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Stacking sequences and symmetry properties of trigonal vacancy-ordered phases (τ phases)

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ABSTRACT

The vacancy-ordered phases known as τ phases are described and the literature dealing with the observed stacking sequences is reviewed. It is shown that the stacking sequences along the threefold axis can be derived from a projection method involving projection on to an axis of type $[rr\bar{q}]$. The structure has alternating filled and empty lamellae parallel to planes of type $(rr\bar{q})$. The particular cases in which r and q are consecutive numbers of the Fibonacci sequence can be regarded as rational approximants to a one-dimensional quasiperiodic structure. Some mathematical properties of the sequences, and their relationship with the three-dimensional structures, are presented.

§ 1. INTRODUCTION

The vacancy-ordered phases known as τ-phases are B2 structures in which the vertices of one of the two constituent primitive cubic lattices are occupied by aluminium atoms and those of the other are occupied by transition-metal atoms or are vacant sites. The (111) planes are either completely filled or completely empty, with characteristic periodic stacking sequences along the [111] direction.

The stacking sequences for a large number of τ phases are now known. A τ_5 phase Al_5Cu_2Ni was reported by Bingham and Haughton (1923) and the structure of the τ_3 phase Al_3Ni_2 was elucidated by Bradley and Taylor (1937). The most extensive investigation is the work of Lu and Chang (1957) in which the Al–Cu–Ni system was explored and stacking sequences determined, for τ_p phases with $p = 5, 6, 7, 8, 11, 13, 15$ and 17. The X-ray diffraction analyses of van Sande *et al.* (1978) confirmed the evidence for

$$\tau_2, \tau_3, \tau_5, \tau_8 \text{ and } \tau_{13} \tag{1}$$

but did not encounter the other members on list given by Lu and Chang.

A very striking feature of the list (1) is as follows: the lengths of the repeat units of the stacking sequences are terms in the Fibonacci sequence. Motivated by this observation, Chattopadhyay *et al.* (1987) were led to the discovery that the actual stacking sequences of these phases are in fact rational approximants to the well-known quasiperiodic sequence generated by the iteration rule $0 \rightarrow 1$, $1 \rightarrow 10$ (Elser

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1985, Katz and Duneau 1986, Levine and Steinhardt 1986). Here and in what follows, 1 and 0 denote occupied and vacant sites respectively.

§ 2. Computation of the periodic sequences

Figure 1 illustrates a particular example: a τ_8 structure, viewed along $[1\bar{1}0]$. Only the transition-metal atoms and vacant sites are indicated (denoted by full and open circles respectively); the aluminium atoms have been omitted. Denoting occupied sites by the symbol 1 and vacant sites by 0, the repeat unit for the stacking sequence along [111] in this example is 11011010. Observe, however, that the sequence along $[33\bar{5}]$ is 11111000. This strongly suggests that the characteristic [111] stacking sequence observed in τ_8 might be a consequence of growth of the structure along $[33\bar{5}]$, whereby lamellae of occupied sites (parallel to the $(33\bar{5})$ planes) alternate with lamellae of vacancies. The purpose of this paper is to generalize this observation.

Consider the effect of the vacancy ordering of the central sites of a cubic lattice produced by the stacking sequence $\ldots 1^q 0^r 1^q 0^r 1^q 0^r \ldots$ along the $[rr\bar{q}]$ direction. It will be convenient to adopt the symbol $\{p/q\}$, where $p = r + q$, to refer to this structure or to its stacking sequence along [111], or to the repeat unit of the sequence. The projection operator for orthogonal projection of 3-space on to the line through the origin, in the $[rr\bar{q}]$ direction, is

$$P = \frac{1}{2r^2 + q^2}\begin{pmatrix} r^2 & r^2 & -rq \\ r^2 & r^2 & -rq \\ -rq & -rq & q^2 \end{pmatrix} \tag{2}$$

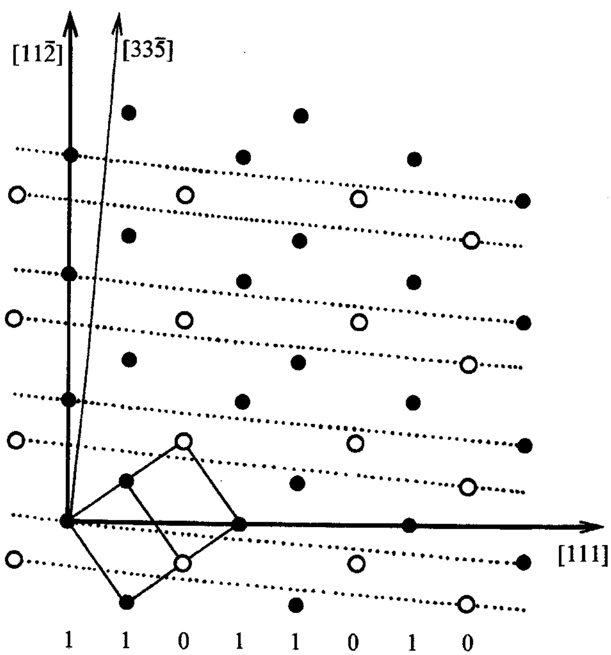

Figure 1. A τ_8 structure viewed along the $[1\bar{1}0]$ axis, showing the periodic stacking of layers perpendicular to $[33\bar{5}]$.

Choosing the origin at an occupied site lying in the first plane of the sequence 1^q0^r, the general point (x, y, z) projects to the point on the line located at distance

$$\frac{r(x+y)-qz}{(2r^2+q^2)^{1/2}}$$

from the origin. The presumed sequence along $[rr\bar{q}]$ then implies that any point (x, y, z) of the lattice of vacant and occupied sites (x, y and z integers) is occupied if and only if

$$r(x+y)-qz = s+Np, \qquad 0 \leqslant s < q, \qquad N \text{ integer.}$$

Defining

$$n = x+y+z, \tag{3}$$

this gives

$$qn+s = 0 \bmod p, \qquad 0 \leqslant s < q. \tag{4}$$

Therefore,

$$n+\beta = \frac{mp}{q}, \qquad 0 \leqslant \beta < 1, \qquad m \text{ integer,}$$

that is

$$n = \left[\frac{mp}{q}\right], \tag{5}$$

where $[x]$ denotes the greatest integer less than or equal to x. Since the projection of (x, y, z) on the [111] axis is distant $n/3^{1/2}$ from the origin, this formula gives the stacking sequence of occupied and vacant layers along [111]. For the specific example $\{8/5\}$ we obtain

m	0	1	2	3	4
mp/q	0	8/5	16/5	24/5	32/5
n	0	1	3	4	6

The sequence along [111] is therefore ...11011010... (as already noted in figure 1).

In general, the repeat unit of the stacking sequence along [111], in the $\{p/q\}$ structure, is $N_0N_1N_2 \ldots N_{p-1}$, where

$$N_n = \begin{cases} 1 & \text{if } n = \left[\dfrac{mp}{q}\right] \text{ for some integer } m, 0 \leqslant m < q-1, \\ 0 & \text{otherwise.} \end{cases} \tag{6}$$

§ 3. Symmetry properties of the sequences

The periodic sequence $\ldots 1^q0^r1^q0^r1^q0^r \ldots$ has obvious symmetries: invariance under reversal about the centre of any 1^q or 0^r grouping. This corresponds to the existence of diad axes in the three-dimensional (3D) structure (perpendicular to the page in figure 1, at obvious positions). This in turn implies that the periodic sequence $\ldots(N_0N_1 \ldots N_{p-1})(N_0N_1 \ldots N_{p-1})\ldots$ also has reversal symmetries. An independent algebraic proof is not without interest.

The reversal symmetry of an infinite sequence $\{N_n\}$ defined by equation (6) is

$$N_n = N_{\kappa - n} \tag{7}$$

for all n, and for certain values of κ.

Proof: Without loss of generality we may take p and q to be mutually prime integers. Then, there exist positive integers $\mu < q$ and $\nu < p$, satisfying

$$\nu q = \mu p + 1. \tag{8}$$

(This follows from the fact that the integers $\rho q \bmod p\,(\rho = 1, 2, \ldots, p-1)$ are all different; since p and q are mutually prime, $(\rho - \rho')q = 0 \bmod \rho$ implies that $\rho = \rho'$. Thus, there exists a ν satisfying $\nu q = 1 \bmod p$. However, this in turn means that there also exists a μ, satisfying $0 < \mu < p$ and equation (8). Then $\mu = (\nu q - 1)/p < q - 1/p < q$.) Define

$$\kappa = \nu - 1. \tag{9}$$

Suppose that $N_n = 1$, that is, $mp = nq + s$, $0 \leqslant s < 1$. Then $m'p = (\kappa - n)q + s'$, where $m' = \mu - m$ and $s' = q - s - 1$. Since $0 \leqslant s < q$, this establishes that $N_{\kappa-n} = 1$. So, $N_n = 1$ implies that $N_{\kappa-n} = 1$. The converse is an obvious consequence. Therefore, for all n, $N_{\kappa-n} = 1$ if and only if $N_n = 1$. This is the property (7). □

Example: For $\{8/5\}$ we have $5\nu = 8\mu + 1$. Then $5\nu = 1 \bmod 8$ gives $\nu = 5$, $\kappa = \nu - 1 = 4$. The infinite sequence generated by the repeat unit 11011010 is therefore symmetrical about the second position $\kappa/2$ and the sixth position $(\kappa + p)/2$:

$$\ldots -2\ -1\,0\,1\,2\,3\,4\,5\,6\,7\,8\,9 \ldots$$

$$\ldots\quad 1\,0\,1\,1\,0\,1\,1\,0\,1\,0\,1\,1 \ldots.$$

Another curious property of the sequences $\{p/q\}$, perhaps of lesser importance, is that the repeat unit $N_0 N_1 N_2 \ldots N_{p-1}$ has the form $1S0$ where S is a *palindrome*.

Proof: $N_0 = 1$, trivially. $N_{p-1} = 0$ because otherwise, from equation (4), we would have $q(p-1) + s' = 0 \bmod p$, $0 \leqslant s < q$, which give the contradiction $s = q \bmod p$. The palindromic property of S, to be proved, is

$$N_n = N_{p-1-n}, \qquad 0 < n < p - 1. \tag{10}$$

Define $n' = p - 1 - n$. Suppose that $N_n = 1$, that is, $qn + s = 0 \bmod p, 0 \leqslant s < q$. Then, $qn' + s = 0 \bmod p$, where $s' = q - s$, which satisfies $0 < s' \leqslant q$. However, $s' = q$ implies that $s = 0$, which corresponds to $n = 0 \bmod p$, $n' = -1 \bmod p$. Therefore, for $0 < n < p - 1$, $0 < n' < p - 1$, $N_n = 1$ implies that $N_{n'} = 1$, and vice versa. This establishes the palindromic property (10). □

§4. Symmetries of the three-dimensional structures

The reversibility property (7) of the stacking sequences implies immediately the existence of diad axes perpendicular to the triad axis.

The 3D structure repeats itself, along its triad axis, whenever the stacking sequence, and the layering abcabc... of the sequence of (111) planes of the underlying cubic lattice, are 'in step'. Therefore, a single repeat unit of length p corresponds precisely to a period of the corresponding τ phase along its triad axis only if p is divisible by 3. Otherwise, three repeat units correspond to a period of the 3D structure.

From these considerations, it is not difficult to deduce the symmetry groups and c/a ratios of the τ phases: symmetry $P\bar{3}m$, $c/a = (p/3)(3/2)^{1/2}$, if $p = 0 \bmod 3$; symmetry $R\bar{3}m$, $c/a = p(3/2)^{1/2}$ otherwise.

For $p = 1 \bmod 3$ the edges of the rhombohedral unit cell, referred to the cubic reference system, are $(p+2,\ p-1,\ p-1)/3$ and cyclic permutations and for $p = -1 \bmod 3$ they are $(p-2, p+1, p+1)/3$ and cyclic permutations.

The rhombus in figure 2 (*a*) illustrates a unit cell of $R\bar{3}m$. (The hexagon indicates one of the cubes of the underlying cubic lattice.) The numbers indicate the positions of transition-metal atoms along the triad axes in the structure {8/5} (i.e. the same

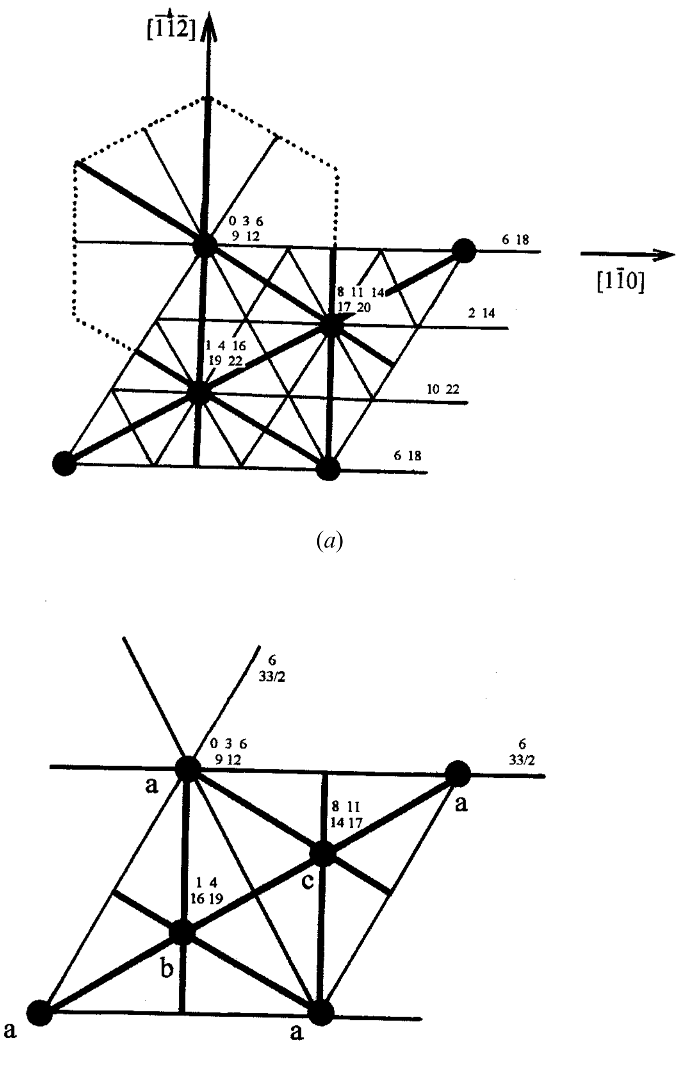

Figure 2. Unit cells of vacancy ordered phases, viewed along the threefold axis: (*a*) {8/5} phase, symmetry $R\bar{3}m$; (*b*) {21/13} phase, symmetry $P\bar{3}m1$.

structure as in figure 1), and positions of the diad axes, in units of $c/24$. Figure 2 (*b*) illustrates a unit cell of $P\bar{3}m1$ with the positions of transition-metal atoms in {21/13} and of the diads, given in units of $c/21$.

The ubiquitous factor $(3/2)^{1/2}$ is the c/a ratio of Frank's (1965) 'cubic hexagonal' lattice. This comes about because $(3/2)^{1/2}$ is the ratio of a main diagonal to a face diagonal of a cube; Frank's hexagonal lattice is a sublattice of the primitive cubic lattice. The τ phases contain (decorated) hexagonal prisms with $c/a = (3/2)^{1/2}$, which can be regarded as the 'building blocks' of these structures. Ranganathan *et al.* (2002) have emphasized the importance of the cubic hexagonal lattice in the context of other kinds of trigonal and hexagonal structures.

§ 5. Fibonacci and non-Fibonacci τ phases

The Fibonacci scheme discovered by Chattopadhyay *et al.* (1987) is obviously a dominant and important feature of the systematics of the τ phases. The τ phases 'of Fibonacci type' (which correspond, in our present notation, to the cases in which r, q, p are successive terms in the Fibonacci sequence) can be regarded as rational approximants to a 'one-dimensional (1D) quasicrystal'. In the present scheme this quasiperiodic phase would arise from alternating empty and filled lamellae perpendicular to the irrational axis $[11\bar{\tau}]$, the ratio of thicknesses being τ. The periodic stacking sequences given by equation (5) are rational approximants to the prescription

$$n = [m\tau]. \qquad (11)$$

As mentioned earlier, Lu and Chang (1957) gave stacking sequences for the 'non-Fibonacci' τ phases $\tau_6, \tau_7, \tau_{11}$ and τ_{17}, which the later investigations of van Sande *et al.* (1978) did not encounter; these workers found *only* Fibonacci-type phases. Shastry *et al.* (1980) reported the existence of a τ_{12} phase. van Tendeloo *et al.* (1989) found τ_{18}, τ_{31} and τ_{38} and noted that 18 and 31 belong to non-standard sequence 8, 5, 13, 18, 31, 49, ... Amelinckx *et al.* (1990) identified the Fibonacci phases τ_{34} and τ_{55}, as well as the non-Fibonacci phases τ_{18}, τ_{31} and τ_{38} and used the 'cut-and-projection' method to obtain plausible stacking sequences.

Lu and Chang (1957) gave the sequences of filled (F) and empty (E) unit cubes of the aluminium lattice, for a string of cubes along the triad axis, rather that the stacking sequences of occupied (O) and vacant (V) planes perpendicular to the triad axis. (The VO notation was introduced by van Sande *et al.* (1978) and has been adopted by subsequent researchers.) If we denote F by 1 and E by 0, the sequences $M_0 M_1 \ldots M_{p-1}$ of Lu and Chang are clearly related to the stacking sequences according to

$$M_n = N_{n+3}. \qquad (12)$$

(The subscripts here are integers mod p.)

It is not clear what the structures τ_6 and τ_{15} found by Lu and Chang (1957) could have been. The reported sequences are F^4E^2 and $F^5E^3F^5E^2$ respectively. Since p in both these cases is a multiple of 3, one cannot extract stacking sequences from this information. In their tabulation, van Sande *et al.* (1978) omitted to give stacking sequences for these two cases (obviously, they had encountered this same difficulty). It is conceivable that the supposed τ_6 was actually a misidentified τ_{18}; {18/11} gives the stacking sequence 110110101101011010 and the length-six sequences F^4E^2, $F^2E^2F^2$ and E^2F^3E along the three kinds of triad axis.

Other stacking sequences deduced by van Sande *et al.* from the data of Lu and Chang are all derivable from the prescription (4). They correspond to the cases

$$\{2/1\}, \{3/2\}, \{5/3\}, \{7/5\}, \{8/5\}, \{13/8\} \text{ and } \{17/12\}.$$

The work of Amelinckx *et al.* (1990) added new members to the list of known τ phases; (in our notation) the Fibonacci types $\{34/21\}$ and $\{55/34\}$, and the non-Fibonacci types $\{18/11\}$, $\{31/19\}$ and $\{38/23\}$.

van Sande *et al.* (1978) expressed doubts about the τ_{11} obtained by Lu and Chang (1957), on the grounds that the sequence 00110110011 contains consecutive pairs of vacant layers, a feature that is absent from all the other phases. They suggested the more evenly distributed sequence 11010101010. This is precisely the sequence given by equation (4) for the case $\{11/6\}$.

This question of the 'evenness' of distribution of the observed sequences warrants further investigation. Observe that almost all the sequences observed in the τ phases have the property that no two vacant planes occur consecutively, and no three occupied planes occur consecutively. Exceptions are τ_1 (no vacancies) and the τ_7 phase ($Al_7(Cu, Ni)_5$) found by Lu and Chang. These have the sequences given by $\{1/1\}$ and $\{7/5\}$. The τ_7 phase given by $\{7/4\}$, however, does satisfy the condition. This particular characteristic of the stacking sequences corresponds to the condition

$$\tfrac{3}{2} \leqslant \frac{p}{q} \leqslant 2. \tag{13}$$

This assertion can be proved by establishing that a sequence $\{p/q\}$ can contain 111 only if $p/q < 3/2$ and can contain 00 only if $p/q > 2$. Suppose that $N_n = 1$, that is, for some integer m, $mp/q = n + \beta$, $0 \leqslant 2\beta < 1$. Then $(m+2)p/q = (n+2) + 2(p/q - 1) + \beta$. Therefore $N_{n+1} = 1$ and $N_{n+2} = 1$ require $0 \leqslant 2(p/q - 1) + \beta < 1$, which implies that $p/q < 3/2$. On the other hand, $N_{n+1} = N_{n+2} = 0$ (i.e. $n+1$ and $n+2$ are not of the form $[m'p/q]$ for any integer m') requires $(m+1)p/q \geqslant n+3$, that is $p/q \geqslant 3 - \beta > 2$.

Note that, in particular, equation (13) is satisfied by all the Fibonacci approximants p/q to the golden number $\tau = (1 + 5^{1/2})/2$ except the first, 1/1. The τ_{12} phase found by Shastry *et al.* is presumably $\{12/7\}$, since, for $p = 12$, 7 is the only number q that is prime to 12 and satisfies equation (13).

The condition (13) can be written in the alternative form

$$1 \leqslant \frac{q}{r} \leqslant 2. \tag{14}$$

In terms of our model, consisting of alternate filled and empty lamellae perpendicular to the $[rr\bar{q}]$ axis (as in figure 1), this has a simple qualitative geometrical interpretation, namely that the 'projection axis' is nearly perpendicular to the triad axis.

Any binary sequence that contains neither 111 nor 00 can be assembled from the subunits 10 and 110. Denoting these units by the symbols 2 and 3 provides an abridged notation for the stacking sequences: the $\{8/5\}$ sequence 11011010, for example, is 332. This abridged notation was introduced by van Sande *et al.* (1978) and has been adopted by subsequent authors.

§6. The golden quasiperiodic sequence

When q and p are successive terms in the Fibonacci number sequence defined by

$$f_0 = 0,\ f_1 = 1, \quad f_{N+1} = f_N + f_{N-1}, \quad q = f_N, \quad p = f_{N+1} \tag{15}$$

(i.e. 1 1 2 3 5 8...), the periodic stacking sequences given by equation (4) converge to the quasiperiodic stacking sequence given by

$$n = [m\tau], \tag{16}$$

where τ is the golden number: $\tau = (1 + 5^{1/2})/2 \approx 1.618\,033\,98\ldots$.

The resulting quasiperiodic stacking sequence $\{F_n\}$ defined by

$$F_n = \begin{cases} 1 & \text{if } n = [m\tau] \text{ for some integer } m \\ 0 & \text{otherwise,} \end{cases} \tag{17}$$

obviously satisfies $F_{-1} = 0$, $F_0 = 1$ and $F_{-n} = F_{n-1}$ except for $n = 0$ or $n = -1$. The beginning of the 'right-hand half' of the sequence is

n	0	1	2	3	4	5	6	7	8	9	10	11	12	13	
m	0	1		2	3		4		5	6		7	8		
F_n	1	1	0	1	1	0	1	0	1	1	0	1	1	0	....

For any Fibonacci approximant to this sequence (i.e. any sequence $\{q/p\}$ where q and p are successive terms of the Fibonacci number sequence),

$$\{p/q\} = N_0 N_1 \ldots N_{p-2} N_{p-1} = F_0 F_1 \ldots F_{p-2} 0. \tag{18}$$

Proof: $N_{p-1} = 0$ has already been established and (trivially) $N_0 = F_0$. It remains to show that

$$\left[\frac{mp}{q}\right] = [m\tau], \quad m = 1, \ldots, q-1. \tag{19}$$

The golden number satisfies the identities

$$p - q\tau = (-\tau)^{-N}, \tag{20}$$

$$q\tau + r = \tau^N. \tag{21}$$

Let β be the fractional part of mp/q, that is, $mp/q = n + \beta$. For $1 \leqslant m \leqslant q-1$, we have

$$\frac{1}{q} \leqslant \beta \leqslant \frac{q-1}{q}. \tag{22}$$

From equation (20), $m\tau = mp/q - m(-\tau)^{-N}$, so that

$$m\tau = n + \beta', \qquad \beta' = \left(\beta - \frac{m(-\tau)^{-N}}{q}\right). \tag{23}$$

Because we are considering only values of m that satisfy $1 \leqslant m \leqslant q-1$,

$$\beta' > \frac{1}{q} - \frac{q-1}{q}\,\tau^{-N} = \frac{1-(q-1)\tau^{-N}}{q}.$$

However, $q - 1 < q\tau + r = \tau^N$. Therefore $\beta' > 0$. Similarly,

$$\beta' < \frac{q-1}{q}\,(1 - \tau^{-N}) = \frac{q-1}{q}\left(1 + \frac{1}{q\tau + r}\right) = \frac{q-1}{q}\,\frac{q\tau + r + 1}{q\tau + r} < 1.$$

We have now shown that β' in equation (23) satisfies $0 < \beta' < 1$. This establishes the result (19). The Fibonacci approximants to the quasiperiodic stacking sequence are therefore given by equation (18). □

A curious companion to equation (19) is

$$\left[\frac{mp}{q}\right] = [m\tau], \quad m = q+1, \ldots, p. \tag{24}$$

We define β and β' as before. For $m = q+1, \ldots, p$, we can write

$$\frac{mp}{q} = \frac{(q+k)p}{q} = p + \frac{kp}{q}, k = 1, \ldots, r.$$

Since β is the fractional part of kp/q, it satisfies equation (22). The rest of the proof is identical with the proof that we have given for equation (19), but with k in place of m.

Since $\tau^{-1} = \tau - 1$, equation (16) can be written in the alternative form

$$n = m + \left[\frac{m}{\tau}\right]. \tag{25}$$

When written in this form, it is seen to be a particular case of a general formula of Socolar and Steinhardt (1986) for 1D 'tilings' obtainable by the 'strip projection' method from a two-dimensional (2D) lattice. With some change in notation to correspond to the notation of the present work, this formula is

$$x = \rho m + \alpha + [m\sigma + \gamma]. \tag{26}$$

It specifies a set of points on the number line. The variable m is an integer; the other parameters are fixed and may independently be rational or irrational. Changing the parameter α corresponds only to a translation of the pattern or, equivalently, to a change of origin. Changing the parameter γ produces 'phason flips' which, for periodic patterns, have the effect of a translation; the aperiodic patterns have the property that, given two patterns with the same ρ and σ but different γ, any arbitrarily long portion of one of them occurs in the other. We shall, accordingly, set $\alpha = \gamma = 0$. The intervals between two successive values of x are the 'tiles', which are of two lengths (L and S, say). The sequence of L and S values is determined only by σ and is periodic or quasiperiodic according to whether σ is rational or irrational respectively. The ratio of interval lengths is given by

$$L : S = (\rho + [\sigma] + 1) : (\rho + [\sigma]). \tag{27}$$

The lengths are commensurate or incommensurate according to whether ρ is rational or irrational respectively.

The 'standard' 1D quasicrystal (produced by projection of a 2D square lattice on to two orthogonal 1D subspaces) is given by $x = m + \tau^{-1}[m\tau^{-1}]$ (Levine and Steinhardt 1986), or, with a scaling factor,

$$x = m\tau + \left[\frac{m}{\tau}\right]. \tag{28}$$

Observe that this gives a quasiperiodic pattern with incommensurate intervals ($\rho = \tau, \sigma = \tau^{-1}$ and hence $L/S = \tau$), whereas for the quasiperiodic stacking sequence given by equation (25) we obtain the same pattern, but with commensurate intervals ($\rho = 1, \sigma = \tau^{-1}$ and hence $L/S = 2$). Equivalently, $\rho = 0$, $\sigma = \tau$ and $L/S = 2$.

The values $L/S = 2$ for spacing of the (111) planes occupied by transition-metal atoms is of course a consequence of the assumption that the underlying B2 structure is undeformed. In actual τ phases this may not be so. It would be intuitively reasonable to expect a deviation of the actual structures away from this simple geometrical model; the minimum-energy configuration would correspond to a shift of atoms from their ideal positions. (The stacking sequences would be unaffected.) The atomic positions determined by Bradley and Taylor (1937) for the τ_3 phase Al_3Ni_2 give $L/S \approx 2.3$ (corresponding to a shift towards each other of adjacent pairs of filled nickel planes). Ramachandrarao and Laridjani (1974) investigated Al_3Cu_2. The observed diffraction patterns agreed very closely with those calculated on the hypothesis that the atomic positions are the same as those given by Bradley and Taylor (1937). Since the deviations of the positions of atoms from their positions in the simplified model are produced by purely local dynamics, the L/S ratio would not be expected to vary greatly in the different τ phases of a family but may depend on the particular transition metal. Clearly, more experimental data are needed for further elucidation of the detailed structures of these phases.

§7. Iterative generation of the Fibonacci sequences

As is well known, the standard Fibonacci quasiperiodic sequence $F_0F_1F_2\ldots$ can be generated by the iterative rule $0 \to 1$, $1 \to 10$. (Binary sequences generated by formulae of the type given by equation (26), and the iterative rules that generate them, were studied by de Bruijn (1981), before the discovery of quasicrystals.) In other words, applying the iterative rule (rule 1)

$$S_{N+1} = S_N S_{N-1}$$

for generating strings of binary digits, to the starting values $S_0 = 0$, $S_1 = 1$, gives

$$S_N = F_1F_2\ldots F_p. \tag{29}$$

This is a consequence of a remarkable 'quasiperiodicity' property of the sequence defined by equation (17); for any two consecutive Fibonacci numbers q and p, $p > 1$,

$$F_n = F_{n+p}, \qquad n = 1, \ldots, q. \tag{30}$$

Proof: Equation (23) can be written as $[(m+q)p/q] = [(m+q)\tau]$, $m = 1, \ldots, r$. Therefore, for $m = 1, \ldots, r$, $[(m+q)\tau] = [(m+q)p/q] = [mp/q] + p = [m\tau] + p$. From this result, and the definition (17) we deduce that, for $n = 1, \ldots, q, F_n = 1$ if and only if $F_{n+p} = 1$. □

Alternatively, the iterative rule (rule 2)

$$S_{N+1} = S_{N-1} S_N$$

gives

$$S_N = F_{-p}\ldots F_{-1}. \tag{31}$$

At each stage of the iteration, one can arbitrarily apply either rule 1 or rule 2. In this way, an infinite number of iterative procedures can be defined. All these iterative procedures give rise to the same sequence. The various strings of length q obtained after N iterations, from the various iterative procedures, differ only by a cyclic permutation. Infinite sequences obtained in the limit therefore differ only by a translation.

The alternating rule (rule 3)

apply rule 1 or rule 2 according to whether N is even or odd,

generates the sequences $\{p/q\}$:

$$S_N = N_0 \dots N_{p-1} = \{p/q\} \tag{32}$$

The sequences in the abridged notation of van Sande *et al.* (1978), in which 2 and 3 denote the subunits 10 and 110, can be generated from the starting values $S_0 = 2$, $S_1 = 3$, by applying the following rule (rule 4):

apply rule 1 or rule 2 according to whether N is odd or even.

Thus,

$$\begin{gathered}\{2/1\} = 2, \{3/2\} = 3, \{5/3\} = 32, \{8/5\} = 3\,32,\\ \{13/8\} = 332\,32, \{21/13\} = 332\,33232, \dots .\end{gathered}$$

The iterative procedures can of course also be applied to $S_0 = S$, $S_1 = L$, generating directly the sequence of 'tiles' or intervals.

§8. Generation of non-Fibonacci sequences

The Fibonacci family of sequences $\{p/q\}$ with q and p being successive terms in the Fibonacci sequence, accounts for the stacking order of many of the τ phases. However, as discussed in § 5, quite a few τ phases have been observed that do not belong to this family. Their observed sequences, however, are all characterized by having no subunits 111 or 00 and hence can be denoted in the abridged '32' notation of van Sande *et al.* (1978). Exploration of the actual sequences $\{p/q\}$ generated by equations (5) and (6) reveals that all known τ phases are of this type, with $3/2 \leqslant p/q \leqslant 2$. The following list gives all allowed non-Fibonacci $\{p/q\}$ sequences up to $p = 29$:

$\{7/4\} = (32)2$, $\{9/5\} = (32)2^2$, $\{11/6\} = (32)2^3$, $\{11/7\} = 3(332)$,
$\{12/7\} = (32)^2 2$, $\{13/7\} = (32^4)2$, $\{14/9\} = 3^2(332)$, $\{15/8\} = (32)2^5$,
$\{16/9\} = (32)2(32)2^2$, $\{17/9\} = (32)2^6$,

$\{17/10\} = (32)^3 2$, $\{17/11\} = 3^3(332)$, $\{18/11) = 332(32)^2$, $\{19/10\} = (32)2^7$,
$\{19/11\} = (32)^2 2(32)2$, $\{19/12\} = 3(332)^2$, $\{20/11\} = (32)2^2(32)2^3$,
$\{20/13\} = 3^4(332)$,

$\{21/11\} = (32)2^8, \{21/13\} = (332)^2 32, \{22/13\} = (32)^4 2, \{23/12\} = (32)2^9,$

$\{23/13\} = (32)2(32)2(32)22, \{23/14\} = 332(32)^3, \{23/15\} = 3^6(32),$

$\{24/13\} = (32)2^3(32)2^4,$

$\{25/13\} = (32)2^{10}, \{25/14\} = (32)2^2(32)2(32)2^2, \{25/16\} = 3^2(332)3(332),$

$\{26/15\} = (32)^2(32)2(32)2, \{26/17\} = 3^6(332), \{27/14\} = (32)2^{11},$

$\{27/16\} = (32)^5 2, \{27/17\} = 3(332)^3, \{28/15\} = (32)2^4(32)2^5,$

$\{28/17\} = (332)(32)^4, \{29/15\} = (32)2^{12}, \{29/16\} = ((322)2)^3 2,$

$\{29/17\} = (32)^3 2(32)^2 2, \{29/18\} = (332)^3 32, \{29/19\} = 3^7(332).$

It turns out that families of $\{p/q\}$ sequences exist, generated by the iterative procedures (rule 3 or 4) of § 7. For example taking $S_0 = \{8/5\}$ and $S_1 = \{5/3\}$ and denoting these strings by the symbols 8 and 5, and applying rule 3, we obtain, successively, $\{8/5\} = 8$, $\{5/3\} = 5$, $\{13/8\} = 85$, $\{18/11\} = 855$, $\{31/19\} = 85\,855$, $\{49/30\} = 85855\,855, \ldots$. The first five members have all been observed as stacking sequences of τ phases. The non-Fibonacci τ_{31} was reported by Amelinckx *et al*. (1990). Their τ_{38} belongs to a family that begins

$$\{5/3\} = 5, \{33/20\} = 85^5, \{38/23\} = 85^6, \{71/43\} = 85^6 85^5, \ldots .$$

Frangis *et al*. (1989, 1990) have extensively investigated alloys that have structures analogous to those of the τ phases. They are, like the τ phases, modulated B2 structures, with characteristic stacking sequences along a [111] axis, but the binary sequences are composed of two kinds of atom, rather than of atoms and vacancies. The sequences have been observed to be built from units of length 5 and 7, of the form 10101 and 1010101. Denoting $\{7/4\} = 332$ by 7 and $\{5/3\} = 32$ by 5 and applying rule 4, we obtain the family $\{7/4\} = 7$, $\{5/3\} = 5$, $\{12/7\} = 57$, $\{17/10\} = 557$, $\{29/17\} = 557\,57$, $\{46/27\} = 557\,55757, \ldots$. These stacking sequences are (apart from irrelevant cyclic permutations corresponding to translation of the infinite periodic sequences) precisely those observed by Frangis *et al*.!

It should be remarked that these remarkable families of $\{p/q\}$ sequences (and many others) have been found empirically by examining the sequences belonging to the first few members of these families. We have no mathematical proof that the iterations would continue to yield $\{p/q\}$ sequences; that is a conjecture.

§ 9. Concluding remarks

The predominance of the irrational number τ in the metric properties of quasicrystals exhibiting fivefold or tenfold symmetry is not a mystery; the structures are built in various ways from clusters with icosahedral symmetry; the irrational number τ is the length of the diagonal of a regular pentagon of unit edge length, and the circumradius of a regular decagon of unit edge length. The occurrence, in the structure of the ‘approximants’ associated with these quasicrystals of the rational fractions p/q, where p and q are consecutive terms in the Fibonacci sequence 1 1 2 3 5 8 ... comes from the fact that the limit of these fractions is τ.

The reason for the occurrence of the Fibonacci numbers in the τ phases is not clear. (It is a surprising coincidence that Lu and Chang called them the 'τ phases' before this was recognized.) As we have shown, the Fibonacci-type τ phases can arise as approximants to a 1D trigonal quasicrystal produced by growth along a $[11\bar{\tau}]$ direction of the underlying cubic lattice. Perhaps this is a clue, but it is not apparent why this particular direction should be favoured. It is perhaps not entirely irrelevant to note another quite different context in which Fibonacci numbers occur in nature: in the arrangements of leaf buds and florets in many plant species. A completely satisfactory explanation has proved elusive, although there has been much theoretical speculation (it is essentially a problem of optimal close packing of similar units). It seems unlikely, but not inconceivable, that the two problems are related.

The standard '1D quasicrystal' (known to date only as a substructure of 2D and 3D patterns with fivefold symmetries) is characterized by an 'L/S ratio' equal to τ. In the vacancy-ordered phases discussed here, fivefold symmetry is not present. However, it is interesting to note that approximations to pentagonal and icosahedral structures in the B2 structure have been pointed out by Dong (1995, 1996) and Dong *et al.* (1999) who have explored reasons for regarding B2 structures as 'approximants' to quasicrystals. Zhang and Kuo (1989) have observed that the τ phases can occur in conjunction with decagonal quasicrystalline phases, with a surprising (and mysterious) orientation relation between the two phases: the tenfold axis and two perpendicular diads of the decagonal phase are aligned with [110], [001] and $[1\bar{1}0]$ of the underlying B2 structure of the τ phase.

The simple systematic iterative generation of the stacking sequences, and the alternating sequence of filled and empty lamellae parallel to the $(rr\bar{q})$ planes, are probably also clues to the nature of the dynamic processes that produce the vacancy-ordering characteristic of the τ phases.

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