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LETTER TO THE EDITOR

On the equivalence of ANNNI model polytypes formed by square wave modulation and branching mechanisms

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Abstract. It is proved that long-period structures formed by a square wave modulation of a lattice are identical to those of stable phases found in the ANNNI model. The proof is based on a continued fraction expansion of the modulation half period, producing structural formulae shown to be equivalent to those obtained by a structure-combination branching process. The same structures have been observed experimentally by high-resolution transmission electron microscopy in certain ordered alloys.

In order to interpret certain x-ray diffraction patterns of ordered alloys featuring satellite reflections, Fujiwara (1957) proposed that the crystal structure was *modulated* by a periodic function $f(x)$, in which the coordinate x represented a continuous variable in the (crystallographic) direction of the observed long-wavelength modulation. In particular, Fujiwara showed that a square wave modulation could account quite well for both the positions and relative intensities of the satellite reflections. The modulation wavelength was written as $\Lambda = 2Ma_0$, the number M thus representing the half wavelength expressed in units of the lattice parameter a_0 in the direction of the modulation. Actually, it is not necessary for the $f(x)$ profile to be a sharp square wave: it suffices for the zeros of the modulating function to be equidistant on the x axis, a property which Fujiwara described as that of *uniform mixing*, as explained elswhere (de Fontaine and Kulik 1984, henceforth to be referred to as FK). A more proper condition on $f(x)$ is that it posess a Fourier spectrum containing only odd harmonics. For simplicity, however, we shall continue to refer to that class of modulations as 'square wave'; the set of all such modulations of half period $M = P/Q$ (where P and Q are relative primes) will be denoted by the symbol S_q. The numerator P, or *commensuration number* (FK), is seen to be equal to the number of lattice planes between two successive *commensurations*, where the lattice and the modulation are in step; the denominator Q is then equal to the number of half periods of the modulation within an interval of P planes.

Figure 1(a) illustrates the effect of a square wave modulation of half-period $M = \frac{8}{5}$ on a lattice. The open and closed symbols may represent, respectively, (predominantly) positive (spin up) and negative (spin down) lattice plane magnetisation, or A-rich and B-rich planes in a binary AB alloy, or positive and negative antiphase shifts if the lattice planes have two-dimensional order (FK) etc. It is seen that the modulation creates a *polytype* of the original structure, with new unit cell of lattice parameter Pa_0 if Q is even and twice that if Q is odd. The commensuration number P is here equal

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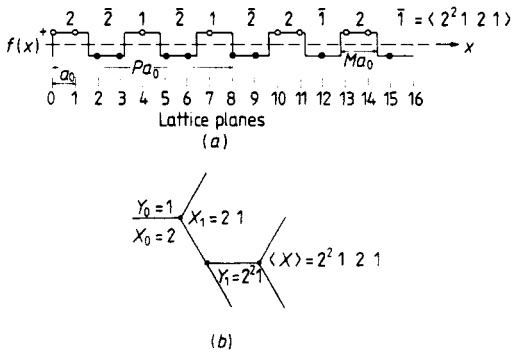

Figure 1. Fujiwara phase $\langle 2^2121\rangle$: (*a*) square wave modulation $f(x)$ of period $2Ma_0$, with polytype period $2Pa_0$ where a_0 is the (unmodulated) lattice parameter; (*b*) equivalent graph of corresponding structure-combination branching process, with partial domains X_i, Y_i determined by continued fraction expansion algorithm.

to 8. The *structural formula* for this polytype is indicated just above the modulation profile in figure 1(*a*), and written in shorthand notation as $\langle 2^2121\rangle$, a notation pioneered by Fisher and Selke (1981).

Polytypes resulting from the set of S_q modulations were called *Fujiwara phases* (FW) in FK. In that paper, it was shown that the corresponding structural formulae could be derived by a *continued fraction algorithm*, proposed independently by Hubbard (1978) and by Pokrovsky and Uimin (1978) in a quite different context. The algorithm, in the notation of FK, is as follows: one first expands the half period M in a continued fraction

$$M = \frac{P}{Q} = n_0 + \cfrac{\gamma_0}{n_1 + \cfrac{\gamma_1}{n_2 + \cfrac{\gamma_2}{\ddots \; n_{k-1} + \cfrac{\gamma_{k-1}}{n_k}}}}. \tag{1}$$

Since M can be approximated as closely as desired by the rational fraction P/Q, the continued fraction expansion must terminate at some level, say k. At any intermediate level i, the integers n_i are determined uniquely by the remainder (r) at level $i-1$:

$$1/r_{i-1} = n_i + \gamma_1 r_i \tag{2}$$

with

$$-\tfrac{1}{2} < r_i \leqslant +\tfrac{1}{2} \tag{3}$$

so that

$$\gamma_i = r_i/|r_i| = \pm 1. \tag{4}$$

Now define the sequences $\{X\}$ and $\{Y\}$ by the recursion formulae

$$X_0 = n_0, \qquad Y_0 = n_0 + \gamma_0, \tag{5a, b}$$

$$X_i = (X_{i-1})^{n_i - 1} Y_{i-1} \qquad (5c)$$

$$Y_i = (X_{i-1})^{n_i + \gamma_i - 1} Y_{i-1} \qquad (i = 1, 2, \ldots, k-1). \qquad (5d)$$

The formula for polytype of half period M is then

$$\langle X \rangle = X_k. \qquad (6)$$

At any level $0 < i < k$, X_i and Y_i will be called *partial domains*; X_0 and Y_0 will be called *majority* and *minority domains*, respectively. The set of polytypes whose structural formulae result from the application of the above algorithm will be designated as the C_f set. Since the sets S_q and C_f have been shown elsewhere (FK) to be identical, both S_q and C_f polytypes may be called FW phases.

Thus far, the description of FW phases has been purely geometrical. However, in a remarkable paper, Fisher and Selke (1981) showed that such structures could well result from a statistical mechanical model, the so-called *axial next-nearest neighbour Ising* (ANNNI) *model.* In particular, these authors showed that a low-temperature expansion of the exact free energy yielded (rigorously) stable phases of structural formulae $\langle 2^j 3 \rangle$, provided that the ratio of next-nearest ($J_2 < 0$) to nearest ($J_1 > 0$) neighbour interactions in the axial direction were greater than $\frac{1}{2}$ in magnitude. A change of sign of J_1 (antiferromagnetic) produced structures of the type $\langle 2^j 1 \rangle$, stable at low temperatures (FK). More generally, it appears (FK) that a scheme of interactions J can always be found which will yield stable low-temperature polytypes of structural formulae $\langle X_0^j Y_0 \rangle$, where X_0 and Y_0 are, respectively, the 'majority' and 'minority' domains defined above. These phases have been called FS phases, for short (FK); they are FW phases resulting from a continued fraction expansion terminating at level one.

Fisher and Selke (1981) also mentioned that, at higher temperatures, the common boundary between two successive FS phases, say $\langle 2^j 3 \rangle$ and $\langle 2^{j+1} 3 \rangle$, may become unstable and split to produce the intermediate phase $\langle 2^j 32^{j+1} 3 \rangle$. In later papers, Duxbury and Selke (1983) and Selke and Duxbury (1984) showed, by mean-field calculations, that higher-temperature stable phases could indeed result from, as they put it, a *structure-combination branching process.* The set of structures derived in this manner will be denoted as the B_r set, for short. The purpose of this communication is to prove the equivalence of C_f and B_r mechanisms:

$$C_f \rightleftarrows B_r \qquad (7)$$

In each direction, the proof will be carried out by induction.

First note that the branching process in question can be represented by a graph, in fact by a (*rooted*) *tree* (figure 2). A particular structural formula, say $\langle X \rangle = X_k$, must be found at some branching point, or *node* of the tree, from which the path to the 'root' is unique. That path may be regarded as the 'trunk' of the tree, with 'branches' springing 'right' and 'left'. Any two successive branches may lie either on the same side of the trunk (parallel configuration), or on opposite sides (anti-parallel configuration), as illustrated by branches at points t and u in figure 2(b) and (a), respectively. Assignment of domain symbols X and Y to interbranch regions of the graph will turn out to depend on the nature of the branching, parallel or antiparallel.

Let us prove that any C_f structure can be obtained by a B_r process. Assume that partial domains X_{i-1} and Y_{i-1} have been obtained correctly by the appropriate branching tree. For arbitrary integer l (>1), it is clearly possible to produce the formula $x_{i-1}^{l-1} Y_{i-1}$ by successive parallel branchings, as shown in figure 2, nodes p to s. The next two domains beyond points s and t, which we wish to relabel X_i and Y_i, must

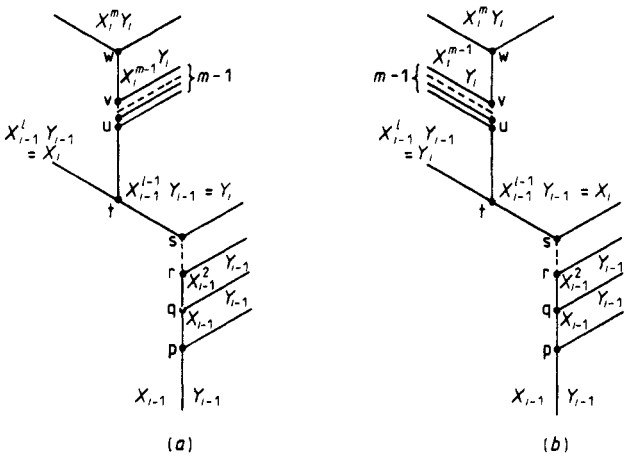

Figure 2. Sub-trees used in proof of equivalence of C_f and B_r processes: (a) antiparallel branching at (t, u); (b) parallel branching at (t, u).

result from antiparallel branching (otherwise we would simply go on raising the 'power' l). One alternative, $X_{i-1}{}^{l-1}Y_{i-1} = Y_i$, $X_{i-1}{}^{l}Y_{i-1} = X_i$, corresponding to $\gamma_i = -1$ in equation ($5d$), is then obtained by branching at point u in antiparallel fashion (figure 2(a)), the opposite alternative, corresponding to $\gamma_i = +1$, is graphed by branching at u in parallel fashion (figure 2(b)). Arbitrarily high 'powers' of X_i can then be obtained by successive parallel branchings beyond node u, to reach, at w, the desired structural formula for level i: $X_i{}^m Y_i$. Assignment of symbols X_{i+1} or Y_{i+1} to that domain proceeds in a like manner. Since the procedure is obviously valid for transition from level 0 to 1 (producing FS phase $\langle X_0{}^j Y_0\rangle$), the $C_f \rightarrow B_r$ part of the proof is completed.

We now prove the converse: that any 'structure-combination branching process' gives rise to structural formulae conforming to the continued fraction algorithm. Assume that interbranch regions of the representative graph have been correctly labelled by X and Y symbols up to level $i-1$. Beyond that level, arbitrary branching processes can be represented in all generality by a succession of sub-trees of the types illustrated in figure 2. Parallel branching from point p to s unambiguously leads to the strucutral formula $X_{i-1}{}^{l-1}Y_{i-1}$ at s. Since antiparallel branching occurs at (s, t), resulting domains must be relabelled, the choice of symbols X_i or Y_i depending on the type of branching at (t, u). If the latter branching is antiparallel, Y_i must be located at s, and X_i at t, from consecutive antiparallel branching, yielding formula X_iY_i, can be lifted by parallel, labelling of domains must be inverted, and $\gamma_i = +1$ (figure 2(b)). Thus, it is seen that structural formulae of the C_f set can be assigned unambiguously to interbranch regions of an arbitrary sub-tree from level $i-1$ to i. The ambiguity which may result from consecutive antiparallel branching, yielding formula X_iY_i, can be lifted by adopting the convention embodied in inequalities (3). Since the process just described is obviously valid in going from level 0 to 1, the $B_r \rightarrow C_f$ part of the proposition is proved. Hence, the complete bijection (7) is proved. As an example, consider the FW polytype $\langle 2^2121\rangle$, pictured as a square wave modulation in figure 1(a). Its continued fraction expansion is

$$M = \tfrac{8}{5} = 2 - 1/(2 + \tfrac{1}{2}),$$

with partial domains X_i, Y_i $(i = 0, 1, 2)$ shown in the equivalent graph of figure 1(*b*), in complete agreement with the results of the continued fraction algorithm.

By this proof, and the one given in Appendix 1 of FK, it is thus established that polytypes resulting from (a) the square wave modulation mechanism S_q, (b) the continued fraction algorithm C_f, and (c) the structure-combination branching process B_r are identical. The practical significance of this result is that structural formulae which were introduced for the purpose of explaining certain diffraction patterns from long-period superstructures in ordered alloys are precisely the ones which also minimise the free energy of the ANNNI model. Added confirmation is provided by high-resolution transmission electron microscopy on, for instance, Ag_3Mg alloys with periodic anti-phase boundaries (Portier *et al* 1980). In these alloys, polytype structures can be analysed directly in real space: FS phases $\langle 2^j 1 \rangle$ are clearly seen, possibly also more general FW phases. Furthermore, since the low-temperature expansion of Fisher and Selke (1981) can be extended to the face-centred cubic lattice, a very good case indeed can be made for direct application of the ANNNI model to certain classes of long-period superstructures in ordered alloys: diffraction evidence, direct structure analysis, and statistical mechanics all converge to produce the same set of structural formulae, that of the *Fujiwara phases* (FW).

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