Possible disordered ground states for close-packed polytypes and their diffraction patterns

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Abstract

It has recently been shown that one-dimensional Ising problems can have degenerate, disordered ground states (GSs) over a finite range of coupling constants, i.e., without ‘fine tuning’. The disorder is however of a special kind, consisting of arbitrary mixtures of a short-period structure and its symmetry-degenerate partner or partners. In this exploratory study, we assume that the energetics of close-packed polytypes can be represented by an Ising Hamiltonian (which includes, in principle, all terms allowed by symmetry), and that (for simplicity) the close-packed triangular layers are unfaulted and monatomic. We then calculate the diffraction patterns along the stacking direction for the various possible kinds of disordered GSs. We find that some disordered GSs give diffraction patterns which are only weakly distinguished from their periodic counterparts, while in others the disorder is more clearly evident beneath the delta functions. Finally, in some cases, the long-ranged order of the layers is destroyed by the interference among the short-period structures and their symmetry-related partners, giving a diffraction spectrum which is purely continuous.
I. INTRODUCTION

For one dimensional $k$–state models it is known that the ground state is ‘almost always’ periodic. Radin and Schulman [1] showed that, for such models, any nondegenerate ground state is periodic, and that, for the degenerate case, there always exists at least one periodic ground state. In each case the period is at most $k^r$ where $r$ is the range of interaction. For $k = 2$ (Ising model) Teubner [2] obtained the same results using the directed graph $G_k^{(k)}$ (called the de Bruijn diagram after N. G. de Bruijn’s paper [3]). Recently Canright and Watson (CW) [4] considered the mathematically ‘exceptional’ (but physically unexceptional) case of Hamiltonians constrained by symmetry. CW showed that, for many values of $k$ and $r$, the restriction to symmetric Hamiltonians leads to the possibility of degenerate and disordered GSs over a finite fraction of coupling-parameter space. (This finite fraction is of course negligible in the higher-dimensional space of all possible Hamiltonians, unconstrained by symmetry.) That is, if one allows the physically unexceptional ‘fine tuning’ of parameters arising from symmetry, then in most cases one can find degenerate and disordered GSs without any further fine tuning of parameters. The disorder arises since, in such cases, there are degenerate periodic states (phases) such that the energy of a domain wall between the degenerate phases is zero. Hence any arbitrary (and so in general aperiodic) mixture of the degenerate states is also a ground state.

Such ground states have a finite entropy per spin, and so suggest the possibility of (weak) exceptions to the third law of thermodynamics [5]. It is therefore of interest to inquire whether CW’s theoretical results may be applied to any real physical systems. Here we consider close-packed polytypes [6], which are well modeled as classical Ising ($k = 2$) chains. As a first step in the study of this special kind of one-dimensional disorder, we examine in this paper the possible kinds of diffraction patterns (along the stacking axis) for the disordered GSs found by CW. Our goal is to try to see how the constrained disorder described above (ie, mixtures of two distinct stacking sequences which are related by symmetry) may be realized in the experimentally accessible form of the diffraction pattern.
II. DIRECTED GRAPHS

Our approach, like that of CW, relies on the representation of a Hamiltonian \( H_r^{(k)} \) (with \( r \) the range of interaction, and \( k \) the number of states per site) as a directed graph \( G_r^{(k)} \). Hence, in this section, we provide a brief description of this representation, including the modifications introduced by CW to represent the effects of symmetry.

From here on we will restrict our attention on the Ising model \((k = 2)\), and so drop the superscript \( k \) everywhere. An infinite Ising chain with interaction range \( r \) can be viewed as a successive sequence of spin configurations, each of length \( r \). There are \( 2^r \) such configurations; these become the nodes \((\mathcal{N})\) of the graph \( G_r \). To complete the graph, two nodes \( \mathcal{N}_1 = \sigma_1...\sigma_r \) and \( \mathcal{N}_2 = \sigma'_1...\sigma'_r \) are connected by an arrow (directed arc) only if the last \((r - 1)\) spins of \( \mathcal{N}_1 \) are identical to the first \((r - 1)\) spins of \( \mathcal{N}_2 \). This arc then represents a transition \( \mathcal{N}_1 \rightarrow \mathcal{N}_2 \), effected by the addition of the spin \( \sigma'_r \) to the chain (which we imagine as growing from the left). The \( 2^r \) nodes in \( G_r \) are thus connected by \( 2^r+1 \) arcs, each of which can be labeled with \((r + 1)\) sequential spin values. The graph \( G_r \) then represents the Hamiltonian \( H_r \) as follows. A unique weight (energy cost resulting from adding a spin \( \sigma'_r \) to the chain) can be associated with each arc. Any infinite Ising chain of spins can be then represented as a path through the graph \( G_r \), with the energy of the chain being simply the sum of the energies (weights) of the arcs in the path. Since the graph has a finite number of nodes, any infinite path must visit at least one node more than once; hence, ignoring boundary effects, such a chain must be a closed cycle in \( G_r \). Furthermore, if we define a simple cycle (SC) as a non-decomposable (ie, non-self-intersecting) cycle, then all the cycles in \( G_r \) can be uniquely decomposed into SCs.

The general periodicity of the ground state can now be understood in terms of SCs. The ground state is the repetition of that SC which has the minimum energy per spin, and the period of any SC is \( \leq 2^r \) (the number of nodes of \( G_r \)). In the case that the parameters in \( H_r \) are ‘fine tuned’ to precise values (as can occur from symmetry), there can be more than one SC with the least energy per spin in the graph \( G_r \)—that is, there can be degenerate
ground states which are related by symmetry. We are interested here in the two symmetries $S$ (spin inversion) and $I$ (space inversion). These symmetries force the degeneracy of pairs of SCs in $G_r$. Now assume that such a pair has the lowest energy per spin. If these two minimal-energy SCs share a node, then the GS is infinitely degenerate, since it includes arbitrary mixtures of the two SCs. If on the other hand they do not share any nodes, it is evident that jumping from one cycle to another costs energy, and so gives a configuration which is not a GS. CW found that the former case (infinitely degenerate GS, arising from a pair of minimal-energy SCs which share a node or nodes) occurs for many values of $k$ and $r$, assuming only $S$ or $I$ symmetry. We will follow their terminology and call such a pair a ‘D-pair’. That is, a D-pair is a pair of SCs in $G_r$ which (i) can be minimal-energy configurations for a range of parameter values in $H_r$; (ii) are related by symmetry and hence degenerate; (iii) share one or more nodes.

For the Ising model (more precisely for even $k$) CW found that $S$ symmetry alone never gives rise to disordered ground states (D-pairs). For the case of $I$ symmetry, CW showed that (again for $k = 2$) D-pairs do exist, but only for $r \geq 5$. Combining the two symmetries (denoted $S + I$ symmetry), CW found that the Ising case has D-pairs only for $r \geq 6$.

These results may seem somewhat surprising, from the following point of view. It is easy to find SCs of the graph $G_r$ which are related by symmetry and hence satisfy (ii) above, while also satisfying (iii). Hence one might think that D-pairs should be ubiquitous. However, it turns out that the imposition of symmetry often makes satisfaction of (i) impossible, even as it enforces (ii), for a pair of SCs. Hence CW turned to modified graphs $X G_r^{(k)}$ (where $X$ is the symmetry $S$, $I$, or $S + I$) whose SCs always satisfy (i). For the polytype problem we will concentrate on $S + I G_r$.

The graph $S + I G_r$ is most readily constructed (for details see CW) by first operating on $G_r$ with $S$ (giving $S G_r$), and then operating on the latter with $I$. Similarly, a SC of $S + I G_r$ is mapped to its counterparts in $G_r$ by reversing this sequence: first undoing $I$ (hence ‘unfolding’ the SC into $S G_r$), then undoing $S$. This unfolding of a SC of $S + I G_r$ will yield one, two, or more generally four SCs of $G_r$. We are interested in those SCs of $S + I G_r$ which,
upon unfolding, yield multiple node-sharing cycles. Although the precise identification of distinct pairs may be complicated by the simultaneous presence of two symmetries, such unfolded cycles are the analogs of the D-pairs identified by CW; we will use the same term for these (multiple, unfolded) cycles in $G_r$.

It is useful to classify the D-pairs into topological types. CW found two topological SCs of any graph of the form $I^r G$ (which includes $S^r I G_r$) which represent D-pairs in $G$. Expansion of one type gives any of four topologically different types (I-IV) of D-pairs in $G_r$ (Fig. 1). Expansion of the other type (which is found in $S^r I G_r$ only for $r \geq 8$) yields either a type IV or type V D-pair in $G_r$.

Let us briefly describe the five types of D-pairs. First we may have a type I D-pair in which a cycle $\text{cyc}$ shares the node $\mathcal{N}$ with its $I$ symmetry partner $\overleftarrow{\text{cyc}}$ [Fig. 1(a)]. A type II D-pair is composed of $\text{cyc}$ and its $SI$ symmetry partner $\overleftarrow{\text{cyc}}$ sharing a node $\mathcal{N}$ [Fig. 1(b)]. Both type I and II D-pairs are always accompanied by another D-pair, related to the first by $S$ symmetry (hence sharing the node $\overleftarrow{\mathcal{N}}$). Taking the length of the cycle $\text{cyc}$ (in the Ising or ‘01’ representation—see below) to be $T_{01}$, and assuming a random mixture of the two node-sharing cycles, we get the entropy $[7]$ of types I and II as $\ln 2$ per $T_{01}$ layers.

Fig. 1(c) and 1(d) shows type III and IV D-pairs. We can think of these types as a pair of cycles, which however share two nodes: $\mathcal{N}$ and $\overleftarrow{\mathcal{N}}$ for type III, and $\mathcal{N}$ and $\overleftarrow{\mathcal{N}}$ for type IV. It is clear from the figures that four distinct (but degenerate) cycles may be formed from a type III or IV D-pair. Hence the entropy for these is $\ln 4$ per $T_{01}$ layers.

In general, as with types I and II, types III and IV D-pairs imply the existence of other D-pairs, related by $S$. However such general (asymmetric) D-pairs only occur for $r \geq 8$ — a range which we have not studied systematically. Hence we have instead shown the symmetric cases, for which $S(D\text{-pair}) = D\text{-pair}$. Such a symmetric pair will give cycles with period $T_{01}$ which is twice that of the ‘folded’ D-pair in $S^r I G_r$ (hence even). These symmetric type III and IV D-pairs map to themselves under either $S$ or $I$; hence [unlike Fig. 1(a) and 1(b)] there are not other pairs implicit in Fig. 1(c) and 1(d).

In a type V [Fig. 1(e)] D-pair, all four symmetry related nodes $\mathcal{N}, \overleftarrow{\mathcal{N}}, \overline{\mathcal{N}}, \overline{\overleftarrow{\mathcal{N}}}$ are shared.
as shown. Again, there are no other implicit pairs. Since there are two choices of path at each shared node, there are \(2^4 = 16\) cycles (again, all degenerate) represented by a type V D-pair, giving \(S = \ln 16 = 4 \ln 2\) per \(T_{01}\) layers.

We note here that, besides the entropy, we can quantify the complexity of the kinds of GS under study. Here we will use the definition of Crutchfield and Young [8], which is trivially computed for our D-pairs, since it relies upon the representation of chains as probabilistic, finite-state automata. Thus we take the complexity as \(C = -\sum p_n \ln(p_n)\), where \(n\) runs over the nodes of the automaton (D-pair), and \(p_n\) is the node probability. We can easily obtain a general expression for \(C\) for all the types of D-pair in Fig. 1, as follows. Let \(n_s\) be the number of shared nodes in the D-pair (1 for types I and II, 2 for types III and IV, and 4 for type V), and let \(n_u = 2(T_{01} - n_s)\) be the number of unshared nodes. Then \(p_s = 1/T_{01}\) and \(p_u = 1/(2T_{01})\). Thus the complexity of a D-pair is \(C_D = \ln(2T_{01}) - \frac{n_s}{T_{01}} \ln 2\), which exceeds the complexity \(C_{per} = \ln(T_{01})\) of a periodic chain of the same \(T_{01}\) by \(C_D - C_{per} = \ln 2(1 - \frac{n_s}{T_{01}})\).

Hence we see that a D-pair is less complex, by this definition, than a periodic chain of period \(2T_{01}\); but its entropy is higher.

We wish to compute and study the diffraction patterns for these five types of D-pairs. To do this we will translate Ising spin configurations into an \(ABC\)-sequence of close-packed layers, using the standard mapping between the two, as follows. Any pair in the sequence \(A \rightarrow B \rightarrow C \rightarrow A\) is denoted by 1 (or +, in Hägg’s notation [9]); and a pair from the sequence \(A \rightarrow C \rightarrow B \rightarrow A\) is a 0 (−).

We next introduce some notation, using an example for clarity. One D-pair from \(S^{+I}G_6\), for example, consists of \(\text{cyc} = (0010111)\) (with Zhdanov symbol [10] \(\text{cyc} = (2113)_3\)) and its \(SI\)-symmetry partner \(\overleftarrow{\text{cyc}} = (0001011)\). (The shared node is 001011.) If the number of 1’s and 0’s in a cycle is denoted by \(n_1\) and \(n_0\), a parameter \(\Delta\) can be defined by \(\Delta \equiv (n_1 - n_0) \pmod{3}\). Hence a cycle with \(\Delta = 0\), if repeated periodically, gives a hexagonal polytype, while one with \(\Delta = \pm 1\) gives a rhombohedral polytype. The example shown above has \(\Delta = 1\), and, as one may notice, the cycle does not complete a period in \(ABC\) notation: The cycle is mapped to \((ACBCBCA)(B\ldots)(C\ldots)\) (starting from \(A\)). This reflects the fact that
the rhombohedral polytypes must be repeated three times to complete the hexagonal unit cell \( \mathbb{H} \) (as indicated by the subscript 3 in the Zhdanov symbol). It is convenient to define two different periods \( T_{01} \) and \( T \): \( T_{01} \) is the period of a cycle in 01 notation, and \( T \) in ABC notation. Thus \( T = T_{01} \) for \( \Delta = 0 \) and \( T = 3T_{01} \) for \( \Delta = \pm 1 \).

As noted above, both \( S \) and \( I \) are good symmetries of the Ising model as applied to polytypes. We now want to address how these operators, defined in 01 notation, appear in the (somewhat more physical) \( ABC \) notation. We will use a different example, a SC cyc = (101000001) (from \( S+IG_7 \)).

In 01 language the operator \( S \) takes the form \( 0 \xrightarrow{S} 1 \), while space inversion \( I \) is given by \( (\sigma_1\sigma_2\ldots\sigma_N) \xrightarrow{I} (\sigma_N\sigma_{N-1}\ldots\sigma_1) \). Hence \( S \) applied to cyc is

\[
\begin{align*}
1 & 0 1 0 0 0 0 0 1 \\
A & B & A & B & A & C & B & A & C & A
\end{align*} \xrightarrow{S} \begin{align*}
0 & 1 0 1 1 1 1 1 0 \\
A & C & A & C & A & B & C & A & B & A
\end{align*}
\] (2.1)

As we can see here, the \( S \) operation leaves one layer type invariant (here arbitrarily chosen to be \( A \)), and takes \( B \leftrightarrow C \).

\( I \)(cyc) is then

\[
\begin{align*}
1 & 0 1 0 0 0 0 0 1 \\
A & B & A & B & A & C & B & A & C & A
\end{align*} \xrightarrow{I} \begin{align*}
1 & 0 0 0 0 0 1 0 1 \\
A & B & A & C & B & A & C & A & C & A
\end{align*}
\] (2.2)

Thus, in \( ABC \) notation, \( I \) corresponds to the composite operation of (spatial inversion)\( \circ (B \leftrightarrow C) \).

Given the above, it is clear that physically sensible Hamiltonians for close-packed polytypes will be invariant under both \( S \) and \( I \) operations. We now proceed to examine the diffraction patterns of some possible disordered ground states for Hamiltonians with \( S+I \) symmetry. Such ‘possible disordered ground states’ are of course the D-pairs obtained from \( S+IG_r \), as described above.
III. DIFFRACTION PATTERNS AND PROBABILITIES

For the purpose of our study, we assume that the polytypic crystals consist of un-faulted two-dimensional layers, stacked as prescribed by the chosen SC of $S^+1G_r$. Hence the diffracted intensity needs to be calculated only for wavevectors normal to the close-packed layers (i.e., along $c$). This problem has been addressed previously [11–13] for perfect crystals and for various stacking defects; hence here we only need apply old results to a novel kind of disorder. The intensity of X-ray diffraction from close-packed crystals can be expressed in terms of the number $N$ of layers in the chain, and the average structure factor product $J(n)$, as 

\[ I(l) = N_{ab} \sum_{n=-N}^{N} (N - |n|)J(n) \exp(i2\pi nl). \]  

(3.1)

where $N_{ab}$ is a constant coming from a summation over the basal planes, $l$ is a continuous variable which determines the wavevector $k = 2\pi l/c$, and $n$ is an integer number of units of the primitive lattice vector $c$. The average structure factor product $J(n)$ can be written as a function of interlayer correlations, or probabilities, as follows. Let $P_{AA}(n)$ be the probability that two layers $n$ apart be $A \cdots A$, and similarly define $P_{AB}$ for $A \cdots B$, $P_{BA}$ for $B \cdots A$, and so on. With these probabilities $J(n)$ can be written as

\[ J(n) = P_{AA}(n)F_AF_A^* + P_{BB}(n)F_BF_B^* + P_{CC}(n)F_CF_C^* + P_{AB}(n)F_AF_B^* + P_{BC}(n)F_BF_C^* + P_{CA}(n)F_CF_A^* + P_{BA}(n)F_BF_A^* + P_{CB}(n)F_CF_B^* + P_{AC}(n)F_AF_C^*. \]  

(3.2)

The structure factors $F_A$, $F_B$ and $F_C$ for the hexagonal $A$, $B$ and $C$ layers are also well-known [11]. They differ from each other only in phase since the layers represent identical structures related by a rotation. $F_B$ and $F_C$ can be written in term of the normalized structure factor of $A$ layer ($F_A = 1$) as

\[ F_B = \exp[i2\pi m_0/3] \]

\[ F_C = \exp[-i2\pi m_0/3] \]  

(3.3)
where \( m_0 = h_0 - k_0 \) is an integer constant determined by the components \((h_0, k_0)\) parallel to the layers. For \( m_0 = 3m \), \( m \) any integer, the structure factors are all unity, and, as we can see from Eq. (3.2), \( J(n) \) does not depend on the probabilities at all. Hence for this case, by Eq. (3.1), the intensity is zero. Taking \( m_0 = 3m + 1 \) and inserting \( F \) values (the case \( m_0 = 3m - 1 \) is trivially related), \( J(n) \) reduces to

\[
J(n) = P_{AA}(n) + P_{BB}(n) + P_{CC}(n) + [P_{AB}(n) + P_{BC}(n) + P_{CA}(n)] \exp(-i2\pi/3) + [P_{BA}(n) + P_{CB}(n) + P_{AC}(n)] \exp(i2\pi/3).
\] (3.4)

Eq. (3.4) shows that the intensity of the diffraction pattern depends on the sums of the probabilities that two layers \( n \) units apart are in \( A \cdots A \), in \( A \cdots B \) or in \( A \cdots C \) relationship. After some algebra, using the fact \( P_{AB}(n) = P_{BA}(-n) \), the intensity \( I(l) \) reduces to

\[
I(l) = \frac{\sin^2(\pi N l)}{\sin^2(\pi l)} - 2\sqrt{3} \sum_{n=1}^{N} (N - n)[Q_c(n) \cos(2\pi nl + \frac{\pi}{6}) + Q_r(n) \cos(2\pi nl - \frac{\pi}{6})]
\] (3.5)

where \( Q_c(n) \equiv P_{AB}(n) + P_{BC}(n) + P_{CA}(n) \) and \( Q_r(n) \equiv P_{BA}(n) + P_{CB}(n) + P_{AC}(n) \). [Here we use \( c \) for ‘cyclic’ and \( r \) for ‘reverse’. We also define \( Q_s(n) = P_{AA}(n) + P_{BB}(n) + P_{CC}(n) = 1 - (Q_c(n) + Q_r(n)) \) (\( s \)=‘same’) for future use.] Thus, in order to calculate the diffracted intensity, one needs only the lumped probabilities \( Q_c(n) \) and \( Q_r(n) \).

For perfectly periodic crystals these probabilities are periodic, giving \( \delta \)-function peaks in the diffraction pattern. On the other hand, for disordered crystals, the periodicity of the probabilities may (or may not) be destroyed, depending on the type of disorder which is introduced. If the correlations are not periodic, then the diffraction pattern is of course continuous.

Previous work (that we are aware of) on disorder in close-packed polytypes has concentrated on the random introduction, with various probabilities, of various kinds of stacking faults in otherwise perfect structures [12,13]. This approach gives nonperiodic probabilities \((Q_c, Q_r)\) which decay to 1/3 at large \( n \).

The disorder we are dealing with however is different: the only type of ‘stacking fault’ we consider is a zero-energy fault consisting of a free choice among multiple paths in \( G_r \), at one
or more points in an otherwise completely deterministic stacking sequence. Furthermore, the distinct paths considered are always related by symmetry. Our unfaulted or reference configuration, an ordered or periodic polytype, is formed by choosing only one cycle, among the two or more symmetry-related ones, to form an infinite chain. Hence the earlier methods for computing the probabilities are not appropriate for our case. We found instead a simple rule for calculating the probabilities $Q_x (x = s, c, r)$ for both the ordered and disordered close-packing sequences. Some useful properties of these correlations are proved in the Appendix.

We now examine the correlations $Q_x$, comparing those for a perfect crystal with those for a disordered chain built from a D-pair. Fig. 2(a) shows $Q_s(n)$ for a perfect ($\Delta = -1$) stacking sequence with $T_{01} = 14$. We can see that the period is $T = 3T_{01} = 42$. $Q_s(n)$ and $Q_r(n)$ very similar, being related to $Q_s(n)$ by a shift in $n$.

We now consider the disordered case. Disordered chains were constructed by computer, using a pseudo random number generator. For type I and II D-pairs, this involves starting from a shared node $N$ [for example see Fig. 1(a), 1(b)] and choosing one cycle (either $cyc$ or $\overleftarrow{cyc}$ for type I, or $cyc$ or $\overleftarrow{cyc}$ for type II) randomly; adding the chosen cycle brings us back to $N$, and the choice is made again. For type III and IV D-pairs, four half cycles share two nodes [Fig. 1(c), 1(d)]. There are two possible half cycles to be selected at each node; again the choice is made randomly, with equal probability. Given the symmetries of the problem, we believe that the assumption of equal probabilities is reasonable for a real physical system. In this manner a long disordered chain (over 50,000 layers) is produced, and its diffraction pattern computed from the correlations.

In the disordered case the value of $\Delta$ plays an important role in determining the properties of the correlations. Suppose the value of $\Delta$ of a cycle, say $cyc$, is $+1$ or $-1$, and let the number of 1’s (0’s) be $n_1$ ($n_0$). In the cycle $\overleftarrow{cyc} = I(cyc)$, $n_1$ and $n_0$ will remain unchanged, so that $\Delta$ remains unchanged. On the other hand, if the other half of the D-pair is $\overleftarrow{cyc} = SI(cyc)$, $n_1$ and $n_0$ of $cyc$ are exchanged, so that the value of $\Delta$ is switched to $-\Delta$.

When a disordered chain is built up from $cyc$ and $\overleftarrow{cyc}$ [Fig. 1(a)], the $\Delta$s of both cycles are
the same. Somewhat surprisingly, the result, as shown in Fig. 2(b), is that the probabilities $Q_s(n)$ are periodic, with period $T$ (recall that $T = 3T_{01}$ for $\Delta = \pm 1$ and $T = T_{01}$ for $\Delta = 0$), when $n$ is greater than a threshold value $n_c$ (see Appendix). It turns out that $n_c$ is a small number which is always less than $T_{01}$, but the ‘noise’ in this small region makes a bump in the intensity (see below). When $n > n_c$ we can expect (see Appendix for details) that the basic properties of periodic correlations can be applied for this case, so that the diffraction patterns are very similar to those for the periodic case. In particular, the locations of the $\delta$ functions are unchanged.

The correlations of a disordered chain grown by using D-pairs of types II–V show a special behavior when $\Delta = \pm 1$. For example, a chain produced by a random mixture of cyc and $\overleftarrow{cyc}$ (type II) gives an arbitrary mixture of cycles with $\Delta = 1$ and $-1$. The other D-pairs (types III–V) also have this feature, as may be seen from Fig. 1. In the Appendix we show that the correlations, in these cases, decay exponentially and approach $1/3$ [Fig. 2(c)] (note that the same result was obtained by Wilson [12] using difference equations for disordered hcp polytypes). However when $\Delta$ is 0 for any of types II–V, the result is similar as that for a $cyc-\overleftarrow{cyc}$ D-pair: the chain has periodic probabilities for $n > n_c$ [with however $Q_c(n) = Q_r(n)$], and irregular ‘noise’ below $n_c$.

IV. DIFFRACTION PATTERNS

After growing a close-packed but disordered crystal from a D-pair, we calculate the probabilities $Q_s(n), Q_c(n)$ and $Q_r(n)$, and then calculate the intensity diffracted from these structures by feeding these probabilities to Eq. (3.3).

Fig. 3 shows the intensity from a perfect crystal for various $\Delta$. As noted above, the perfect crystals are constructed by repetition of one cycle of a given D-pair. For $\Delta = 0$ where $T = T_{01}$, in general, all $T$ diffraction lines occur at $l = h/T$ with $h$ an integer. Figure 3(a) shows the peaks in the range $0 \leq l \leq 1$. We see in contrast from Fig. 3(b) and 3(c) that $\delta$ function intensities occur only at the positions $h = Tl = 3k + 1$ for $\Delta = 1$ and $3k - 1$
for $\Delta = -1$. Then the number of peaks in the range $1 \leq h \leq T$ is $T_{01} = T/3$. These are well-known results; we only reproduce them here to facilitate the comparison with the disordered cases. The extinction of $2/3$ of the peaks, for $\Delta = \pm 1$, is proved in the Appendix.

In Fig. 4 we show the intensity diffracted from disordered lattices. When the disordered lattice is type I with $\Delta = 0$ [Fig. 4(a)], $\Delta = 1$ [Fig. 4(b)] and $\Delta = -1$ [Fig. 4(c)], we can see that the sharp peaks occur at the same positions [compare, for example, Figs. 3(a) and 4(a)] as for the periodic cases, but the intensities of the lines change. We note also that there occurs a small intensity bump on the base line of the patterns. This is the only evidence of the disorder in the chain; we see that it can in fact be quite small, and hence difficult to detect experimentally.

There are two reasons why the disorder is so well hidden in these cases. One is of course the identity of $\Delta$ for the two halves of the D-pair, which preserves long-range correlations as noted above. The second reason is that the two cycles (say cyc and $\overline{\text{cyc}}$) must share at least one node, and so have at least $r$ bits which are identical. This leaves at most only $(T_{01} - r)$ bits which can differ between the two cycles. The actual number of differing bits can be as small as one; hence the amplitude of the continuous part of the spectrum can be quite small.

When the disordered lattice is built from type II–V D-pairs the diffraction patterns can show very different behavior. For $\Delta = 0$, the result is similar to that of type I: all $T$ sharp peaks occur at the regular positions, with an intensity bump due to the irregular part of the correlations [Fig. 5(a)]. [One difference is that, for this case, the intensity lines are symmetrically placed about the axis $l = 0.5$, due to the fact that $Q_c(n) = Q_r(n)$].

Fig. 5(b) shows that some structures, which are possible ground states of a class of symmetric Hamiltonians, show a completely diffuse diffracted intensity with no $\delta$-function peaks. When the D-pair is of type II through V, with $\Delta = \pm 1$, the sharp $\delta$-function lines are destroyed by the random mixture of cycles (or parts of cycles) related by $SI$ (types II–V), or simply by $S$ (types III–V). This can perhaps be understood in an intuitive way as follows. Suppose two cycles, constituting the D-pair, have different $\Delta$ values: one has $+1$ and the
other has $-1$. Then, of course, if we have a perfect crystal (ie, all one cycle) the sharp peaks tend to occur at (respectively) $h = 3k + 1$ and $h = 3k - 1$. Mixing the two cycles arbitrarily, the sharp peaks of one cycle (say $cyc$) will be destroyed by any significant fraction of the other cycle (say, $\overleftarrow{cyc}$) since the positions of lines of $cyc$ corresponds to the positions of zero intensities of $\overleftarrow{cyc}$.

Fig. 5(b) is for the case of an equal mixture of the two cycles. In Fig. 6 we vary the ratio of the two cycles, in order to clarify how the disordered, continuous pattern is related to the two discrete spectra obtained for the pure periodic cases ($cyc$ and $\overleftarrow{cyc}$). We see from Fig. 6 that, as claimed above, the intensity is changed from discrete to continuous by any finite fraction of the symmetry-related cycle. It is also clear that the peaks are smoothly shifted, as a function of the mixture ratio, from one limit ($3k + 1$) to the other ($3k - 1$). (We are of course not aware of any physical mechanism which would bias the ratio away from $1/2$; we include Fig. 6 simply to clarify the behavior of the continuous spectra for these types of D-pairs.)

V. D-PAIRS

We have compiled a modest catalog of the D-pairs which may occur for $r = 6$ and $r = 7$, always assuming $S + I$ symmetry. To do this, we drew the graphs $S^+I G_6$ and $S^+I G_7$ by hand, and picked out by inspection the simple cycles which satisfy the CW rules for D-pairs [4]. We also found a few D-pairs for $r = 8$, since this is the smallest $r$ giving type V D-pairs for $S + I$ symmetry. Our method rapidly becomes cumbersome for larger $r$, and is already rather unwieldy for $r \geq 7$. Hence, if any further search for D-pairs at larger $r$ is warranted, it should be automated (which is possible) and carried out by a machine.

Our manual search is however extensive enough to uncover both types of D-pair in $S^+I G_r$ found by CW. Therefore, we believe that the five types of Fig. 1 represent all the topological types of D-pairs that can occur in $G_r$. Hence we feel that the present study has revealed all the qualitative features of disorder which may occur for Ising Hamiltonians.
In Table I, we list all the D-pairs we found from $S^+IG_6$. Table I is actually not typical of larger $r$, since $r = 6$ is the smallest value, given $S + I$ symmetry, for which D-pairs occur at all. However the D-pairs for larger $r$ are very numerous; hence we just summarize those results here.

For $r = 7$ we found 66 D-pairs, of which 38 gave $\delta$-function patterns and 28 gave pure continuous spectra. The periods $T_{01}$ for the $\delta$-function spectra included 9–15, 17–19, 22, 24, 26, 28, and 30; for the continuous spectra we found periods 9, 10, 14, 16, 18, 20, 22, 26, 28, 30, 34, and 38. There are no type V D-pairs for $r = 7$, since $S^+IG_7 \sim IG_6$ [4]. We did find (with help from a computer search) type V D-pairs in $S^+IG_8$; typically, they involve nonzero $\Delta$ values and so give continuous patterns. Hence the principal feature which distinguishes this type (besides their topological structure in the graph) is their higher entropy per $T_{01}$ layers (which may or may not yield a higher entropy per layer, depending on $T_{01}$).

We note finally that, for $r = 6$ or 7, odd-period D-pairs with continuous diffraction patterns are rare. The reason is that such patterns are only obtained, for these $r$ values, from type II pairs with nonzero $\Delta$. Type I pairs always give $\delta$-function patterns, and types III–V always have even period (because all these types, for $r < 8$, are $S$-symmetric, ie, they ‘unfold’ into two doubled cycles rather than four distinct ones). From Table I, the continuous spectra with odd period do not appear to be uncommon; however, they represent only 2 out of 66 D-pairs for $r = 7$.

VI. DISCUSSION AND SUMMARY

Recent work by Canright and Watson (CW) [4] has proposed a novel type of disordered ground state for classical one-dimensional chains whose Hamiltonians obey certain symmetries. This disorder involves arbitrary mixtures of simple sequences (cycles) which are related by symmetry. Our goal in the present work has then been to ask how this kind of disorder might appear in an experimentally accessible signal. We chose to view the 1D chains as stackings of identical layers, ie, as polytypes, and computed the the diffraction
patterns along the stacking direction. In particular, we assumed, as appropriate for closepacked polytypes, that the distinct ways of stacking the layers gave simple phase shifts in
the scattering.

Given these assumptions, we found that the diffraction patterns fell into two classes: discrete, with a continuous baseline, or pure continuous. In the former case the baseline can be quite small [see for example Fig. 5(a)], giving a pattern strongly similar to that for a periodic structure; or it can be larger [Fig. 4(a)]. In the latter case [Fig. 5(b)], the disorder is obvious; however the remnant periodicity is also clear. Briefly (see the Appendix for details), the reasons for the two classes are as follows. In binary notation, there is long-ranged order (LRO) for all types of D-pairs, because the shared nodes (which represent at least \( r \) bits) recur with perfect periodicity. However, when the binary chain is translated to a close-packed \( ABC \) sequence, this LRO may or may not be lost, depending on the relative symmetries of the pieces which are mixed by the degeneracy, and on the parameter \( \Delta \) which determines the net shift in spatial phase after one period.

These results, being based on an entire class of generic Hamiltonians, are as yet purely theoretical. It remains to be seen whether or not real materials might be governed by any of that fraction of Hamiltonians which give disordered ground states. Such Hamiltonians should apply to any compound whose structure consists of stacked identical layers, with the layers restricted to a discrete number (in this paper, two) of states (say, orientations). Here we have assumed the simplest of such structures, ie, close-packed polytypes.

There are many well-known polytypic materials whose structures obey the \( ABC \) state restriction. SiC, perhaps the most well-studied case, does not look promising \[3\,4\], for two reasons. First, the effective interlayer potentials \[4\] are likely to have a periodic ground state, because they fall off too rapidly (being very small for \( r \gtrsim 5 \)). It is of course of interest to see whether these potentials are close to any of those which give disordered ground states. The answer to this question however requires further work; specifically, the ‘inverse problem’ of finding the set of Hamiltonians which correspond to a given ground state (eg, a D-pair)
must be solved. We plan to address this question in future work.

Besides the ‘classical’ polytypes such as SiC, there are polytypic structures among simple metals and metallic alloys [15]. Here the effective potentials are long-ranged, and highly frustrated. The approach of CW [1,2,4] is strictly valid only for finite-ranged interactions. However there remains the possibility that the ground state for the long-ranged interactions is already determined by those up to some range \( \hat{r} \), so that our logic may be useful even for this case. Zangwill and Bruinsma [16] have argued that the ground states for this class of problem form a ‘devil’s staircase’ as a function of the average valence \( Z \) of the metallic alloy. This argument implies a periodic ground state for all \( Z \). This result depends on allowing elastic displacements of the layers from perfectly periodic \( c \)-axis spacing; this feature is also absent from the simple discrete state space considered here. Thus, it seems that the best current logic predicts periodic ground states for metallic polytypes; however, there is clearly room for, and need for, further work on this question.

Our theoretical approach to polytypes, and many other approaches, share the common feature of reducing a three-dimensional, quantum-mechanical problem to a one-dimensional classical problem. We believe such an approach is well justified by the large mass of the layers. However, one must consider the possibility that true quantum-mechanical solids [17] may not sample the entire range of possibilities of classical interlayer Hamiltonians, even after allowing for symmetry. This question also we plan to address in future work.

In summary, our study of the diffraction patterns of D-pairs is motivated by an interest in determining whether the kind of disordered ground states identified by Canright and Watson [4] may arise in real materials. We find that, depending on the details of the disordered structure, a D-pair may give either a diffraction spectrum (\( \delta \) functions) very much like that for a perfect crystal (with however some continuous spectrum as well); or one may find a purely continuous spectrum, in which the underlying disorder is obvious. These results are an essential component of any search for disordered ground states in polytypes.

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APPENDIX A:

1. Probabilities for the Periodic Chain

In this Appendix we prove various properties of the probabilities \( Q_x \), which are useful for understanding the diffraction patterns. We begin, in this section, with some general properties for the periodic case. The following sections will then consider the presence or absence of sharp lines for the periodic and disordered (D-pair) cases, respectively.

Define \( \Delta(l) \) to be the \( \Delta \) of a set of \( l \) spins within an interval, from the \( (q + 1) \)st to the \( (q + l) \)th spin \( (q, l \) integers with \( q \geq 0 \) and \( l \geq 1 \) ) in an infinite Ising chain. (Hence \( \Delta(l) = \Delta_q(l) \) strictly depends on \( q \) as well; but we will usually ignore the \( q \) dependence.) The \( \Delta \) defined in the main text is then \( \Delta(T_{01}) \) in this notation. Also define \( n_s(l), n_c(l) \) and \( n_r(l) \) to be the number of sets which give \( \Delta(l) = 0, +1, \) and \( -1 \) respectively when we scan \( q \) from 0 to \( T_{01} - 1 \). Then, for the periodic case,

\[
\begin{align*}
Q_s(mT + n) &= \frac{n_s(n)}{T_{01}} \\
Q_c(mT + n) &= \frac{n_c(n)}{T_{01}} \\
Q_r(mT + n) &= \frac{n_r(n)}{T_{01}} \quad (m \geq 0)
\end{align*}
\]

We can prove these relations as follows. First consider a set of \( n \) spins and a corresponding close-packing sequence. If the stacking sequence begins with \( A \) \( (B, C) \) then after \( n \) further layers the position will be \( A \) \( (B, C) \) if \( \Delta(n) = 0 \), or will be \( B \) \( (C, A) \) if \( \Delta(n) = +1 \), or \( C \) \( (A, B) \) if \( \Delta(n) = -1 \). Thus, for example, \( n_s(n) \) is the number of pairs of layers, \( n \) apart, which are in the same (hence ‘s’) orientation: \( A \cdots A, B \cdots B \) or \( C \cdots C \). (Similarly, as in the main text, ‘c’ stands for ‘cyclic’ and ‘r’ for ‘reverse’.)

Let \( N_p(n) \) be the number of layer-pairs, \( n \) apart, over a whole chain, and \( n_s^{(\infty)}(n) \) be the number of pairs among \( N_p(n) \) which gives \( \Delta(n) = 0 \). For a periodic chain composed of \( N_u \) unit cycles with period \( T_{01} \) we will have \( N_p = T_{01}N_u \) and \( n_s^{(\infty)}(n) = n_s(n)N_u \). With this notation \( Q_s(n) \) can be written as
\[ Q_s(n) = \frac{n_s(n)}{T_{01}} \quad (1 \leq n < \infty). \] (A2)

Since the chain is periodic it is useful to write \( n \) as \( n = mT + n' \), \( m \geq 0 \) and \( 1 \leq n' \leq T \). Then \( n_s(n) = n_s(mT + n') = n_s(n') \) [since \( \Delta(mT + n') = \Delta(mT) + \Delta(n') = \Delta(n') \)]. Finally we can drop the prime, giving

\[ Q_s(mT + n) = \frac{n_s(n)}{T_{01}} \] (A3)

Other equations in Eqs. (A1) can be derived using the same method. Thus we do not need to count the number of layer-pairs over a whole chain in order to calculate the probabilities \( Q_s(n) \), \( Q_c(n) \) and \( Q_r(n) \). Instead only one to three unit cycles are enough in calculating the probabilities (see below).

In the remainder of this section we will take \( \Delta = +1 \) for concreteness. (Generalizations to other \( \Delta \) are obvious.) We want to derive relationships between \( n_x(n) \) and \( n_x(n') \), where \( n \) and \( n' \) differ by a multiple of \( T_{01} \). For example, let us show that \( n_r(T_{01} + n) = n_c(n) \) and \( n_r(2T_{01} + n) = n_s(n) \) for the case \( \Delta = +1 \). We will use the modular arithmetic properties of \( \Delta(n) \):

\[ (\pm 1) + (\pm 1) = \mp 1 \quad \text{and} \quad (\pm 1) - (\pm 1) = 0. \] (A4)

A set of \( T_{01} + n \) spins contributes to \( n_r \) (\( n_c, n_s \)) if \( \Delta(T_{01} + n) = -1 \) (\(+1, 0\)). Thus (for example) \( \Delta(T_{01} + n) = -1 = \Delta(T_{01}) + \Delta(n) \) implies that \( \Delta(n) \) should be +1, since \( \Delta \equiv \Delta(T_{01}) = +1 \). With this argument we can see that \( n_r(T_{01} + n) = n_c(n) \). Similarly, if \( \Delta(2T_{01} + n) \) is \(-1\), then \( \Delta(n) = 0 \), since \( \Delta(2T_{01}) \) is \(-1\) for the case of \( \Delta = +1 \). Hence \( n_r(2T_{01} + n) = n_s(n) \). Finally we see that

\[ Q_r(T_{01} + n) = Q_c(n) \]
\[ Q_r(2T_{01} + n) = Q_s(n). \] (A5)

We can consider properties under subtraction, as well as under addition. Noting that \( \Delta_q(T - n) = \Delta(T) - \Delta_{q-n}(n) \), and averaging to eliminate the \( q \) dependence, we find, for example,
\[ Q_r(n) = Q_c(T - n). \quad (1 \leq n \leq T) \] (A6)

This result is independent of \( \Delta \) since it only uses the fact that \( \Delta(T) = 0 \).

With the logic described above it is not hard to derive a number of relations among the probabilities. In the next section we will use such relations as needed.

2. Extinction of Diffraction Lines

Using the properties shown in section I, we can show that the lines indexed \( 3k \) and \( 3k - 1 \) \((k \geq 0)\) are extinguished for a periodic chain with \( \Delta = +1 \). Rewrite the intensity equation [Eq. \ref{eq:3.5}] as

\[
I(l) = \frac{\sin^2(\pi N l)}{\sin^2(\pi l)} - 2\sqrt{3} \sum_{n=1}^{N} (N - n) [Q_c(n) \cos(2\pi nl + \frac{\pi}{6}) + Q_r(n) \cos(2\pi nl - \frac{\pi}{6})]
\]
\[\equiv \frac{\sin^2(\pi N l)}{\sin^2(\pi l)} - S. \] (A7)

Using the fact that the probabilities \( Q_c(n) \) and \( Q_r(n) \) are periodic and that \( Q_c(T - n) = Q_r(n) \) we can simplify the summation in Eq. \ref{eq:A7} as

\[
S \equiv \frac{2\sqrt{3}N^2}{T} \sum_{n=1}^{T_01} Q_r(n) \cos(2\pi nl - \frac{\pi}{6}). \] (A8)

Next, using \( Q_r(T_01 + n) = Q_c(n) \) and \( Q_r(2T_01 + n) = Q_s(n) \), \( S \) can be written as

\[
S = \frac{2\sqrt{3}N^2}{T} \sum_{n=1}^{T_01} [Q_r(n) \cos(2\pi nl - \frac{\pi}{6}) + Q_c(n) \cos(2\pi T_01 l + 2\pi nl - \frac{\pi}{6})]
+ Q_s(n) \cos(4\pi T_01 l + 2\pi nl - \frac{\pi}{6})]. \] (A9)

Let \( l = h/T \) (\( h=\)integer). The first term in Eq. \ref{eq:A7} is 0 everywhere except \( h = 0 \) and \( h = T \). Thus if \( S \) vanishes for any other \( h \), \( 0 < h < T \), then the intensity lines are extinguished.

(i) \( h = 0 \) or \( T \)

\[ S = N^2 \] and then the intensity \( I = N^2 - N^2 = 0. \)

(ii) \( h = 3k \)

\[
S = \frac{2\sqrt{3}N^2}{T} \sum_{n=1}^{T_01} [Q_r(n) + Q_c(n) + Q_r(n)] \cos\left(\frac{2\pi kn}{T_01} - \frac{\pi}{6}\right). \] (A10)
The sum of all three probabilities is always 1, and the summation of the cosine term can be carried out to be 0. Thus \( I(3k) = 0 \).

(iii) \( h = 3k + 2 = 3k - 1 \)

Using \( Q_c(n) = Q_s(T_{01} - n) \), the last two terms in Eq. (A9) cancel. Hence \( S \) becomes

\[
S = \frac{2\sqrt{3}N^2}{T} \sum_{n=1}^{T_{01}} Q_r(n) \cos \left( \frac{2\pi n(3k - 1)}{3T_{01}} - \frac{\pi}{6} \right). \tag{A11}
\]

By straightforward algebra we can show the above equation also vanishes, using \( Q_r(n) = Q_r(T_{01} - n) \). Hence \( I(3k - 1) = 0 \).

Thus we find that only one-third of the allowed lines appear in the rhombohedral case \( \Delta = +1 \); the same conclusion holds for \( \Delta = -1 \). In the hexagonal case (\( \Delta = 0 \)) all \( T \) lines appear.

### 3. Disordered Case

For the disordered case, we need to consider the average values for \( n_s(n) \), \( n_c(n) \) and \( n_r(n) \) over the entire chain. (For the remainder of this section we will use the notation \( n_x(n) \), earlier defined for periodic chains, to denote this average.) For simplicity, we will assume that the chain is built from a random mixture of two symmetry-related cycles, present with equal probability. Hence our derivation will be strictly valid only for type I and II D-pairs; however our conclusions (periodic probabilities and \( \delta \)-function spectra for pairs with the same \( \Delta \), decaying probabilities and loss of sharp diffraction lines for mixtures of cycles of opposing \( \Delta \)) are valid in general.

We consider two cycles \( c \) and \( c' \), related by symmetry (\( I \) or \( SI \)), with bit parities \( \Delta \) and \( \Delta' \), respectively. We will need to distinguish the case that \( \Delta = \Delta' \) (‘same-\( \Delta \)’ case; type I D-pairs, or type II with \( \Delta = 0 \)) from that with \( \Delta = -\Delta' \) (‘opposing-\( \Delta \)’ case; type II with \( \Delta = \pm 1 \)).

Our strategy is to first calculate the short-ranged \( Q \)'s, then the longer-ranged ones, building from the short-ranged values. For \( n \) sufficiently large (\( \geq 2T_{01} + 1 \)), there is always
at least one complete cycle, of length $T_{01}$, which appears unchanged in all sums involved in the averaging process used to compute the $n_x(n)$ and hence the $Q_x(n)$ ($x = s, c, r$). We call such a cycle ‘lumped’. If a cycle, or fraction of a cycle, is included but not lumped, we say it is ‘scanned’.

(i) $n = 1$

We begin with $n = 1$. For a same-$\Delta$ pair, $n_1$ and $n_0$ are the same for either $c$ or $c'$. Thus it is clear that $Q_c(1) = n_1 N_u/N = n_1/T_{01}$, $Q_r(1) = n_0 N_u/N = n_0/T_{01}$ and $Q_s(1) = 0$. These are the same as for the periodic case. In the opposing-$\Delta$ case the probabilities will depend on the probabilities of the two cycles. Taking an equal fraction of the two cycles, the probabilities (neglecting edge effects) are

$$Q_c(1) = Q_r(1) = (1/2)(n_1 + n_0)/T_{01} = 1/2.$$  

(ii) $2 \leq n \leq T_{01} + 1$

If $2 \leq n \leq T_{01} + 1$ the length of spin sets involved in the counting process will be up to $2T_{01}$—that is, two cycles are scanned [from the first spin ($q = 0$) to $2T_{01}$th spin ($q = T_{01} - 1$)] [18]. Since we scan more than one cycle in this case, we need to compute the $n_x(n)$ by averaging over the four possible combinations of two cycles: $cc$, $cc'$, $c'c$, $c'c'$. We find that, in the same-$\Delta$ case, there exists a threshold ($n_c$) between 1 and $T_{01}$, above which the probabilities $Q_x$ are periodic. Since the most general bound is $n_c < T_{01} + 1$, we will confine ourselves to showing the periodicity for $n > T_{01} + 1$.

(iii) $T_{01} + 1 < n \leq 2T_{01}$

For $n$ in this range, three unit cycles are scanned. Therefore the $n_x(n)$ should be calculated by averaging over eight possible combinations of the two cycles ($ccc$, $ccc'$, etc). Let these averaged values be $\bar{n}_s^{(0)}(n)$, $\bar{n}_c^{(0)}(n)$ and $\bar{n}_r^{(0)}(n)$. Then the probabilities can be written as

$$
Q_s(n) = \frac{\bar{n}_s^{(0)}(n)}{T_{01}},
Q_c(n) = \frac{\bar{n}_c^{(0)}(n)}{T_{01}} \quad (T_{01} + 1 < n \leq 2T_{01}).
$$  

$$Q_r(n) = \frac{\bar{n}_r^{(0)}(n)}{T_{01}} \quad (T_{01} + 1 < n \leq 2T_{01}).$$
(iv) $2T_{01} + 1 \leq n \leq 3T_{01}$

In this region there exists one unit cycle which is lumped (i.e., makes an invariant addition to the sum) when we scan $q$ from 0 to $T_{01} - 1$. This cycle can be either $c$ or $c'$ with equal probability, and the $\Delta(T_{01}) = \Delta$ of this cycle will be 0, +1 or −1 depending on the D-pair considered. Let $f_1^{(s)}$, $f_1^{(c)}$ and $f_1^{(r)}$ be the probabilities [we will use the term 'cycle-probability' in order to distinguish these probabilities from the $Q_x(n)$] that the $\Delta$ of the lumped cycle is 0, +1, or −1 respectively. For example, for a type II D-pair, in which the $\Delta$ of $cyc$ is +1 and that of $\overline{cyc}$ is −1, $f_1^{(s)} = f_1^{(r)} = 1/2$ and $f_1^{(s)} = 0$. Recalling the modular arithmetic of the $\Delta$’s, the $n_x(n)$ in this range can be written in terms of the cycle-probabilities and $\overline{n}_s^{(0)}(n)$, $\overline{n}_c^{(0)}(n)$ and $\overline{n}_r^{(0)}(n)$:

$$
\overline{n}_s(2T_{01} + n) = f_1^{(s)}\overline{n}_s^{(0)}(n) + f_1^{(r)}\overline{n}_r^{(0)}(n) + f_1^{(c)}\overline{n}_c^{(0)}(n)
$$

$$
\overline{n}_c(2T_{01} + n) = f_1^{(c)}\overline{n}_c^{(0)}(n) + f_1^{(s)}\overline{n}_s^{(0)}(n) + f_1^{(r)}\overline{n}_r^{(0)}(n)
$$

$$
\overline{n}_r(2T_{01} + n) = f_1^{(r)}\overline{n}_r^{(0)}(n) + f_1^{(c)}\overline{n}_c^{(0)}(n) + f_1^{(s)}\overline{n}_s^{(0)}(n).
$$

(A13)

Dividing Eq. (A13) by $T_{01}$, we can calculate the probabilities $Q_s(n)$, $Q_c(n)$ and $Q_r(n)$.

(v) Larger $n$

If $n$ is in the range $3T_{01} + 1 \leq n \leq 4T_{01}$, there are two lumped cycles. The cycle-probabilities $f_2^{(s)}$, $f_2^{(c)}$, and $f_2^{(r)}$ can then be obtained using those obtained before: $f_2^{(s)} = f_1^{(s)}f_1^{(s)} + f_1^{(r)}f_1^{(c)} + f_1^{(c)}f_1^{(r)}$ and so on. From these cycle-probabilities we can calculate the $n_x(n)$ as before.

In general, if $n$ is in the range $(p + 1)T_{01} + 1 \leq n \leq (p + 2)T_{01}$ ($p \geq 1$), we can use the following formulae:

$$
f_p^{(s)} = f_{p-1}^{(s)}f_1^{(s)} + f_{p-1}^{(r)}f_1^{(c)} + f_{p-1}^{(c)}f_1^{(r)}
$$

$$
f_p^{(c)} = f_{p-1}^{(c)}f_1^{(s)} + f_{p-1}^{(s)}f_1^{(c)} + f_{p-1}^{(r)}f_1^{(r)}
$$

$$
f_p^{(r)} = f_{p-1}^{(r)}f_1^{(s)} + f_{p-1}^{(c)}f_1^{(c)} + f_{p-1}^{(s)}f_1^{(r)}.
$$

(A14)

Since $f_1^{(s)}$, $f_1^{(c)}$ and $f_1^{(r)}$ can be determined by the $\Delta$ of the D-pair, we can obtain the cycle-probabilities for any $p$ using these recursion relations. Using Eqs. (A14) we can finally get
Thus, once we know \( \pi_s(0) \), \( \pi_c(0) \) and \( \pi_r(0) \), and the \( f_p(x) \) from the recursion relations, we can calculate the probabilities \( Q_x((p + 1)T_01 + n) \) by dividing Eqs. (A15) by \( T_01 \).

When \( \Delta = +1 \) in a type I D-pair, for example, we know that \( f_1^{(s)} = 0 \), \( f_1^{(c)} = 1 \), and \( f_1^{(r)} = 0 \). The recursion relations (A14) for this case will be

\[
\begin{align*}
  f_p^{(s)} &= f_{p-1}^{(r)} \\
  f_p^{(c)} &= f_{p-1}^{(s)} \\
  f_p^{(r)} &= f_{p-1}^{(c)}
\end{align*}
\]

so that the probabilities are given by

\[
\begin{align*}
  Q_s(2T_01 + n) &= \frac{\pi_r(0)}{T_01} \\
  Q_s(3T_01 + n) &= \frac{\pi_c(0)}{T_01} \\
  Q_s(4T_01 + n) &= \frac{\pi_s(0)}{T_01} \\
  Q_r(2T_01 + n) &= \frac{\pi_c(0)}{T_01} \\
  Q_r(3T_01 + n) &= \frac{\pi_s(0)}{T_01} \\
  Q_r(4T_01 + n) &= \frac{\pi_r(0)}{T_01} \\
  Q_c(2T_01 + n) &= \frac{\pi_s(0)}{T_01} \\
  Q_c(3T_01 + n) &= \frac{\pi_r(0)}{T_01} \\
  Q_c(4T_01 + n) &= \frac{\pi_c(0)}{T_01}.
\end{align*}
\]  

(A17)

Thus, even for the disordered chain, we can see that the probabilities are periodic, when \( n > n_c \), with period \( 3T_01 \equiv T \) for the \( \Delta = +1 \) case. In that region of \( n \) the properties of periodic probabilities (see above) can be applied to this disordered case. Therefore we can expect that the diffraction lines (\( \delta \) function) in Fourier space occur at the same positions as those for a periodic chain, as derived above. With the same method we can show the periodicity of probabilities for any same-\( \Delta \) case, ie, any type I D-pair, or for a type II D-pair with \( \Delta = 0 \). It is clear that the proof generalizes to types III–V, as long as \( \Delta = 0 \) for all possible cycles which can be formed.

On the other hand, for the opposing-\( \Delta \) cases (type II–V D-pairs, with \( \Delta \neq 0 \)) we have a different story. The initial cycle-probabilities for this case are different from the previous
example: they are $f^{(s)}_1 = 0$ and $f^{(c)}_1 = f^{(r)}_1 = 1/2$. From Eqs. (A14) and the initial cycle-probabilities it is not hard to get the following recursion relation,

$$f^{(x)}_p = \frac{1}{2} (f^{(x)}_{p-1} + f^{(x)}_{p-2})$$

(A18)

(Ther again $x = s, c, r$); here we have used the fact that $f^{(c)}_p = f^{(r)}_p$. We can solve (A18) to get

$$\delta_p \equiv f_p - f_{p-1} = C \left(-\frac{1}{2}\right)^p$$

(A19)

with $C = 4(f_2 - f_1)$. We then sum (A13) to get, for large $p$,

$$f^{(x)}_{p \to \infty} = f^{(x)}_1 + \frac{2}{3} (f^{(x)}_2 - f^{(x)}_1).$$

(A20)

With initial conditions appropriate to $\Delta = \pm 1$ (ie, $f^{(s)}_1 = 0$ and $f^{(s)}_2 = 1/2$, or equivalently, $f^{(c,r)}_1 = 1/2$ and $f^{(c,r)}_2 = 1/4$) we can show that all three cycle-probabilities decay to $1/3$ at large $p$. With Eqs. (A13), $\pi_s(n)$ (large $n$) can be found to be $(1/3)T_{01}$, using the fact that $\pi^{(0)}_s(n) + \pi^{(0)}_c(n) + \pi^{(0)}_s(n) = T_{01}$. Finally, the probabilities for large $n$ are

$$Q_s(n) = \frac{\pi^{(0)}_s(n)}{T_{01}} = \frac{1}{3} = Q_c(n) = Q_r(n).$$

(A21)

The diffraction pattern for the opposing-$\Delta$ case is thus diffuse, without any $\delta$ functions.
TABLES

TABLE I. D-pairs found in $^{S+I}G_6$. The first column gives the D-pairs in binary notation. The type II pairs are always $cyc/cyc$. The type III pairs [see Fig. 1(c)] can be decomposed in several ways; here we give them as $cyc/cyc$. The (binary) periods of the paired cycles are given, as these are apparent even in the disordered diffraction patterns [see, eg, Fig. 5(b)]. The $\Delta$ value and type determines whether the diffraction pattern has $\delta$ functions, or is continuous.

| $r$ | D-pair        | $T_{01}$ | $\Delta$ Values$^a$ | Type | Spectrum     |
|-----|---------------|----------|----------------------|------|--------------|
| 6   | 10111100100001 | 14       | 0, 0, −1, +1         | III  | continuous   |
|     | 00111101100001 |          |                      |      |              |
| 6   | 101111001000001 | 16       | 0, 0, −1, +1         | III  | continuous   |
|     | 0011111011000001 |         |                      |      |              |
|     | 1001011        | 7        | +1, −1               | II   | continuous   |
|     | 0001011        |          |                      |      |              |
| 6   | 0001010011101011 | 16       | 0, 0, +1, −1         | III  | continuous   |
|     | 1001010001101011 |         |                      |      |              |
| 6   | 1011111001000001 | 18       | 0, 0, −1, +1         | III  | continuous   |
|     | 00111111011000001 |        |                      |      |              |
|     | 100101011      | 9        | +1, −1               | II   | continuous   |
|     | 000101011      |          |                      |      |              |

$^a$Each entry has two or four values depending on the type of D-pair. (see Fig. 1)
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FIGURES

FIG. 1. Schematic drawings of the five topological types of D-pair, assuming $S+I$ symmetry for the Ising Hamiltonian. (a) Type I: $\text{cyc}$ and $\overrightarrow{\text{cyc}} \equiv I(\text{cyc})$. (b) Type II: $\text{cyc}$ and $\overrightarrow{\text{cyc}} \equiv SI(\text{cyc})$. (c) Type III: There are four possible cycles, sharing two nodes. Here and in (d) (type IV), we have shown symmetric D-pairs which are invariant under $S$, because such symmetry holds for these types for $r < 8$, which represents the majority of cases studied in this work. (d) Type IV: There are four possible cycles sharing two nodes. (e) Type V: There are sixteen possible cycles sharing four nodes. Type V D-pairs are invariant under any combination of $S$ and $I$.

FIG. 2. The probabilities $Q_s(n)$ for $T = 42$. (a) For a perfect chain with $\Delta = -1$. Other probabilities are related to $Q_s(n)$ by $Q_r(n) = Q_s(14 + n)$ and $Q_c(n) = Q_s(28 + n)$. (b) For a disordered chain; type II D-pair with $\Delta = 0$. We can see the irregular part only for the first few $n$. In general, the probabilities are periodic for this (‘same-$\Delta$’) type of D-pair, for $n > n_c$, with $n_c < T_{01}$. (c) For a disordered chain; type II D-pair with $\Delta = \pm 1$. The probability decays exponentially to $1/3$. Others ($Q_c, Q_r$) show the same behavior.

FIG. 3. Diffraction patterns from perfect chains with various $\Delta$. (a) For $\Delta = 0$, $T = T_{01} = 13$. Basically all lines occur; the number of lines is $T$. Some lines are too small to see. (b) For $\Delta = +1$, lines at $l = h/T$, with $h = 3k$ and $h = 3k - 1$, are extinguished. (c) For $\Delta = -1$, $3k$ and $3k + 1$ lines are extinguished.

FIG. 4. Diffraction patterns from disordered chains (type I) with various $\Delta$. (a) Pattern for a disordered chain built from a D-pair (shown); the pattern for a perfect chain from half of this D-pair is shown in Fig. 3(a). Relative to Fig. 3(a), the positions of the lines are not changed; but there is a smooth background, with a visible ‘bump’. (b) $\Delta = +1$; compare with Fig. 3(b). (c) $\Delta = -1$; compare with Fig. 3(c).
FIG. 5. Diffraction patterns from disordered chains built from a type II D-pair. The lines are symmetric with respect to $l = 0.5$, due to $Q_c(n) = Q_r(n)$. (a) $\Delta = 0$. Here we still have a same-$\Delta$ pair, and hence sharp lines in the spectrum. (b) When $\Delta \neq 0$ we have an ‘opposing-$\Delta$’ pair. [An example of probabilities for an opposing-$\Delta$ case is shown in Fig. 2(c).] In this case, as shown in the Appendix, the probabilities are not periodic, and there are no sharp lines in the diffraction spectrum.

FIG. 6. The diffracted intensity with varying probabilities (as shown) for mixing the two cycles, $cyc$ and $\overleftarrow{cyc}$, from a type II D-pair with $\Delta = \pm 1$. We can see the positions of maximum intensity moving from $3k - 1$ to $3k + 1$ as the fraction of $\overleftarrow{cyc}$ increases (top to bottom). We have drawn a few dotted lines as a guide to the eye. Fig. 5(b) shows the case of a 50:50% mixture.