On the Crystalline Approximants of the Al-Mn, Al-Pd and Al-Mn-Pd Type Decagonal Quasicrystals

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On the Crystalline Approximants of the Al-Mn, Al-Pd and Al-Mn-Pd Type Decagonal Quasicrystals*

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On the basis of atomic clusters of decagonal quasicrystals, subunits of decagonal quasicrystals are proposed as the results of aggregation of the atomic clusters. The structure of the crystalline approximants can be characterized as some simple periodic tiling of the subunits. This is shown as a new approach to study the structure of the new crystalline approximants.

KEYWORDS: decagonal quasicrystal, crystalline approximant

1. Introduction

Decagonal quasicrystal (DQC) was first discovered in a rapidly quenched Al_4Mn alloy[1,2] and later was found in many binary and ternary alloys of Al and transition metals. The characteristic of the phase is shown as a tenfold two-dimensional (2D) quasiperiodic reciprocal plane and periodic axis in the perpendicular direction. Soon after the discovery of the DQCs, some crystalline phases related to the DQC were noticed. Their diffraction patterns are resemblance to those of the DQCs, i.e., the distribution of the strong diffraction spots, although on periodic arrays, has a pseudo-tenfold symmetry. These phases were latterly called crystalline approximants of the DQCs. It is believed that the structures of the DQC and crystalline approximants are composed of the same atom cluster, packing aperiodically in the former and periodically in the latter.

If the structure of one crystalline phase (C1) has been determined among the crystalline approximants (C1, C2, C3, ...) in the same alloy or isotypical ones. Then atom clusters can be separated out and re-aggregated to form structural subunits of the DQCs according to the high-resolution electron microscopy (HREM) image of the DQCs. Aperiodic (random or quasiperiodic) packings of the subunits provide the structures of the DQCs. On the other hand, structural models for other crystalline approximants C2, C3, ... can be constructed by periodic packing of subunits. This is very helpful in the structural determination of the crystalline approximants. We will use the concept of the subunit in the construction of the structural models, since the subunit includes not only the atom clusters and also the local arrangement of the atom clusters. The subunits are the biggest common motives in the structures of the DQCs and crystalline approximants.

In this paper, firstly a survey on the atom clusters and the subunits of the Al-Mn, Al-Pd and Al-Mn-Pd type DQCs is given. Then we show that the structures of the crystalline phases related to these DQCs can be described as periodic packings of subunits. Finally structural models of two new approximants proposed by this approach are shown as examples.

2. Atom clusters and subunits of decagonal quasicrystals

Al_3Mn (Pnma, a=1.484, b=1.246, c=1.251 nm) and Al_3Pd ($Pna2_1$, a=2.336, b=1.232, c=1.659 nm) phases are the approximants of the Al-Mn and Al-Pd DQCs, respectively[3,4]. Thanks to the determination of the two crystalline phases[5-8], the atom clusters of the Al-Mn type and Al-Pd type DQC can be deduced. Fig. 1 shows (a) the schematic illustration of the Al_3Mn structure in the [010] projection, in which the unit-cells are outlined by dotted lines and (b) the atom cluster. The structure of the Al_3Mn phase is composed of pentagonal atom clusters, which appear as pentagonal columns and is briefly represented as

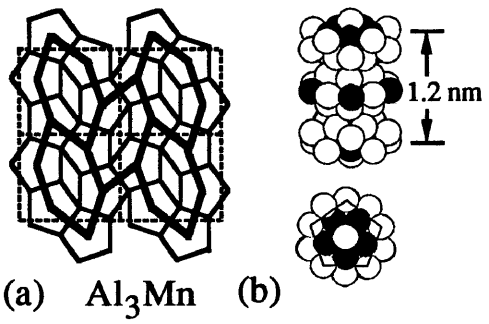

Figure 1. (a) Schematic illustration of the Al_3Mn structure in the [010] projection and (b) atom cluster as a pentagon prism.

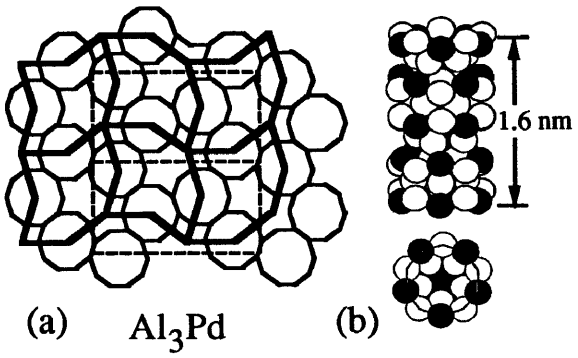

Figure 2. (a) Schematic illustration of the Al_3Pd structure in the [001] projection and (b) atom cluster as a decagonal prism.

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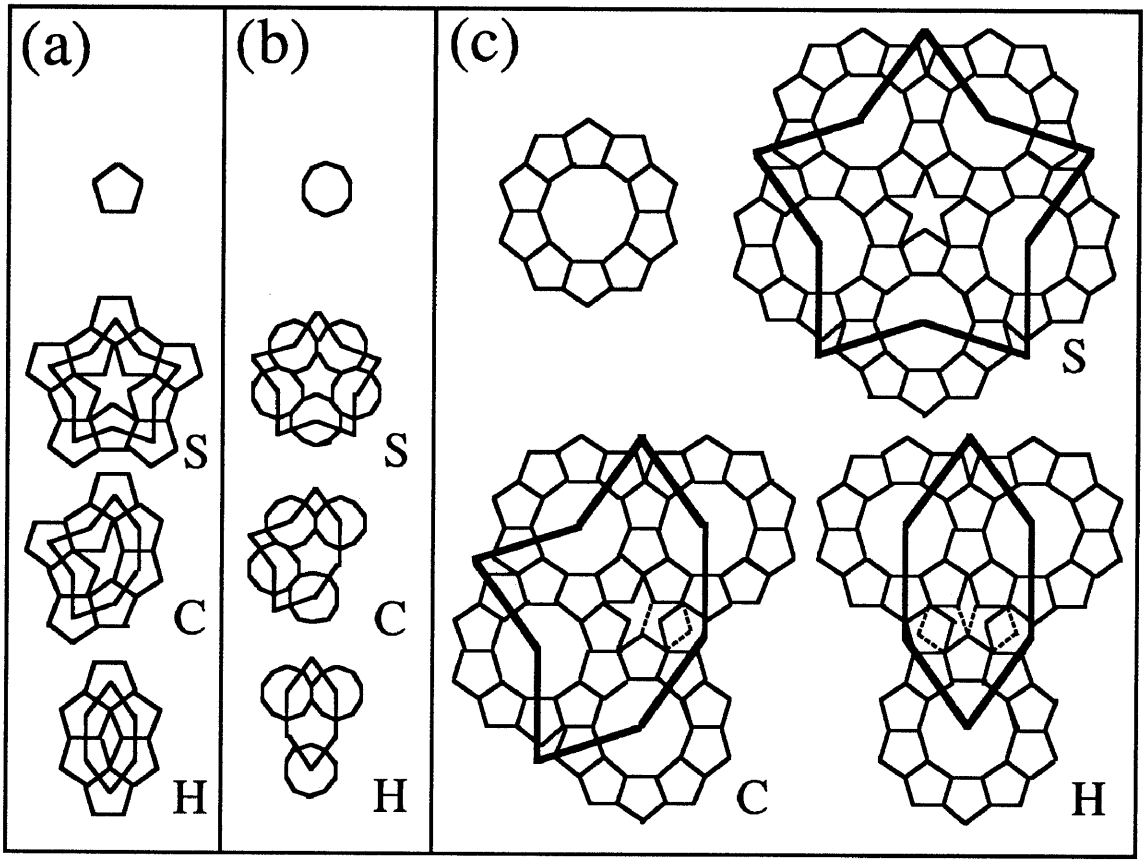

Figure 3. Schematic illustration of the structural subunits, in (a) Al-Mn type DQC, (b) Al-Pd type DQC and (c) Al-Mn-Pd type DQC.

pentagon in Fig. 1(a). The structure can be also described by flat (F, mirror plane) and puckered (P, p) layers perpendicular to the b axis in a sequence of PFpP'F'p' ..., where P'F'p' is related to PFp by a 2_1 screw operation. Fig. 2 shows (a) the schematic illustration of the Al_3Pd structure in the [001] projection, in which the unit-cells are outlined by dotted lines and (b) the atom cluster. The structure of the Al_3Pd phase is composed of decagonal atom clusters, which appear as decagonal columns and is briefly represented as decagon in Fig. 2(a). The structure can be also described by layers A, B, C, D perpendicular to the c axis in a sequence of ABCDA'B'C'D'..., where A'B'C'D' is related to ABCD by a 2_1 screw operation.

The possible local arrangements of the pentagonal and decagonal clusters are shown in Fig. 3, which can be briefly represented by the kinds of tiles, (H)exagon, (C)rown and (S)tar. These tiles are considered to be the subunits of the Al-Mn type and Al-Pd type DQCs, when atom decoration are filled in according to the structure of the Al_3Mn and Al_3Pd phases, respectively. We note that more larger decagonal cluster are possibly formed by the above pentagonal clusters and new decagonal core in the center[9,10]. Fig. 3 (c) shows that the atom cluster in the Al-Mn-Pd DQC and again the subunits can be represented as the tiles H, C and S, but τ^2 larger than ones in the Al-Mn DQC. The atom clusters proposed above have been observed in the HREM images of the Al-Mn, Al-Pd and Al-Mn-Pd DQCs[11-13].

3. Periodic tilings for crystalline approximants

Some orthorhombic phases as the approximants of the DQCs are listed in Table 1. The structures of these crystalline approximants can be characterized by packing the three kinds of tiles (H, C and S), as shown in Fig. 4. In these structures, some of them were determined by single-crystal X-ray analysis and the others are structural models, which have been checked by comparing the simulation of the HREM image or the powder X-ray diffraction pattern to the experimental ones.

4. Examples on modeling the structures of the crystalline approximants

Two examples are given here to show that the reasonable models of the crystalline approximants can be constructed by the approach discussed above. One is the O-AlCrPd ($Al_{77}Cr_{14}Pd_9$) approximant of the Al-Mn type DQC and the other is the $Al_{75}Pd_{13}Ru_{12}$ approximant of the Al-Pd type DQC.

The O-AlCrPd approximant[22] was found in a ternary $Al_{72}Pd_{18}Cr_{10}$ alloy annealed at 800 °C for 36 hours. This is an orthorhombic phase with the lattice parameters, a=2.38, b=1.25 and c=3.28 nm. Electron diffraction study shows that the phase is a crystalline approximant of the Al-Mn type DQC. A structural model of the O-AlCrPd phase has been constructed by the subunits of the Al-Mn DQC. Like the structure of the Al_3Mn phase, the structure can be described in the flat (F,

Table 1. Lattice parameters of some orthorhombic crystalline phases (the axis in bold type is along the pseudo-tenfold axis). Approximants of the Al-Mn, Al-Pd and Al-Mn-Pd type DQCs are classified as A, B and C, respectively.

Type	Phase	Lattice parameters (nm)	Reference
A	π–AlMn	a=2.36, **b=1.24**, c=0.77	(14)
	$Al_{60}Mn_{11}Ni_4$	a=2.38, **b=1.25**, c=0.775	(15)*
	$Al_{20}Mn_3Cu_2$	a=2.42, **b=1.25**, c=0.772	(16)
	T3-AlMnZn	a=2.38, **b=1.26**, c=0.778	(17)*
	Al_3Mn	a=1.484, **b=1.246**, c=1.251	(6,7)*
	Y-AlMnCu	a=1.48, **b=1.24**, c=1.26	(16)
	O3-AlCuFeCr	a=1.458, **b=1.232**, c=1.236	(18)
	C1-AlMnPd	a=1.48, **b=1.24**, c=1.26	(19)
	O2-AlCuFeCr	a=2.36, **b=1.22**, c=2.01	(20)
	O1-AlCuFeCr	a=3.25, **b=1.22**, c=2.37	(20)
	C_{3I} AlMnNi	a=2.40, **b=1.24**, c=3.27	(21)
	O-AlCrPd	a=2.38, **b=1.25**, c=3.28	(22)
B	(2/1,1/1)AlCoNiTb	a=2.00, b=1.38, **c=1.65**	(23)
	R-AlPdMn	a=1.99, b=1.42, **c=1.66**	(24)
	Al_3Pd	a=2.336, b=1.232, **c=1.659**	(8)*
	(1/1,2/1)AlCoNiTb	a=2.30, b=1.26, **c=1.65**	(23)
	$Al_{75}Pd_{13}Ru_{12}$+	a=2.388, b=3.280, **c=1.669**	(25)
	$Al_{75}Pd_{15}Fe_{10}$	a=2.35, b=3.24, **c=1.66**	(24)
C	C2-AlMnPd	a=6.14, **b=1.24**, c=1.48	(19,24)
	C3-AlMnPd	a=5.05, **b=1.24**, c=3.78	(19,24)
	C4-AlMnPd	a=8.4, **b=1.24**, c=6.2	(19)

* indicates the structure of the crystalline phase has been determined by single-crystal X-ray analysis.
+ The $Al_{75}Pd_{13}Ru_{12}$ phase is exception. Its space group is Cm, however, it has a pseudo-orthorhombic lattice due to ß≈90°.

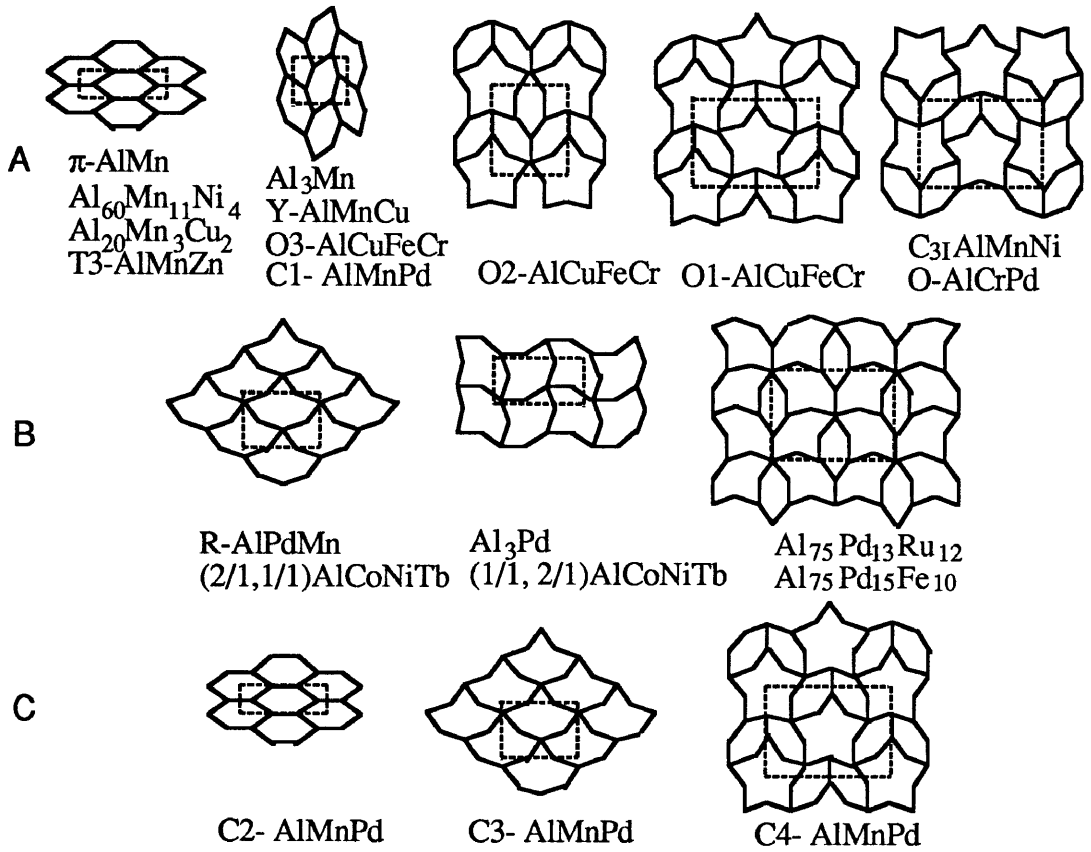

Figure 4. Periodic tilings for the structures of some crystalline approximants of the Al-Mn type DQC, Al-Pd type DQC and Al-Mn-Pd type DQC.

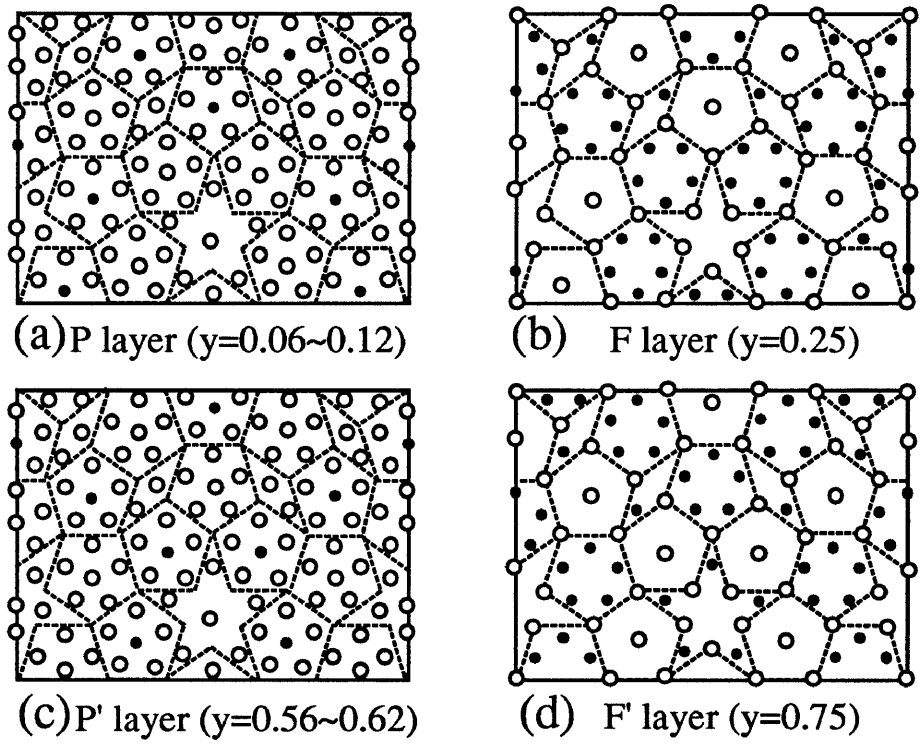

Figure 5. Structural model of the O-AlCrPd crystalline approximant, atom arrangements in (a) the P layer, (b) the F layer, (c) the P' layer and (d) the F' layer. Open circles for Al atoms and solid circles for Cr/Pd atoms.

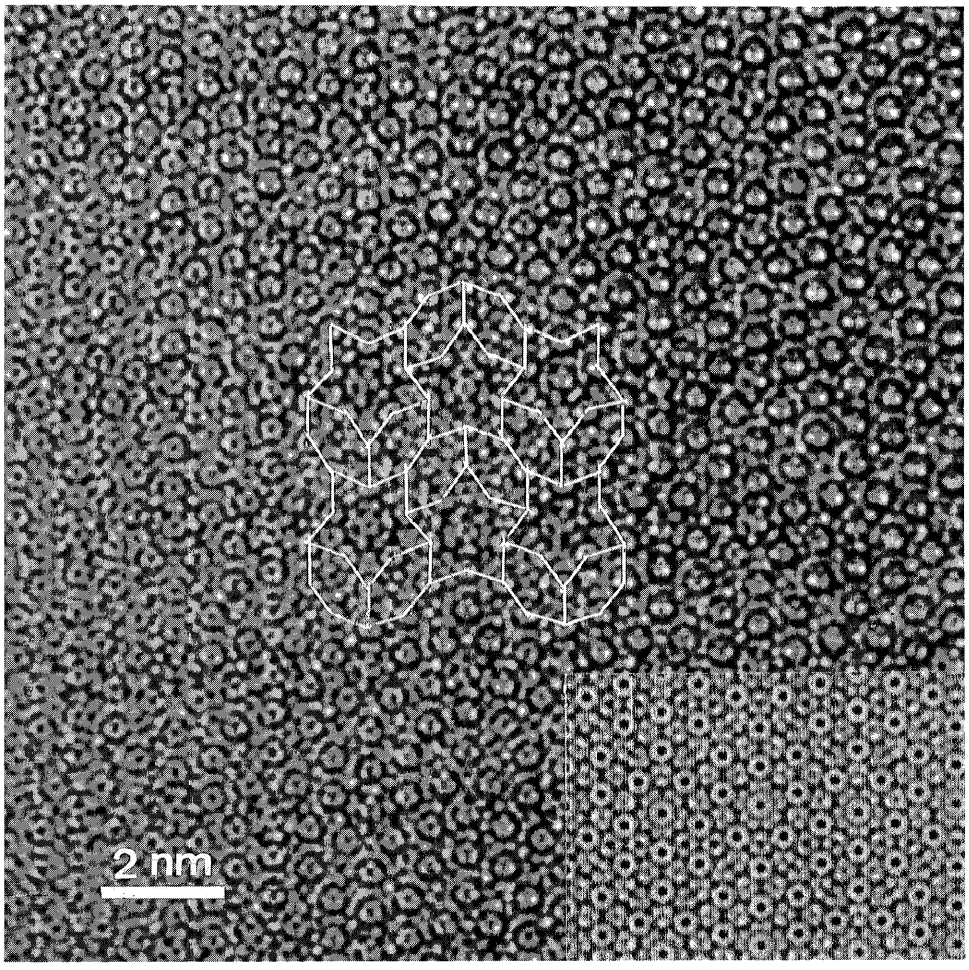

Figure 6. High-resolution structure image of the O-AlCrPd crystalline approximant and the inset is a simulation image based on the structural model described in the text.

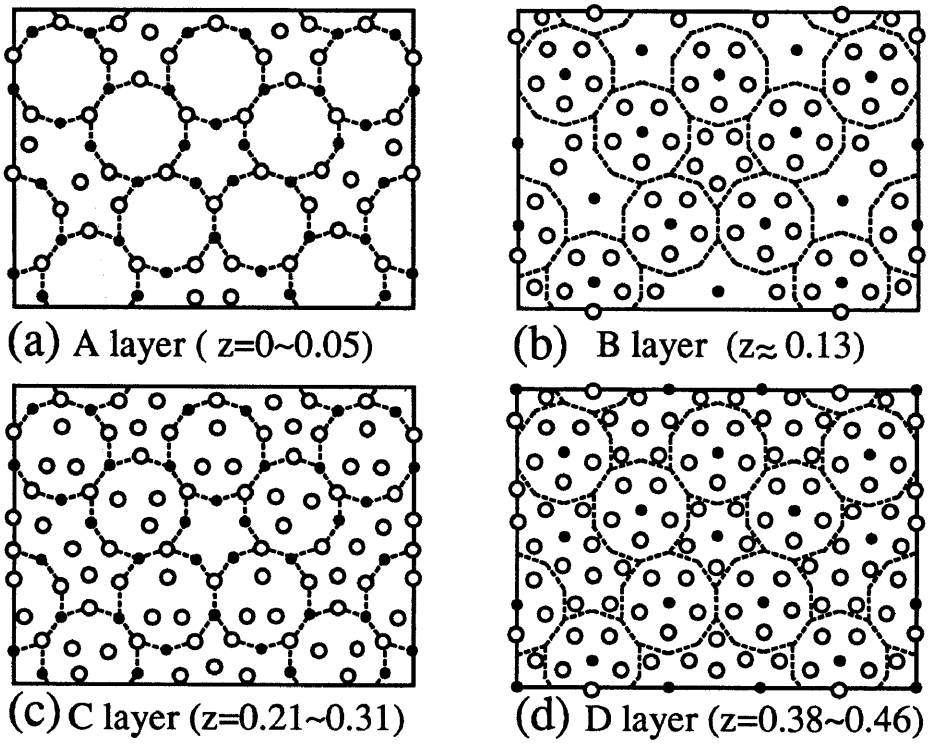

Figure 7. Structural model of the $Al_{75}Pd_{13}Ru_{12}$ crystalline approximant, atom arrangements in A, B, C, and D layers. open circles for Al atoms and solid circles for Pd/Ru atoms.

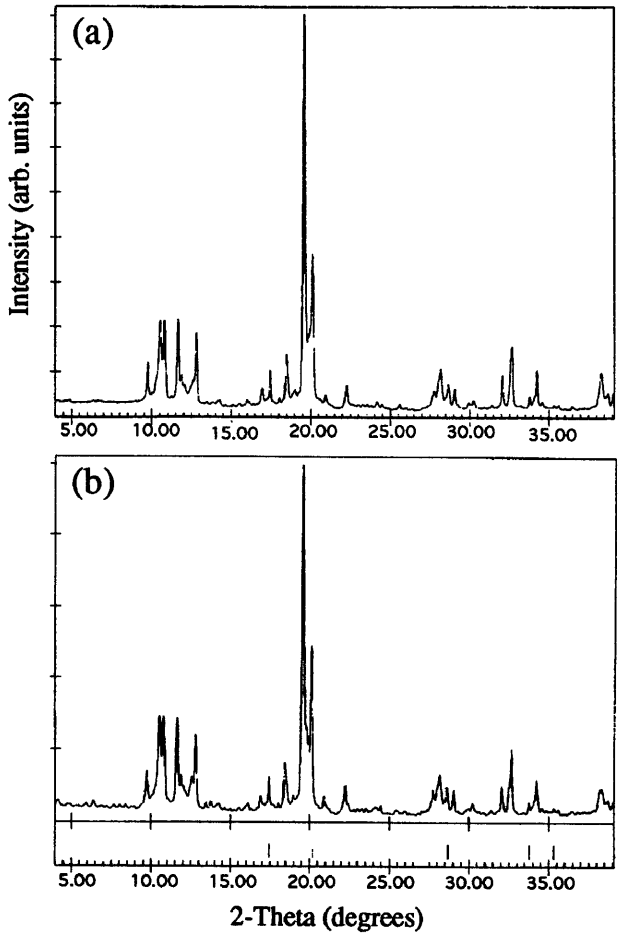

Figure 8. Powder X-ray diffraction pattern of the $Al_{75}Pd_{13}Ru_{12}$ crystalline approximant, (a) the experimental one and (b) the simulated one based on the structural model described in text.

mirror plane) and the puckered (P and p) layers and the stacking sequence are PFpP'F'p'..., in which the P'F'p' layers are related to the PFp layers by the atom clusters but there is no symmetric relation between them in this case. Fig. 5 shows the atom arrangements in (a) the P layer, (b) the F layer, (c) the P' layer and (d) the F' layer. Fig. 6 shows the HREM image of the O-AlCrPd phase taken with incident electron beam along the b axis. A periodic tiling of H and S tiles is outlined to show the feature of the image. A calculated image by using the model is shown as an inset. It is found that the calculated image fits quite well with the experimental one, which means that the structural model is basically correct.

The $Al_{75}Pd_{13}Ru_{12}$ approximant[25] was obtained as needle-shape crystals from a ternary $Al_{80}Pd_{10}Ru_{10}$ alloy by slowly solidification. This is an orthorhombic phase with the lattice parameters, a=2.39, b=3.28 and c=1.67 nm. X-ray diffraction study (precession photograph) shows that the phase is a crystalline approximant of the Al-Pd type DQC. A structural model has been proposed as periodic packing of the subunits of the Al-Pd DQC. Like the structure of the Al_3Pd phase, the structure can be described in the layers A (A'), B(B'), C(C') and D(D') with a stacking sequence of ABCDA'B'C'D', here the A'B'C'D' layers are related to ABCD by the atom clusters, but there is no symmetric relation between them. Fig. 7 shows the atom arrangements in the A, B, C and D layers. Fig. 8 shows (a) the experimental powder X-ray diffraction pattern and (b) the simulated one on the basis of the structural model. It is obvious that the simulation matchs quite well to the experimental one, which means that the structural model is basically correct.

In summary, the structures of the DQCs and the crystalline approximants are related by the subunits (or atom cluster). In order to study the structures of the DQCs, one can start with the structures of the crystalline approximants. On the other hand, the subunits of the DQCs can be used to study the structures of the new crystalline approximants. The approach to the structure of the crystalline phases has been demonstrated by two examples: one is a crystalline approximant of the Al-Mn type DQC and the other is a crystalline approximant of the Al-Pd type DQC.

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