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Structure of Al–Mn Decagonal Quasicrystal. I. A Unit-Cell Approach

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Abstract

Based on the fact that the Al_3Mn phase is closely related to the Al–Mn decagonal quasicrystal, three subunits of the Al–Mn decagonal quasicrystal are deduced from the structure of the Al_3Mn phase. The existence of these subunits is confirmed by the high-resolution electron microscopy image of the Al–Mn decagonal quasicrystal. The structure of the Al–Mn decagonal quasicrystal is suggested to be a random aggregation of these subunits. The local atomic arrangements in the present model agree well with those obtained by the single-crystal X-ray structure analysis of the Al–Mn decagonal quasicrystal.

1. Introduction

Structure determination is an urgent subject in the study of decagonal quasicrystals (DQC). Two methods are often used in the structure study of the DQC, one is the high-dimensional approach, which suggests the structure of the DQC is an irrational section of a high-dimensional periodic structure with a three-dimensional super-plane (Janssen, 1986; Steurer & Kuo, 1990; Steurer, 1991), the other is the unit-cell approach, which is established on a hypothesis that the DQC and the crystalline approximant possess the same or similar atomic clusters, packed aperiodically in the former and periodically in the latter (Kumar, Sahoo & Athithan, 1986; Li & Kuo, 1992*a*; Li & Dubois, 1994).

The two-dimensional DQC was firstly found in a rapidly solidified Al–Mn alloy (Bendersky, 1985; Chattopadhyay, Lele, Ranganathan, Subbanna & Thangaraj, 1985). Many models have been proposed to elucidate the structure of the Al–Mn DQC, *e.g.* a single-crystal X-ray structure analysis of the Al–Mn DQC has been performed using the high-dimensional approach by Steurer (1991); Li & Kuo (1992*a*) proposed a model for the Al–Mn DQC on the basis of the orthorhombic π-Al_4Mn phase; Niizeki (1993) suggested that a modified pentagonal Penrose pattern should be used as the quasilattice for the Al–Mn DQC.

In the present paper, we propose a new structural model for the Al–Mn DQC, which explains the experimental observation on the Al–Mn DQC better than the models published before. A unit-cell approach is used in this paper and a high-dimensional description of the structure is presented in a separate paper (Li & Frey, 1995). The content of the present paper is organized as follows. In §2, the structure of the Al_3Mn phase (Li, Shi & Kuo, 1992; Hiraga, Kaneko, Matsuo & Hashimoto, 1993; Shi, Li, Ma & Kuo, 1994) is analysed and the high-resolution electron microscopy (HREM) image of the Al–Mn DQC (Hirabayashi & Hiraga, 1987) is re-examined. Based on the two aspects, the structural subunits of the Al–Mn DQC are derived. In §3, the quasilattice of the Al–Mn DQC is discussed. The comparison of the present model with the result of the single-crystal X-ray analysis of the Al–Mn DQC is given in §4, conclusions are given in §5.

2. Structural subunits

The Al–Mn DQC is closely related to two orthorhombic crystalline phases: (i) the Al–Mn DQC was found coexisting with the Al_3Mn phase in melt spun ribbons of Al–24%Mn (Fitz Gerald, Withers, Stewart & Calka, 1988); (ii) the Al–Mn DQC was found transforming to the π-Al_4Mn phase after a heat treatment of 873 K for 2 h (Li & Kuo, 1992*a*). The electron-diffraction patterns of the two crystalline phases resemble those of the Al–Mn DQC. This means that the three phases are possibly composed by the same (or similar) atomic clusters. Li & Kuo (1992*b*) found that the Al_3Mn and π-Al_4Mn phases are indeed composed of the same type of flattened hexagonal subunit. Therefore, the structures of the two crystalline phases can be regarded as a starting point to interpret the structure of the Al–Mn DQC.

2.1. *The structure of the* Al_3Mn *crystalline approximant*

Fig. 1(*a*) shows a schematic illustration of the Al_3Mn phase, the plane unit-cell with **a** and **c** outlined. The

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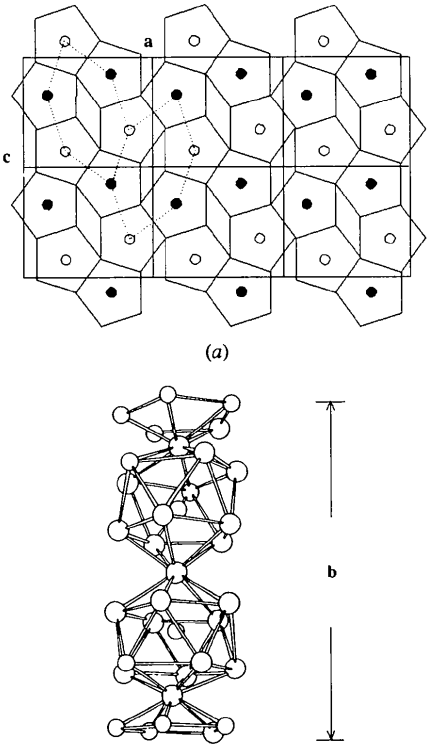
structure of the Al_3Mn phase can be described by a framework of Al pentagonal prisms and a column of atomic clusters inside. The *b*-period of the Al framework is 1/2**b**. The column of atomic clusters is an icosahedral chain [see Fig. 1(*b*)]. The icosahedral chains in the pentagonal prisms denoted by solid circles are 1/2**b**-shifted with respect to those in the pentagonal prisms denoted by open circles. The structure of the Al_3Mn phase can also be described by two types of layers, namely flat (*F*, a mirror plane*) and puckered (*P* and *p*) layers, stacking in the sequence *PFpP′F′p′*, in which the sequence *P′F′p′* is related to the sequence *PFp* by a 2_1-screw axis. The atomic arrangements are more easily shown in these layers (see §2.3).

Flattened hexagonal subunits can be found in the structure of the Al_3Mn phase, which is an accumulation of six atomic clusters, by sharing the side faces of the Al pentagonal prisms. Thus, the structure of the Al_3Mn phase can be interpreted as a tessellation of the flattened hexagonal subunits in alternating different orientations. The flattened hexagonal subunit is also observed in the HREM image of the Al_3Mn phase, since the icosahedral chain can be considered as a type of atomic channel (Li *et al.*, 1992; Hiraga *et al.*, 1993). The edge length of the flattened hexagon in the HREM image is *ca* 6.5 Å.

2.2. *HREM image of the* Al–Mn *DQC*

A HREM study of the Al–Mn DQC has been reported by Hirabayashi & Hiraga (1987), the HREM image taken with the incident beam along the tenfold symmetry axis shows a pattern of aperiodic arrangement of two types of tiles, which are consistent with the Penrose rhombuses (edge length 6.5 Å). This result gives a valuable insight into the structure of the Al–Mn DQC. A schematic illustration of the HREM image (Hirabayashi & Hiraga, 1987) is reproduced in Fig. 2(*a*). Re-examining the HREM image, we find that the two Penrose rhombuses are not totally randomly packed, but assemble into three new tiles, which are shown in Fig. 2 (*b*) and denoted as a flattened hexagon (H), crown (C) and star (S).

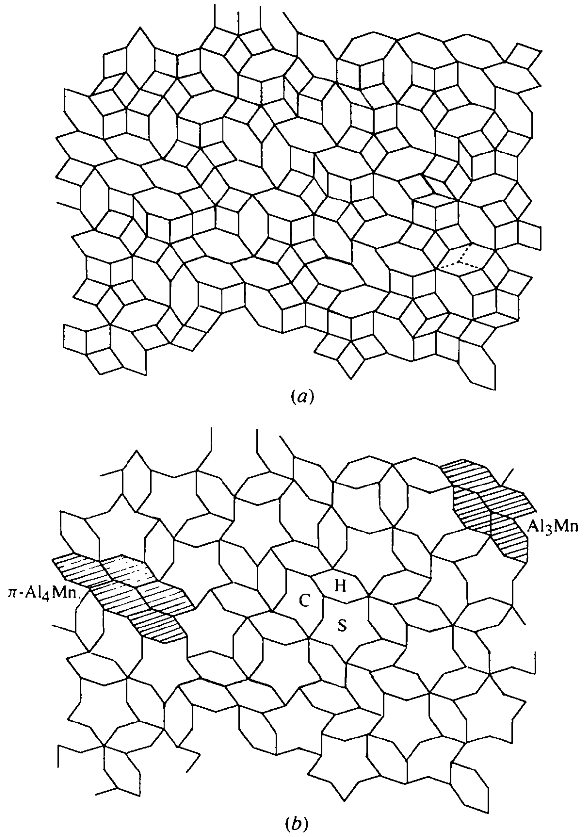
By considering the close structural relationship between the Al–Mn DQC and Al_3Mn phase, we suggest that the Al–Mn DQC is also composed of the same type



(*a*)

(*b*)

Fig. 1. The structure of the Al_3Mn phase can be described by (*a*) a framework of Al pentagonal prisms and (*b*) a column of the atomic clusters inside. The plane unit-cell with **a** and **c** is outlined. Flattened hexagonal subunits are also shown.



(*a*)

(*b*)

Fig. 2. (*a*) Tiling by two types of Penrose rhombuses, which is formed by connecting the bright dots in the observed image of the Al–Mn DQC with lines (Hirabayashi & Hiraga, 1987). (*b*) Tiling pattern is composed of three types of tiles, denoted as a flattened hexagon (*H*), crown (*C*) and star (*S*), which can be used to describe the same image.

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* This has been determined as a pseudo-mirror plane in the paper by Shi *et al.* (1994).

of structural motif as that of the Al_3Mn phase. The following experimental observations imply a way of obtaining the subunits of the Al–Mn DQC: (i) a crown subunit was also observed in a grain-boundary of the Al_3Mn phase (Li *et al.*, 1992); (ii) the aggregation of the flattened hexagonal subunits corresponding to the π-Al_4Mn and Al_3Mn phases can be found in the local area of the Al–Mn DQC, which are indicated by shaded lines in Fig. 2(*b*). The three tiles in Fig. 2(*b*) are suggested to be the subunits of the Al–Mn DQC.

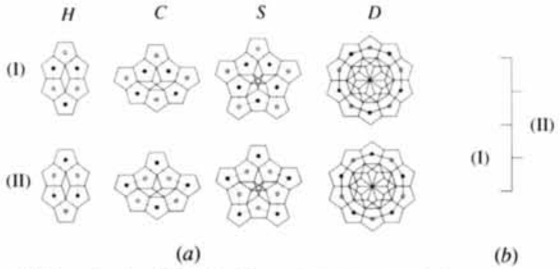

Fig. 3. The subunits of the Al–Mn and Al–Mn–Pd DQCs formed by the initial aggregation of the atomic clusters, flattened hexagon *H*, crown *C*, star *S* and decagon *D*.

2.3. *Structural subunits of the* Al–Mn DQC

Based on the analysis given above, we construct the structural subunits of the Al–Mn DQC in the following way. Firstly we assume that the initial aggregation of the atomic clusters should be with fivefold rotational symmetry. In this way, the aggregated states *S* and *D* can be obtained. Meanwhile, two shrunken states of the subunit *S* (no shrunken state for the subunit *D*) are also considered. One is the aggregated state with a flattened hexagonal shape (*H*), which appears in the Al_3Mn structure and the other is the aggregated state with a crown shape (*C*), which is also observed in the grain boundary of the Al_3Mn phase. These initial aggregated states are shown in Fig. 3(*a*).

There are two types of subunits* (I and II) with the same shapes of the hexagon, crown, star and decagon. The relationship between them is shown in Fig. 3(*b*), a periodic stack of type (I) subunits is indicated as the vertical line and type (II) subunits can be obtained by reselecting the building block. Therefore, type (II) subunits can be expressed by their counterparts, type (I) subunits.

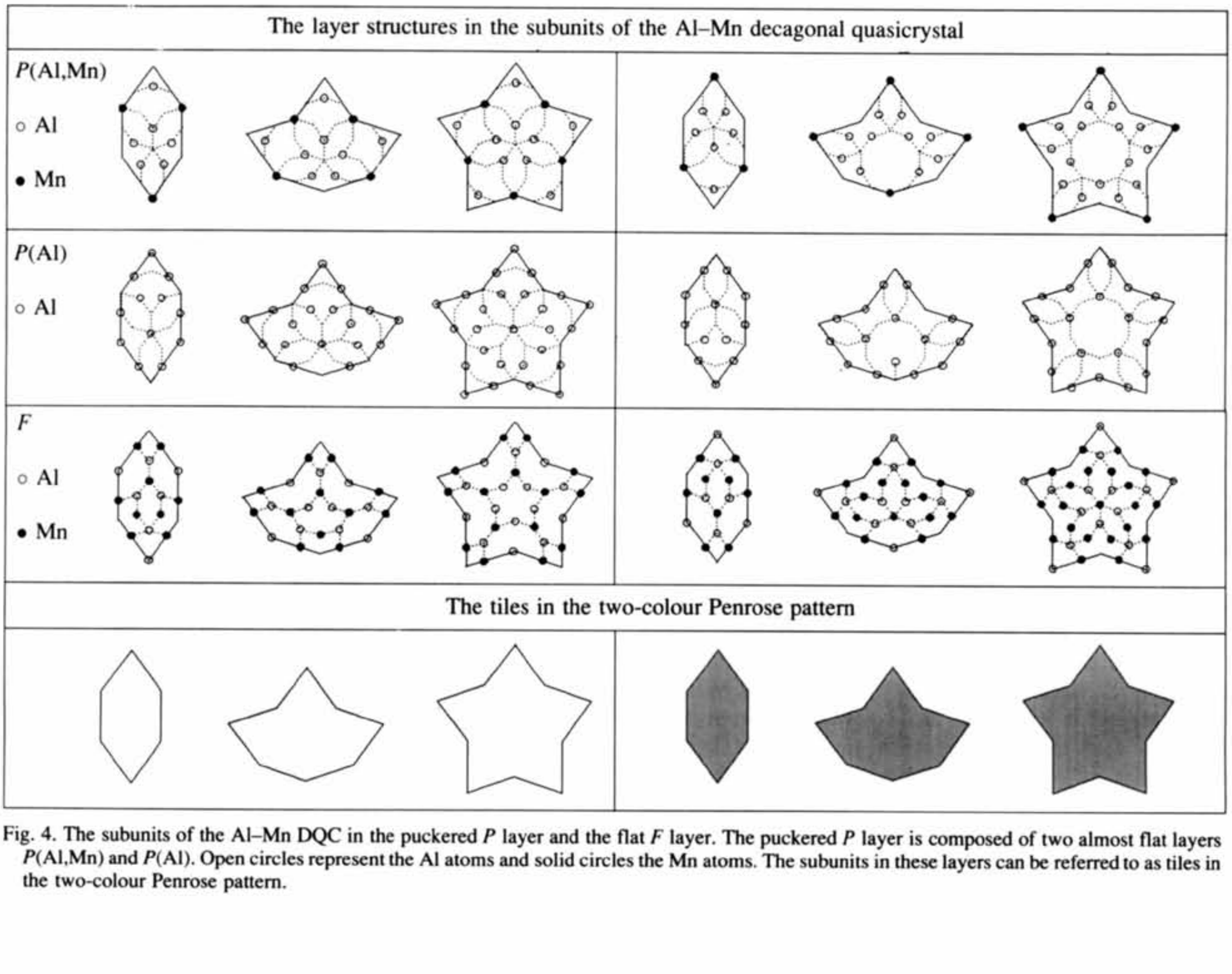

Fig. 4. The subunits of the Al–Mn DQC in the puckered *P* layer and the flat *F* layer. The puckered *P* layer is composed of two almost flat layers *P*(Al,Mn) and *P*(Al). Open circles represent the Al atoms and solid circles the Mn atoms. The subunits in these layers can be referred to as tiles in the two-colour Penrose pattern.

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* For the subunits *H* and *D*, types (I) and (II) are the same. However, they also obey the relationship shown in the text below.

We use type (I) subunits to describe the structure of the Al–Mn DQC hereafter. It is clear that only the first three of the subunits (*H*, *C* and *S*) exist in the Al–Mn DQC, as shown in the HREM image of the Al–Mn DQC. The fourth subunit (*D*) is found existing in the Al–Mn–Pd DQC (Li & Dubois, 1994).

The atomic arrangements in the subunits of the Al–Mn DQC can be shown in the flat (*F*) and puckered (*P*) layers as the structural description of the Al_3Mn phase. The layers in the subunits of the Al–Mn DQC are stacked in the sequence $PFp\bar{P}\bar{F}\bar{p}$. Layer p ($\bar{p}$) is related to layer P ($\bar{P}$) by the mirror plane at layer F ($\bar{F}$). The relationship between PFp and $\bar{P}\bar{F}\bar{p}$ will be given below. As a matter of fact, the *P* layer is composed of two almost flat layers, that near the *F* layer is composed of only Al atoms and referred to as the *P*(Al) layer, while the other is composed of Al and Mn atoms and referred to as the *P*(Al,Mn) layer. Fig. 4 shows the subunits in the puckered layer *P*(Al,Mn) and *P*(Al), and the flat layer (*F*), respectively. The Al atoms are represented by open circles and the Mn atoms by solids circles. The atomic arrangements in Fig. 4 are stacked in the following way in the three-dimensional subunits: when the atomic arrangements in the left part of Fig. 4 appear in the layer F (P), the atomic arrangements in the right parts of Fig. 4 appear in the $\bar{F}$ ($\bar{P}$) layer, respectively, and *vice versa*.

3. Quasilattice

3.1. *Quasiperiodic lattice*

A two-colour Penrose pattern (Li, Dubois & Kuo, 1994) is composed of tiles with shapes of a flattened hexagon (*H*), crown (*C*) and star (*S*) in white or black, which is a variety of the (original) Penrose pattern. The frequencies of the subunits in two-colour Penrose pattern are $F_H{:}F_C{:}F_S = 5\tau{:}5{:}2\tau - 1$, in which $\tau = (5^{1/2} + 1)/2 = 1.618\ldots$ is the golden mean. The two-colour Penrose pattern is a quasiperiodic lattice with fivefold rotational symmetry, in contrast to the tenfold rotational symmetry of the Penrose pattern. A two-dimensional quasiperiodic and one-dimensional periodic lattice can be constructed by stacking the two-colour Penrose pattern in a sequence of $T\bar{T}T\bar{T}\ldots$, where $\bar{T}$ is T in reverse colour, as shown in Fig. 5.

The subunits of the Al–Mn DQC in each layer can be referred to as the two-colour Penrose tiles if the different atomic decorations are considered as different colours (see Fig. 4). Thus, the subunits in each layer can form a quasiperiodic lattice with a fivefold rotational symmetry. The stacking sequence of these quasiperiodic layers is determined by the relationship of the different layers in the subunits. We find that the ideal quasiperiodic lattice for the Al–Mn DQC belongs to a three-dimensional lattice formed by the periodic stack of the two-colour Penrose pattern in the sequence $T\bar{T}T\bar{T}\ldots$. For further details, see the subsequent paper by Li & Frey (1995).

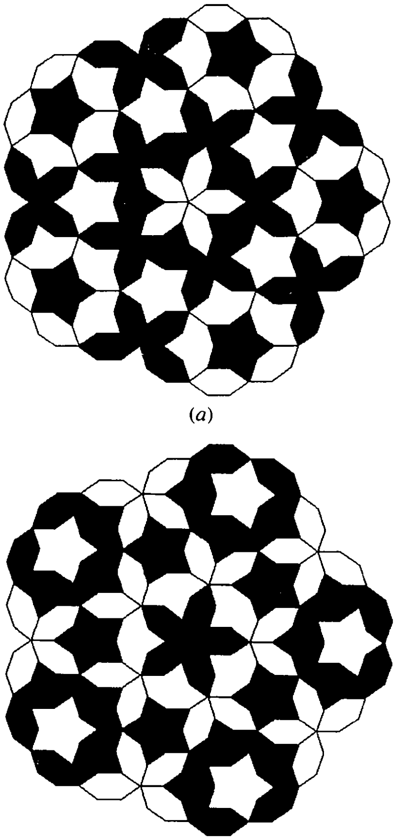
3.2. *Quasilattice for the* Al–Mn *DQC*

It should be pointed out that the structural subunits of the Al–Mn DQC can be packed in a quasiperiodic way, such as the two-colour Penrose lattice, but it should not be forced. As shown in the HREM image [Fig. 2(*b*)], the subunits are packed in a random way in the structure of the (true) Al–Mn DQC.

We propose that the quasilattice of the Al–Mn DQC is a random aggregation of the three subunits. The frequencies of each subunit in this quasilattice should be close to those in the ideal quasiperiodic lattice. Such a quasilattice can be obtained from an ideal quasiperiodic lattice by introducing phason strains.

4. Comparison with the result of the single-crystal X-ray analysis

The structure of the Al–Mn DQC has been determined by a single-crystal X-ray analysis and five-dimensional approach (Steurer, 1991). There are four five-dimensional atoms in the asymmetric unit generating one flat and one strongly puckered quasiperiodic atom layer in physical space. The experimental result provides the


(*a*)

(*b*)

Fig. 5. Two-colour Penrose patterns composed of tiles with the shapes of a flattened hexagon, crown and star and each tile is in white or black. The pattern $\bar{T}$ (*b*) is the pattern T (*a*) in reverse colour.

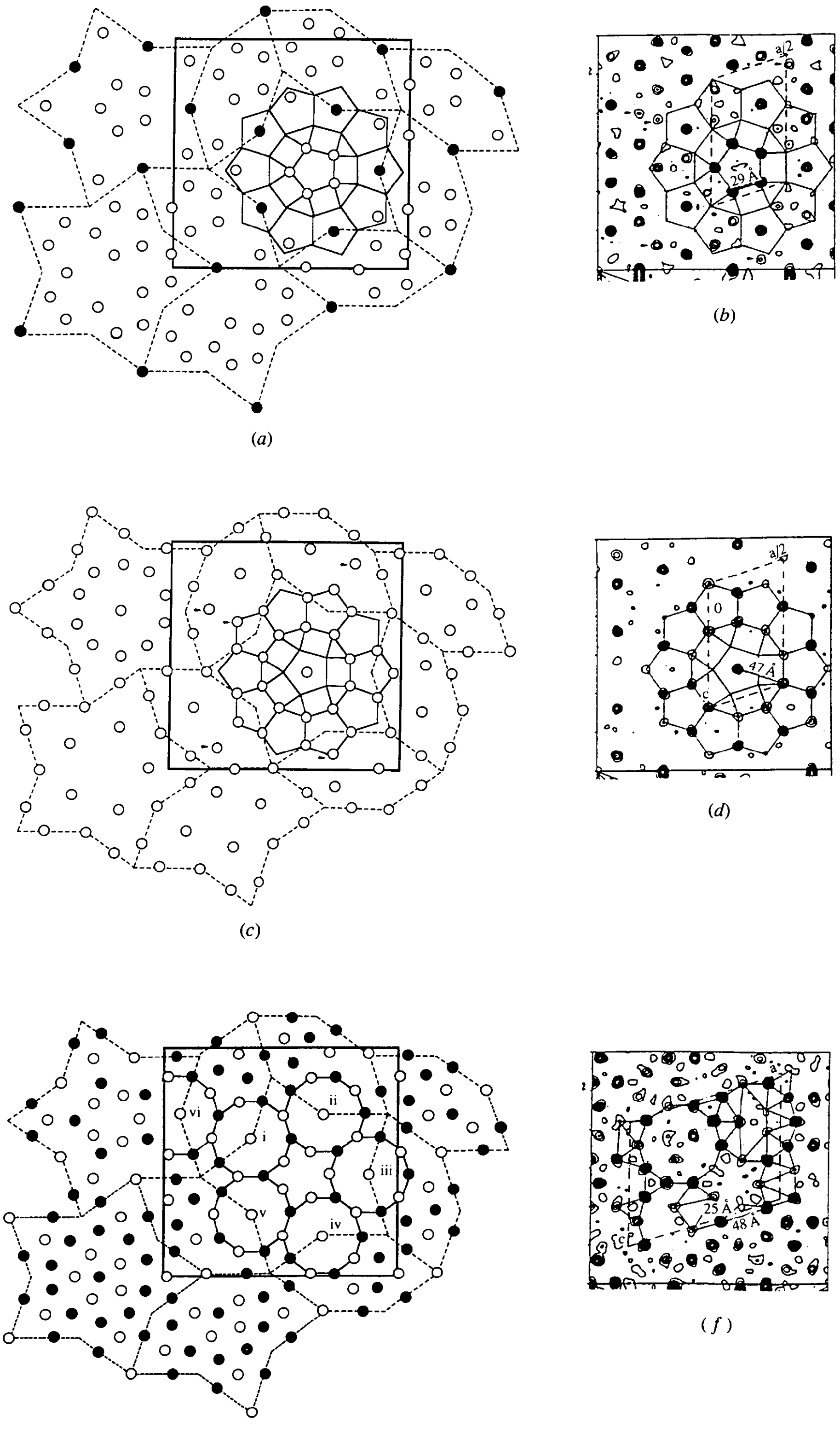


Fig. 6. Partial structure in the present model and the result of the single-crystal X-ray analysis on the Al–Mn DQC (Steurer, 1991). (*a*) *P*(Al,Mn), (*c*) *P*(Al) and (*e*) *F* in the present model are compared with the quasiperiodic (11 000) sections of the five-dimensional Fourier function at (*b*) $x_3 = 0.064$, (*d*) $x_3 = 0.124$ and (*f*) $x_3 = 0.25$, respectively. For details, see text.

information of an average structure only, since the diffuse scattering is not considered in the structure determination (Steurer, 1991). The correct local structural information, such as coordination polyhedra, structural motifs and bond lengths, can be determined from the averaged quasiperiodic structure, even if the sample used is any type of random tiling-like (but not quasiperiodic) structure (Steurer, Haibach, Zhang, Kek & Lück, 1993). Therefore, it is necessary to compare the present model with the results of the single-crystal X-ray structure analysis of the Al–Mn DQC.

The local area in the present model [Figs. 6(*a*), (c) and (*e*)] is compared with the X-ray result (Steurer, 1991), which are reproduced in Figs. 6(*b*), (*d*) and (*f*). Atomic arrangements in layers (*a*) *P*(Al,Mn), (*c*) *P*(Al) and (*e*) *F* in Fig. 6 can be compared with the quasiperiodic (11 000) sections of the five-dimensional Fourier function at (*b*) $x_3 = 0.064$, (*d*) $x_3 = 0.124$ and (*f*) $x_3 = 0.25$, respectively. It is obvious that most of the atom positions in the present model are consistent with the X-ray results by Steurer (1991). Divergences are also noticed: in the puckered layer, a few atoms (indicated by arrow heads) in Fig. 6(*c*) have no corresponding peaks in Fig. 6(*d*), but in Fig. 6(*b*). This difference between the present model and X-ray result is not essential, since *P*(Al,Mn) and *P*(Al) are very close and they form one puckered layer; in the flat layer, one Al atom lies in the center of the atom decagon [marked with i, ii, iii, iv, v and vi in Fig. 6(*e*)], while one weak peak in the corresponding site and two or three strong peaks inside the decagon in Fig. 6(*f*). These excess strong peaks are possible due to averaging in the structure determination. It shows that the coordination polyhedra, structure motifs and bond lengths in the present model agree well with the X-ray experimental results.

The structure of the Al–Mn–Pd stable DQC (Beeli, Nissen & Robadey, 1991) is recently determined by a single-crystal X-ray analysis and a five-dimensional approach (Steurer, Haibach, Zhang, Beeli & Nissen, 1994). The result shows that the stable Al–Mn–Pd DQC is isostructural with the metastable Al–Mn DQC. In our point of view, the atomic cluster in Al–Mn–Pd and Al–Mn DQCs is similar, but the subunits in the Al–Mn–Pd DQC are much larger than those in the Al–Mn DQC, since the electron diffraction and HREM experiments clearly show longer range correlations in the Al–Mn–Pd DQC than that in the Al–Mn DQC (Hirabayashi & Hiraga, 1987; Hiraga, 1993). The structural relationship between the two DQC phases is recently discussed by Li & Dubois (1994), showing that the average structure of the Al–Mn and Al–Mn–Pd DQCs, determined by the high-dimensional approach, is more suitable to the Al–Mn–Pd DQC than to the Al–Mn DQC. This is consistent with the fact that the diffuse scattering in the Al–Mn DQC is much more essential than that in the Al–Mn–Pd DQC and the diffuse scattering was neglected in the structure determination of the two DQCs.

5. Concluding remarks

In conclusion, the structural subunits of the Al–Mn decagonal quasicrystal can be derived based on the structure of the Al_3Mn crystalline phase and the HREM image of the Al–Mn DQC. Quasiperiodic tessellation of the subunits corresponds to a three-dimensional lattice formed by the periodic stack of the two-colour Penrose quasilattices in the sequence $T\bar{T}T\bar{T}$.... The quasilattice for the (true) Al–Mn DQC is a random aggregation of the subunits, which can be regarded as a case of an ideal quasiperiodic lattice with a strong phason strain. The local atomic arrangements in the present model agree with those in the single-crystal X-ray structure analysis of the Al–Mn DQC.

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