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Possible disordered ground states for layered solids and their diffraction patterns

Jaichul Yi and Geoff S. Canright
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200

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It has recently been shown, assuming only certain (physical) symmetries of the Hamiltonian, that one-dimensional Ising problems can have degenerate, disordered ground states (GS's). This result is of interest since it implies a weak violation of the third law of thermodynamics. The ground-state 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 study, we address the question of how this constrained disorder may appear in an experimentally accessible signal, namely, the diffraction pattern. To calculate the latter, we assume (as is commonly done with known polytypes) that the Ising Hamiltonian represents the energetics of stacking of close-packed layers of some hypothetical polytypic material. We then calculate the diffraction patterns along the stacking direction for the various possible kinds of disordered GS's. We find that some disordered GS's give diffraction patterns which are only weakly distinguished from their periodic counterparts, while in others the long-ranged correlations among the layers is destroyed by the disorder, giving a diffraction spectrum which is purely continuous.

I. INTRODUCTION

One of the simplest problems in classical statistical mechanics is the one-dimensional spin chain, with the spins taking only values from a discrete set of k states. The most well-known example is of course the Ising problem, where $k=2$. For general k-state models in one dimension, it is known that the ground state is "almost always" (in the sense of for "almost all" possible Hamiltonians) periodic. That is, 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 (among other results) these same results, using the directed graph $G_r^{(k)}$ (called the de Bruijn diagram,[3] and described in more detail below). Recently, Canright and Watson (CW) (Ref. 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* ground states (GS's) 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; hence there is no contradiction between the CW result and that of Radin and Schulman.) That is, if one allows the physically unexceptional "fine tuning" of parameters arising from symmetry, then in many cases one can find degenerate and disordered GS's without any further fine tuning of parameters. The disorder arises since, in such cases, there are multiple 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] Furthermore, since such disordered GS's do not require fine tuning of the parameters of the Hamitonian to precise values, it is at least plausible that such exceptions may be found in some real materials whose energetics may be represented by a one-dimensional, k-state Hamiltonian.

It is therefore of some interest to inquire whether CW's theoretical results may be applicable to any real physical systems. In the pursuit of this idea, two obvious questions immediately arise. (i) Are there any real materials which may be described by such a Hamiltonian? (ii) If so, and if such materials do in fact have a disordered ground-state structure of the type found by CW, how might the disorder appear experimentally?

(i) is readily answered: besides possible magnetic systems, there is a multitudes of layered solids (polytypes[6]) which may be described by such Hamiltonians, in the following sense: there is a low probability of intralayer defects, while packing constraints force the layers to choose one of a small, discrete set of relative stacking orientations. A one-dimensional, k-state Hamiltonian may then be usefully employed to represent the energy (or free energy for $T>0$) of the various ways of stacking the layers.[7] We should of course make it clear at this point that such a Hamiltonian is by no means restricted to near-neighbor couplings, nor even to two-body terms. In fact, there is no justification for excluding any term up to range r, except those which violate the assumed symmetry of the Hamiltonian H. This broad class of Hamiltonians is the same class studied by CW.

Hence we are led by the results of CW to imagine a layered solid for which the ground state consists of a disordered stacking of layers. The disorder is however of a special kind, namely, the random mixture of two (or more—see below) stacking sequences, with the different sequences related by symmetry. It is not obvious what experimental consequences might arise from such a constrained form of disorder. In the present work, as a partial answer to question (ii) above, we study the diffraction patterns, along the stacking direction, of

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such hypothetical layered materials. We will refer to our hypothetical material as an h polytype: it is a polytype in the broad sense of the term; however, we prefix the "h" to distinguish our hypothetical layered solid from the well-studied classical polytypes such as SiC.[6]

In this work we consider the simplest possible h polytype, namely, a close-packed solid, which may be modeled as a classical Ising ($k=2$) chain.[6] We assume our h-polytype has a disordered ground state of the type found by CW, and examine the possible kinds of diffraction patterns (along the stacking axis) which may result from such a structure. Our goal is to try to see how the constrained disorder described above (i.e., 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, ISING SPINS, AND CLOSE-PACKED STACKINGS

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 first provide a brief description of this representation, including the modifications introduced by CW to represent the effects of symmetry. Subsequently, we show how to translate a cycle of Ising spins into a stacking sequence of close-packed layers. This is a standard procedure, but we include it here (briefly) for completeness, and to show how the relevant symmetry operations on the Ising spins appear in the language of layer sequences.

A. Directed graphs, cycles, and degenerate pairs ("*D* pairs")

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 $\mathcal{N}_1=\sigma_1 \ldots \sigma_r$ and $\mathcal{N}_2=\sigma_1' \ldots \sigma_r'$ 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 σ_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 σ_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 nondecomposable (i.e., non-self-intersecting) cycle, then all the cycles in G_r can be uniquely decomposed into SC's.

The general periodicity of the ground state can now be understood in terms of SC's. The gound state is the repetition of that SC which has the minimum energy per spin, and the period of any SC is $\leqslant 2^r$ (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 SC's in G_r. Now assume that such a pair has the lowest energy per spin. If these two minimal-energy SC's share a node, then the GS is infinitely degenerate, since it includes arbitrary mixtures of the two SC's. 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 SC's 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 SC's 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 $r \geqslant 5$. Combining the two symmetries (denoted $S+I$ symmetry), CW found that the Ising case has D pairs only for $r \geqslant 6$.

These results may seem somewhat surprising, from the following point of view. It is easy to find SC's 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 SC's. Hence CW turned to modified graphs ${}^X G_r^{(k)}$ (where X is the symmetry S, I, or $S+I$) whose SC's 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 SC's of G_r. We are interested in those SC's 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 SC's of any graph of the form ${}^I G$ (which includes ${}^{S+I}G_r$) 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 ${}^{S+I}G_r$ only for $r \geqslant 8$) yields either a type IV or type V D pair in G_r.

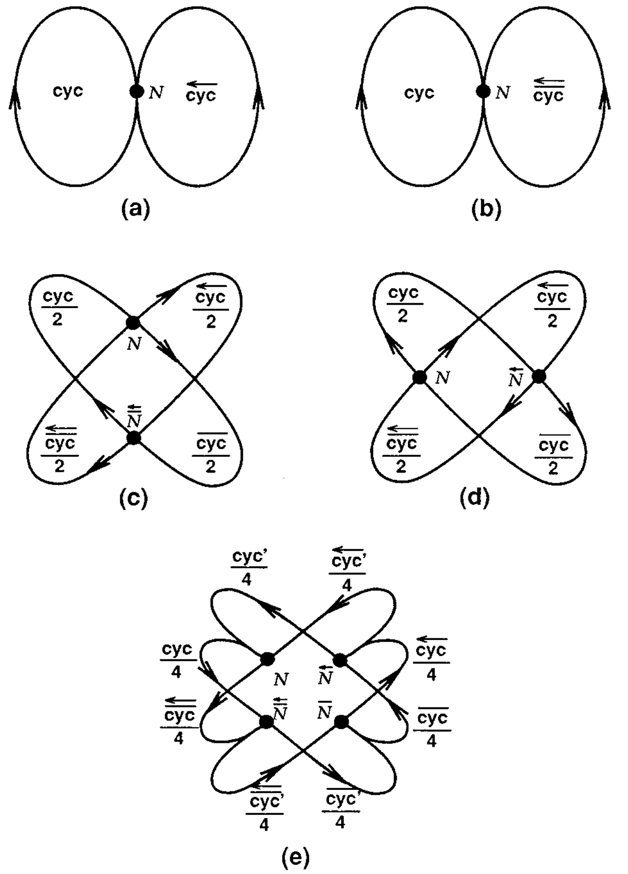

FIG. 1. Schematic drawings of the five topological types of D pair, assuming $S+I$ symmetry for the Ising Hamiltonian. (a) Type I: cyc and $\overleftarrow{cyc} \equiv I(cyc)$. (b) Type II: cyc and $\overline{\overleftarrow{cyc}} \equiv SI(cyc)$. (c) Type III: there are four possible cycles, sharing two 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.

Let us briefly describe the five types of D pairs. First we may have a type-I D pair in which a cycle cyc shares the node $\mathcal{N}$ with its I symmetry partner $\overleftarrow{cyc}$[Fig. 1(a)]. A type II D pair is composed of cyc and its SI symmetry partner $\overline{\overleftarrow{cyc}}$ 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 $\overline{\mathcal{N}}$). Taking the length of the cycle 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[8] of types I and II as ln2 per T_{01} layers.

Figures 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 $\overline{\overleftarrow{\mathcal{N}}}$ 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 ln4 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, with the *pairs* of D pairs related by S symmetry. However, such general (asymmetric) D pairs only occur for $r \geqslant 8$—a range which we have not studied systematically. Hence we have instead shown the symmetric cases, for which $S(D\text{ pair}) = D$ pair. Such a symmetric pair will give cycles with period T_{01} which is twice that of the "folded" D pair in ${}^{S+I}G_r$ (hence even). These symmetric type III and IV D pairs map to themselves under either S or I; hence [unlike Figs. 1(a) and 1(b)] there are not other pairs implicit in Figs. 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,[9] 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 $C = -\Sigma_n p_n \ln(p_n)$, 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 $C_D = \ln(2T_{01}) - (n_s/T_{01})\ln 2$, which exceeds the complexity $C_{\text{per}} = \ln(T_{01})$ of a periodic chain of the same T_{01} by $C_D - C_{\text{per}} = \ln 2[1 - (n_s/T_{01})]$. Hence we see that a D pair—that is, a *disordered* stacking sequence whose building blocks are of length T_{01}—is less complex, by this definition, than a periodic chain of period $2T_{01}$. (Its entropy per layer is, of course, higher.)

B. Layer stackings and Ising spins

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[10]); and a pair from the sequence $A \rightarrow C \rightarrow B \rightarrow A$ is a 0 (−). It is worth pointing out here that the Ising (+/−) variables are *relative* coordinates, while the ABC notation refers to absolute layer positions.

We next introduce some notation, using an example for clarity. One D pair from ${}^{S+I}G_6$, for example, consists of $cyc = (0010111)$ [with Zhdanov symbol[11] $cyc = (2113)_3$] and its SI-symmetry partner $\overline{\overleftarrow{cyc}} = (0001011)$. (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 Δ can be defined by $\Delta \equiv (n_1 - n_0)$ (mod 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[6] (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 (real or h). 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 ${}^{S+I}G_7$).

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

$$\begin{array}{cccccccccccccccccccc} & 1 & & 0 & & 1 & & 0 & & 0 & & 0 & & 0 & & 0 & & 1 & & \\ A & & B & & A & & B & & A & & C & & B & & A & & C & & A \end{array} \overset{S}{\Leftrightarrow} \begin{array}{cccccccccccccccccccc} & 0 & & 1 & & 0 & & 1 & & 1 & & 1 & & 1 & & 1 & & 0 & & \\ A & & C & & A & & C & & A & & B & & C & & A & & B & & A \end{array}. \tag{2.1}$$

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

$$\begin{array}{cccccccccccccccccccc} & 1 & & 0 & & 1 & & 0 & & 0 & & 0 & & 0 & & 0 & & 1 & & \\ A & & B & & A & & B & & A & & C & & B & & A & & C & & A \end{array} \overset{I}{\Rightarrow} \begin{array}{cccccccccccccccccccc} & 1 & & 0 & & 0 & & 0 & & 0 & & 0 & & 1 & & 0 & & 1 & & \\ A & & B & & A & & C & & B & & A & & C & & A & & C & & A \end{array}. \tag{2.2}$$

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 ${}^{S+I}G_r$, as described above.

III. DIFFRACTION PATTERNS: METHOD OF CALCULATION

For the purpose of our study, we assume that crystals of the h polytype consist of unfaulted two-dimensional layers, stacked as prescribed by the chosen SC of ${}^{S+I}G_r$. Hence the diffracted intensity needs to be calculated only for wave vectors normal to the close-packed layers (i.e., along **c**). This problem has been addressed previously[12–14] for perfect crystals and for various stacking defects; hence here we only need apply old results to another 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[14]

$$I(l)=N_{ab}\sum_{n=-N}^{N}(N-|n|)J(n)\exp(i2\pi nl), \tag{3.1}$$

where N_{ab} is a constant coming from a summation over the basal planes, l is a continuous variable which determines the wave vector $k=2\pi l/c$, 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

$$\begin{aligned} J(n)=&P_{AA}(n)F_AF_A^*+P_{BB}(n)F_BF_B^*+P_{CC}(n)F_CF_C^*\\ &+P_{AB}(n)F_AF_B^*+P_{BC}(n)F_BF_C^*+P_{CA}(n)F_CF_A^*\\ &+P_{BA}(n)F_BF_A^*+P_{CB}(n)F_CF_B^*+P_{AC}(n)F_AF_C^*. \end{aligned} \tag{3.2}$$

The structure factors F_A, F_B, and F_C for the hexagonal A, B, and C layers are also well-known.[12] They differ from each other only in phase since the layers represent identical structures related by a rotation. If we divide out the common amplitude of the three structure factors by setting $F_A=1$, then F_B and F_C can be written as

$$\begin{aligned} F_B&=\exp[i2\pi m_0/3],\\ F_C&=\exp[-i2\pi m_0/3], \end{aligned} \tag{3.3}$$

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

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

Equation (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

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

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 δ-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.

A common approach to disorder in close-packed polytypes is to assume the random introduction, with various probabilities, of various kinds of stacking faults in otherwise perfect structures.[6,13,14] This approach gives nonperiodic probabilities (Q_c, Q_r) which decay to 1/3 at large n. In real polytypes, the defects (stacking faults) are often not random, however (see, e.g., Sebastian and Krishna in Ref. 6), so that long-range periodicity of correlation functions cannot be ruled out. As an interesting example, which (as we will see) is closely related to the present work, we cite the study by Kabra and Pandey[15] of the $2H\rightarrow 6H$ (or in Zhdanov notation, $\langle 1\rangle\rightarrow\langle 3\rangle$) transformation in SiC. In this work it was shown that certain types of stacking faults do not destroy the long-range order, so that the metastable structures at which the transformation is arrested may be described as having "long-range order without short-range order."

The disorder we are dealing with here is unusual: 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. Hence the common 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. Figure 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 $Q_r(n)$ are very similar, being related to $Q_s(n)$ by a shift in n.

We next consider the disordered case. Disordered chains were constructed by computer, using a pseudorandom number generator. For type I and II D pairs, this involves starting from a shared node $\mathcal{N}$ [for example, see Figs. 1(a), 1(b)] and choosing one cycle (either cyc or $\overset{\curvearrowleft}{cyc}$ for type I, or cyc or $\overleftarrow{cyc}$ for type II) randomly; adding the chosen cycle brings us back to $\mathcal{N}$, and the choice is made again. For type III and IV D pairs, four half cycles share two nodes [Figs. 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.

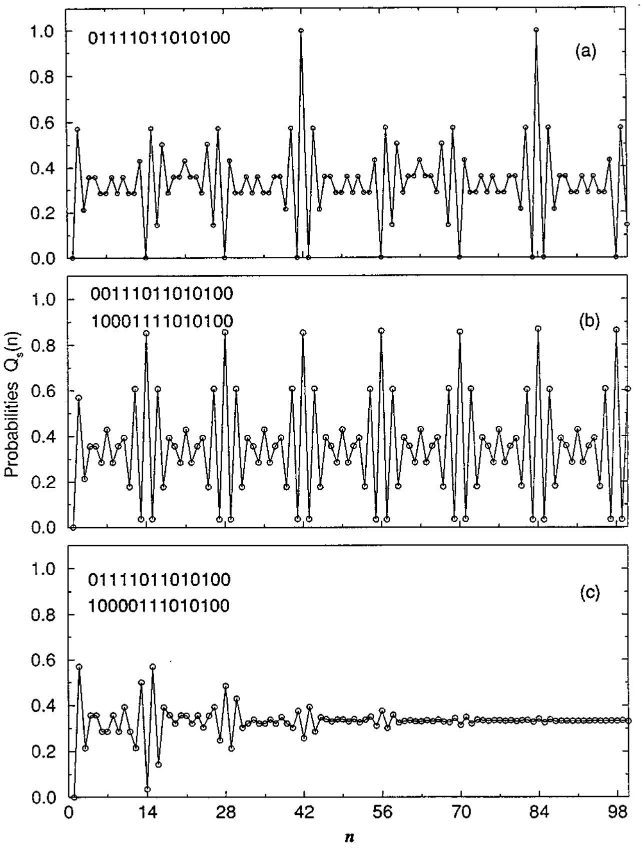

FIG. 2. The probabilities $Q_s(n)$ for $T=42$. (a) For a perfect chain with $\Delta=-1$. Other probabilities are related to $Q_s(n)$ by $Q_r(n)=Q_s(14+n)$ and $Q_c(n)=Q_s(28+n)$. (b) For a disordered chain; type II D pair with $\Delta=0$. We can see the irregular part only for the first few n. In general, the probabilities are periodic for this ("same-Δ") 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.

In the disordered case the value of Δ plays an important role in determining the properties of the correlations. Suppose the value of Δ 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 $\overset{\curvearrowleft}{cyc}=I(cyc)$, n_1 and n_0 will remain unchanged, so that Δ 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 Δ is switched to $-\Delta$.

When a disordered chain is built up from cyc and $\overset{\curvearrowleft}{cyc}$ [Fig. 1(a)], the Δs of both cycles are the same. Somewhat surprisingly, the result, as shown in Fig. 2(b), is that the probabilities $Q_x(n)$ 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 irregularity 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 δ 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[13] using difference equations for disordered hcp polytypes). However, when Δ 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: RESULTS

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. (3.5).

Figure 3 shows the intensity from a perfect crystal for various Δ. 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 $0\leqslant l\leqslant 1$. We see in contrast from Figs. 3(b) and 3(c) that δ 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 $1\leqslant h\leqslant T$ 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 Δ 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 $\overleftarrow{cyc}$) 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.

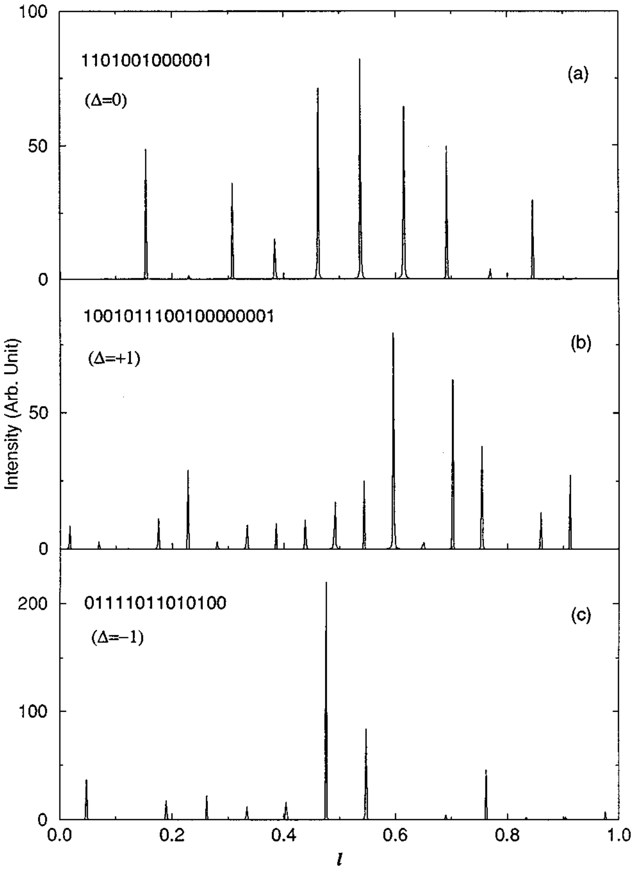

FIG. 3. Diffraction patterns from perfect chains with various Δ. (a) For $\Delta=0$, $T=T_{01}=13$. Basically all lines occur; the number of lines is T. Some lines are too small to see. (b) For $\Delta=+1$, lines at $l=h/T$, with $h=3k$ and $h=3k-1$, are extinguished. (c) For $\Delta=-1$, $3k$ and $3k+1$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

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 $Q_c(n)=Q_r(n)$.]

Figure 5(b) shows that some structures, built from D pairs, show a completely diffuse diffracted intensity with no δ-function peaks. That is, we see here that the equilibrium, zero-temperature structures of our h polytype may have an entirely continuous diffraction spectrum, like that seen for highly disordered but metastable structures in known polytypes. When the D pair is of type II through V, with $\Delta=\pm 1$, the sharp δ-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 Δ values: one has $+1$ and the other has -1. Then, of course, if we have a perfect crystal (i.e., 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

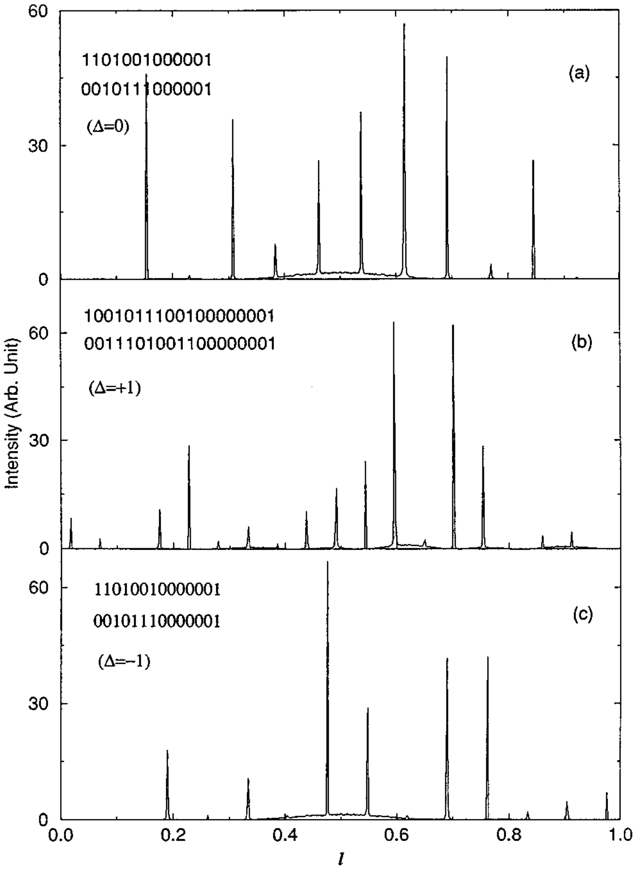

FIG. 4. Diffraction patterns from disordered chains (type I) with various Δ. (a) Pattern for a disordered chain built from a D pair (shown); the pattern for a perfect chain from half of this D pair is shown in Fig. 3(a). Relative to Fig. 3(a), the positions of the lines are not changed; but there is a smooth background, with a visible "bump." (b) $\Delta=+1$; compare with Fig. 3(b). (c) $\Delta=-1$; compare with Fig. 3(c).

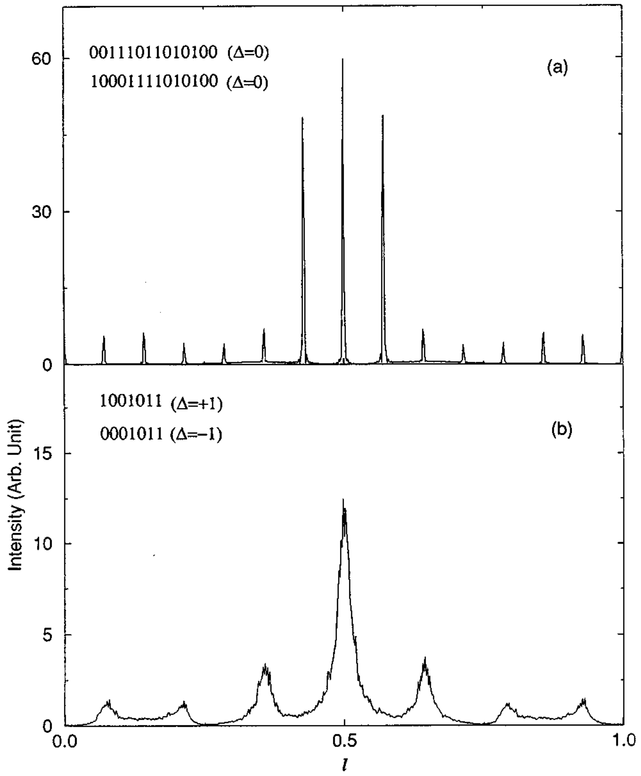

FIG. 5. Diffraction patterns from disordered chains built from a type II D pair. The lines are symmetric with repect to $l=0.5$, due to $Q_c(n)=Q_r(n)$. (a) $\Delta=0$. Here we still have a same-Δ pair, and hence sharp lines in the spectrum. (b) When $\Delta\neq0$ we have an "opposing-Δ" pair. [An example of probabilities for an opposing-Δ 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.

cycle (say, $\overleftarrow{cyc}$) since the positions of lines of cyc corresponds to the positions of zero intensities of $\overleftarrow{cyc}$.

Figure 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 $r\geqslant7$. 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 ${}^{S+I}G_6$. 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 δ-function patterns and 28 gave pure continuous spectra. The periods T_{01} for the δ-function spectra included 9–15, 17–19,

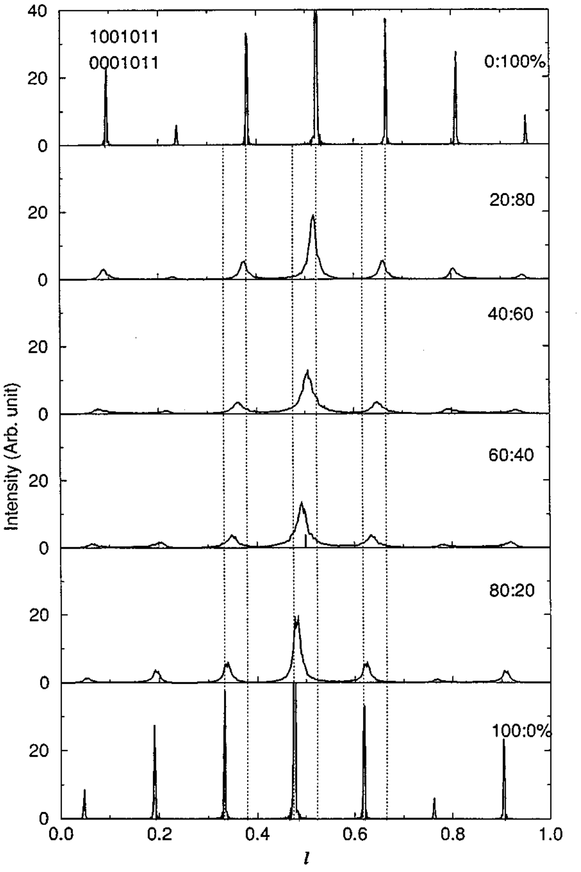

FIG. 6. The diffracted intensity with varying probabilities (as shown) for mixing the two cycles, cyc and $\overleftarrow{cyc}$, from a type II D pair with $\Delta = \pm 1$. We can see the positions of maximum intensity moving from $3k-1$ to $3k+1$ as the fraction of $\overleftarrow{cyc}$ increases (top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

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 ${}^{S+I}G_7 \sim {}^{I}G_6$.[4] We did find (with help from a computer search) type V D pairs in ${}^{S+I}G_8$; typically, they involve nonzero Δ 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 Δ. Type I pairs always give δ-function patterns, and types III–V always have even period (because all these types, for $r<8$, are S symmetric, i.e., 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) (Ref. 4) has proposed a 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 one-dimensional (1D) chains as stackings of identical close-packed layers, i.e., as (hypothetical) polytypes, and computed the the diffraction patterns along the stacking direction. In particular, we assumed, as appropriate for close-packed 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.[15] 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 Δ 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, i.e., those built from close-packed layers.

There are many well-known polytypic materials whose structures obey the ABC state restriction. SiC and ZnS, which are among the most well-studied "classical" polytypes, can almost certainly be ruled out as candidate materials for realization of the zero-temperature disorder described by CW,[4] and here. For these materials, there are good estimates[7] of the effective interlayer couplings in the Ising Hamiltonian. These couplings point to a simple periodic ground state; in particular, they fall off too rapidly, being very small for $r \gtrsim 5$ (recall that CW showed that all ground states are periodic for $r<6$). It is also likely (though not certain) that the other classical polytypes will also have interactions of a range too short to give rise to the phenomena studies here. It is of course of interest to see whether these potentials, or any other known potentials for real polytypic materials, 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

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 $cyc/\overleftarrow{\overline{cyc}}$. The type III pairs [see Fig. 1(c)] can be decomposed in several ways; here we give them as $cyc/\overleftarrow{cyc}$. The (binary) periods of the paired cycles are given, as these are apparent even in the disordered diffraction patterns [see, e.g., Fig. 5(b)]. The Δ value and type determines whether the diffraction pattern has δ functions, or is continuous.

r	D pair	T_{01}	Δ values [a]	Type	Spectrum
6	10111100100001 00111101100001	14	$0,0,-1,+1$	III	Continuous
6	1011111001000001 0011111011000001	16	$0,0,-1,+1$	III	Continuous
6	1001011 0001011	7	$+1,-1$	II	Continuous
6	0001010011101011 1001010001101011	16	$0,0,+1,-1$	III	Continuous
6	101111110010000001 001111110110000001	18	$0,0,-1,+1$	III	Continuous
6	100101011 000101011	9	$+1,-1$	II	Continuous

[a] Each entry has two or four values depending on the type of D pair (see Fig. 1).

the set of Hamiltonians which correspond to a given ground state (e.g., 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.[16] Here the effective potentials are long ranged, and highly frustrated. The approach of CW (Refs. 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[17] 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[18] 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 (δ 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 layered solids.

ACKNOWLEDGMENTS

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APPENDIX

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 Δ of a set of l spins within an interval, from the $(q+1)$st to the $(q+l)$th spin (q,l integers with $q\geqslant 0$ and $l\geqslant 1$) 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 Δ 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,

$$Q_s(mT+n)=\frac{n_s(n)}{T_{01}},$$

$$Q_c(mT+n)=\frac{n_c(n)}{T_{01}}, \tag{A1}$$

$$Q_r(mT+n)=\frac{n_r(n)}{T_{01}} \quad (m\geqslant 0).$$

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

$$Q_s(n)=\frac{n_s(n)}{T_{01}} \quad (1\leqslant n<\infty). \tag{A2}$$

Since the chain is periodic it is useful to write n as $n=mT+n'$, $m\geqslant 0$ and $1\leqslant n'\leqslant T$. 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

$$Q_s(mT+n)=\frac{n_s(n)}{T_{01}}. \tag{A3}$$

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 Δ 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 $\Delta(n)$:

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

A set of $T_{01}+n$ spins contributes to n_r (n_c, n_s) if $\Delta(T_{01}+n)$ is -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

$$Q_r(T_{01}+n)=Q_c(n),$$

$$Q_r(2T_{01}+n)=Q_s(n). \tag{A5}$$

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,

$$Q_r(n)=Q_c(T-n) \quad (1\leqslant n\leqslant T). \tag{A6}$$

This result is independent of Δ 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 Sec. I, we can show that the lines indexed $3k$ and $3k-1$ ($k\geqslant 0$) are extinguished for a periodic chain with $\Delta=+1$. Rewrite the intensity equation [Eq. (3.5] as

$$\begin{aligned} I(l)=&\frac{\sin^2(\pi Nl)}{\sin^2(\pi l)}-2\sqrt{3}\sum_{n=1}^{N}(N-n)\left[Q_c(n)\cos\left(2\pi nl+\frac{\pi}{6}\right)\right.\\ &\left.+Q_r(n)\cos\left(2\pi nl-\frac{\pi}{6}\right)\right]\\ \equiv&\frac{\sin^2(\pi Nl)}{\sin^2(\pi l)}-\mathscr{S}. \end{aligned} \tag{A7}$$

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. (A7) as

$$\mathscr{S}\equiv\frac{2\sqrt{3}N^2}{T}\sum_{n=1}^{T}Q_r(n)\cos\left(2\pi nl-\frac{\pi}{6}\right). \tag{A8}$$

Next, using $Q_r(T_{01}+n)=Q_c(n)$ and $Q_r(2T_{01}+n)=Q_s(n)$, $\mathscr{S}$ can be written as

$$\begin{aligned} \mathscr{S}=\frac{2\sqrt{3}N^2}{T}\sum_{n=1}^{T_{01}}&\left[Q_r(n)\cos\left(2\pi nl-\frac{\pi}{6}\right)\right.\\ &+Q_c(n)\cos\left(2\pi T_{01}l+2\pi nl-\frac{\pi}{6}\right)\\ &\left.+Q_s(n)\cos\left(4\pi T_{01}l+2\pi nl-\frac{\pi}{6}\right)\right]. \end{aligned} \tag{A9}$$

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

(i) $h=0$ or T. $\mathscr{S}=N^2$ and then the intensity $I=N^2-N^2=0$.

(ii) $h=3k$

$$\mathscr{S}=\frac{2\sqrt{3}N^2}{T}\sum_{n=1}^{T_{01}}[Q_r(n)+Q_c(n)+Q_r(n)]\cos\left(\frac{2\pi kn}{T_{01}}-\frac{\pi}{6}\right). \tag{A10}$$

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 $\mathscr{S}$ becomes

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

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 δ-function spectra for pairs with the same Δ, decaying probabilities and loss of sharp diffraction lines for mixtures of cycles of opposing Δ) are valid in general.

We consider two cycles c and c', related by symmetry (I or SI), with bit parities Δ and Δ', respectively. We will need to distinguish the case that $\Delta=\Delta'$ ("same-Δ" case; type I D pairs, or type II with $\Delta=0$) from that with $\Delta=-\Delta'$ ("opposing-Δ" 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 $(\geqslant 2T_{01}+1)$, 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-Δ pair, n_1 and n_0 are the same for either c or c'. Thus it is clear that $Q_c(1)=n_1N_u/N=n_1/T_{01}$, $Q_r(1)=n_0N_u/N=n_0/T_{01}$, and $Q_s(1)=0$. These are the same as for the periodic case. In the opposing-Δ 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) $2\leqslant n\leqslant T_{01}+1$. If $2\leqslant n\leqslant T_{01}+1$ 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 $(q=T_{01}-1)$].[19] 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-Δ 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) $T_{01}+1<n\leqslant 2T_{01}$. 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 $\overline{n}_s^{(0)}(n)$, $\overline{n}_c^{(0)}(n)$, and $\overline{n}_r^{(0)}(n)$. Then the probabilities can be written as

$$Q_s(n)=\frac{\overline{n}_s^{(0)}(n)}{T_{01}},$$

$$Q_c(n)=\frac{\overline{n}_c^{(0)}(n)}{T_{01}}, \tag{A12}$$

$$Q_r(n)=\frac{\overline{n}_r^{(0)}(n)}{T_{01}} \quad (T_{01}+1<n\leqslant 2T_{01}).$$

(iv) $2T_{01}+1\leqslant n\leqslant 3T_{01}$. 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 $\Delta(T_{01})\equiv\Delta$ 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 Δ of the lumped cycle is 0, $+1$, or -1, respectively. For example, for a type II D pair, in which the Δ 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 Δ'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 $\overline{n}_r^{(0)}(n)$:

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

$$\overline{n}_c(2T_{01}+n)=f_1^{(c)}\overline{n}_s^{(0)}(n)+f_1^{(s)}\overline{n}_c^{(0)}(n)+f_1^{(r)}\overline{n}_r^{(0)}(n), \tag{A13}$$

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

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 $3T_{01}+1\leqslant n\leqslant 4T_{01}$, 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 $(p+1)T_{01}+1\leqslant n\leqslant(p+2)T_{01}$ $(p\geqslant 1)$, we can use the following formulas:

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

$$f_p^{(c)}=f_{p-1}^{(c)}f_1^{(s)}+f_{p-1}^{(s)}f_1^{(c)}+f_{p-1}^{(r)}f_1^{(r)}, \tag{A14}$$

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

Since $f_1^{(s)}$, $f_1^{(c)}$, and $f_1^{(r)}$ can be determined by the Δ of the D pair, we can obtain the cycle probabilities for any p using these recursion relations. Using Eqs. (A14) we can finally get $n_x[(p+1)T_{01}+n]$:

$$\overline{n}_s[(p+1)T_{01}+n]=f_p^{(s)}\overline{n}_s^{(0)}(n)+f_p^{(r)}\overline{n}_c^{(0)}(n)+f_p^{(c)}\overline{n}_r^{(0)}(n),$$

$$\overline{n}_c[(p+1)T_{01}+n]=f_p^{(c)}\overline{n}_s^{(0)}(n)+f_p^{(s)}\overline{n}_c^{(0)}(n)+f_p^{(r)}\overline{n}_r^{(0)}(n),$$

$$\overline{n}_r[(p+1)T_{01}+n]=f_p^{(r)}\overline{n}_s^{(0)}(n)+f_p^{(c)}\overline{n}_c^{(0)}(n)+f_p^{(s)}\overline{n}_r^{(0)}(n)$$

$$(p\geqslant 2,1\leqslant n\leqslant T_{01}). \tag{A15}$$

Thus, once we know $\overline{n}_s^{(0)}(n)$, $\overline{n}_c^{(0)}(n)$, and $\overline{n}_r^{(0)}(n)$, 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

$$f_p^{(s)}=f_{p-1}^{(r)}f_p^{(c)}=f_{p-1}^{(s)}f_p^{(r)}=f_{p-1}^{(c)} \tag{A16}$$

so that the probabilities are given by

$$Q_s(2T_{01}+n)=\frac{\overline{n}_r^{(0)}(n)}{T_{01}},\quad Q_s(3T_{01}+n)=\frac{\overline{n}_c^{(0)}(n)}{T_{01}},$$

$$Q_s(4T_{01}+n)=\frac{\overline{n}_s^{(0)}(n)}{T_{01}},$$

$$Q_r(2T_{01}+n)=\frac{\overline{n}_c^{(0)}(n)}{T_{01}},\quad Q_r(3T_{01}+n)=\frac{\overline{n}_s^{(0)}(n)}{T_{01}},$$

$$Q_r(4T_{01}+n)=\frac{\overline{n}_r^{(0)}(n)}{T_{01}}, \tag{A17}$$

$$Q_c(2T_{01}+n)=\frac{\overline{n}_s^{(0)}(n)}{T_{01}},\quad Q_c(3T_{01}+n)=\frac{\overline{n}_r^{(0)}(n)}{T_{01}},$$

$$Q_c(4T_{01}+n)=\frac{\overline{n}_c^{(0)}(n)}{T_{01}}.$$

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 (δ 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-Δ case, i.e., 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-Δ 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 $f_1^{(s)}=0$ and $f_1^{(c)}=f_1^{(r)}=1/2$. From Eqs. (0.14) and the initial cycle probabilities it is not hard to get the following recursion relation:

$$f_p^{(x)}=\frac{1}{2}(f_{p-1}^{(x)}+f_{p-2}^{(x)}) \tag{A18}$$

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

$$\delta_p\equiv f_p-f_{p-1}=C\left(-\frac{1}{2}\right)^p, \tag{A19}$$

with $C=4(f_2-f_1)$. We then sum (A19) to get, for large p,

$$f_{p\rightarrow\infty}^{(x)}=f_1^{(x)}+\frac{2}{3}(f_2^{(x)}-f_1^{(x)}). \tag{A20}$$

With initial conditions appropriate to $\Delta=\pm 1$ (i.e., $f_1^{(s)}=0$ and $f_2^{(s)}=1/2$, or equivalently, $f_1^{(c,r)}=1/2$ and $f_2^{(c,r)}=1/4$) we can show that all three cycle probabilities decay to 1/3 at large p. With Eqs. (A13), $\overline{n}_s$ (large n) can be found to be $(1/3)T_{01}$, using the fact that $\overline{n}_s^{(0)}(n)+\overline{n}_c^{(0)}(n)+\overline{n}_s^{(0)}(n)=T_{01}$. Finally, the probabilities for large n are

$$Q_s(n)=\frac{\overline{n}_s(n)}{T_{01}}=\frac{1}{3}=Q_c(n)=Q_r(n). \tag{A21}$$

The diffraction pattern for the opposing-Δ case is thus diffuse, without any δ functions.

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