. Mag.* **43** 775
- [19] Robinson K 1954 *Acta Crystallogr.* **7** 494
- [20] Damjanovic A 1961 *Acta Crystallogr.* **14** 982
- [21] Kang S S and Dubois
- [21] Kang S S and Dubois J M 1992 *J. Phys.: Condens. Matter* **4** 10 169
- [22] Li X Z, Dubois J M and Kuo K H 1993 *Phil. Mag. Lett.* **69**