

Up to now two kinds of stacking faults related to the ratios of iron and oxygen atoms have been proved. The chemical composition will deviate from the regular value of magnetite in local areas in the presence of such defects and the average chemical composition will be unchanged if these two kinds of stacking faults occur in equal numbers. It may be noticed that the framework of oxygen in any of them is perfect and the stacking faults are caused by the arrangement of cations occupying different polyhedral coordinated positions. This suggests that there is some degree of

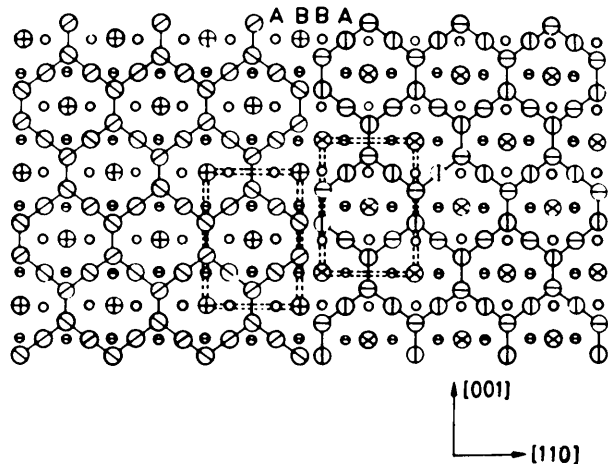


Fig. 10. Stacking fault with an iron to oxygen ratio 1:1 showing a possible arrangement of the iron atoms in the case of cation excess (see *E* in Fig. 8).

freedom for the occupation of the cations in the framework at the initial stage of nucleation when the fluctuation of cations happened in local areas and this remains in the growing process. In other words, the fluctuation of cations may cause the non-stoichiometry by forming defects in the stoichiometric structure.

All the defects observed are located on the inter-phase boundaries or in coulsonite, implying that they were pre-existing defects formed in the process of crystallization of an average structure and these positions were favourable for the nucleation of coulsonite when it separates from the average structure in order to reduce the total free energy of the system on cooling. In our observations, cations are always in deficit, although the presence of excess cations is possible in local areas.

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## Description of Hexagonal Frank-Kasper Phases by a Projection Method

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### Abstract

The structure of hexagonal Frank-Kasper (FK) phases can be described by the projection of the seven-dimensional (7D)  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$  cubes in a suitable projection subspace onto a 3D hyperplane. The close relationship between hexagonal FK phases and the dodecagonal quasicrystal with 12-fold rotational symmetry is discussed.

### 1. Introduction

Significant activity has been generated among condensed-matter physicists and crystallographers by the recent discovery of Bragg diffraction patterns with icosahedral symmetry corresponding to a new quasicrystalline phase of matter. Several 2D and 3D tiling models with noncrystallographic symmetry have been proposed based on the view that a quasilattice is a projection of a higher-dimensional periodic lattice in a defined projection subspace onto a lower-dimensional hyperplane. According to Elser &

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Henley (1985) and Yang & Kuo (1987), this projection method can be used to describe both periodic and quasiperiodic patterns. Using this method, Yang & Kuo (1987) have recently derived the structure of both the crystalline pentagonal Frank-Kasper (FK) phases as well as that of the icosahedral quasicrystal. The method involves the projection of a 6D  $\text{MgCu}_2$  cube onto a 3D rational or irrational hyperplane. As a continuation of this prior work on pentagonal FK phases, we shall discuss in this paper the development of this projection method to describe the hexagonal FK phases.

In the following, we describe these structures by using a projection of a 7D cubic lattice onto a 3D hyperplane. The hexagonal FK phases (Frank & Kasper, 1958, 1959) have been described as tetrahedrally close-packed structures consisting of hexagonal antiprisms. The simplest cases are the cubic  $\text{Cr}_3\text{Si}$  and hexagonal  $\text{Zr}_4\text{Al}_3$  structures. These may be considered as elementary building blocks of the other five known hexagonal FK phases (Li & Kuo, 1986). The centers of the hexagonal antiprisms of these hexagonal FK phases form a net consisting of squares and equilateral triangles corresponding to the  $\text{Cr}_3\text{Si}$  unit and one half of the  $\text{Zr}_4\text{Al}_3$  unit, respectively. We therefore attempt to obtain these structures by the projection of 7D  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$  cubes in some subspace onto a 3D hyperplane related directly to the symmetry of these structures. Recently, the discovery of two kinds of dodecagonal quasicrystal have been reported (Ishimasa, Nissen & Fukano, 1985; Chen, Li & Kuo, 1988). The corresponding high-resolution electron images show that the new quasicrystals also consist of  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$  units but the corresponding tilings are now quasiperiodic. Structural models of these quasicrystals have already been derived from their close relationship to the hexagonal FK phases (Yang & Wei, 1987; Kuo, Feng & Chen, 1988). The projection method is found to be a very useful tool in describing the structure of the hexagonal FK phases as well as those of the dodecagonal quasicrystals.

The organization of this paper is as follows. In § 2, after giving a brief description of the principles involved, we generate the projection method for calculating the structure of these hexagonal FK phases. In § 3, a concrete example of the method is given along with all the calculations involved. Finally, the close relationship between the hexagonal FK phases and the dodecagonal quasicrystal is discussed.

## 2. The principle of the method

Yang & Kuo (1987) have previously explored the projection method in detail in order to describe the pentagonal FK phases, therefore we just give a simple survey here in connection with the hexagonal FK phases. It is well known that a 1D projection structure

can be obtained by the projection of a 2D lattice in a strip subspace onto a 1D physical space. When both the strip and the 1D physical space are irrational, the corresponding projection structure is incommensurate. A commensurate structure consisting of the same unit cells, however, can also be obtained simply by changing the direction of the strip into a rational one. It is obvious that a projection structure is determined by two major factors – namely the projecting subspace in the higher-dimensional space and the lower-dimensional projection plane (projection direction). The former determines the method of packing while the latter determines the shape and size of the basic unit of a system. In our case, we choose the projection direction which gives rise to the  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$  unit in 3D physical space. Each of the hexagonal FK phases corresponds to a projection of a cubic lattice consisting of 7D  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$  cubes in a certain rational subspace of 7D space.

Let  $B$  be the column matrix of the basis  $\{\mathbf{b}_i\}_{i=1,7}$  of a 7D cell and  $\mathbf{r}$  a lattice vector in a 7D space, then

$$\mathbf{r} = \sum_{i=1}^7 m_i \mathbf{b}_i = \tilde{M}B, \quad (1)$$

where  $m_i$  are integers and  $\tilde{M} = (m_1 \ m_2 \ \dots \ m_7)$ ;  $\tilde{B} = \{\mathbf{b}_1 \ \mathbf{b}_2 \ \dots \ \mathbf{b}_7\}$ . After projecting onto a 3D hyperplane with the basis  $\tilde{I} = \{\mathbf{i} \ \mathbf{j} \ \mathbf{k}\}$  in a 3D Cartesian system,  $\mathbf{r}$  becomes  $\mathbf{r}_p$  and we have

$$\mathbf{r}_p = \tilde{M}Q \quad (2)$$

and

$$Q = PB = UI. \quad (3)$$

$P$  is a projection operator with the property  $P = PP$ .  $U$  is a representation matrix of the projection of the basis vectors of a 7D cube onto a 3D hyperplane. This description of the projector  $P$  has been given by Yang & Kuo (1987). The calculation of the vector  $Q$  can be carried out by establishing either the projection matrix  $P$  or the representation matrix  $U$ . Using  $U$  is more convenient than using  $P$ . The seven star vectors  $\tilde{Q} = \{\mathbf{q}_1 \ \mathbf{q}_2 \ \dots \ \mathbf{q}_7\}$  are the projection of a set of 7D cell basis vectors onto a 3D physical space. Six of this set of basis vectors are coplanar with an angle of  $30^\circ$  between adjacent vectors while the seventh is orthogonal to them (see Fig. 1). Obviously, one can combine two of these coplanar basis vectors to derive the square and  $60^\circ$  rhombus corresponding to the  $\text{Cr}_3\text{Si}$  or  $\text{Zr}_4\text{Al}_3$  cells in 3D space. The matrix  $U$  thus has the form:

$$U = 1/(2 \times 3^{1/2}) \begin{pmatrix} 2 & 0 & 0 \\ 3^{1/2} & 1 & 0 \\ 1 & 3^{1/2} & 0 \\ 0 & 2 & 0 \\ -1 & 3^{1/2} & 0 \\ -3^{1/2} & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \quad (4)$$

Similar matrices have been used to obtain a dodecagonal quasilattice (see Yang & Wei, 1987; Gahler & Rhyner, 1986). It is clear from this that the structure of the dodecagonal quasicrystal is closely related to the structure of the hexagonal FK phases.

If the subspace in the 7D space within which  $\mathbf{r}$  is located is defined, the lattice vector  $\mathbf{r}_p$  in the projected structure can be calculated through the  $U$  matrix.

Let

$$C = SB, \quad (5)$$

where  $S$  is the  $7 \times 7$  transformation matrix for choosing a subspace. Therefore, the vector set  $C$  can be considered as a set of 7D subspace vectors.

$$B = S^{-1}C = VC, \quad (6)$$

i.e.  $V = S^{-1}$ .

From (1) and (6), a lattice vector  $\mathbf{r}$  can be expressed as

$$\mathbf{r} = \tilde{M}B = \tilde{M}VC$$

or

$$\mathbf{r} = \sum_{i=1}^7 w_i \mathbf{c}_i$$

and

$$w_i = \sum_{j=1}^7 m_{ij} v_j. \quad (7)$$

Following Elser (1986) and Yang & Kuo (1987),  $\mathbf{r}$  is located within a predetermined subspace with

$$\begin{aligned} -\infty < w_1, w_2, w_3 < \infty \\ k_{1i} < w_i < k_{2i}, \quad i = 4, 5, 6, 7. \end{aligned} \quad (8)$$

If all the elements of  $S$  are rational numbers, the projection structure is a periodic one. From the formulae for calculating lattice constants and atomic coordinates, the lattice constants  $\tilde{A} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$  of the primitive cell of the projected structure are the projections of  $\mathbf{c}_1, \mathbf{c}_2$  and  $\mathbf{c}_3$ , respectively. Then we have

$$A = S^{(3)}UI \quad (9a)$$

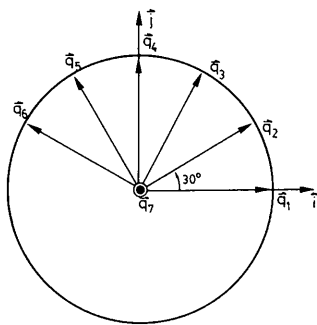
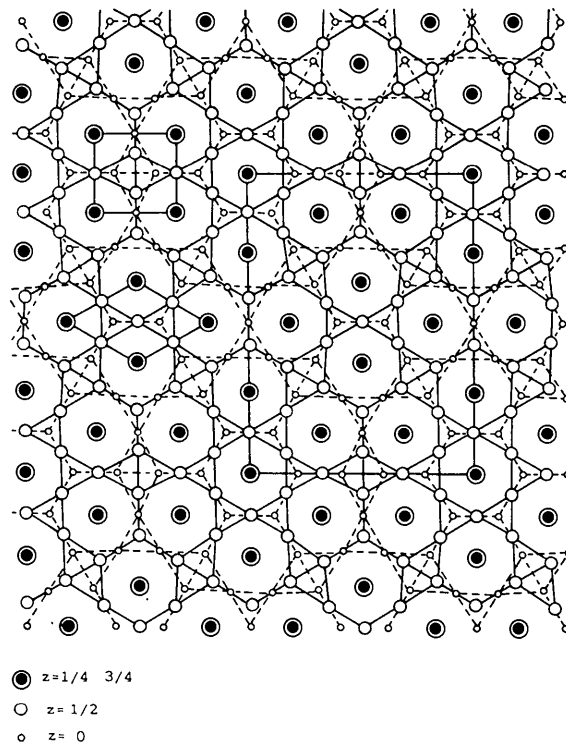
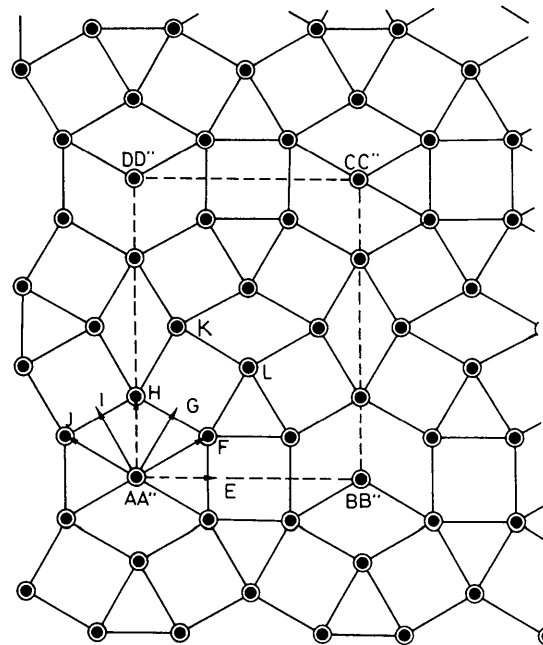


Fig. 1.  $q_i$  are seven basis vectors and represent the projection of a set of 7D cube basis vectors onto a 3D physical space.



(a)



(b)

Fig. 2. (a) Structural model of the  $K$  phase projected on (001). The rectangle shows the primitive cell of the  $K$  phase. The primitive cells of  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$  correspond to the small square and rhombus, respectively. (b) The secondary layer of the  $K$  phase,  $z = \frac{1}{2}$  and  $\frac{3}{4}$ , illustrating its unit cell  $ABCDA'B''C''D''$ , and the projection vectors  $AE, AF, AG, AH, AI, AJ$  of the selection 7D subspace.

and

$$I = (S^{(3)}U)^{-1}A. \tag{9b}$$

$S^{(3)}$  denotes the first three rows of the matrix  $S$ . Sometimes the origin of the 3D unit cell is displaced from that of the 7D one by  $r_0 = \tilde{M}_0 B$ , from (2) and (9b) then

$$r_p = (\tilde{M} - \tilde{M}_0)U(S^{(3)}U)^{-1}A = (x, y, z)A, \tag{10}$$

where  $\tilde{M}_0 = (m_{01} m_{02} \dots m_{07})$  are fractional numbers. Equation (10) gives the atomic coordinates  $(x, y, z)$  in the projected structure.

### 3. Hexagonal FK phases and the calculated results

In discussing the structure of hexagonal FK phases, Frank & Kasper (1959) took up the tilings composed of squares and equilateral triangles and showed that the atoms in  $\text{Cr}_3\text{Si}$  form deformed hexagonal antiprisms arranged in a square pattern and those in  $\text{Zr}_4\text{Al}_3$  are arranged in a hexagonal pattern. Along the unique axis (or hexagonal tunnels) of these systems, they are layer structures consisting of four layers. For example, consider the  $K$ -phase model given in Fig. 2(a): the primary layer has a hexagonal-triangle network at 0 or  $\frac{1}{2}$  height denoted by open circles; the secondary layer at  $\frac{1}{4}$  or  $\frac{3}{4}$  height has square-triangle networks located at the centers of these hexagonal antiprisms. We can also find the  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$  cells which are the basis for further calculations. In the following, starting with the matrix  $U$ , we first focus on the square-equilateral triangle network, i.e. the secondary layer of the hexagonal FK phases. We change the direction of the subspace concerned, and give the quantitative results.

As mentioned above, an important step in obtaining a projected structure is to define a suitable subspace by choosing the matrix  $S$ . For the  $K$  phase, the layer structure can be represented by the secondary layer as shown in Fig. 2(b). In this secondary layer, the filled circles and letters without a prime represent the nodes at  $z = \frac{1}{4}$ , while the open circles and letters with a double prime represent those at  $z = \frac{3}{4}$ .

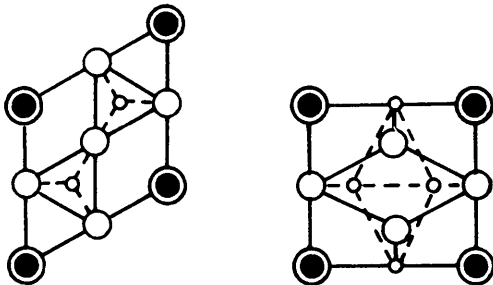


Fig. 3. Structural models of  $\text{Cr}_3\text{Si}$  and  $\text{Zr}_4\text{Al}_3$ .

Table 1. Calculated lattice constants of the hexagonal FK phases by the projection method compared with experimental results

FK phase	b/a	c/a	Calculated			Experimental			Matrix S	K <sub>11</sub>	K <sub>12</sub>	K <sub>21</sub>	K <sub>22</sub>	K <sub>31</sub>	K <sub>32</sub>	K <sub>41</sub>	K <sub>42</sub>	References
			α (°)	β (°)	γ (°)	c/a	α (°)	β (°)										
Zr <sub>4</sub> Al <sub>3</sub>	1.0	1.0	90	90	120	0.992	90	90	120	0	0	0	0	0	0	0	0	(a)
Cr <sub>3</sub> Si	1.0	1.0	90	90	90	1.0	90	90	90	0	0	0	0	0	0	0	0	(a)
σ	1.0	0.518	90	90	90	0.517	90	90	90	-1	0	0	0	0	0	0	0	(a)
H	3.732	1.0	90	90	90	3.889	90	90	90	-1	0	-1	1	0	0	0	0	(b)
F	1.0	0.366	90	90	90	0.360	90	90	90	-1	0	0	0.5	0	0	0	0	(c)
J	2.732	0.366	90	90	90	0.360	90	90	90	-1	-1	-1	-1	0	0	0	0	(c)
K	1.366	0.366	90	90	90	0.360	90	90	90	-2	2	-1	-1	0	0	-1	1	(c)

Limit conditions	S1	S2	S3	S4	S5	S6	S7
Calculated	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 1 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 1 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$

References: (a) Sinha (1972); (b) Ye, Li & Kuo (1984); (c) Li & Kuo (1986).

Table 2. Comparison of calculated atomic positions with the experimental results:  $\sigma$  phase (Fe-Cr)

P4/mmm; $a = b = 8.7995$ , $c = 4.5442$ Å, $\alpha = \beta = \gamma = 90^\circ$ .			
Atomic position	Experimental	Calculated	
	x y z	x y z	
2A(a)	0 0 0	0 0 0	
4B(f)	0.4 0.6 0	0.394 0.606 0	
8C(i)	0.133 0.533 0	0.133 0.533 0	
8D(i)	0.067 0.727 0	0.067 0.750 0	
8E(j)	0.817 0.817 0.25	0.817 0.817 0.25	
	The average of $\Delta d/d$ is 2.9%. $D_{\min} = 4.2$ Å. Origin: (0.00 0 $-\frac{1}{2}$ $-\frac{1}{4}$ )		
	$m_1$ $m_2$ $m_3$ $m_4$ $m_5$ $m_6$ $m_7$	$w_4$ $w_5$ $w_6$ $w_7$	$\Delta d$ (Å)
	(0.000 0.000)+(0.000 0.000 $-\frac{1}{2}$ 0.000 $-\frac{1}{4}$ )	-0.5 0 0 0	0
	(1.000 0.000)+(0.100 0.100 0.000 $-\frac{1}{4}$ )	$\frac{2}{3}$ $-\frac{1}{3}$ 0 $\frac{1}{3}$	0.07
	(0.000 0.000)+(0.200 0.000 0.000 $-\frac{1}{4}$ )	$\frac{2}{3}$ 0 0 0	0.07
	(0.000 0.000)+(0.100 0.000 0.000 $-\frac{1}{4}$ )	$\frac{1}{2}$ 0 0 0	0.15
	(1.001 0.000)	1 1 1 0	0.004

The average of  $\Delta d/d$  is 2.9%.  $D_{\min} = 4.2$  Å. Origin: (0.00 0  $-\frac{1}{2}$   $-\frac{1}{4}$ )

Table 3. Comparison of calculated atomic positions with the experimental results: H phase

Cmmm - D; $a = 4.5$ , $b = 17.5$ , $c = 4.5$ Å, $\alpha = \beta = \gamma = 90^\circ$ , $z = 30$ .			
Atomic position	Experimental	Calculated	
	x y z	x y z	
2A(a)	0 0 0	0 0 0	
4B(e)	0.25 0.25 0	0.25 0.25 0	
4C(i)	0 0.2892 0	0.2892 0 0	
4C(i)	0 0.4206 0	0.4330 0 0	
4D(j)	0 0.3677 0.5	0.3660 0.5 0	
8E(h)	0 0.125 0.25	0.1340 0.25 0	
4F(h)	0.200 0 0.250	0 0.250 0	
	The average of $\Delta d/d$ is 4.2%. $D_{\min} = 2.45$ Å. Origin: (0.00 0 $-\frac{1}{2}$ 0 $-\frac{1}{4}$ )		
	$m_1$ $m_2$ $m_3$ $m_4$ $m_5$ $m_6$ $m_7$	$w_4$ $w_5$ $w_6$ $w_7$	$\Delta d$ (Å)
	(0.000 0.000)+(0.000 0.000 $-\frac{1}{2}$ 0.000 $-\frac{1}{4}$ )	0.5 0 0 0	0
	(0.000 0.000)+(0.000 0.100 0.000 $-\frac{1}{4}$ )	0.5 0 0 0	0
	(0.000 0.000)+(0.000 0.100 0.000 $-\frac{1}{4}$ )	$\frac{2}{3}$ 0 0 0	0
	(0.000 1.000)+(0.100 0.000 0.000 $\frac{1}{4}$ )	$\frac{2}{3}$ 1 0 0	0.0217
	(0.000 1.000)+(0.100 0.000 0.000 $-\frac{1}{4}$ )	1 1 0 0	0.003
	(0.000 0.000)	0 0 0 0	0.016
	(0.000 0.000)+(0.100 0.000 $-\frac{1}{2}$ 0.000 $\frac{1}{4}$ )	0.5 0 0 0	0.023

The average of  $\Delta d/d$  is 4.2%.  $D_{\min} = 2.45$  Å. Origin: (0.00 0  $-\frac{1}{2}$  0  $-\frac{1}{4}$ )

Table 4. Comparison of calculated atomic positions with the experimental results: J phase

Pmmm; $a = 4.5$ , $b = 12.5$ , $c = 4.5$ Å, $\alpha = \beta = \gamma = 90^\circ$ .			
Atomic position	Experimental	Calculated	
	x y z	x y z	
1A(a)	0 0 0	0 0 0	
1B(g)	0 $\frac{1}{2}$ 0	$\frac{1}{2}$ 0 0	
2C(j)	0.259 0 0.250	0.250 0 0.250	
2D(m)	0 0.387 0	0.394 0	
2E(o)	0.060 0.060 0	0.092 0	
2F(o)	0.280 0.280 0	0.289 0	
2G(p)	0.167 0.167 0	0.183 0	
2H(i)	$\frac{1}{2}$ $\frac{1}{2}$ 0	$\frac{1}{2}$ $\frac{1}{2}$ 0	
4J(u)	0 0.167 0	0.183 0	
4J(z)	0.259 $\frac{1}{2}$ 0.250	0.342 0.250 0.250	
	The average of $\Delta d/d$ is 5.7%. $D_{\min} = 2.37$ Å. Origin: (0.00 0 $-\frac{1}{2}$ 0 $-\frac{1}{4}$ )		
	$m_1$ $m_2$ $m_3$ $m_4$ $m_5$ $m_6$ $m_7$	$w_4$ $w_5$ $w_6$ $w_7$	$\Delta d$ (Å)
	(0.000 0.000)+(0.000 0.000 $-\frac{1}{2}$ 0.000 $-\frac{1}{4}$ )	0.5 0 0 0	0
	(0.010 0.000)+(0.100 0.000 0.000 $-\frac{1}{4}$ )	0.5 0 0 0	0
	(0.000 0.000)+(0.100 0.000 $-\frac{1}{2}$ 0.000 $-\frac{1}{4}$ )	0.5 0 0 0	0.004
	(0.000 0.000)+(0.100 0.000 0.000 $-\frac{1}{4}$ )	$\frac{1}{3}$ 0 0 0	0.009
	(0.000 0.000)+(0.100 0.000 0.000 $-\frac{1}{4}$ )	0.25 0 0 0	0.04
	(0.000 0.000)+(0.100 0.000 0.000 $-\frac{1}{4}$ )	0 0 0 0	0.011
	(0.000 0.000)	0 0 0 0	0.02
	(0.010 0.000)	0 0.5 0 0	0
	(0.000 0.000)	0 0 0 0	0.02
	(0.000 0.000)+(0.000 0.100 0.000 $\frac{1}{4}$ )	0 0.25 0 0	0.001

The average of  $\Delta d/d$  is 5.7%.  $D_{\min} = 2.37$  Å. Origin: (0.00 0  $-\frac{1}{2}$  0  $-\frac{1}{4}$ )

Table 5. Comparison of calculated atomic positions with the experimental results: *F* phase  
*P6/mmm*; *a* = *b* = 12.5, *c* = 4.5 Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

Atomic position	Experimental			Calculated			<i>z</i>	<i>m</i> <sub>1</sub> <i>m</i> <sub>2</sub> <i>m</i> <sub>3</sub> <i>m</i> <sub>4</sub> <i>m</i> <sub>5</sub> <i>m</i> <sub>6</sub> <i>m</i> <sub>7</sub>	<i>w</i> <sub>4</sub>	<i>w</i> <sub>5</sub>	<i>w</i> <sub>6</sub>	<i>w</i> <sub>7</sub>	$\Delta d$ (Å)
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>							
2A( <i>d</i> )	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	(0 0 0 1 0 0 0) + (0 0 $\frac{1}{2}$ 0 $\frac{1}{2}$ 0 $\frac{1}{2}$ )	$-\frac{1}{2}$	$\frac{2}{3}$	$-\frac{1}{2}$	$\frac{1}{2}$	0	
2B( <i>e</i> )	0	0	$\frac{1}{4}$	0	0	$\frac{1}{4}$	(0 0 0 0 0 0)	0	0	0	0	0	
6C( <i>j</i> )	0.233	0	0	0.2113	0	0	(0 0 0 0 0) + (0 $\frac{1}{2}$ 0 0 $-\frac{1}{2}$ 0 $-\frac{1}{2}$ )	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0.015	
6D( <i>j</i> )	0.444	0	0	0.444	0	0	(0 1 0 0 0) + ( $\frac{1}{2}$ 0 0 $-\frac{1}{2}$ 0 0 $-\frac{1}{2}$ )	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0.044	
6E( <i>k</i> )	$\frac{1}{2}$	0	$\frac{1}{2}$	0.317	0	$\frac{1}{2}$	(0 1 0 0 0) + (0 0 $-\frac{1}{2}$ 0 $\frac{1}{2}$ 0 $\frac{1}{2}$ )	1	$-\frac{1}{2}$	0	0	0.020	
6F( <i>l</i> )	0.390	0.780	0	0.394	0.789	0	(0 0 1 0 0) + ( $-\frac{1}{2}$ 0 0 0 0 $-\frac{1}{2}$ )	$-\frac{1}{2}$	1	$-\frac{1}{2}$	1	0.014	
6G( <i>m</i> )	0.112	0.223	$\frac{1}{2}$	0.106	0.213	$\frac{1}{2}$	(0 0 0 0 0) + (0 0 $\frac{1}{2}$ 0 0 $\frac{1}{2}$ )	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0.019	
6H( <i>m</i> )	0.444	0.888	$\frac{1}{2}$	0.447	0.894	$\frac{1}{2}$	(0 0 1 0 0) + ( $-\frac{1}{2}$ 0 0 $\frac{1}{2}$ 0 0 $\frac{1}{2}$ )	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1	0.010	
12I( <i>o</i> )	0.233	0.446	$\frac{1}{4}$	0.2113	0.423	$\frac{1}{4}$	(0 0 0 1 0 0)	0	0	0	0	0.039	

The average of  $\Delta d/d$  is 8.4%.  $D_{\min} = 2.763$  Å. Origin: (0 0 0 0 0  $-\frac{1}{4}$ ).

Table 6. Comparison of calculated atomic positions with the experimental results: *K* phase

*Pmmn*; *a* = 12.5, *b* = 17.1, *c* = 4.5 Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 82^\circ$ , *z* = 82.

Atomic position	Experimental			Calculated			<i>z</i>	<i>m</i> <sub>1</sub> <i>m</i> <sub>2</sub> <i>m</i> <sub>3</sub> <i>m</i> <sub>4</sub> <i>m</i> <sub>5</sub> <i>m</i> <sub>6</sub> <i>m</i> <sub>7</sub>	<i>w</i> <sub>4</sub>	<i>w</i> <sub>5</sub>	<i>w</i> <sub>6</sub>	<i>w</i> <sub>7</sub>	$\Delta d$ (Å)
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>							
1A( <i>e</i> )	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0	(0 0 1 1 0 0 0) + ( $-\frac{1}{2}$ 0 0 0 0 0 $-\frac{1}{2}$ )	$\frac{1}{2}$	1	0	$-\frac{1}{2}$	1	0
1B( <i>h</i> )	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	(0 1 1 0 0 0) + (0 0 0 $\frac{1}{2}$ 0 0 $\frac{1}{2}$ )	1	1	0	0	1	0
2C( <i>i</i> )	0.220	0	0	0.211	0	0	(0 0 0 0 0) + (0 $\frac{1}{2}$ 0 0 $-\frac{1}{2}$ 0 $-\frac{1}{2}$ )	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0.001
2D( <i>j</i> )	0.442	0	0	0.408	0	0	(0 0 0 0 0) + ( $\frac{1}{2}$ 0 0 $-\frac{1}{2}$ 0 0 $-\frac{1}{2}$ )	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0.042
2E( <i>j</i> )	$\frac{1}{2}$	0	$\frac{1}{2}$	0.317	0	$\frac{1}{2}$	(0 1 0 0 0) + (0 0 0 $-\frac{1}{2}$ 0 0 $\frac{1}{2}$ )	1	1	0	0	0	0.020
2F( <i>k</i> )	0.392	$\frac{1}{2}$	0	0.394	$\frac{1}{2}$	0	(0 1 0 0 0) + (0 0 $\frac{1}{2}$ 0 0 $\frac{1}{2}$ )	1	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0.003
2G( <i>n</i> )	0	0.143	$\frac{1}{2}$	0	0.134	$\frac{1}{2}$	(0 0 0 0 0) + (0 0 0 $\frac{1}{2}$ 0 0 $-\frac{1}{2}$ )	0	0	0	0	0	0.015
2H( <i>n</i> )	0	0.430	$\frac{1}{2}$	0	0.423	$\frac{1}{2}$	(0 0 1 0 0) + (0 0 0 $\frac{1}{2}$ 0 0 $\frac{1}{2}$ )	0	0	0	0	0	0.013
2I( <i>o</i> )	$\frac{1}{2}$	0.143	0	$\frac{1}{2}$	0.134	0	(0 1 0 0 0) + ( $\frac{1}{2}$ 0 0 0 0 0 $-\frac{1}{2}$ )	0	0	$\frac{1}{2}$	0	0	0.015
2J( <i>p</i> )	0.072	0	0	0.067	0	0	(0 1 0 0 0) + ( $\frac{1}{2}$ 0 0 0 0 0 $-\frac{1}{2}$ )	0	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	0.009
2K( <i>p</i> )	0.216	0.216	$\frac{1}{2}$	0.201	0.201	$\frac{1}{2}$	(0 1 0 0 0) + ( $\frac{1}{2}$ 0 0 0 0 0 $\frac{1}{2}$ )	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0.026
2L( <i>q</i> )	0	0	0	0	0	0	(0 0 0 0 0 0)	0	0	0	0	0	0
4M( <i>u</i> )	0	0.286	0	0	0.268	0	(0 0 1 0 0 0)	0	1	0	0	0	0.031
4N( <i>v</i> )	$\frac{1}{2}$	0.358	$\frac{1}{2}$	$\frac{1}{2}$	0.366	$\frac{1}{2}$	(0 1 1 0 0 0)	0	1	0	0	1	0.014
4O( <i>x</i> )	0.167	$\frac{1}{2}$	0	0.183	$\frac{1}{2}$	0	(0 0 1 0 0 0)	0	0	0	0	0	0.020
4P( <i>y</i> )	0.085	0.376	0	0.092	0.384	0	(0 0 1 0 0 0) + (0 0 0 0 0 0 $-\frac{1}{2}$ )	$\frac{1}{2}$	0	0	0	0	0.015
4Q( <i>y</i> )	0.110	0.143	0	0.105	0.134	0	(0 0 0 0 0) + (0 $\frac{1}{2}$ 0 0 $-\frac{1}{2}$ )	$\frac{1}{2}$	0	0	0	0	0.017
4R( <i>y</i> )	0.220	0.286	0	0.204	0.259	0	(0 1 0 0 0) + (0 0 0 0 0 $-\frac{1}{2}$ )	1	1	0	0	0	0.058
4S( <i>y</i> )	0.415	0.253	0	0.409	0.250	0	(0 1 0 0 0) + (0 0 0 0 0 $-\frac{1}{2}$ )	1	1	0	0	0	0.009
4U( <i>y</i> )	0.277	0.358	0	0.296	0.375	0	(0 1 0 0 0) + (0 0 0 0 0 $-\frac{1}{2}$ )	1	1	0	0	0	0.038
4V( <i>z</i> )	0.167	0.072	0	0.158	0.067	0	(0 0 0 0 0) + (0 $\frac{1}{2}$ 0 0 0 $\frac{1}{2}$ )	0	0	0	0	0	0.014
4W( <i>z</i> )	0.167	0.216	0	0.158	0.201	0	(0 1 0 0 0) + (0 0 0 0 0 $\frac{1}{2}$ )	1	0	0	0	0	0.028
4X( <i>z</i> )	0.167	0.358	0	0.171	0.350	0	(0 1 0 0 0) + (0 0 0 0 0 $\frac{1}{2}$ )	1	0	0	0	0	0.015
4Y( <i>z</i> )	0.286	0.286	0	0.329	0.283	0	(0 1 0 0 0) + (0 0 0 0 0 $\frac{1}{2}$ )	1	1	0	0	0	0.007
4Z( <i>z</i> )	$\frac{1}{2}$	0.428	$\frac{1}{2}$	0.342	0.433	$\frac{1}{2}$	(0 1 0 0 0) + (0 0 0 0 0 $\frac{1}{2}$ )	1	1	0	0	0	0.013
8Aa( <i>d</i> )	$\frac{1}{2}$	0.143	$\frac{1}{4}$	0.317	0.134	$\frac{1}{4}$	(0 1 0 0 0 0)	1	1	0	0	0	0.026

The average of  $\Delta d/d$  is 7.1%.  $D_{\min} = 2.75$  Å. Origin: (0 0 0 0 0  $-\frac{1}{4}$ ).

$ABCDAB''C''D''$  represents a unit cell of the  $K$  phase with  $\mathbf{a}_1 = AB$ ,  $\mathbf{a}_2 = AD$ , and  $\mathbf{a}_3 = AA''$ . Let  $AE$ ,  $AF$ ,  $AG$ ,  $AH$ ,  $AI$ ,  $AJ$  and  $AA''$  denote the projected vectors  $\mathbf{q}_1$ ,  $\mathbf{q}_2$ ,  $\mathbf{q}_3$ ,  $\mathbf{q}_4$ ,  $\mathbf{q}_5$ ,  $\mathbf{q}_6$  and  $\mathbf{q}_7$ , in the 3D hyperplane projected from the vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$ ,  $\mathbf{b}_3$ ,  $\mathbf{b}_4$ ,  $\mathbf{b}_5$ ,  $\mathbf{b}_6$  and  $\mathbf{b}_7$  respectively, of a 7D cube. Then  $AB = \mathbf{q}_1 + \mathbf{q}_2 - \mathbf{q}_6$ ;  $AC = \mathbf{q}_3 + 2\mathbf{q}_4 + \mathbf{q}_5$ ;  $AA'' = \mathbf{q}_7$ ;  $AK = \mathbf{q}_3 + \mathbf{q}_4$ ;  $AH = \mathbf{q}_4$ ;  $AF = \mathbf{q}_2$  and  $AJ = \mathbf{q}_6$  are the projected vectors onto the 3D hyperplane of vectors  $\mathbf{c}_1$ ,  $\mathbf{c}_2$ ,  $\mathbf{c}_3$ ,  $\mathbf{c}_4$ ,  $\mathbf{c}_5$ ,  $\mathbf{c}_6$  and  $\mathbf{c}_7$ , thus

$$S = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 2 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 \end{pmatrix}$$

with the limiting conditions

$$-2 < w_4 < 2; \quad -1 < w_5, w_7 < 1; \quad 0 < w_6 < 1.$$

All the lattice points in the secondary layer as well as the lattice parameters of the primitive cell of the  $K$  phase can thus be calculated. The latter are given by  $b/a = 1.366$ ,  $c/a = 0.366$ ,  $\alpha = \beta = \gamma = 90^\circ$  - in good agreement with experimental data (see Table 1). In Table 1 the calculated results for  $Zr_4Al_3$ ,  $Cr_3Si$  and five other hexagonal FK phases are also given. The deviation from experiment for most of the calculated lattice-parameter magnitudes is less than 1.6% with a maximum deviation of 4.0%. In order to calculate all atom positions of these phases, we will analyze the primitive cells of  $Cr_3Si$  and  $Zr_4Al_3$  (see Fig. 3), respectively. The primitive cell of  $Cr_3Si$  is a cube with an edge length equal to 1, and it contains eight atoms. The edge vectors of the cube should take  $\mathbf{q}_i$  and  $\mathbf{q}_j$  with  $|i-j|=3$ , and the cube itself has six different orientations. When  $i=1$ , the 7D coordinates of each atom are: two Si's at  $(\frac{1}{2}00000\frac{3}{4})$  and  $(000\frac{1}{2}00\frac{1}{4})$  and six Cr's at  $(0000000)$ ,  $(000000\frac{1}{2})$ ,  $(\frac{1}{2}00\frac{1}{4}00\frac{1}{4})$ ,  $(\frac{1}{2}00\frac{3}{4}00\frac{1}{4})$ ,  $(\frac{1}{4}00\frac{1}{2}00\frac{3}{4})$  and  $(\frac{3}{4}00\frac{1}{2}00\frac{3}{4})$ , respectively. Similarly, for  $Zr_4Al_3$  the primitive cell is a  $60^\circ$  rhombus of seven atoms with an edge length 1 and it also has six different orientations. Thus the corresponding edge vectors are  $\mathbf{q}_i$  and  $\mathbf{q}_j$  with  $|i-j|=2$ . When  $i=1$ , the 7D coordinates of each atom are: five Zr's at  $(0000000)$ ,  $(000000\frac{1}{2})$ ,  $(\frac{1}{2}00000\frac{1}{4})$ ,  $(\frac{1}{2}0\frac{1}{2}000\frac{1}{4})$  and  $(00\frac{1}{2}000\frac{1}{4})$  and two Al's at  $(\frac{1}{3}0\frac{1}{3}000\frac{2}{3})$  and  $(\frac{2}{3}0\frac{2}{3}000\frac{2}{3})$ , respectively. Following the above description, the atom positions in the other hexagonal FK phases can be calculated as shown in Tables 2-6.

It should be noticed that our calculated result for the  $\sigma$  phase is in good agreement (2.9%) with experiment data for the atom positions (see Table 2), but that the deviation of our results for the other hexagonal FK phases compared with the previous results of Li & Kuo (1986) and Ye, Li & Kuo (1984) is rather larger (5.0%). In the latter case, regular hexagonal antiprisms were used in constructing the structure of these new phases. In fact, hexagonal antiprisms in these FK phases are always somewhat distorted. Unless some distortion occurs, the distance between some atoms in the primary layer is too short to accommodate two atoms.

In summary, we have presented detailed quantitative calculations for the seven hexagonal FK phases using the projection method. The square-triangle networks used for describing these structures are all periodic. With an irrational subspace, however, a quasiperiodic array of such tilings can be obtained which may be used to propose a structural model for the dodecagonal quasicrystal. Based on experimental evidence, Yang & Wei (1987) and Kuo, Feng & Chen (1988) have given atomic models for this new quasicrystal. In these cases,  $Cr_3Si$  and  $Zr_4Al_3$  cells were packed quasiperiodically or aperiodically with a 12-fold bond orientational order. In fact, they can be distinguished by different subspaces in the projection method. For the random model, the subspace is a random one but its average direction is irrational and related to dodecagonal symmetry. Once the 3D hyperplane used to generate the basic unit cell is defined, it will be interesting to investigate a quasicrystal growth model by considering a series of subspaces. The existence of transition structures intermediate between the dodecagonal quasicrystal and the hexagonal FK phases can also be anticipated.

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