

A complicated quasicrystal approximant ε_{16} predicted by the strong-reflections approach

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The structure of a complicated quasicrystal approximant ε_{16} was predicted from a known and related quasicrystal approximant ε_6 by the strong-reflections approach. Electron-diffraction studies show that in reciprocal space, the positions of the strongest reflections and their intensity distributions are similar for both approximants. By applying the strong-reflections approach, the structure factors of ε_{16} were deduced from those of the known ε_6 structure. Owing to the different space groups of the two structures, a shift of the phase origin had to be applied in order to obtain the phases of ε_{16} . An electron-density map of ε_{16} was calculated by inverse Fourier transformation of the structure factors of the 256 strongest reflections. Similar to that of ε_6 , the predicted structure of ε_{16} contains eight layers in each unit cell, stacked along the b axis. Along the b axis, ε_{16} is built by banana-shaped tiles and pentagonal tiles; this structure is confirmed by high-resolution transmission electron microscopy (HRTEM). The simulated precession electron-diffraction (PED) patterns from the structure model are in good agreement with the experimental ones. ε_{16} with 153 unique atoms in the unit cell is the most complicated approximant structure ever solved or predicted.

1. Introduction

The question regarding the exact atomic positions in quasicrystals has confused crystallographers for more than two decades since the discovery of the icosahedral quasicrystal in rapidly solidified Al–Mn alloys (Shechtman *et al.*, 1984). Although quasicrystals are well ordered on the atomic scale, they are not periodic. Furthermore, the presence of defects has made it very difficult to solve their structures by single-crystal X-ray diffraction. An effective way to study the structure of quasicrystals is to start from quasicrystal approximants which often coexist with quasicrystals. This is because the latter normally have similar local atomic structures as quasicrystals. A series of quasicrystal approximants are often closely related in terms of their structures. Until today, many quasicrystal approximants have been found, but only a few of these structures have been solved by X-ray crystallography. One of the examples is the family of ε approximants in the Al–TM (TM = transition metal) alloys (Klein *et al.*, 1996; Sun & Hiraga, 1996; Balanetsky, Grushko, Velikanova & Urban, 2004), where the lattice parameters a ($\simeq 23.5$ Å) and b ($\simeq 16.8$ Å) are essentially the same, while the c parameters of the regular structures are $\simeq 12.3$, 32.4, 44.9 or 57.0 Å. They are designated as ε_6 , ε_{16} , ε_{22} , ε_{28} . . . (Balanetsky, Grushko, Velikanova & Urban, 2004), where the subscript is the index l of the strong ($00l$) reflection corresponding to the interplanar spacing of ~ 0.2 nm. Earlier investigations of Al–TM alloys revealed that it was difficult to synthesize Al–TM

Table 1

List of quasicrystal approximants solved by the strong-reflections approach.

Known structure						Deduced structure						
Phase	Space group	Lattice parameters (Å)				Phase	Space group	Lattice parameters (Å)				Ref.
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)			<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	
<i>m</i> -Al ₁₃ Co ₄	<i>C2/m</i>	15.2	8.1	12.4	108	τ^2 -Al ₁₃ Co ₄	<i>P2/m</i>	39.9	8.1	32.2	108	Christensen <i>et al.</i> (2004)
μ_3 -ZnMgRE	<i>P6₃/mmc</i>	14.6		8.6		μ_5 -ZnMgRE	<i>P6₃/mmc</i>	23.5		8.6		Zhang, Zou <i>et al.</i> (2006)
λ -Al ₄ Mn	<i>P6₃/m</i>	28.38		12.39		μ_7 -ZnMgRE	<i>P6₃/mmc</i>	33.6		8.9		Zhang, He <i>et al.</i> (2006)
ε_6	<i>Pnma</i>	23.5	16.8	12.3		$\tau(\mu)$ -AlCrSi	<i>P6₃/mmc</i>	32.3		12.4		He <i>et al.</i> (2007)
						μ' -AlCrSi	<i>P6₃/mmc</i>	20.1		12.4		This work
						ε_{16}	<i>B2mm</i>	23.5	16.8	32.4		

samples with only a single type of ε phase. The crystals often consist of different transitional states that are aperiodic in one direction. Owing to the difficulty in growing large ordered single crystals and the complexity of their structures, most of the approximant structures remain unsolved. Indeed, only the ε_6 structure (also known as ξ') was solved by single-crystal X-ray diffraction (Boudard *et al.*, 1996). This situation has

significantly slowed down the further investigations of quasicrystal structures.

The structures of crystals too small for single-crystal X-ray diffraction can be determined by electron crystallography. Electrostatic potential maps can be obtained by combining the structure-factor phases from HRTEM images with amplitudes from HRTEM images or electron-diffraction patterns. A

successful application is to the complicated quasicrystal approximant ν -AlCrFe with space group *P6₃/m*, *a* = 40.687 and *c* = 12.546 Å (Zou *et al.*, 2003). A three-dimensional electrostatic potential map was calculated by combining the structure-factor phases from HRTEM images and amplitudes from selected-area electron-diffraction (SAED) patterns of 13 zone axes. 124 of the 129 unique atoms in the unit cell were found from the electrostatic potential map. However, this method requires extensive experimental work for the determination of complicated structures such as quasicrystal approximants. First, a sufficient number of high quality images which contain phase information needs to be collected. Unfortunately, the phases from HRTEM are affected by many uncertain factors, such as defocus, astigmatism, crystal thickness and orientation. Extracting the real phases therefore relies on advanced image processing that takes into account these experimental conditions (Klug, 1978–1979; Hovmöller *et al.*, 1984; Zou *et al.*, 1996). Secondly, in order to obtain enough intensity information, many electron-diffraction patterns of different zone axes must be

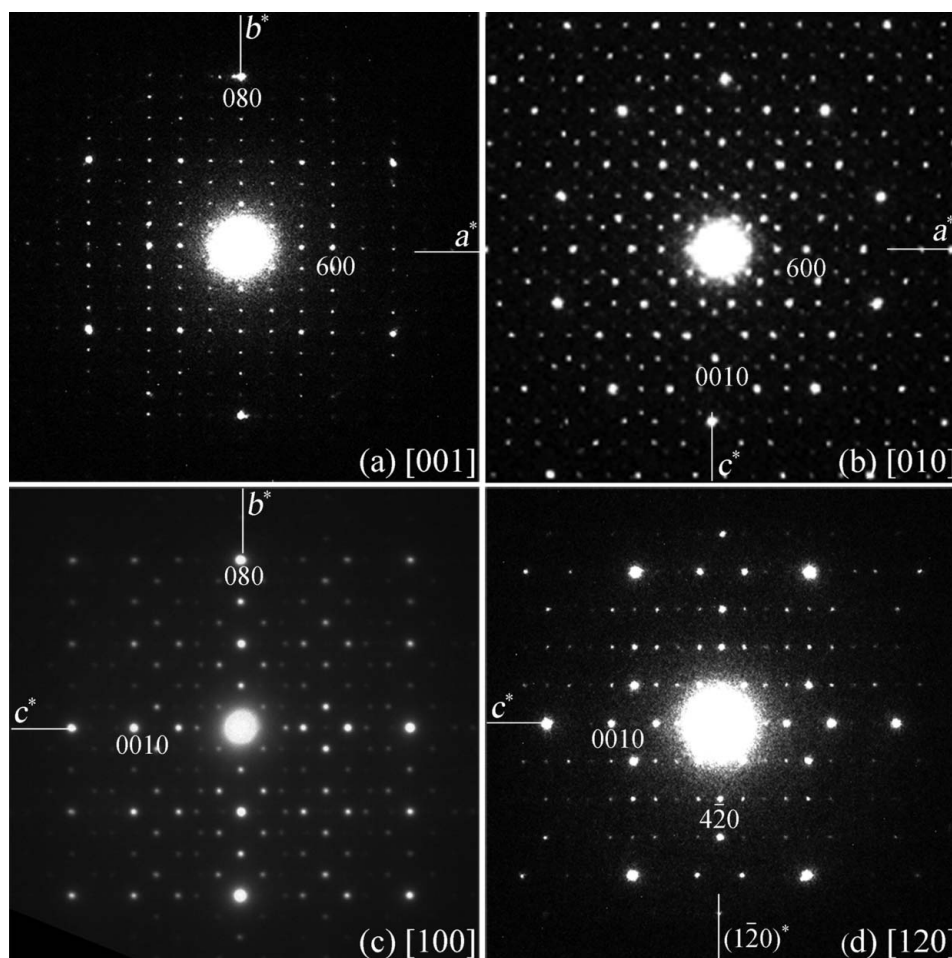


Figure 1

Selected-area electron-diffraction patterns of ε_{16} along the (a) [001], (b) [010], (c) [100] and (d) [120] directions.

taken. However, as with HRTEM images, high quality kinematic electron-diffraction data are very difficult to obtain, owing to the multiple scattering of electrons (Zou & Hovmöller, 2008).

Another effective way of determining approximant structures, namely the *strong-reflections approach*, was proposed by some of the present authors (Zou & Hovmöller, 2008; Christensen *et al.*, 2004). This approach is based on the fact that the strongest reflections largely determine the atomic positions in a structure. By analyzing the relationship of the structure-factor amplitudes and phases of reflections from a series of quasicrystal approximants, we found that the strong reflections that are close to each other in reciprocal space have similar structure-factor amplitudes and phases for all the approximants in the series (Zhang, Zou *et al.*, 2006). Therefore, the structure-factor amplitudes and phases of strong reflections for an unknown approximant can be estimated from those of a known related approximant. Atomic positions in the unknown approximant are then obtained directly from the three-dimensional electron-density map calculated by inverse Fourier transformation of the structure-factor amplitudes and phases of the strong reflections. It is important to find the orientation matrix that relates the known and the unknown approximants, and re-index the reflections from the known approximant to the unknown approximant.

Structural models of five compounds in three groups of approximants (see Table 1) have been successfully deduced from their known related structures by the strong-reflections

approach (Christensen *et al.*, 2004; Zhang, Zou *et al.*, 2006; Zhang, He *et al.*, 2006; He *et al.*, 2007). For all these five cases listed in Table 1, the phase origins (defined by the space groups) are the same for all structures in the same group. The structure-factor phases of the known approximant are therefore the same as those of the unknown approximant. Here we present the structure of the ε_{16} approximant in an Al–Rh alloy, deduced by the strong-reflections approach from the known structure of the ε_6 approximant in the same Al–Rh system. The structure determination in the present case is more complicated since the origins in space groups $Pnma$ (known structure ε_6) and $B2mm$ (unknown structure ε_{16}) are different. The structure-factor phase relations of the symmetry-related reflections are not consistent in the two structures. In order to utilize their structure-factor phases, a non-standard origin was first used and then shifted to the final origin for ε_{16} . The ε_{16} approximant has the most complicated structure ever predicted/determined by electron crystallography or the strong-reflections approach. Details are presented below.

2. Experimental

Sample alloys with nominal composition $\text{Al}_{75}\text{Rh}_{25}$ and $\text{Al}_{77}\text{Rh}_{23}$ were prepared according to the Al–Rh phase diagram (Grushko *et al.*, 2000). In order to obtain ε_6 and ε_{16} , additional annealing was applied for up to 69 h at 1323 K to $\text{Al}_{75}\text{Rh}_{25}$ and for 2 h at 1369 K to $\text{Al}_{77}\text{Rh}_{23}$. Samples for transmission electron microscopy observation were crushed

and dispersed on holey carbon films on Cu grids. Selected-area electron-diffraction (SAED) and precession electron-diffraction (PED) patterns were recorded in a Jeol 2000FX electron microscope operated at 200 kV. PED patterns of ε_6 and ε_{16} were taken with a precession angle of $\sim 1.1^\circ$, using the Spinning Star Precession Unit (Aivilov *et al.*, 2007). The 16-bit digitized SAED and PED patterns were analysed by the program *ELD* (Zou *et al.*, 1993). HRTEM images were recorded on a Jeol 3010 electron microscope with a point resolution of 0.17 nm operated at 300 kV. The projection symmetry of the crystal was determined from the HRTEM images by crystallographic image processing using the program *CRISP* (Hovmöller, 1992). The program *eMap* (Oleynikov, 2006) was used for calculating structure factors from the structure model, calculating three-dimensional electron-density maps from crystal structure factors, determining peak

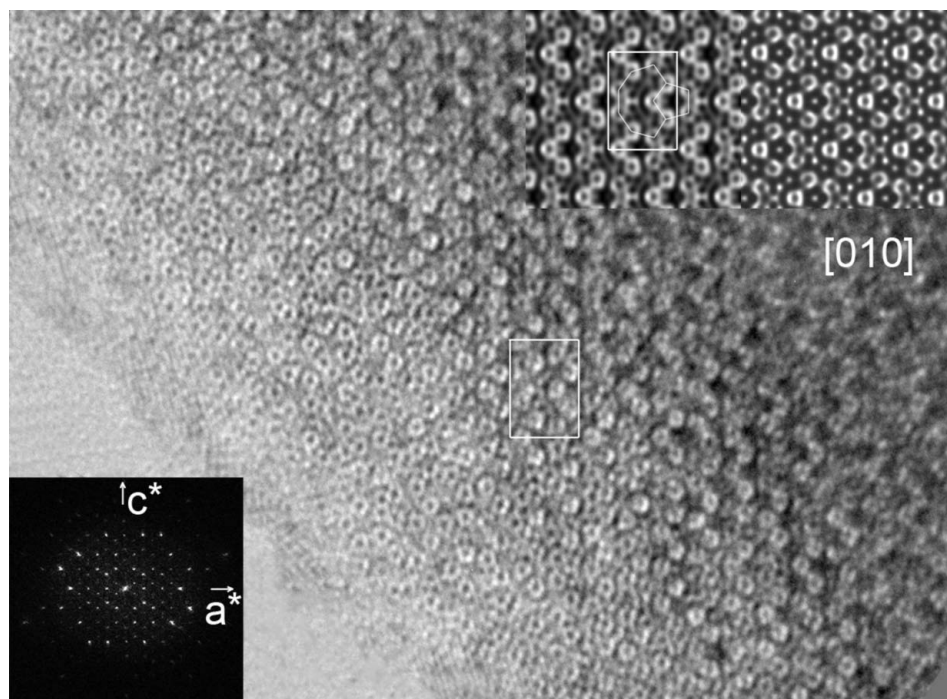


Figure 2 HRTEM image of ε_{16} taken along the b axis. The Fourier transform of the HRTEM image, a symmetry-imposed image (left) and a simulated image (right) are inserted. There is only one mirror symmetry, perpendicular to the c axis. Unit cells are marked and the banana-shaped tile and the pentagonal tile are outlined in the symmetry-imposed image. The simulation was carried out with -25 nm defocus and 6.6 nm thickness.

positions from the electron-density maps and simulating HRTEM images and precession electron-diffraction patterns from the structure model.

3. Results and discussion

3.1. Unit-cell and space-group determination

There are several ways to identify crystallographic features from electron microscopy. For example, by comparing the net

of reflections between ZOLZ (zero-order Laue zone) and FOLZ (first-order Laue zone) that emerge at precession angles $> 0.5^\circ$, the Bravais lattice and glide planes can be inferred (Morniroli *et al.*, 2007). The point group may also be deduced from convergent-beam electron-diffraction (CBED) patterns. Here we determine the space group of ϵ_{16} by combining SAED and HRTEM techniques. Four electron-diffraction patterns of ϵ_{16} along the [001], [010], [100] and [120] directions are shown in Fig. 1. From these, the unit cell

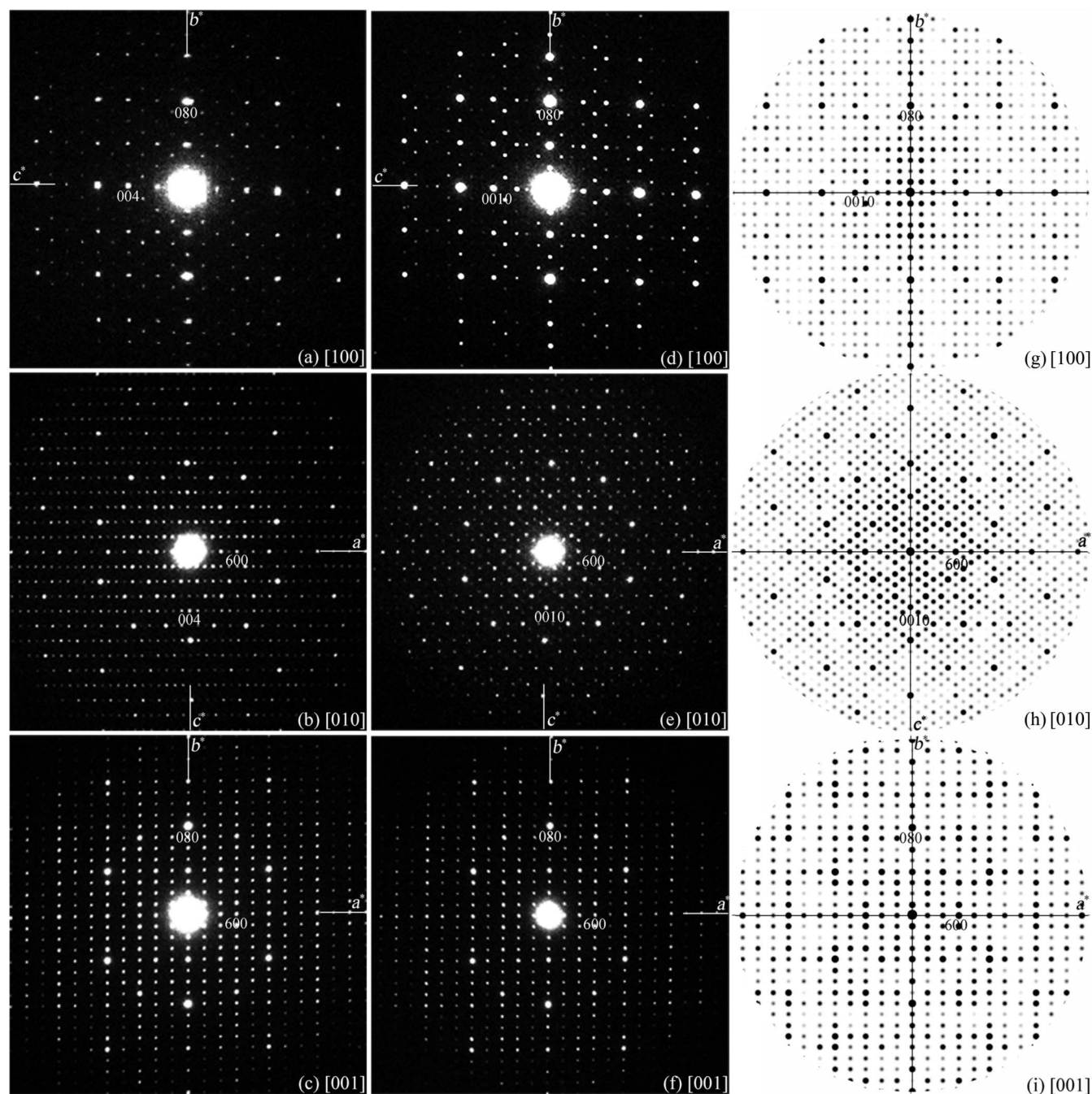


Figure 3 Precession electron-diffraction patterns of (a)–(c) ϵ_6 and (d)–(f) ϵ_{16} , and (g)–(i) the simulated precession electron-diffraction patterns from the derived structure model of ϵ_{16} . The kinematical simulation conditions are: voltage 200 kV, precession angle 1.1° , and crystal thicknesses (g) 400 Å, (h) 500 Å and (i) 400 Å. The intensity distributions in reciprocal space are similar for ϵ_6 and ϵ_{16} . The corresponding reflections have the same h and k , but $l(\epsilon_{16}) \simeq \tau^2 l(\epsilon_6)$, such that the very strong reflection (006) in ϵ_6 corresponds to (00,16) in ϵ_{16} .

Table 2

List of structure-factor amplitudes and phases of 45 strongest independent reflections of ε_6 (with $Pnma$) and ε_{16} (with $P1$ and $B2mm$).

After the origin has been shifted from that of ε_6 to (0, 0.25, 0.15625), the phases of symmetry-related reflections [Phase ε_{16} ($P1$)] are close to those required by the space group $B2mm$, with an average phase error of 7.8° and a maximum phase error of 22.5° compared with phases after imposing the $B2mm$ symmetry.

ε_6	Amplitude ε_6 and ε_{16}	Phase				ε_{16}	Origin shifted (0, 0.025, 0.15625)				Phase ε_{16} ($B2mm$)
		ε_6 ($Pnma$) and ε_{16}									Symmetry-imposed
$h\ k\ l$		hkl	$hk-l$	$h-k-l$	$h-kl$	$h\ k\ l$	hkl	$h-kl$	$hk-l$	$h-k-l$	hkl
0 8 0	2815	0	0	0	0	0 8 0	0	0	0	0	0
0 0 10	2338	0	0	0	0	0 0 26	23	23	338	338	0
8 4 3	2279	0	180	180	0	8 4 8	90	90	90	90	90
18 0 3	2262	180	0	0	180	18 0 8	270	270	270	270	270
10 4 0	2259	180	180	180	180	10 4 0	180	180	180	180	180
11 0 8	2211	180	0	0	180	11 0 21	281	281	259	259	270
3 4 5	2205	180	180	180	180	3 4 13	191	191	169	169	180
7 0 5	2036	0	0	0	0	7 0 13	11	11	349	349	0
11 0 2	2021	0	180	180	0	11 0 5	281	281	259	259	270
0 0 6	2018	180	180	180	180	0 0 16	0	0	0	0	0
0 16 0	1567	0	0	0	0	0 16 0	0	0	0	0	0
26 4 0	1471	0	0	0	0	26 4 0	0	0	0	0	0
8 4 13	1471	0	180	180	0	8 4 34	113	113	68	68	90
0 8 10	1457	0	0	0	0	0 8 26	23	23	338	338	0
18 8 3	1454	180	0	0	180	18 8 8	270	270	270	270	270
21 4 8	1433	0	180	180	0	21 4 21	101	101	79	79	90
11 8 8	1406	180	0	0	180	11 8 21	281	281	259	259	270
8 12 3	1288	0	180	180	0	8 12 8	90	90	90	90	90
13 7 5	1275	0	0	180	180	13 7 13	281	281	259	259	270
19 4 5	1269	0	0	0	0	19 4 13	11	11	349	349	0
16 7 0	1269	0	0	180	180	16 7 0	270	270	270	270	270
10 4 10	1256	180	180	180	180	10 4 26	203	203	158	158	180
5 7 8	1241	0	180	0	180	5 7 21	11	11	349	349	0
0 4 0	1234	180	180	180	180	0 4 0	180	180	180	180	180
15 4 8	1216	0	180	180	0	15 4 21	101	101	79	79	90
10 12 0	1194	180	180	180	180	10 12 0	180	180	180	180	180
0 8 6	1181	180	180	180	180	0 8 16	0	0	0	0	0
21 4 2	1178	180	0	0	180	21 4 5	101	101	79	79	90
3 4 11	1169	0	0	0	0	3 4 29	191	191	169	169	180
5 7 2	1163	180	0	180	0	5 7 5	11	11	349	349	0
3 12 5	1162	180	180	180	180	3 12 13	191	191	169	169	180
11 8 2	1151	0	180	180	0	11 8 5	281	281	259	259	270
7 8 5	1126	0	0	0	0	7 8 13	11	11	349	349	0
18 0 7	1057	0	180	180	0	18 0 18	293	293	248	248	270
2 7 3	1038	0	180	0	180	2 7 8	0	0	0	0	0
0 14 0	1035	180	180	180	180	0 14 0	0	0	0	0	0
8 11 3	1010	180	0	180	0	8 11 8	180	180	180	180	180
7 0 11	998	180	180	180	180	7 0 29	11	11	349	349	0
10 0 0	973	0	0	0	0	10 0 0	0	0	0	0	0
15 4 2	970	180	0	0	180	15 4 5	101	101	79	79	90
10 11 0	961	180	180	0	0	10 11 0	90	90	90	90	90
3 11 5	959	180	180	0	0	3 11 13	101	101	79	79	90
22 0 0	955	180	180	180	180	22 0 0	180	180	180	180	180
8 4 7	952	180	0	0	180	8 4 18	113	113	68	68	90
19 12 5	903	0	0	0	0	19 12 13	11	11	349	349	0

was determined as B-centered orthorhombic with $a = 23.5$, $b = 16.8$ and $c = 32.4$ Å. ε_{16} has almost the same a and b parameters as ε_6 (unit-cell parameters $a = 23.5$, $b = 16.8$, $c = 12.3$ Å), but c is τ^2 times that of ε_6 ($\tau \simeq 1.618$ is the golden ratio).

The reflection conditions of ε_{16} deduced from the SAED patterns are hkl : $h + l = 2n$.

According to the *International Tables for Crystallography* (Hahn, 2002), four space groups – $B222$ (No. 21), $Bm2m$ (No. 35), $B2mm$ (No. 38) and $Bmmm$ (No. 65) – fulfill these reflection conditions. These four space groups are possible for ε_{16} and cannot be distinguished by the reflection conditions only. Fortunately, the projection symmetries along the b axis

are different for these space groups: cm for $B2mm$ and cmm for the others. It is possible to determine the projection symmetry of ε_{16} by analyzing the phases extracted from the Fourier transform of the HRTEM images taken along the b axis. This was performed by the program *CRISP* (Hovmöller, 1992). The projection symmetry of ε_{16} was determined as cm since the HRTEM image gave a much lower average phase error for cm (phase residual = 19.5°) than that for cmm (phase residual = 44.8°). This is also directly confirmed from the HRTEM image taken along [010] shown in Fig. 2. Only one mirror perpendicular to the c axis appears in the [010] image, and no mirror perpendicular to the a axis was found. Thus, the projected symmetry along [010] was determined as cm but

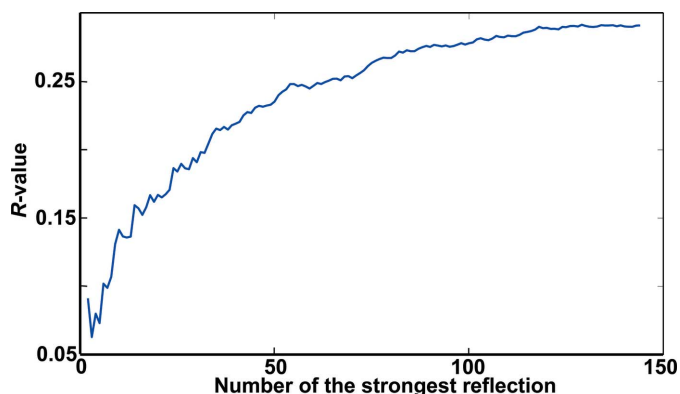


Figure 4
R values against the number of corresponding strongest reflections in ε_6 and ε_{16} . For the 30 strongest reflections, an *R* value of 0.19 shows good correspondence for the strong reflections in ε_6 and ε_{16} . As more and more moderately strong reflections are included, the *R* value increases, reaching 0.29 for the 146 strongest reflections.

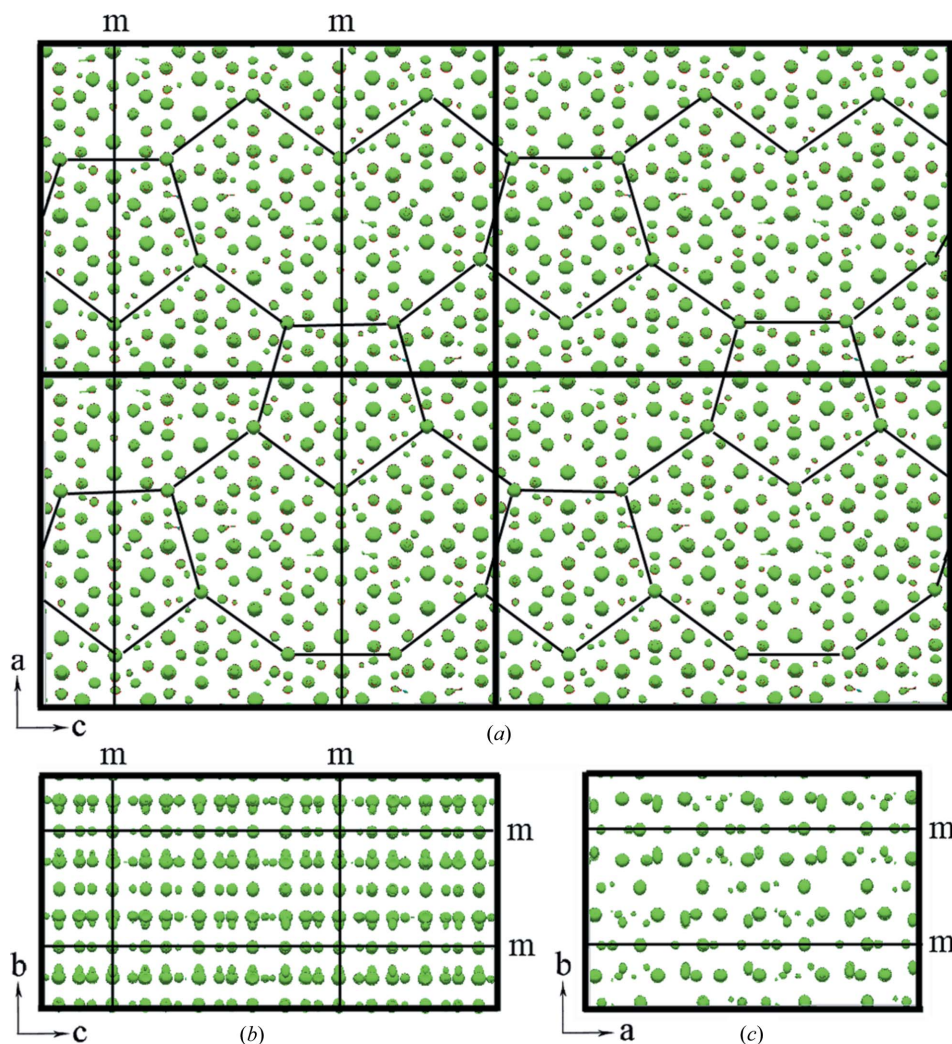


Figure 5
 A three-dimensional electron-density map of ε_{16} calculated from 1590 (256 independent) strong reflections using the space group *P1*. (a), (b) and (c) are three-dimensional density maps viewed along the *b*, *a* and *c* axes, respectively. Four unit cells are outlined in (a). The symmetry elements can be identified from the density map, with mirrors perpendicular to the *b* and *c* axes (marked). The new origin is set on $2mm$. The origin shifts obtained from the electron-density maps are $\Delta x = 0$, $\Delta y = 0.25$ and $\Delta z = 0.15625$. Banana-shaped clusters and pentagonal clusters²¹ are outlined in (a).

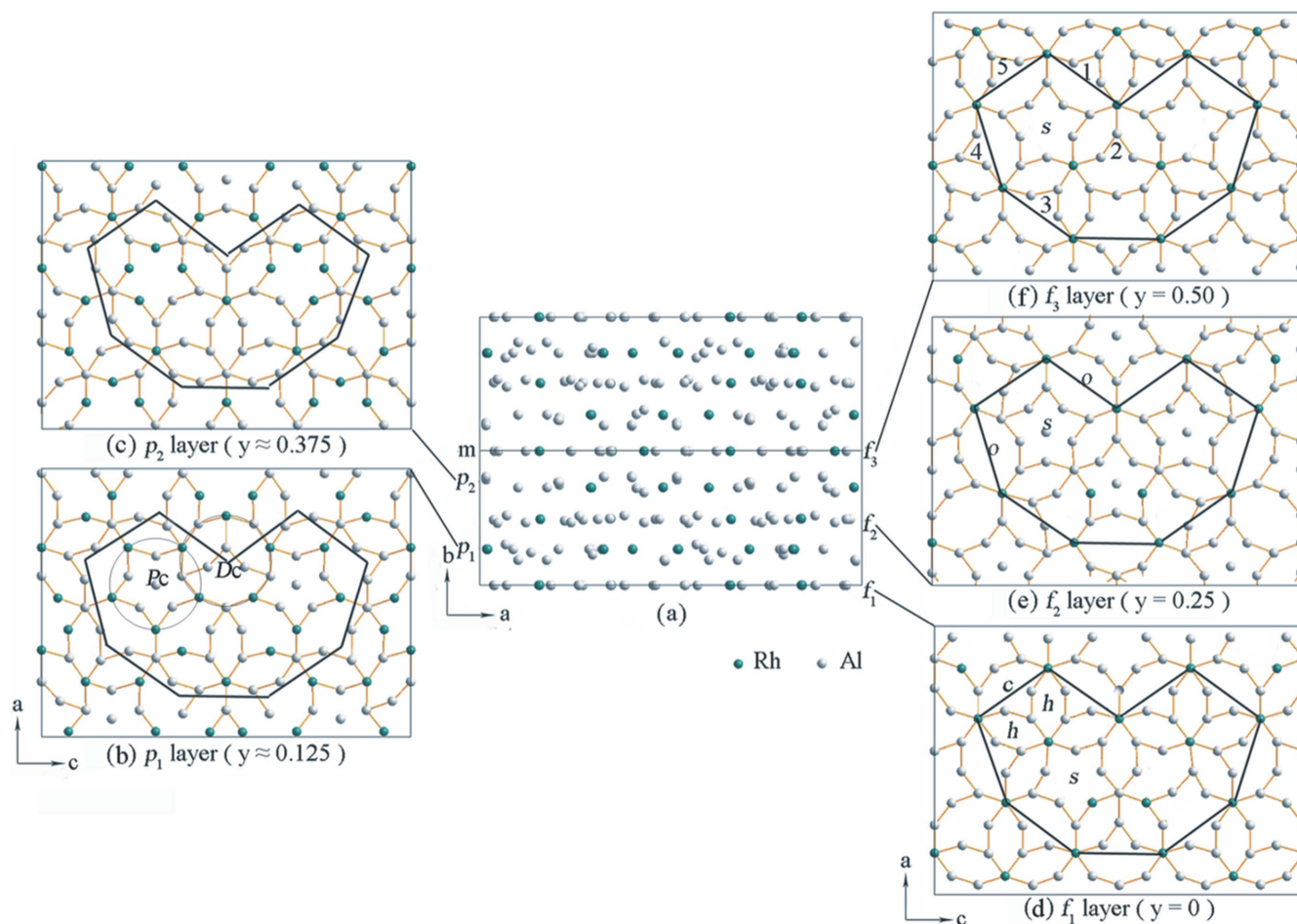
not *cm*m and the only possible space group for ε_{16} is *B2mm*.

3.2. Deducing a structure model

Once the space group has been determined, we are ready to deduce the structure model of ε_{16} from the structure of ε_6 using the strong-reflections approach. The most important condition for the strong-reflections approach is that the intensity distribution of the strongest reflections between the known and unknown structures should be similar. Thus, the first step is to identify and relate the corresponding strong reflections of ε_{16} to those of ε_6 using electron diffraction. For such a purpose, precession electron-diffraction patterns were taken as shown in Fig. 3, since they are less dynamical and show higher resolution (about 0.9 Å) than those of the SAED patterns in Fig. 1. The less-dynamical diffraction intensities

obtained by precession electron diffraction make the identification of the corresponding strong reflections easier. As can be seen from the experimental precession electron-diffraction patterns of ε_6 and ε_{16} in Fig. 3, all the strong reflections in ε_{16} coincide with the strong reflections in ε_6 . Since the *a* and *b* parameters are similar for ε_{16} and ε_6 , and the *c* parameter of ε_{16} (32.4 Å) is about τ^2 times that of ε_6 (12.3 Å, $32.4/12.3 = 2.634$), the (*hkl*) indices of the strong reflections in these two approximants are related by $(h k l_{\varepsilon_{16}}) = (h k \tau^2 l_{\varepsilon_6})$. Here, the golden number $\tau = (1 + 5^{1/2})/2$ is associated with fivefold rotational symmetry of an icosahedral quasicrystal. Elser *et al.* (Elser & Henley, 1985) used the rational ratio of two successive Fibonacci numbers (1, 1, 2, 3, 5, 8, 13, 21, ..., F_n , ...; $F_n = F_{n-1} + F_{n-2}$) as an approximation to substitute for the irrational τ to obtain the crystalline approximant of an icosahedral quasicrystal. According to the Fibonacci series, (*h k 8*) in ε_{16} is related to (*h k 3*) in ε_6 , (*h k 10*) in ε_{16} is related to (*h k 4*) in ε_6 , (*h k 26*) in ε_{16} is related to (*h k 10*) in ε_6 , and so on.

To confirm the similarity of the ε_{16} and ε_6 structures, the *R* value against the number of corresponding strongest reflections was plotted in Fig. 4 without any corrections (such as absorption


Figure 6

The atomic structure of ε_{16} (a) viewed along the c axis. Eight layers, including four flat layers (f) and four puckered layers (p), are stacked along the b axis. Five independent layers are identified; at $y = 0$ (f_1), ~ 0.125 (p_1), 0.25 (f_2), ~ 0.375 (p_2) and 0.5 (f_3). The structure can be described as $f_1 p_1 f_2 p_2 f_3 p_2 f_2 p_1 f_1$, where $p_2' f_2' p_1'$ are obtained from the layers $p_1 f_2 p_2$ by a mirror symmetry at $y = 0.5$. (b)–(f) The five independent layers viewed along the b axis. Three basic tilings: squashed hexagon (h), pentagonal star (s) and crown (c) are indicated in (d). A decagonal column (Dc) and a pentagonal column (Pc) are marked in (b). A squashed octagon (o) is marked in (e). A pentagonal star (s) surrounded by five hexagonal columns is marked in (f).

correction, Lorenz correction and so on). The detailed reflection lists are given as supporting information.¹ The reflections from different orientations were merged using their common reflections. It shows that the intensities of the strong corresponding reflections are very close to each other ($R = 0.19$) for the 30 strongest reflections. As more and more moderately strong reflections are included, the R value increases, reaching 0.29 for the 146 strongest reflections. This kind of R value is close to a typical internal R value for electron-diffraction data obtained from different particles of the same structure. Thus, we think there is obvious similarity in the ε_{16} and ε_6 structures. Note that here we only compared the experimental strong reflections along the three main zone axes, but they constitute a major part of all data. For the 256 strongest reflections (the 45 strongest of which are listed in Table 2), the amplitudes along these three main zone axes sum up to 45% of the total amplitudes in ε_6 .

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: DR5024). Services for accessing these data are described at the back of the journal.

The strong reflections in ε_{16} are then deduced from the corresponding reflections in the known ε_6 according to the relations described above. In order to determine the number of independent strong reflections that are needed to obtain a sufficiently good electron-density map, we first checked the procedure on the ε_6 structure. Generally speaking, the structure-factor amplitude sum of the strong reflections must be more than 50% of the total amplitude sum in order to generate an electron-density map that represents the structure (Zhang, He *et al.*, 2006). Here we choose the 256 strongest reflections of ε_6 among the total 2640 independent reflections within 1.0 Å resolution. Table 2 lists 45 of them, together with their structure-factor amplitudes and phases. The 256 reflections sum up to 57% of the total amplitude and they were expanded to 1590 reflections according to the symmetry of ε_6 . A three-dimensional electron-density map was calculated from the structure-factor amplitudes and phases of these 1590 reflections by inverse Fourier transformation, using the program *eMap* (Oleynikov, 2006). All the atomic positions of ε_6 as determined by single-crystal X-ray diffraction (Boudard *et al.*, 1996) could be found in the three-dimensional density

map. This indicates that the 256 strong reflections are sufficient to obtain a correct structure model of ε_6 . Since the strong reflections in ε_{16} coincide with the strong reflections in ε_6 , a reasonable structure model of ε_{16} should be obtained using the 256 strong reflections of ε_{16} deduced from those of ε_6 .

The structure-factor amplitudes of ε_{16} were assigned from those of the corresponding reflections in ε_6 , calculated from the single-crystal X-ray structure model (Table 2). We did not use the amplitudes from the experimental PED data since it was difficult to collect a complete three-dimensional PED data due to mixed phases in the same particle. A new technique, called electron-diffraction tomography, is being developed in our department (Zhang *et al.*, 2010) and may be applied in the future for collecting complete three-dimensional electron-diffraction data. Our earlier studies have shown that the amplitudes taken from the corresponding known approximants are enough to deduce the structure model.

Different from our previous studies (Christensen *et al.*, 2004; Zhang, He *et al.*, 2006; Zhang, Zou *et al.*, 2006; He *et al.*, 2007), the structure-factor phases for the strong reflections of ε_{16} cannot be taken directly from those of ε_6 , since the choice of origin for the space group of ε_{16} ($B2mm$) is different from that of the space group for ε_6 ($Pnma$). Consequently, the phase relations between the symmetry-related reflections in the two space groups are different. For the space group $Pnma$, the relations are (Table 2):

(i) If $h + l = 2n$ and $k = 2n$

$$\begin{aligned} \varphi_{hkl} &= \varphi_{-hk-l} = \varphi_{h-kl} = \varphi_{-h-k-l} = \varphi_{hk-l} = \varphi_{-h-kl} \\ &= \varphi_{-hkl} = \varphi_{h-k-l} \quad (\varphi: \text{structure-factor phase}). \end{aligned} \quad (1)$$

(ii) If $h + l = 2n$ and $k = 2n + 1$:

$$\begin{aligned} \varphi_{hkl} &= \varphi_{hk-l} = \varphi_{-h-k-l} = \varphi_{-h-kl} = \pi + \varphi_{h-k-l} = \pi + \varphi_{h-kl} \\ &= \pi + \varphi_{-hkl} = \pi + \varphi_{-hk-l}. \end{aligned} \quad (2)$$

(iii) If $h + l = 2n + 1$ and $k = 2n$:

$$\begin{aligned} \varphi_{hkl} &= \varphi_{h-kl} = \varphi_{-h-k-l} = \varphi_{-hk-l} = \pi + \varphi_{hk-l} = \pi + \varphi_{h-k-l} \\ &= \pi + \varphi_{-h-kl} = \pi + \varphi_{-hkl}. \end{aligned} \quad (3)$$

(iv) If $h + l = 2n + 1$ and $k = 2n + 1$:

$$\begin{aligned} \varphi_{hkl} &= \varphi_{h-k-l} = \varphi_{-h-k-l} = \varphi_{-hkl} = \pi + \varphi_{hk-l} = \pi + \varphi_{h-kl} \\ &= \pi + \varphi_{-h-k-l} = \pi + \varphi_{-hk-l}. \end{aligned} \quad (4)$$

For the space group $B2mm$, the relations are simpler

$$\begin{aligned} \varphi_{hkl} &= \varphi_{h-kl} = \varphi_{hk-l} = \varphi_{h-k-l} = -\varphi_{-hkl} = -\varphi_{-h-k-l} \\ &= -\varphi_{-hk-l} = -\varphi_{-h-k-l}. \end{aligned} \quad (5)$$

One way to overcome the problem of the different phase relationships is to first assume the space group $P1$ for ε_{16} . Starting from 256 strong reflections in ε_6 , they are expanded into 1590 reflections using $Pnma$ symmetry. Based on the

strong-reflection approach, each of these strong reflections in ε_6 structure has one corresponding reflection in the ε_{16} structure in $P1$ symmetry with the same phases and amplitudes but different indices [see Table 2, column Phase ε_6 ($Pnma$) and ε_{16} ($P1$)]. This ε_{16} structure in $P1$ symmetry turns out to be very close to $B2mm$ symmetry. Note that although the phase relations between the symmetry-related reflections in the two space groups $Pnma$ and $B2mm$ are different, the phase relations for the strongest reflections in the two structures are almost the same.

The three-dimensional electron-density map of ε_{16} in $P1$ symmetry gives well resolved peaks that can be assigned to atomic positions, as shown in Fig. 5. From the density map viewed along the b axis (Fig. 5a), the banana-shaped tiles and pentagonal tiles (Balanetsky, Grushko & Velikanova, 2004) can be identified. The two types of tiles are alternating along the a and c directions and connected to each other. Similar tiles and connections are observed in the [010] HRTEM image in Fig. 2. The symmetries can be identified from the three-dimensional electron-density map as follows: B -centering, $2 // a, m \perp b, m \perp c$, which agrees with the space group $B2mm$. An origin that is compatible with the space group $B2mm$ was found at a $2mm$ Wyckoff position, (0, 0.25, 0.15625). Thus, the origin was shifted to this position and the new structure-factor phases were calculated using the following equation

$$\varphi'(hkl) = \varphi(hkl) + 360^\circ \times (h \times 0 + k \times 0.25 + l \times 0.15625). \quad (6)$$

The new structure factor phases of 45 reflections from the 256 independent strong reflections are listed in Table 2, together with the symmetry-imposed phases. The average deviation of the phases from the symmetry $B2mm$ is only 7.8° , and the largest phase error is 22.5° . The amplitudes together with the phases of the 256 reflections after imposing the symmetry $B2mm$ were used to calculate a new three-dimensional electron-density map of ε_{16} . The three-dimensional density map is very similar to that with $P1$ symmetry, but the electron densities at symmetry-related positions become exactly identical instead of just similar to each other.

There were 150 unique peaks corresponding to the atomic positions of ε_{16} identified from the three-dimensional density map and the atomic coordinates were determined. There were 33 of them assigned as Rh, and the remaining 117 were Al. The assignment of Rh positions was based on:

- (i) the peak height (the highest peaks) and
- (ii) chemical knowledge.

Since ε_{16} and ε_6 are both members of the same series of icosahedral quasicrystal approximants, they are expected to have very similar local atomic structures. Atoms in similar clusters should have a similar environment, and thus atoms in ε_{16} were assigned to form similar clusters as those in ε_6 . In addition, three Al atoms were added to complete the structure based on the geometry and similarity to ε_6 , see Table 3 in the supplementary material. Most of the atoms have reasonable distances to their neighbors, ranging from 2.2 to 3.1 Å. The

final composition of our ε_{16} model is $\text{Al}_{340}\text{Rh}_{99}$, which fits the synthesis stoichiometry ($\text{Al}_{77}\text{Rh}_{23}$) very well.

The precession electron-diffraction patterns simulated using the derived ε_{16} structure model (Figs. 3*g–i*) agree well with the experimental precession electron-diffraction patterns (Figs. 3*d–f*). A least-squares refinement was performed with only four refined parameters (overall scale factor, extinction parameters and isotropic atomic displacement parameters for Rh and Al) using the experimental ε_{16} intensities from PED patterns (659 independent reflections within 1.0 Å resolution) in the *SHELXL* program (Sheldrick, 2008). The refinement converged with $R_1 = 0.33$. Thus, the structure model deduced for ε_{16} from ε_6 can be taken as a good preliminary model.

3.3. Structure description

The final structure of ε_{16} viewed along the c axis is shown in Fig. 6(*a*). There are eight layers that are perpendicular to the b axis in each unit cell, including four flat (f) and four puckered (p) layers. Five of the layers, at $y = 0$ (f_1), ~ 0.125 (p_1), ~ 0.25 (f_2), ~ 0.375 (p_2) and 0.5 (f_3), are independent (Figs. 6*b–f*). The other three can be generated by a mirror located at $y = 0.5$. The atoms within the f_2 layer deviate slightly from $y = 0.25$. Since this deviation is very small (< 0.019), f_2 is still considered as a flat layer. Therefore, the structure can be described as $f_1 p_1 f_2 p_2 f_3 p_2' f_2' p_1' f_1$, where $p_2' f_2' p_1'$ are related to the layers $p_1 f_2 p_2$ by a mirror operation at $y = 0.5$. Each layer contains three common basic tilings: a squashed hexagon (h), a pentagonal star (s) and a crown (c) (marked in Fig. 6*d*). Two h tilings together with one c tiling form a decagonal ring. Each s tiling is surrounded by five inter-connected decagonal rings (marked in Fig. 6*f*). An additional eight-ring tiling (o) is also found in the layer f_2 (marked in Fig. 6*e*).

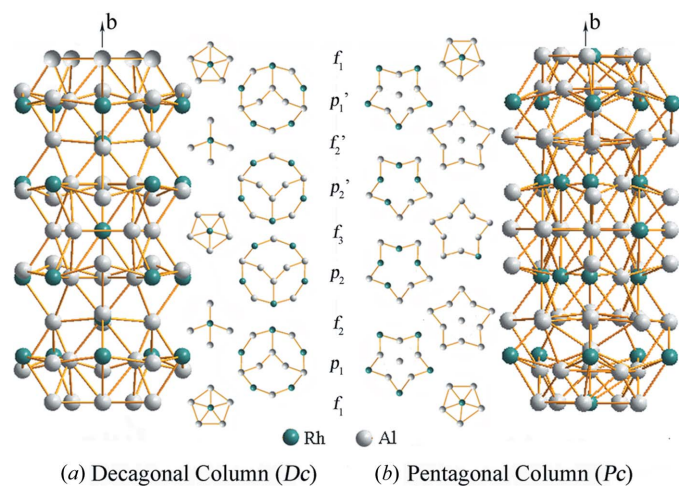


Figure 7

Two types of columns related to decagonal quasicrystals. (*a*) Side view of the decagonal column. Each puckered layer contributes a decagonal ring to the decagonal column. Between the decagonal rings are small pentagons (in f_1 and f_3) and irregular subunits (in f_2) that are alternating along the b axis. (*b*) Side view of the pentagonal column. The pentagonal column is constructed by pentagonal stars or pentagons that are stacked along the b axis. The centers of the decagonal columns are always occupied by the heavy Rh atoms.

The structure of ε_{16} can be described using two types of columns along the b axis: a decagonal column (Dc) and a pentagonal column (Pc) (marked in Fig. 6*b*). The construction of the decagonal and pentagonal columns is given in Fig. 7. Each puckered layer contributes a decagonal ring to the decagonal column. Between the decagonal rings are small pentagons (in f_1 and f_3) and irregular tilings (in f_2) that are alternating along the b axis (Fig. 7*a*). The pentagonal column is constructed by pentagonal stars or pentagons that are stacked along the b axis (Fig. 7*b*). The centers of the decagonal columns are always occupied by the heavy Rh atoms. The decagonal columns are connected to each other through edge-sharing (*via* two common atoms). Five decagonal columns form a pentagonal tile with a pentagonal column inside (Fig. 6*b*). Nine decagonal columns form a banana-shaped tile with

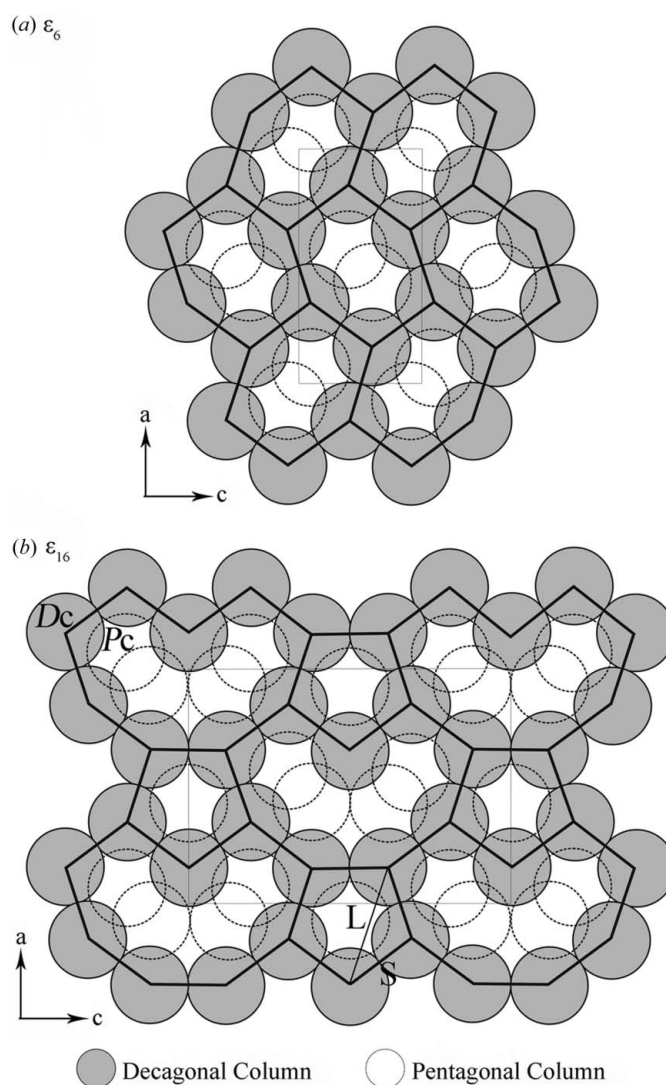


Figure 8

The construction of ε_6 and ε_{16} from the decagonal columns (Dc) and pentagonal columns (Pc) running along the b axis. The structure of ε_6 is constructed by only one type of hexagonal tiles (outlined) built from six decagonal columns with two intersecting pentagonal columns inside. The structure of ε_{16} is constructed by two types of tiles alternating along the a and c axes (outlined): a banana-shaped tile and a pentagonal tile.

two pairs of intersecting pentagonal columns inside. The banana-shaped and pentagonal tiles are seen in the HRTEM images (see Fig. 2). Similar decagonal and pentagonal columns have also been observed in the decagonal quasicrystal d-Al-Pd (Li *et al.*, 1996).

A comparison of the structure features of ε_6 and ε_{16} is given in Fig. 8. Both structures can be described by the decagonal and pentagonal columns. All decagonal columns in ε_6 and ε_{16} are connected by edge-sharing. The structure of ε_6 is constructed by only one type of hexagonal tile built from six decagonal columns with two intersecting pentagonal columns inside. The structure of ε_{16} is constructed by two types of tiles: a banana-shaped tile and a pentagonal tile. The diameter of decagonal and pentagonal columns is about 7.6 Å in both structures. This is also the edge length (marked by thick lines in Fig. 8) of the different tiles. We designate this edge length as 'S', as the short distance in a Fibonacci series as found in quasicrystal structures. The diagonal distance of the pentagonal tile is τ times longer than S, and thus defined as 'L'. As shown in Fig. 8, the c parameters can be given by S and L as follows: ε_6 : $c = L = \tau S \simeq 12.3$ Å; ε_{16} : $c = S + L + L \simeq 32.2$ Å. Consequently the c parameters for the other approximants in the series are: ε_{22} : $c = S + L + L + L \simeq 44.5$ Å; ε_{28} : $c = S + L + L + L + L \simeq 56.8$ Å. They are related by 1: $(1 + \tau)$: $(2 + \tau)$: $(3 + \tau)$.

We expect that it will be possible to obtain the structures of the complete ε series and describe them using the stacks of decagonal and pentagonal columns. Furthermore, a detailed structure model of the decagonal quasicrystal (d-Al-TM) can possibly be deduced from these common features.

4. Conclusion

A series of approximants of quasicrystals are expected to be built from similar atomic clusters, resulting in similar intensity distributions of reflections in reciprocal space. The similarity of the intensity distributions leads to similar structure-factor amplitudes and phases of the related reflections, especially for the strongest reflections. Based on this knowledge, the structure-factor amplitudes and phases of an unknown structure can be deduced from those of a related known structure. A structure model can be deduced from the three-dimensional electron-density map obtained by inverse Fourier transformation of the structure factors. Such a case was demonstrated here successfully on the complex and unknown structure of ε_{16} based on the related known structure of ε_6 . The derived structure model agrees well with the experimental precession electron-diffraction patterns and high-resolution transmission electron microscopy images. The structure of ε_{16} with 153 unique atoms within the unit cell is the most complex quasi-

crystal approximant predicted or solved so far. The strong-reflections approach has once again proven to be an effective method for predicting and solving unknown quasicrystal approximants.

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