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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.

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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 zeroes of the modulating function to be equidistant on the \( x \) axis, a property which Fujiwara described as that of uniform mixing, as explained elsewhere (de Fontaine and Kulik, 1984; henceforth to be referred to as FK, for short). A more proper condition on \( f(x) \) is that it possess 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 \( M = 8/5 \) 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 $P_a$ if $Q$ is even and twice that if $Q$ is odd. The commensuration number $P$ is here equal to 8. The structural formula for this polytype is indicated just above the modulation profile in Fig. 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 formulas 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

$$M = \frac{P}{Q} = n_0 + \frac{1}{n_1 + \frac{1}{n_2 + \frac{1}{\ldots + \frac{1}{n_{k-1} + \frac{1}{n_k}}}}}$$

(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 $i-1$:

$$\frac{1}{r_{i-1}} = n_i + \frac{1}{r_i}$$

(2)
with
\[-1/2 < r_i \neq 1/2\] (3)
so that
\[\gamma_i = r_i/1r_i1 = \pm 1\] (4)
Now define the sequences \(\{X\}\) and \(\{Y\}\) by the recursion formulas
\[X_0 = n_0\] (5a)
\[Y_0 = n_0 + \gamma_0\] (5b)
\[X_i = (X_{i-1})^{n_i-1} Y_{i-1}\] (5c)
\[Y_i = (X_{i-1})^{n_i+\gamma_i-1} Y_{i-1}\] (5d)
The formula for polytype of half-period \(M\) is then
\[\langle X \rangle = X_k\] (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 formulas 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 Neighbor 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 \(\langle 2^13^2 \rangle\), provided that the ratio of next-nearest \((J_2<0)\) to nearest \((J_1>0)\) neighbor interactions in the axial direction were greater than 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 \( \langle 2^j 3 2^{j+1} 3 \rangle \). In later papers, Duxbury and Selke (1984) 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:

\[
C_f \uparrow B_r
\]

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 (Fig. 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 Fig. 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 $\ell$ (>1), it is clearly possible to produce the formula $X_{i-1}^{\ell-1}Y_{i-1}$ by successive parallel branchings, as shown in Fig. 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 result from antiparallel branching (otherwise we would simply go on raising the "power" $\ell$). One alternative, $X_{i-1}^{\ell-1}Y_{i-1} = Y_i$, $X_{i-1}^{\ell}Y_{i-1} = X_i$, corresponding to $\gamma_i = -1$ in Eq. (5d), is then obtained by branching at point $u$ in antiparallel fashion (Fig. 2a), the opposite alternative, corresponding to $\gamma_i = +1$, is graphed by branching at $u$ in parallel fashion (Fig. 2b). 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 $i$: $X_i Y_i$. 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 $<X_0 Y_0>$), 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 formulas conforming to the continued fraction algorithm. Assume that interbranch regions of the representative graph have been correctly labeled 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 Fig. 2. Parallel branching from point p to s unambiguously
leads to structural formula $X_{i-1}^{2-1}Y_{i-1}$ at $s$. Since antiparallel branching occurs at $(s,t)$, resulting domains must be relabeled, 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 which it is concluded that $\gamma_i = -1$ (Fig. 2a). Conversely, if the branching is parallel, labeling of domains must be inverted, and $\gamma_i = +1$ (Fig. 2b). Thus, it is seen that structural formulæ of the $C_4$ 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 $X_i Y_i$, 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 $B_r + C_4$ part of the proposition is proved. Hence, the complete bijection (7) is proved. As an example, consider the FW polytype $<22121>$, pictured as a square wave modulation in Fig. 1 (a). Its continued fraction expansion is

$$M = 8/5 = 2 - 1/(2 + 1/2)$$

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

By this proof, and the one given in Appendix I of FK, it is thus established that polytypes resulting from (a) the square wave modulation mechanism $S_q$, (b) the continued fraction algorithm $C_4$, and (c) the structure-combination branching process $B_r$ are identical. The practical significance of this result is that structural formulæ which were introduced for the purpose of explaining certain diffraction patterns from long-period superstructures in ordered alloys are precisely the ones which also minimize the free energy of the ANNNI model. Added confirmation is
provided by high-resolution transmission electron microscopy on, for instance, Ag$_3$Mg alloys with periodic antiphase boundaries (Portier et al., 1980). In these alloys, polytype structures can be analyzed directly in real space: FS phases ($2^1$) 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-centered 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 formulas, that of the Fujiwara phases (FW).

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References

de Fontaine D and Kulik J 1984 to be published


Fisher M E and Selke W 1981 Proc. R. Soc. A 302 1


Selke W and Duxbury P M 1984 to be published in Z. Physik B
Figure Captions

Figure 1. Fujiwara phase $<2\bar{1}21>$: (a) square wave modulation $f(x)$ of period $2M_0$, with polytype period $2P_0$, 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.

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 $(t,u)$. 
Figure 1.

(a) Lattice planes

(b) 

$Y_0 = 1$

$X_0 = 2$

$X_1 = 2^{\frac{1}{2}}$

$Y_1 = 2^{2^{1}}$

$\langle X \rangle = 2^{2^{1}} 2^{1}$

$f(x) \sim \frac{1}{x}$

$b^x$
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