

The crystal problem for polytypes

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Recent work on discrete classical problems in one-dimensional statistical mechanics has shown that, given certain elementary symmetries, such problems may not have a periodic (crystalline) ground state, even in the absence of fine tuning of the couplings. Here these results are applied to several families of well known polytypic materials. The families studied are those represented by the compounds SiC, CdI₂ and GaSe, and also the micas and kaolins. For all families but SiC, it is found that there is a finite probability for the ground state to be degenerate and disordered.

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1. Introduction

The crystal is by far the most common state of bulk matter at low temperature. The ‘crystal problem’ is then the problem of understanding, or even proving, why this is so. The crystal problem remains largely unsolved; see Miękisz & Radin (1987) for some recent discussions. In this paper, we consider the crystal problem as applied specifically to polytypes and polytypism. In polytypic materials (Verma & Krishna, 1966; O’Keeffe & Navrotsky, 1981; Pandey & Krishna, 1982; Sebastian & Krishna, 1994), one finds a three-dimensional structure built up from identical two-dimensional layers; here we call such layers ‘modular layers’ or MLs. Various stacking sequences of these MLs then give a bulk three-dimensional solid. The ‘poly’ aspect comes in because, although there are in general constraints on how the MLs may be stacked one upon another, these constraints do not uniquely determine the stacking sequence giving rise to the three-dimensional structure. Instead they allow a variety of sequences and hence many structures.

One can phrase this discussion in terms of energy scales. The unique structure assigned to the ML comes from chemical bonding with a large energy scale. The stacking constraints then arise from another large energy scale: inter-(modular)layer bonding may be weaker than intralayer bonds, but the extensive nature of the interlayer interface makes very large energy penalties for any relative stacking orientations outside a discrete set. Finally, there are residual small energy terms that can distinguish among the various stacking sequences allowed by the constraints. These terms are small because the nature of the ML, plus the stacking constraints, typically ensure that the coordination of all constituent atoms is independent of stacking sequence at the level of first, second or even higher neighbors.

Given this discrepancy of energy scales, it is then reasonable, at low T , to assume that the large-energy degrees of

freedom (MLs and stacking orientations) are restricted to their lowest-energy configurations – perfect MLs, and perfectly obeyed stacking constraints. Hence one can view polytypism as a limited version of the crystal problem: one assumes crystallinity in two dimensions (the ML), and then asks: is there necessarily crystalline order in the third dimension, *i.e.* in the stacking sequence?

Here the crystal problem is formally one-dimensional. The discrete set of stacking orientations may then be thought of as ‘spins’ lying on a one-dimensional chain. Furthermore, given the large mass of the ML, it is appropriate to view these spins as classical. The stacking energetics is then expressed (Cheng *et al.*, 1987; 1988; Heine, 1987; Pandey, 1989) by a one-dimensional classical spin Hamiltonian H_{1D} , with the spins σ_i taking one of a set of k possible values. Another integer parameter r gives the range of the effective spin–spin (*i.e.* interlayer) interaction. This effective interaction is of course determined by the energetics of interacting quantum-mechanical electrons in the potential of the constituent ions. However, for insulating polytypes, for which the Fermi energy lies in a gap, the range of interlayer interactions is finite (Cheng *et al.*, 1988), and so it is appropriate to consider r finite. [For metals (Blandin *et al.*, 1966; Krause & Morris, 1974), r is effectively infinite.]

Given a finite k and r , there are in fact only a finite set of independent couplings that can be used to define H_{1D} . A typical term in H_{1D} is of the form

$$J_{p_0 p_1 \dots p_r} \sum_i \sigma_i^{p_0} \sigma_{i+1}^{p_1} \dots \sigma_{i+r}^{p_r} \quad (1)$$

There is one such term (and so one coupling J) in H_{1D} for each choice of the exponents $\{p_l\}$ (with $1 \leq p_0 \leq k-1$; and $0 \leq p_l \leq k-1$, $l > 0$) (Canright & Watson, 1996). The total number of independent couplings, which is thus the dimension of the coupling-parameter space unconstrained by symmetry,

is $d = (k - 1)k'$. We shall not in general have much to say about the couplings in H_{1D} , which we loosely refer to as J 's – beyond the facts that they are finite in number and may be constrained (some of them) by symmetry. The crystal problem for Hamiltonians of this form – again, appropriate to insulating polytypes – has been studied by Radin & Schulman (1983), by Teubner (1990) for $k = 2$, and by Canright & Watson (1996) (CW). Radin & Schulman showed that the ground state (GS) for H_{1D} is in general periodic – as did Teubner for $k = 2$. These results appear to leave the crystal problem solved for polytypism. However, CW pointed out that the words ‘in general’, for the previous results, mean *barring fine tuning of the coupling parameters J in H_{1D}* . That is, if one chooses couplings freely from the d -dimensional space spanned by the J 's of H_{1D} , one finds couplings giving a periodic and nondegenerate GS with probability one. CW then pointed out that nature does *not* choose freely from this d -dimensional space – instead, because of the presence of *symmetry*, at least some of the J 's are fine tuned. In other words, when H_{1D} respects certain elementary physical symmetries, the couplings are constrained to a space of dimension $d_s < d$. CW then showed that, in this reduced (symmetric) space of couplings, there is a finite fraction of the space giving degenerate and disordered GSs for many values of k and r and certain elementary symmetries.

We emphasize that these disordered ground states are *equilibrium* structures. They are thus conceptually distinct from the nonequilibrium disorder studied by Kabra & Pandey (1988) and by Shrestha & Pandey (1996, 1997) – although, in some cases, the nature of the disorder is qualitatively similar (Yi & Canright, 1996). They also require *no fine tuning* of the couplings in H_{1D} – in contrast to the degeneracy and disorder found in models such as the ANNNI model (Yeomans, 1987) at lines or points in a higher-dimensional space of couplings. The methods of CW instead predict degeneracy and disorder, in equilibrium at zero temperature, over a finite subvolume of the coupling-parameter space.

This finite fraction is however never 100%. Hence the results of CW give two possible answers to the question ‘Is the GS of a given polytypic material crystalline?’, namely, possibly not or necessarily yes. In this paper, we abbreviate these possibilities as, respectively, PNC (possibly noncrystalline) or C (crystalline). Here we should be quite clear what we mean by possible or impossible: we consider any fine tuning of the J 's, other than that enforced by symmetry, to be ‘impossible’ – *i.e.* infinitely unlikely. We also consider defects in the MLs or violation of the stacking rules to be impossible, since we neglect them. However, our approach (and that of CW) does allow for relaxation of the MLs from their ideal structure, as long as that relaxation does not alter the symmetry of the MLs and hence of the problem. (For an example, see §7 on micas.) This restriction is necessary since our approach relies heavily on symmetry.

In this paper, we ask the above question (is the GS crystalline?) for a variety of known polytypic materials, or rather families of materials, characterized by the symmetry of the MLs, by the nature of the ‘spins’ and by the stacking rules.

Since we reason purely from the symmetries and constraints, we can only give the answers C or PNC. In the PNC case, one must look to the actual energetics of the interlayer couplings (the J 's) in order to obtain a definite answer. These couplings can be obtained in principle and sometimes in practice (Cheng *et al.*, 1987, 1988; Heine, 1987; Shaw & Heine, 1990; Engel & Needs, 1990; Engel, 1990); but we shall not address that problem here.

Our method is as follows. Given the symmetry of the MLs, the definition of the spins and the nature of the stacking constraints, we can obtain, by basic geometric and symmetry considerations detailed below, the elementary symmetries that must apply to the couplings J of the layer Hamiltonian H_{1D} . These symmetries will form a group \mathcal{G} . Knowing this group, plus the number of states k per spin and the range r of interlayer interactions, we can determine whether the ground state of the resulting problem is C or PNC, using the methods of CW. However, the range r of interlayer interactions – like the couplings themselves – is not known for most polytypic materials. Hence we reason as follows. The results of CW, as well as our own experience, imply that, if a material is PNC for some r_{\min} , then it is also PNC for all $r > r_{\min}$. Hence our answer takes one of two forms: PNC for $r > r_{\min}$ (and we determine r_{\min}), or C for all r . For cases already studied by CW, we get this answer from Table 1 of CW. However, we have found a rich variety of new possibilities for real polytypes, beyond those studied by CW. In particular, we find that the spins can take on a *vector* character for some polytypes. That is, per ML, one needs an ordered D -tuple of scalars to specify the stacking, with (possibly) $D > 1$. Hence, our one-dimensional formalism must include the possibility of D (the spin dimension) > 1 . Furthermore, given $D > 1$, we find that interesting symmetries are possible for H_{1D} that were not considered by CW. Hence, for these cases, we must determine the GS structure of H_{1D} (C or PNC as a function of k , r and symmetries) ‘from scratch’.

The plan of the rest of the paper is as follows. In §2, we give the logic that enables us to obtain the symmetry group \mathcal{G} of H_{1D} for real polytypic materials. Then in §3 we present a brief review of the graph-based analysis of CW, as well as a preview of its extension to $D > 1$. In §§4–8, we then present our results for five polytype families, represented by SiC, CdI₂, GaSe, micas and kaolins/cronstedtites. Finally, in §9, we summarize our results and discuss their implications.

2. Symmetry group of H_{1D}

We wish to study the ground states of a one-dimensional Hamiltonian H_{1D} which represents a family of polytypes. This Hamiltonian is one-dimensional because we make the usual assumptions for polytypes: that the modular layers (MLs) are invariant and have no defects, and that they stack upon one another in relative positions/orientations chosen from a discrete set. H_{1D} then gives the energetics (which can, in principle, be exact) for the possible stacking sequences (chosen from this set). We call the discrete degrees of freedom of H_{1D} ‘spins’. In our approach, it is useful to distinguish

'absolute' from 'relative' spins. The former are absolute in the sense that their position and orientation is fixed [modulo operations in the layer group (LG)] with respect to a fixed coordinate system. We find it helpful to think of this fixed coordinate system as a ML at $z = -\infty$; we call this the 'reference' modular layer or RML. The RML then defines the absolute position and orientation, *i.e.* the 'absolute spin', of any other ML, as well as the stacking (\hat{z}) axis. 'Relative' spins are then spins that are defined by comparing absolute spins. We write H_{1D} in terms of relative spins for the same reason that the microscopic Hamiltonian is in terms of relative positions – that is, we assume that no external fields bias the absolute position of the MLs.

Given the discreteness of these relative spins and the (assumed) finite range of effective interlayer interactions, there are in general a finite number (Radin & Schulman, 1983; Teubner, 1990) of possible ground states for H_{1D} , and hence for the polytype family. However, Canright & Watson (1996) showed that symmetries of H_{1D} can alter this conclusion, such that there are, in some *finite-volume* regions of coupling space, an exponential (in layer number N) number of ground states, essentially all of which are disordered. Our goal in the present work is to use the symmetries and stacking rules of a given polytype family to determine whether the ground states of the resulting H_{1D} include this kind of disorder and degeneracy. In this section, we outline the logic that allows us to determine the symmetry group \mathcal{G} of H_{1D} . In the following section, we discuss how to determine whether or not there are such degenerate and disordered ground states for H_{1D} , given its symmetry group \mathcal{G} .

What are the symmetries of H_{1D} ? Clearly, they derive from the symmetries of the microscopic interactions giving rise to the condensed solid. In particular, we know that the microscopic energetics H_{3D} must be invariant under any proper or improper rotation R in $O(3)$. Our goal is then to find a set of rotations $\{R^*\} \subset O(3)$ that tell us the symmetries of H_{1D} . This works as follows: we take a finite sample of MLs, stacked according to the rules of the polytype family, and assign to it a sequence \mathcal{S}_r of relative spins σ_i (where i is a layer index). Then a 'useful' rotation R^* , when applied to this three-dimensional sample, will give us another sample that (i) is oriented such that we can also assign a spin sequence \mathcal{S}'_r to it, *using the same conventions as those used for \mathcal{S}_r* ; and (ii) has $\mathcal{S}'_r \neq \mathcal{S}_r$.

'Useless' rotations (much more numerous) will fail (i) or (ii). For instance, noncrystallographic rotations fail (i): if we rotate a sample by an arbitrary amount about an arbitrary axis, its energy doesn't change, but we cannot assign a spin sequence to the result because (in general) we have lost orientation with respect to the (fixed) RML. That is, the RML provides us with a reference frame that must be used to evaluate any new stacking sequence *as spins*. Without the RML, the exercise is empty.

Other rotations will satisfy (i) but simply give the identity. This group may include elements of the LG but not necessarily; the LG leaves the MLs invariant but may alter the spins. In any case, rotations giving the identity in spin space are also clearly not useful; hence criterion (ii).

In order to satisfy (i), we confine ourselves to those crystallographic rotations appropriate to layers. [This is a necessary but not sufficient condition for satisfying (i).] In fact – since the group structure of rotations carries over into the group structure of symmetry operations on spins – we need only consider a sufficient set of generators for the layer groups, in order to find a sufficient set of generators for the group \mathcal{G} of H_{1D} . We take these layer-group generators from a table in Goodman (1984). This is a short list, from which one quickly finds those R^* that fail neither (i) nor (ii) and so give us the symmetry group \mathcal{G} for the polytype. Specifically, a (sufficiently general) 'seed' sequence \mathcal{S}_a of absolute spins is chosen, and its corresponding relative-spin sequence \mathcal{S}_r determined. Then a useful rotation R^* gives a new configuration that also may be written as a list of well defined absolute spins, using the same reference coordinates (*i.e.* the RML) as the original sample. This new list \mathcal{S}'_a then gives a new relative list \mathcal{S}'_r . The operation relating \mathcal{S}_r to \mathcal{S}'_r is then a symmetry of H_{1D} – because the sequences \mathcal{S}_r and \mathcal{S}'_r (representing stacking sequences differing only by a rigid rotation) must be degenerate.

In order to illustrate our methods and logic, we consider a simple example: close-packed layers of identical spheres. This example in fact is not wholly academic, as it may be used to describe some elemental metals; however, metals (Blandin *et al.*, 1966; Krause & Morris, 1974) do not conform to our assumption of finite r . Hence we use this example primarily for illustrative purposes.

First we define the MLs. These are two-dimensional close-packed layers with the full symmetry of the hexagonal net: the LG [here we use notation following Vainshtein (1981)] is $p6/mmm$. Next we define the 'absolute spins'. We recall that these are defined with respect to a fixed reference modular layer or RML. For the current (close-packing) example, we take the RML to be (say) an A layer. Then the absolute spin of any other ML is an A , B or C . We can define the relative spins using the usual Hägg notation: $\sigma_i = \pm 1$. This definition incorporates the only stacking constraint, namely, that the occurrence of adjacent like absolute spins (AA , BB or CC) is forbidden. We follow the standard convention that $+$ represents $A \Rightarrow B$, $B \Rightarrow C$ or $C \Rightarrow A$ (cyclic sequences), while $-$ labels the anticyclic pairs.

For the purposes of our analysis, it is important to make explicit what is implicit in the above, and in fact in all cases: the definition of relative spins *includes or implies a convention for a positive stacking vector $+\hat{z}$* . This positive stacking vector may be thought of as attached to the RML. The point here is that relative spins always refer to the *change* in absolute spin upon moving in the $+\hat{z}$ direction. Our logic then requires that this convention (*i.e.* the sign of \hat{z}) not change under rotations (proper or improper) which change $\mathbf{z} \rightarrow -\mathbf{z}$.

Having defined the MLs and their symmetry, relative and absolute spins, and stacking constraints, we are ready to find the symmetry group \mathcal{G} of H_{1D} . We introduce a 'seed' sequence to determine the effects of physical rotations on a sample. The only constraint on the choice of seed is that it should be general enough to distinguish all the possible symmetries of H_{1D} . For the close-packing problem, let this seed sequence be

$S_a = (ABCBACBC)$. We can write this in terms of relative spins as $S_r = (+ + - - - +)$. Let us consider three rotations acting on S . For the first, let us rotate the sample by 60° about an axis parallel to the stacking direction – this operation being more briefly denoted ‘ 6_z ’ – centering the axis on a site in an A layer. This will leave the A spins unaffected but exchange B and C . The rotated absolute spin sequence is then $(ACBCACBC)$, giving a relative rotated spin sequence of $(- - + + + -)$. If the identification of $+$, $-$ as spin inverse pairs is made, then the rotated relative spin sequence is the spin inverse of the original relative spin sequence. We then say that spin inversion (S) is a symmetry of the Hamiltonian describing this system.

For the second rotation, consider rotating the sample by 180° about a primitive translation vector (along x , y or u) of the hexagonal net. (We denote this operation as 2_{xyu} .) Let the origin of this axis again be centered on an A site. Then A sites will be brought back to A sites, while B and C sites exchange; and finally the entire stacking order of the spins is reversed. So the rotated absolute spins will now be $(BCBACBCA)$. This will give a relative spin sequence of $(+ - - - - +)$. Comparison with the original relative spin sequence shows that this has just altered the order of the spins. We therefore say that the Hamiltonian has spatial inversion (I) symmetry.

Finally, consider the improper rotation $m_z \equiv [z \rightarrow -z]$. This rotation will leave the absolute spins unchanged but reverse their stacking order. So the rotated absolute spin sequence will be $(CBCABCBA)$. This gives a relative spin sequence of $(- + + + + -)$. This is just the product of spin and spatial inversion SI operating on the original sequence. Hence our third rotation is redundant: it gives us an element SI of the symmetry group \mathcal{G} , which we already knew we had from the two elements S and I . All other rotations on our list are also redundant. In fact, for $D = 1$ (which is the case here), we have never found a larger group than that generated by S and I . We denote this group by $\mathcal{G} = S + I$; this is the symmetry group of H_{1D} for any polytype formed of close-packed layers of spheres.

3. Disordered ground states, graphs and D pairs

In this section, we first briefly review concepts and terminology from previous work (Canright & Watson, 1996), which we will use in the present work. We then extend these ideas to D -dimensional spins – this extension being necessary for several of the polytype families we consider.

The essential idea is to represent the Hamiltonian H_{1D} as a directed graph G_r^k . Simple cycles (non-self-intersecting closed paths) in this graph then represent the possible ground states for the given Hamiltonian. For finite k and r , there is a finite number of such simple cycles (SCs); as one varies the finite number of J 's in H_{1D} , one selects in general one of these SCs as the ground state. CW also defined a symmetry-reduced graph ${}^X G_r^k$, where X represents some symmetry of H_{1D} . The point of ${}^X G_r^k$ is simply that, if H_{1D} is constrained by a symmetry X , then, as one varies the J 's within this constrained subspace, the ground state is one of the SCs of ${}^X G_r^k$. However, it can happen

that, for some k , r and X , a SC of ${}^X G_r^k$ represents a pair of (symmetry-related) SCs of G_r^k , with zero surface tension between the two ground states. This pair in G_r^k is called a ‘ D pair’: when the J 's are such that the D pair has lowest energy, then there are an uncountable number of degenerate and disordered ground states for the problem. There are a number of technicalities involved in the construction of ${}^X G_r^k$ and the identification of its SCs (particularly those that represent D pairs); we refer the reader to Canright & Watson (1996) for details. Here we simply emphasize that, in studying a given polytype family, a search for disordered ground states becomes a search for D pairs; and, when the graph G_r^k for a given polytype has D pairs, we answer the question of crystallinity with PNC: possibly noncrystalline ground state.

All these ideas extend naturally to vector spins, *i.e.* to $D > 1$. However, for $D > 1$, new symmetries are possible besides S and I (see *e.g.* GaSe). Also, even for the symmetries considered by CW, the graphs (and hence simple cycles) for $D > 1$ are different from those for $D = 1$. (We give a specific example in §5, see Fig. 1.) Hence the question of existence, or not, of D pairs needs to be re-examined for higher D . To indicate which graph we mean, we use the notation ${}^X G_r^{[k]}$. (Here the set $\{k\}$ includes, in principle, one k value for each spin component; see the kaolins, below.) Thus, regardless of the symmetry group \mathcal{G} for a polytype, the CW analysis must be

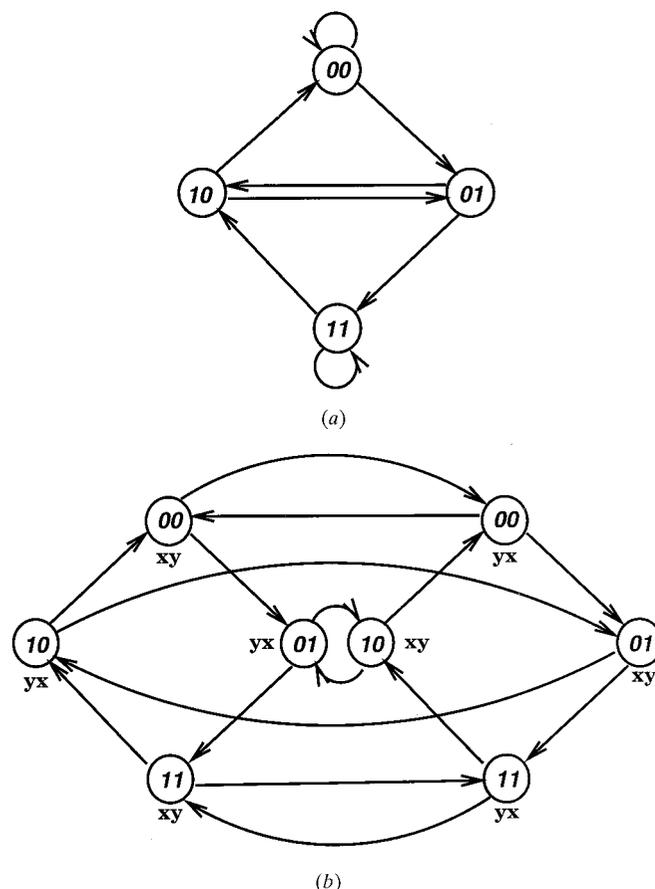


Figure 1
The graphs (a) G_2^2 and (b) $2G_2^2$. The latter graph has twice as many nodes and arcs; it also includes many simple cycles not found in G_2^2 .

redone for any polytype with $D > 1$. That is, the new graphs must be examined, either schematically, or in specific detail, in order to determine at which r values (if any) D pairs exist.

For $D = 1, k = 2$ and Hamiltonians respecting both S and I symmetry, Canright & Watson (1996) found that the effective interlayer interaction must extend through at least six modular layers for there to be a chance of a disordered ground state – *i.e.* for there to be D pairs. For effective interlayer interactions of shorter range than this, the ground state is guaranteed to be periodic. In our present shorthand, these conclusions may be stated as: PNC for $r \geq 6$ for the sphere-packing problem. We remind the reader that we know of no *finite-range* polytype that may be modeled as the close packing of spheres. However, the close-packing problem serves as a useful illustration of our logic. It also introduces notation and language that will be useful in our analysis of several polytype families (SiC, CdI₂, GaSe), for which the MLs are composed of close-packed sublayers. Let us now discuss these families in turn.

4. SiC

SiC is one of the more well known and well studied of the polytypic materials. It shows a rich variety of polytypic structures (Verma & Krishna, 1966; Sebastian & Krishna, 1994) with the simplest being a repeated sequence of two modular layers and the more complex periodic structures consisting of as many as 900 Si–C layers in a unit cell. Weakly or even highly disordered structures are also found. SiC polytypes may be viewed as alternate two-dimensional layers of close-packed Si and C atoms. Adjacent layers (of unlike atoms) then obey the constraint that all atoms in the structure have tetrahedral coordination. An SiC modular layer can be taken to be two of these sublayers, one of Si and the other of C. Absolute and relative spins can be defined analogously to the close-packing problem. The absolute spins can be labeled $A_\alpha, B_\alpha, C_\alpha$, with $\alpha = \text{Si}$ or C designating the sublayer. A convenient convention (Shaw & Heine, 1990) then takes a C sublayer as the ‘lower’ sublayer of a ML and requires the subsequent Si sublayer to have an absolute spin distinct from the C sublayer. This is of course a binary choice; the relative spin representing this choice can be given (again) a + or – symbol. Since these two sublayers form a ML, and their (absolute) positions suffice to define the relative spin without reference to any other ML, we say that the relative spin is an ‘intralayer’ spin. The tetrahedral constraint then forces the next C sublayer (of the next ML) to sit directly above the previous Si sublayer – hence there is no *interlayer* choice (*i.e.* no interlayer relative spin). The resulting MLs have the layer group (LG) $p3m1$. Since we have a single scalar relative spin per ML, we have $D = 1$; and clearly $k = 2$.

We scan Goodman’s (1984) list of crystallographic symmetry operations. We recall that ‘useless’ operations give either the identity or a resulting configuration for which the spins are not well defined, while the ‘useful’ ones give a well defined relative spin sequence that is distinct from the starting or seed sequence. We first note that any operation taking

$\mathbf{z} \rightarrow -\mathbf{z}$ is useless. One can see this from our convention, since $\mathbf{z} \rightarrow -\mathbf{z}$ has as a result a ML with an Si sublayer on the ‘bottom’. We stress however that this result is convention-independent: there is no convention, consistent with the structure, that has well defined relative spins after taking $\mathbf{z} \rightarrow -\mathbf{z}$, for fixed stacking vector $+\hat{\mathbf{z}}$. The reason for this is simply the distinct identities of the two sublayers (Shaw & Heine, 1990): whatever the convention, $\mathbf{z} \rightarrow -\mathbf{z}$ will give configurations that conform to that convention only if one in addition exchanges Si and C atoms – an operation that cannot be a symmetry of the microscopic Hamiltonian H_{3D} .

We consider the remaining operations R on our list. Rotations by 90° about \mathbf{z} (4_z) are also useless: they give configurations that cannot be referred to our reference modular layer (RML), since they do not take the hexagonal net of a ML back to itself, and hence have no well defined absolute spin. Rotations by 120° about \mathbf{z} (3) act as an identity on all absolute spins and stacking sequences, and so are not useful. Reflections (here designated m) about a plane whose normal lies along a primitive translation vector ($\in x, y, u$) are also in the LG and so give identity for the absolute spins, as well as for their stacking order. We are left with two symmetry elements that are not members of the LG, namely sixfold rotations about $\hat{\mathbf{z}}$, and mirror reflections m' about planes parallel to both \mathbf{z} and to primitive translation vectors of the ML. Choosing a seed sequence and performing these operations on it, we find that each is useful: each gives the spin inversion S (*i.e.* $+\iff -$) operation for the relative spins.

We have also considered glides, which are included in Goodman’s list. We have not found glides to be helpful in the case of SiC, or indeed in any case we have considered. While we know of no proof that glides could not give an independent symmetry for H_{1D} , we find that the translational component never affects the relative spins that we have studied so far – while the reflection is of course taken care of by considering it alone. Thus, glides can be ‘useful’ by the technical definition of useful employed here; but we do not find that the translational component adds any new information beyond that obtained from reflection alone. Hence we do not consider glides further in this paper.

There is also a screw operation on our list. It was excluded in the present case (SiC) as it takes $\mathbf{z} \rightarrow -\mathbf{z}$. However, we note here that screws have also not been found helpful for any of the families we have studied, for the same reason that we have not found glides helpful.

We thus exhaust our list of candidate geometric operations. We have found two useful R^* operations, each giving S symmetry for the spins. We do not obtain spatial inversion (I) symmetry. Hence, S is the only good symmetry of the layer Hamiltonian H_{1D} , and so the only generator of the symmetry group \mathcal{G} .

Now we are in a position to ask: might SiC have a noncrystalline ground state? Since $D = 1$, we can use the results of CW. For $k = 2$, they found that only I symmetry or $S + I$ symmetry can lead to disordered ground states. S alone does not give the D pairs that give rise to disordered ground states. Hence, we conclude that SiC must be crystalline in the

ground state: in the language used earlier, we say that SiC is C (crystalline) for all r .

One can also obtain this result by explicitly computing the couplings J in H_{1D} . However, our result is obtained purely from symmetry considerations and so is independent of the specific values of these couplings. This result also applies to any other polytype in the same family as SiC – *i.e.* any other polytype with the same structural and bonding constraints, which give rise to symmetry-equivalent MLs and analogous stacking constraints and spins. To our knowledge, the J 's have been computed only for SiC (Cheng *et al.*, 1988; Shaw & Heine, 1990) and for ZnS (Engel & Needs, 1990; Engel, 1990). Here we find that any polytype isostructural to SiC must have a periodic ground state.

5. CdI₂

5.1. Modular layers, vector spins and symmetry group

Another well known group of polytypic materials is CdI₂ and related compounds isostructural to it, such as CdBr₂ and PbI₂. While we will discuss CdI₂ specifically, our conclusions and analysis will apply to any polytypic compound in the same family. As with SiC, CdI₂ shows a wide variety of polytypic structures: periodic structures with unit cells containing as few as two modular layers up to as many as 120 modular layers; and disordered structures (Verma & Krishna, 1966; Sebastian & Krishna, 1994). CdI₂ can be viewed as a close-packed structure of I ions with Cd ions filling octahedral voids. This is possible because of the disparity of the ionic radii of the constituent ions – 2.16 Å for I and only 0.97 Å for Cd. Since there are twice as many I ions as Cd ions in the structure, only half of the octahedral voids – those between alternating pairs of I sublayers – are filled. A modular layer can be thought of as two close-packed I-ion sublayers, with Cd ions filling the octahedral voids between the I sublayers. Hence a ML is a 'sandwich' of three close-packed layers: I/Cd/I. The bonding in the modular layer (intralayer bonding) is ionic, while the bonding between layers (interlayer bonding) is primarily due to much weaker van der Waals forces. It is thus natural to define a ML as an I/Cd/I sandwich. The LG for such a sandwich is $p\bar{3}m1$.

Just as in the case of the close-packing problem, the absolute spins of the I-ion sublayers may be represented by A , B and C . The stacking constraints for close packing of spheres – namely, that adjacent layers must have different absolute spins – apply also to adjacent sublayers in CdI₂; there is however the further constraint that succeeding I sublayers, whether or not they have an intervening Cd sublayer, must have differing absolute spins. Hence the stacking constraints on the I sublayers is the same as if there were no Cd sublayers; and since the latter, in each ML, must take whatever absolute spin is not taken by the two I sublayers of that ML, the Cd sublayers have no stacking degree of freedom. Furthermore, the Cd sublayers lie on the same two-dimensional net as do the I sublayers, and hence neither add to nor subtract from the symmetry of the problem. Thus we ignore the Cd sublayers in

our analysis. Their presence is reflected in our formalism in the fact that, unlike for the close-packing problem, for CdI₂ we take *two* I sublayers to make up a ML.

Clearly there is a binary relative spin implied by the specification of each ML (*e.g.* an AB ML becomes $+$). This is an intralayer spin. In order to describe the stacking of many MLs, we need (per ML) this intralayer spin, plus an interlayer spin (per ML). The latter gives the relative orientation of the 'bottom' I sublayer of a 'new' ML ($i + 1$) with respect to the 'top' I sublayer of the previous ML (i). We thus find two binary choices per ML. We could then say that $k = 4$ for CdI₂. However, the four states are $++$, $+-$, $-+$ and $--$. That is, the relative spin for a ML is a *vector*: an ordered pair of scalars. The order is important because the chemistry, and hence energetics, differ between inter- and intralayer spins. The formalism must distinguish the two. Furthermore, if we take the above four pairs to be our $k = 4$ spin states but attempt to treat them as scalars (so as to take advantage of the results of CW), we find that the attempt fails. The spatial inversion operator I , applied to these spins treated *as scalars*, has a result that is highly unphysical. The I operation reverses the (stacking) order of scalar spins but fails to reverse the order *within* any 'scalar' ordered pair. A *physical* rotation taking $\mathbf{z} \rightarrow -\mathbf{z}$ must of course reverse both the stacking order and the internal order of the spins. Hence, CdI₂ compels us to consider vector spins. For CdI₂, the dimension of the vector spins is $D = 2$. We also know that the k value for each component of the vector is two. We have not found $D > 2$ for any of the polytype families we have studied. However, we have found a case (kaolins) where the different components have different k values.

At this point, it is worthwhile specifying the form of H_{1D} for vector spins, with $D = 2$. Recall the form of terms in H_{1D} for $D = 1$, as given in (1). In lieu of the σ_i used for the scalar case, we denote the intra- and interlayer spins of ML i by x_i and y_i , respectively. A spin sequence for a given sample is then of the form

$$\dots x_{i-1} y_{i-1} x_i y_i x_{i+1} y_{i+1} \dots \quad (2)$$

Now we wish to build terms like those in (1), using both spin components with interactions out to some given range r . For $D > 1$, we shall define r to be the interaction range in units of spin *components* (half-spins). The form of terms in H_{1D} , for $D = 2$, then depends on whether r is even or odd. For even r , we obtain terms of the form

$$J_{p_0 q_0 p_1 q_1 \dots p_{r/2} q_{r/2}} \sum_i x_i^{p_0} y_i^{q_0} x_{i+1}^{p_1} y_{i+1}^{q_1} \dots x_{i+r/2}^{p_{r/2}} y_{i+r/2}^{q_{r/2}} \quad (3)$$

The exponents obey $0 \leq p_l \leq k_x - 1$ and $0 \leq q_l \leq k_y - 1$, where k_x and k_y are the number of states for, respectively, x and y spins. There are further constraints on the exponents. If $p_0 = 0$, then we must have $q_0 \neq 0$; otherwise we get redundant terms in the \sum_i . Also, to keep only terms of range r , we must have $q_{r/2} = 0$ whenever $p_0 \neq 0$. Given these constraints, and setting $k_x = k_y = k$ and $D = 2$, the total number of distinct J 's is $d_{D=2} = 2(k - 1)k^r$. For odd r , terms are of the form

$$J_{p_0 q_0 p_1 q_1 \dots q_{(r-1)/2} p_{(r+1)/2}} \sum_i x_i^{p_0} y_i^{q_0} x_{i+1}^{p_1} y_{i+1}^{q_1} \dots y_{i+(r-1)/2}^{q_{(r-1)/2}} x_{i+(r+1)/2}^{p_{(r+1)/2}} \quad (4)$$

with the same range for the exponents, and the constraints $p_0 = 0 \implies q_0 \neq 0$ and $p_0 \neq 0 \implies p_{(r+1)/2} = 0$. For $k_x = k_y = k$ and $D = 2$, we get the same number of such terms, namely $d_{D=2} = 2(k-1)k^r$. Hence for CdI₂, with $k_x = k_y = 2$, there are 2^{r+1} independent J 's in H_{1D} – twice the number one obtains for the same r and k with $D = 1$.

We can define R to be the range of interaction in units of modular layers. However, it is not possible to fix the half-spin interaction range at r (as specified above) and, at the same time, to require that MLs have all interactions out to a finite range R and then zero interaction beyond R . This is simply because the interactions coupling x and y spins act on half-layers rather than on entire MLs. We feel that fixing r is neither less nor more realistic than fixing R for the MLs – especially since, in this work, we are asking for a *minimum* range of interaction, beyond which one has the possibility of D pairs, *i.e.* disordered ground states. Given our conventions, interactions in units of spin components (half-spins) reach their limit (at r) in such a way that the range R in units of MLs is half-integer. However, one can simply assume that R is roughly the higher integer value; this gives $R = [(r+1)/2]$, where here '[...]' means 'the integer value of ...'. Thus, r is roughly twice the range of the interaction in terms of MLs. It is r that determines the nature of the graphs representing H_{1D} , through terms of the form (3) or (4). Finally, for $D > 1$, we can define K to be the number of states per ML for a polytype. Unless there are extra stacking constraints beyond those embodied in the definition of the spins themselves, we will have $K = k_x k_y$. Such 'extra' stacking rules do exist for the kaolins and cronstedtites, which then have $K < k_x k_y$.

We now have conventions and notation in place for vector spins with $D = 2$. We know that we will have to redo the graph-based analysis of CW for any problem with $D > 1$, including CdI₂. Let us however work in logical order and begin with finding the symmetry group of H_{1D} for CdI₂. Having defined absolute and relative spins, along with the stacking constraints, we are ready to do so. We consider crystallographic operations from Goodman's list acting on a seed sequence. Since each ML has some degree of symmetry about the Cd sublayer, we expect that operations that take $\mathbf{z} \rightarrow -\mathbf{z}$ will give well defined spins. So we have a more extensive list of operations to consider than we had for SiC. Here we summarize our results. We find that useful operations include the following: 6_z (sixfold rotation about $\hat{\mathbf{z}}$) and m' (reflection about planes containing $\hat{\mathbf{z}}$ and primitive translation vectors) each yield S symmetry for H_{1D} . Reflection (m_z) in a plane perpendicular to the stacking direction has the effect of inverting the stacking order and reversing all the relative spins (as we found in §2 for close packing). So m_z results in SI symmetry. Hence we have that S and SI – or, equivalently, S and I – are generators of \mathcal{G} . As a check, we note that $(6_z)^3 \cdot m_z = \bar{1}$ and hence $\bar{1}$ gives $S^3 \cdot SI = I$ symmetry for H_{1D} (which is also easily verified directly). We find no crystallographic operations yielding any other independent

symmetry so, as in the case of the close-packing problem, we find the symmetry group to be $\mathcal{G} = S + I$. We now ask about the possibility of disordered ground states. Can CdI₂ have a noncrystalline ground state? To answer this, we must determine whether these symmetries can induce D pairs in the symmetry-reduced graphs ${}^{S+I}G_r^{[2,2]}$, for each r . More precisely, we seek the smallest r (r_{\min}) for which D pairs occur, and then assume they also occur for $r > r_{\min}$ (§3). In order to find r_{\min} , we must repeat the CW $D = 1$ study for the case $D = 2$, with the symmetry group $\mathcal{G} = (S + I)$. In order to perform this task, we first need some general results and analysis for the case $D = 2$. These results will be given in the next subsection, after which we give our conclusions for the case of CdI₂ in §5.3.

5.2. Graphs and D pairs for the case $D = 2$

5.2.1. General. We address here the construction of the CW graphs extended to the case of $D = 2$. We begin by noting that in going from $D = 1$ to $D = 2$ we double the number of nodes and arcs. This reflects the fact that one must now distinguish a node (or arc) beginning with an intralayer (x) spin from one beginning with an interlayer (y) spin. Each spin component also in general has a k value associated with it. However, since the k values are identical for each component for both CdI₂ and GaSe, we denote their common value by a single k . (We will be forced to abandon this convention for the kaolins, for which the number of states differs for each component of spin.) With these conventions, the graphs that we study may be denoted ${}_2G_r^k$. Let us first describe the construction of the ${}_2G_r^k$ graph. We draw two copies of each node in G_r^k , labeling one copy (the 'x node') such that the first spin in the sequence begins with an x spin, and the other copy ('y node') begins with a y spin. We then draw the arcs connecting nodes; this is the same as for $D = 1$, except that arcs only connect x nodes to y nodes or *vice versa*. The result, for $k = r = 2$, is shown in Fig. 1(b). We mention some general properties relating the simple cycles (SCs) of the ${}_2G_r^k$ graphs to the SCs of the G_r^k graphs. (I) All of the odd period (p_o) SCs of G_r^k become SCs of period $2p_o$ in ${}_2G_r^k$. An example of this is the SC (001) in Fig. 1(a). As $D = 1$ goes to $D = 2$, this SC expands to $(0_x 0_y 1_x 0_y 0_x 1_y)$ (Fig. 1b). (II) All of the even-period (p_e) SCs of G_r^k break up into two disjoint SCs of period p_e in ${}_2G_r^k$. An example of this is the SC (01) in Fig. 1(a), which breaks up into the two SCs $(0_x 1_y)$ and $(1_x 0_y)$ of Fig. 1(b). (III) Additionally, we find new SCs in ${}_2G_r^k$ that have no analog in G_r^k . For example, the SCs $(0_x 0_y 0_x 1_y)$ and $(0_x 0_y 0_x 1_y 1_x 0_y 1_x 1_y)$ in ${}_2G_2^2$ cannot be simply related to any one SC in G_2^2 .

5.2.2. S symmetry. Next we give some general results concerning S symmetry for the case $D = 2$. CW found that S symmetry never gives rise to D pairs unless there are spin-invariant nodes in the graph G_r^k . Furthermore, they found that there are *always* D pairs when there do exist spin-invariant nodes. That is, they found

$$(\text{disordered ground states}) \iff (\text{spin invariant nodes}). \quad (5)$$

We find that the logic they employed makes no reference to the dimension of the spins, and so holds equally well for the

case $D = 2$. Hence the result (5) also holds for $D = 2$ (and in fact for any D).

CW found that there are always spin-invariant nodes for odd k , but only considered the case of no spin-invariant nodes for even k . We have found that even k can also have spin-invariant nodes; however, we defer a discussion of this case until it is needed, namely when we examine the case of micas.

5.2.3. I symmetry. We have no general results for I symmetry and $D = 2$. We have however examined a number of specific cases for $k = 2$ and 3. For $k = 2$, we find a difference from the $D = 1$ case (which had $r_{\min} = 5$): for $D = 2$, we find no D pairs from I symmetry for $r \leq 5$. We have not constructed the larger- r graphs. For $k = 3$ and $D = 2$, $r_{\min} = 2$ – the same as for $D = 1$.

5.2.4. Isomorphism between ${}^{S+X}G_r^2$ and ${}^XG_{r-1}^2$. CW found that, for $D = 1$, ${}^{S+X}G_r^2 \sim {}^XG_{r-1}^2$. Here X can be either the identity or I ; and the isomorphism \sim means both that the nodes of the two graphs can be placed in one-to-one correspondence and that the *symmetries* (apart from S itself) of the corresponding nodes are the same. This isomorphism is useful in the $D = 1$ case; and it would of course be useful if a similar isomorphism were to hold for $D = 2$. However, we find that such an isomorphism fails for either $X = I$ or $X = \text{identity}$. The isomorphism in fact holds at the level of topology; but the symmetry of the nodes in ${}^{S+X}G_r^2$ is not simply related to those in ${}^XG_{r-1}^2$. Hence we cannot make use of such an isomorphism relation to learn about D pairs in ${}^{S+X}G_r^2$ for the case of CdI_2 .

5.3. D pairs for $D = 2$; CdI_2

We have already noted above that some SCs in G_r^k imply the existence of corresponding SCs (or pairs of SCs) in ${}_2G_r^k$. We have also noted that there are ‘new’ SCs in ${}_2G_r^k$ that have no corresponding SC in G_r^k . In this section, we ask the same questions about D pairs: (i) do D pairs in ${}^XG_r^k$ imply the existence of ‘surviving’ D pairs in ${}_2G_r^k$?; and (ii) are there ‘new’ D pairs in ${}_2G_r^k$? Let us answer these questions in turn, giving only our answers below. (The reasoning is simple, involving only topological and symmetry considerations applied to schematic D pairs, or else proof by example.) The answers to (i) and (ii) will in fact be helpful in understanding the case of CdI_2 .

(i) First we consider S symmetry. Here we find that even-period (p_e) D pairs in ${}^S G_r^k$ (where the period is that of one of the SCs of the D pair) imply the existence of a disjoint pair of period p_e D pairs in ${}_2G_r^k$. On the other hand, for an odd-period (p_o) D pair in ${}^S G_r^k$, we find that there is a ‘ D quadruple’ in ${}_2G_r^k$. A D quadruple is indicated schematically in Fig. 2. It uses two spin-invariant nodes of ${}_2G_r^k$ and represents four degenerate ground-state phases, each of period p_o , all with zero surface tension between them – hence disorder and extensive degeneracy as with a D pair. This combination of topology and symmetry also occurs for $X = S + I$ and $D = 1$; see Yi & Canright (1996, Fig. 1). We note also that a ‘type 4’ D pair (Canright & Watson, 1996) in ${}^I G_r^k$ is in fact topologically a D quadruple.

For I symmetry, the situation is more complicated. There are two topological types (three subtypes) of D pair as listed in Fig. 5 of Canright & Watson (1996): type 2 [which actually has two subtypes, Figs. 5(b) and (e)] and type 4. The survival of a D pair under $D \rightarrow 2$ actually depends on which of the three subtypes it is and whether the period is even or odd. We will not list the results here since we will not need them for any of our families studied. Instead, we proceed to the case $\mathcal{G} = S + I$, which is appropriate to CdI_2 .

For the case of $S + I$ symmetry, there are several topological types of D pairs; see Yi & Canright (1996) for details. We consider only those appearing at $r = 6$ [see Table I of Yi & Canright (1996)]. That fixes r to be even, with p odd for type II [in the notation of Yi & Canright (1996)] D pairs, and p even for type III. We find that the former case gives a D quadruple in ${}^{S+I}{}_2G_r^k$. In the latter case, we find, for $p/2$ odd, a disjoint pair of D quadruples in ${}^{S+I}{}_2G_r^k$; and, for $p/2$ even, no surviving D pairs. We will use these results to find r_{\min} for CdI_2 below.

(ii) We know there are ‘new’ SCs in ${}^X G_r^k$ in general. Are there ‘new’ D pairs as well? We find by example that such can occur, for both S and I symmetry in general. For the case $\mathcal{G} = (S + I)$, we have only studied $k = 2$. For this case, we have constructed ${}^{S+I}G_r^2$ for $1 \leq r \leq 5$, finding no D pairs (and hence no new D pairs) in the graphs. Hence, for the case ${}^{S+I}{}_2G_r^2$ as well as for other cases examined (§5.2.2), we have failed to find ‘new’ ($D = 2$) D pairs wherever there are no ‘old’ ($D = 1$) D pairs. We believe however that there are also new D pairs in general for $S + I$ symmetry.

Finally, with these results we are in a position to find r_{\min} for CdI_2 . There are in fact odd-period type II D pairs, and even-period type III D pairs with $p/2$ odd, in ${}^{S+I}G_6^2$ (Yi & Canright, 1996). These D pairs imply the existence of corresponding D pairs in ${}^{S+I}{}_2G_6^2$. Furthermore, we know (by construction of the graphs) that there are no D pairs in ${}^{S+I}{}_2G_r^2$ for $r < 6$. Thus we find that $r_{\min} = 6$ for CdI_2 . That is, if the intersublayer interactions are significant beyond $r = 6$ (i.e. approximately 3 MLs), then one cannot rule out an infinity of disordered

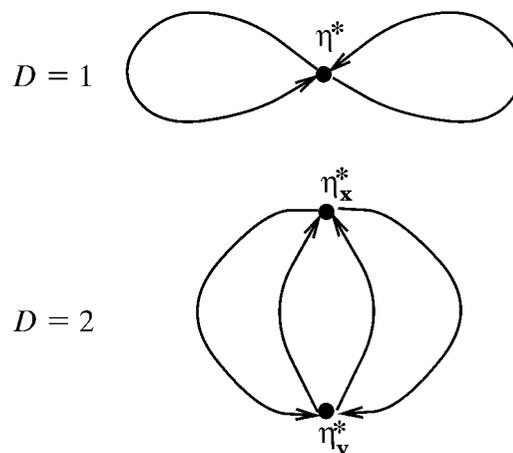


Figure 2

A ‘ D quadruple’, shown schematically. A period p (with p odd) D pair in ${}^S G$ implies a D quadruple (of period $2p$) in ${}_2G$.

ground states for CdI₂ without further investigation of the effective interlayer couplings: CdI₂ is PNC for $r \geq 6$.

6. GaSe

GaSe is a layered compound having strong covalent bonding within a modular layer, with the bonding between adjacent modular layers being primarily due to van der Waals forces. Periodic structures with periodicities as large as 21 MLs have been reported (Sebastian & Krishna, 1994). A modular layer consists of four sublayers, each composed of either Ga or Se in a close-packed hexagonal net. The sublayers are stacked in the sequence Se/Ga/Ga/Se. Each Ga atom is tetrahedrally coordinated with three Se atoms in an adjacent Se sublayer, and has a final bond with the Ga atom in the layer adjacent to it. In fact, the top two sublayers are just the reflection of the bottom two sublayers about a plane perpendicular to the stacking direction placed half way between the Ga sublayers. This can be expressed in terms of the familiar *A, B, C* notation as *L1/L2/L3/L4*, with the two constraints that *L1* and *L4* (the Se sublayers) occupy the same *ABC* positions, and that *L2* and *L3* (the Ga sublayers) also occupy equivalent positions. For the Ga and Se atoms to be tetrahedrally coordinated, they must not occupy the same sites, so *L1* and *L2* differ. Additionally, adjacent Se sublayers must occupy different positions, as in the close-packed problem.

We define the relative and absolute spins analogously to the close-packed problem. For *L1*, which must differ from the upper Se sublayer of the previous ML on which it rests, there are two choices for the relative spin. Likewise, *L2* also has two choices for relative spin. Having specified *L1* and *L2*, the remainder of the ML is rigidly determined. So, just as for CdI₂, we find that $D = 2$, with $k = 2$ for each spin; each ML is described by a two-component vector spin. As in the case of CdI₂, we denote the intra- and interlayer spins of a ML *i* by x_i and y_i . We find the layer group for GaSe to be $p\bar{3}m2$.

The graphical analysis of CW is insufficient to determine the possibility of disordered ground states since $D > 1$. Furthermore, even though $D = 2$ and $k = 2$ (for each spin) as for CdI₂, we find that the graphical analysis performed there does not carry over to GaSe. We will have to rework the graphical analysis because of the presence of new unexpected symmetries. We find these symmetries in the usual way, by choosing a seed sequence and applying useful rotations to them. We recall that the symmetries we have found so far include inversion of the order of spins (*I*), inversion of the spins themselves (*S*), or possibly the product *SI* of these two operations. We will find that GaSe has symmetry operations similar to these; however, owing to the existence of vector spins, we must consider that *S* can act selectively on only one component of the spin. We emphasize that we did not anticipate this possibility, but were led to it by the same procedure that led to finding *S* and *I* for other compounds. It is therefore useful to consider a seed sequence and the effect of rotations on this sequence in some detail.

We take our absolute seed sequence to be $\mathcal{S}_a = (AbbA) (CbbC) (BccB) (CaaC) (AbbA) (BaaB) (AccA) (C\dots)$,

where the parentheses are used for convenience to separate MLs. Upper-case letters refer to Se sublayers and lower-case letters to Ga sublayers. Taking the first component of the spin to be the intralayer component and denoting it by x_i and the second component to be the interlayer component denoted by y_i , we can write the relative spin sequence as $\mathcal{S}_r = (+ - - - + + + + - - -)_x$. The subscript *x* (*y*) reminds us that the sequence begins with an intralayer (interlayer) spin. The first rotation we consider is 6_z centered on an *A* site. As in the case of the close-packing problem, this leaves the *A* sites unaffected while exchanging the *B* and *C* sites. Our rotated absolute sequence is then $\mathcal{S}'_a = (AccA) (BccB) (CbbC) (BaaB) (AccA) (CaaC) (AbbA) (B\dots)$, giving a rotated relative sequence $\mathcal{S}'_r = (- + + + - - - - - + + +)_x$. If the usual identification of $+/-$ is made as spin inverse pairs, \mathcal{S}'_r is just the spin inverse of \mathcal{S}_r . Hence spin inversion *S* is a good symmetry of H_{1D} for GaSe. The next rotation we consider is m_z , which simply reverses the stacking order of the absolute spins. This results in a rotated absolute sequence given by $(\dots C) (AccA) (BaaB) (AbbA) (CaaC) (BccB) (CbbC) (AbbA)$. Writing this in terms of relative spins, we find $\mathcal{S}'_r = (+ - + - - + - + - + +)_y$. Comparison with our original spin sequence shows that not only has the order of the spins been reversed but each interlayer spin has been inverted, while the spin value of the intralayer spins remains unchanged. Since only the interlayer spin has been inverted, we invent a new symbol to denote this operation, S_y . Similarly, we define S_x as acting on a spin sequence to invert only the intralayer spins. The Hamiltonian thus must have, in addition to *S*, the symmetry $S_y I$. The inversion of only one component of the spin may seem surprising, but it is easily understood. Because of the m_z symmetry of an individual ML, *z*-sensitive properties of a single ML, such as the intralayer relative spin, must be invariant under m_z . The value of the intralayer relative spin is thus insensitive to the order in which the sequence is read – as illustrated by the above example. The interlayer spin lacks this property.

We have found two symmetries (*S* and $S_y I$) of the Hamiltonian H_{1D} , and expect that these symmetries should form a group. Clearly these two symmetries alone do not close and form a group, so we must seek other symmetries. The product $SS_y I = (S_x S_y) S_y I = S_x I$ of these symmetries should also be a symmetry of the Hamiltonian. We then expect that some rotation *R* will give this symmetry, and indeed we find that spatial inversion of the sample $\bar{1}$ does just this. We have considered all of the other possible rotations given in Goodman, and find no other symmetries. We only need two of these symmetries to generate the group \mathcal{G} , and we take *S* and $S_x I$ to be the group generators.

We now turn our attention to the graphical analysis to determine whether disordered ground states are possible and, if so, for what minimum *r*. We need to discover whether these new symmetries can induce *D* pairs in the symmetry-reduced graphs ${}^S_2 G_r^2$ or ${}^{S_y I}_2 G_r^2$. These graphs differ from the CdI₂ case because CdI₂ and GaSe do not share the same symmetries. So we are forced to consider the graphs again in detail. While the

novel symmetries of GaSe may seem strange and not as intuitive as the previous ones, all the same criteria for finding D pairs hold, and the construction of the symmetry-reduced graphs proceeds in a similar fashion. We construct the graphs ${}_2G_r^2$, ${}_2^S G_r^2$, ${}_2^{S_x I} G_r^2$ and ${}_2^{S_x I+S} G_r^2$. This is most easily accomplished using the recursive procedure described by Canright & Watson (1996). To search for disordered ground states at a given r , we seek candidate D pairs in ${}_2^S G_r^2$ or ${}_2^{S_x I} G_r^2$. We then require that these D pairs remain simple cycles of the full symmetry-reduced graph ${}_2^{S_x I+S} G_r^2$. Otherwise, they are said to decompose [see Canright & Watson (1996) for a discussion of this term]. We find no candidate ${}^S D$ pairs in ${}_2^S G_r^2$ for any r because there are no spin-invariant nodes (since $k = 2$). Thus we focus on candidate ${}^{S_x I} D$ pairs in ${}_2^{S_x I} G_r^2$. Here we do find candidate D pairs for many r values and must use some care to test if they decompose or not. For $r = 1$, we find candidate D pairs of type 2(a) in ${}_2^{S_x I} G_1^2$ but none survive as simple cycles after the imposition of S symmetry. For $r = 2$, there are no $S_x I$ -symmetric nodes (indeed there are none for any even r) and therefore no possibility of type 2(a) D pairs. Also, there are no joining arcs (JAs) (see Canright & Watson, 1996) in ${}_2 G_2^2$, and hence it is not possible to find type 2(b) or type 4 D pairs. For $r = 3$, there are no joining arcs in ${}_2 G_3^2$, thus no type 2(b) or type 4 D pairs. Also, while ${}_2 G_3^2$ does have $S_x I$ symmetric nodes, none of these support type 2(a) D pairs. At $r = 4$ and 5, we find the following. There are no type 2(a) D pairs (from inspection of the $S_x I$ -symmetric nodes at $r = 5$). However, both ${}_2 G_4^2$ and ${}_2 G_5^2$ have joining arcs. Hence we do find candidate type 2(b) and type 4 D pairs at $r = 4$ and 5.

Here we find it useful to note that there are no JAs in ${}_2^S G_r^2$ for any $r \leq 5$. Given the absence of JAs in ${}_2^S G_r^2$, we can prove that all type 2(b) and type 4 D pairs in ${}_2^{S_x I} G_r^2$ decompose under the application of S symmetry – except for the possible existence of rare cases where a candidate type 4 D pair in ${}_2^{S_x I} G_r^2$ maps to one SC in ${}_2^{S_x I+S} G_r^2$. We have, however, by careful inspection of the graphs, found no such instances for $r \leq 5$. It is only at $r = 6$ that we find JAs in ${}_2^S G_r^2$, and hence D pairs in ${}_2^{S_x I} G_6^2$ that are also simple cycles of ${}_2^{S_x I+S} G_6^2$. We therefore conclude that the range of the interaction must extend at least as far as six spin components (three MLs) for there to be a possibility of disordered ground states. In our previous language, we say that GaSe is PNC for $r \geq 6$ ($R \geq 3$).

7. Micahs

Polytypism in micahs has been studied for some decades (Pauling, 1930; Takeda, 1971; Mogami *et al.*, 1978; Thompson, 1981). The modular layers of micahs can occur in a variety of forms. Here we shall mostly focus on ‘ideal’ micahs, as defined in Thompson (1981). This ideal modular-layer structure consists of an octahedral layer (OL), sandwiched between two tetrahedral layers (TLs). The resulting LG is $C12/m1$. Thompson also defines a pair of orthogonal translation vectors, \mathbf{s} and \mathbf{t} , for the ideal mica ML, which we will make use of. The LG defines a preferred axis in the xy plane by the twofold axis, which also lies along the mirror axis (*i.e.* normal to the mirror plane); Thompson’s \mathbf{t} translation lies along this

axis. The \mathbf{s} axis is then also uniquely defined by the ML; and we follow Thompson in defining a ‘stacking vector’ (SV), which lies parallel to \mathbf{s} . The SV is a true vector, *i.e.* (SV) \neq $-(SV)$, owing to the low symmetry of the mica ML. It is then natural to take the absolute spin of a ML to be its SV. The SV is defined entirely by the OL; in the ideal ML, the TLs are slaved to the OL and so contribute no information to the spin of the ML. The SV is a geometric vector in the real-space xy plane. However, we will not need to resort to vector spins in order to analyze the case of mica. Each ML i is fully specified by its SV s_i . Furthermore, given one ML – for instance, our RML – stacking constraints require that any other ML in a stacking sequence must have its SV lying in one of six positions, equally spaced on a unit circle. Hence the absolute spins take one of six possible values. Relative spins may then be defined by $\sigma_i \equiv s_i - s_{i-1}$. For micahs (unlike the previous cases studied here), σ_i can be zero, *i.e.* two subsequent MLs can have the same SV. In fact, there are no constraints on the σ_i , once we have locked the absolute spins into one of six positions. Hence the relative spins σ_i freely take one of six values, and $k = 6$. Furthermore, a single spin component (per ML) suffices to specify a stacking sequence; hence $D = 1$. We shall simply treat the s_i and σ_i as scalars taking one of six values.

With relative spins so defined, we can find the symmetry group \mathcal{G} of H_{1D} . We take x and y axes in space to lie along the s and t axes, respectively, of a RML. The absolute spins then lie on one of six points on a circle, as shown in Fig. 3(a); here the x axis is horizontal. The same figure can also be taken to depict the relative spin states, with the common conventions that the $+x$ axis represents zero rotation and positive rotations are taken counterclockwise. Now we apply y inversion, *i.e.* $m_y \equiv (y \longleftrightarrow -y)$, to a seed sequence of absolute spins s_i . It is clear from Fig. 3(a) that $m_y s_i = 6 - s_i = -s_i \pmod{6}$. Hence $m_y \sigma_i = -\sigma_i \pmod{6}$ and so S symmetry is a good symmetry of H_{1D} .

In finding this result, we have however run into a case not considered by CW. That is, they assumed that even- k systems must have no S -invariant spin states. Such a case is pictured in Fig. 3(b). This case is also possible but does not pertain to micahs. Hence we digress briefly to attempt to summarize the cases that do seem possible, given the notion of spins as rotations lying on a unit circle. We will continue to assume (as did CW) that the S operation changes the sign of a rotation. For any k , we will also assume that the k states are distributed such that the non- S -invariant states map to one another pairwise, *i.e.* in pairs having the same x coordinate in a figure such as Fig. 3. Under these assumptions, we find that there can be only zero, one or two S -invariant states. This gives three cases.

Case 1: k odd. There must be precisely one S -invariant state.

Case 2: k even, no S -invariant states (Fig. 3b).

Case 3: k even, two S -invariant states (Fig. 3a).

CW considered only cases 1 and 2. Mica falls under case 3 and so we will not be able to use the results of CW’s Table I, even though $D = 1$.

We note here in passing that every polytype family but SiC that we have considered has led us to study possibilities not

considered by CW. In fact, the kinds of spin structures and symmetries that we have found would have been hard to anticipate. Hence we feel that we must append a certain tentativeness to any sort of ‘exhaustive list’ of possibilities – such as the three cases above. They are the only possibilities, given our assumptions about spins and the spin-inversion operation. However, we will soon find (with kaolins) that even the notion of spins as rotations is too narrow. And we will not claim that our other assumptions must hold for all polytype families.

Now we can finish our derivation of the symmetry group \mathcal{G} . We find that uniform \hat{z} rotations are useless (*i.e.* the identity), since the relative spins are relative rotations themselves. It is then sufficient (still neglecting glides and screws) to consider reflections. The reflection m_x has the property $m_x s_i = 3 - s_i \pmod{6}$, and hence also gives S symmetry. The reflection m_z has the effect of inverting each SV in its plane, plus of course reversing the stacking order. We may write these combined effects as $m_z s_i = 3 + s_{-i} \pmod{6}$. This gives in turn $m_z \sigma_i = \sigma_{-i}$; that is, m_z tells us that H_{1D} has I symmetry. There are no further independent useful rotations; so we have $\mathcal{G} = S + I$.

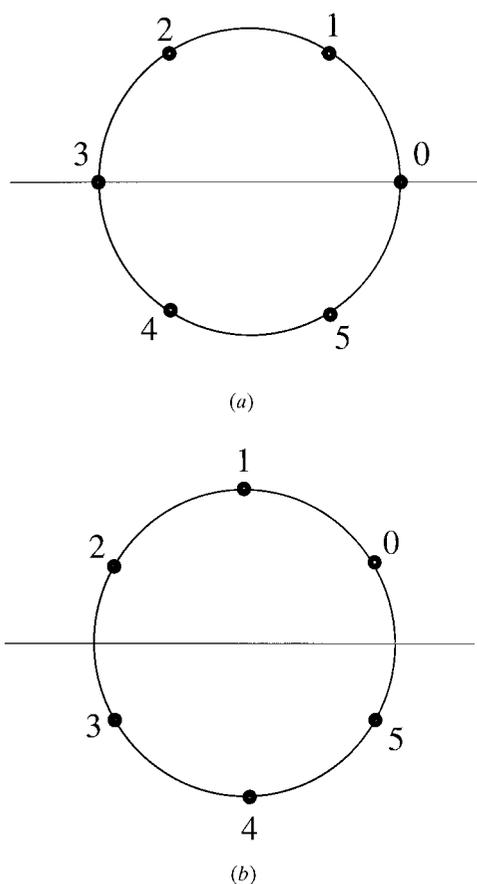


Figure 3
 (a) Locus of absolute (or relative) spins for mica, with $k = 6$ possible states. One can think of the relative spins as rotations; then spin inversion S simply reverses the rotation – which reflects points about the horizontal axis. For micas, there are two spin states that are invariant under S . We call this case 3. (b) A possible $k = 6$ case, with S defined as in (a), in which there are no S -invariant states. We call this case 2.

Now we seek r_{\min} : where are there D pairs for mica? We have not performed a very detailed study of case 3 for various k and r . For one thing, case 3 for $k = 2$ makes the identity out of the S operation; hence it is of no interest. Looking at $k = 4$, we find D pairs already at $r = 1$ for case 3 with $S + I$ symmetry. These D pairs are also found at $k = 6$, since the $k = 4$ graph is a subgraph of the $k = 6$ graph. Hence we find that $r_{\min} = 1, k \geq 4$ (case 3, even k). And so ideal micas may have noncrystalline ground states for any range of interlayer interaction.

Finally, we briefly consider nonideal mica structures. One of the commonest deviations from the ideal structure is a rotation of the tetrahedra in the tetrahedral layers (TLs) (Thompson, 1981). This however does not typically change the symmetry (*i.e.* LG) of the ML – since the ideal TLs have a sixfold rotational symmetry, while the OL has no rotational symmetry about \hat{z} . Hence the above results apply equally well to nonideal micas, when the departure from ideality takes this form.

Another departure from the ideal picture can occur when micas with rotated TLs exhibit a preference for certain σ values over others. Preferences can of course be reflected in energetics (J 's). However, if the ‘preference’ is so strong as to exclude certain possibilities, then we can incorporate it into our formalism. For example, Thompson (1981) states that, in micas with rotated TLs, ‘cross operators’ (our $\sigma_i = 1, 3$ or 5) are not found. In such a case, our $k = 6$ problem simply becomes $k = 3$, and hence case 1. For this case, we know from CW that $r_{\min} = 1$. Thus our conclusion remains unchanged from the ideal mica case: for any range of interaction, one cannot rule out disordered and degenerate ground states.

8. Kaolins/cronstedtites

In this section, we consider a family of phyllosilicates of lower symmetry than micas. This family is termed ‘kaolinites’ in, for example, McLarnan (1981). The MLs consist of an octahedral layer (OL) plus a single tetrahedral silica layer (TL). The MLs are dioctahedral, *i.e.* only 2/3 of the cation sites in the OL are occupied, but in an ordered fashion as expressed in the LG. These minerals are sometimes also called the ‘kaolinite group’, the ‘kaolins’ or ‘kandites’ (Deer *et al.*, 1962). Since ‘kaolinite’ is also used (Brindley, 1946) to refer to a specific crystalline polytype of this family (the commonest one), to avoid confusion we will call the family ‘kaolins’ and reserve the term kaolinite for the specific structure.

Other than this one question of terminology, we will follow McLarnan (1981) in notation and conventions. McLarnan’s article is particularly useful to us because there are strong similarities between the (crystalline) polytype-counting problem studied there (see also Takeda, 1971) and the problem we address here of finding the symmetry group \mathcal{G} of H_{1D} . These similarities come from the fact that, in each case, one is interested in studying allowed sequences of spins and also in determining which distinct allowed strings of spins are related by an overall (proper or improper) rotation of the

sample. Hence we find that McLarnan has performed much of our work for us.

The LG of kaolin MLs is $C1m1$. The twofold axis is lost (compared to mica) owing to the loss of one of the TLs of the sandwich; but the mirror (defined by the missing cation of the dioctahedral layer) remains, at least in ideal kaolins. We shall (as we did with micas) discuss departures from ideality later in this section. This mirror symmetry again allows one to define a preferred axis in the ML. This axis was termed a ‘stacking vector’ for micas; here we follow McLarnan and call it σ . Specifically, we define σ_i to be the displacement from TL_i to OL_i , where the origin of any TL is the center of a hexagon, the origin of an OL is the vacant cation site, and we take the OL to be above the TL in a ML. σ_i is thus a relative spin, since it is measured from an adjacent sublayer rather than from any absolute origin. It is also an intralayer spin. The σ_i can take one of six values, which can be represented as six equal-length vectors differing by 60° rotations (McLarnan, 1981; Zvyagin, 1962; Zvyagin & Drits, 1996) (Fig. 4a). Their components are commonly measured in a basis (a, b) defined by a rectangular unit cell of the RML, with $b = 3^{1/2}a$.

We need an interlayer spin to place the next ML. We take τ_i to be the displacement from TL_{i-1} to TL_i . The allowed τ_i vectors are shown in Fig. 4(b). We have thus two spin components needed per ML to specify any kaolin stacking sequence, so that $D = 2$. However, we also have $k_\sigma = 6$ while $k_\tau = 9 \neq k_\sigma$, i.e. the two k values are different.

Furthermore, unlike any family studied above, we find with kaolins that there are ‘extra’ stacking rules beyond those implicit in the definition of spins. The energetically acceptable stackings bring the lowest oxygen (O) sheet of the TL of ML_{i+1} in registry with the uppermost hydroxyl (OH) sheet of the OL of the i th ML, such that there are short hydrogen bonds between the O and the OH sites. Such a registry depends on the values σ_i and τ_{i+1} . It turns out that not every combination $\sigma_i\tau_{i+1}$ gives a favorable registry. With our conventions (which differ from McLarnan’s by a minus sign), the extra stacking rule states that, if τ has a subscript, then that subscript must differ from that of the previous σ in the sequence by an odd integer. This constraint rules out 18 possible $\sigma_i\tau_{i+1}$ pairs, leaving the well known (McLarnan, 1981; Zvyagin, 1962; Newnham, 1961) 36 possible $\sigma\tau$ pairs. Thus, $K \neq k_\sigma \cdot k_\tau$.

So far we have not mentioned absolute spins. The reason is that, since the relative spins are simply translations, the absolute spins are the same; the two sets of spins are simply related by sum and difference operations. Hence rotations R act upon each in precisely the same way. So in finding the symmetry group \mathcal{G} we shall omit the (usually helpful) step of tracking the fate of absolute spins, and simply let our rotations act directly on the relative spins.

We seek as usual useful rotations which will determine \mathcal{G} . We first rule out (as with SiC) the lower part of Goodman’s table by noting that there is no $(\mathbf{z} \leftrightarrow -\mathbf{z})$ operation in the LG of kaolins. That is, the kaolin MLs are polar. Hence, I will not appear in \mathcal{G} . As noted by McLarnan, the remaining useful operations are reflections (about a and b) and rotations (in

multiples of 60°). McLarnan gives the effects of these operations on the spins. For our purposes, we simply note that each gives a new but allowed spin sequence and hence defines a symmetry of H_{1D} . Reserving capital letters for the latter operators, we denote the symmetry of H_{1D} generated by the 6_z rotation as C (cyclic), and those generated by the mirrors m_a and m_b as M_a and M_b . We note that the latter two operators cannot both be generators of \mathcal{G} however, since (e.g) $M_b = C^3M_a$. In fact, since our spin components are geometric objects (vectors) in a plane, the group \mathcal{G} is isomorphic to a plane point group. We can take the generators to be $6_z = C$ and one mirror M , and the resulting group is the point group $\mathcal{G} \equiv C + M = 6mm$.

Having found \mathcal{G} , we are in principle ready to look for D pairs and r_{\min} . However (as usual), we have some new features with this new problem that require some attention first. The group \mathcal{G} is bigger (of order 12) than any we have faced before; and it is non-abelian. Furthermore, even at $r = 1$ the graph for kaolins is very large; and generating this large graph requires systematically omitting forbidden arcs corresponding to the forbidden sequences in the ‘extra’ stacking rules. Let us examine how these new aspects affect our approach.

Every element of \mathcal{G} is a symmetry of H_{1D} . Thus candidate D pairs may in principle be found in each graph g_2G for every $g \in \mathcal{G}$, $g \neq e$ (where e is the identity). Candidate D pairs must then be tested to see if they decompose under the application of all the other symmetries in \mathcal{G} . That is, one must generate the maximally symmetry-reduced graph G_2G whose nodes and arcs

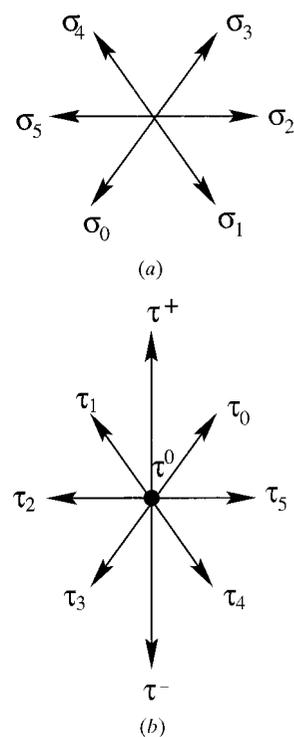


Figure 4
The relative spins for kaolins. Each component (intra- and interlayer) is a translation vector in the ab plane. In these figures, \mathbf{a} is horizontal and \mathbf{b} is vertical. (a) The σ (intralayer) vectors for kaolins. (b) The τ vectors. The τ^0 vector is $(0, 0)$.

are invariant under *every* element of \mathcal{G} . Surviving D pairs among the candidates are then those that appear as simple cycles in ${}^{\mathcal{G}}G$. All of this logic of course holds for every case we have studied, as well as for the work of CW (Canright & Watson, 1996; Yi & Canright, 1996). However, it is the size and complexity of \mathcal{G} that motivates us now to make such logic as precise and explicit as possible.

The fact that our current \mathcal{G} is non-abelian turns out not to require major changes in our approach. The reason is that the deciding criteria are found in the graph ${}^{\mathcal{G}}G$. The nodes \mathcal{N}^* and arcs \mathcal{A}^* of this graph are invariant under all elements $g \in \mathcal{G}$. Thus, for all $g, h \in \mathcal{G}$, $gh \cdot \mathcal{N}^* = hg \cdot \mathcal{N}^*$ (and similarly for the arcs). In a sense the graph ${}^{\mathcal{G}}G$ corresponds to the identity representation of \mathcal{G} , for which it is irrelevant that full representations of \mathcal{G} are non-abelian. (Of course, in any specific algebraic manipulation, one must take care of the fact that $gh \neq hg$ in general.)

It follows from the above that, given a big \mathcal{G} , it is much easier to show that D pairs exist for a given r than to show that they do not. The former requires finding a single example, while the latter requires the examination (by proof or by exhaustion) of all possible symmetry elements g , and all candidate D pairs that they generate.

We are fortunate here in that we can easily find surviving D pairs at the level $r = 1$ for kaolins. Hence we have no need to show that there are none for any r because we find that $r_{\min} = 1$. Hence we have no need to generate (by hand or computer) any complete graph ${}^{\mathcal{G}}G$, thus avoiding the problem of the large *size* of the graphs for this problem. To find a surviving D pair, we simply need to take a candidate D pair, which is a small piece of gG for some g , and verify that it remains a simple cycle of ${}^{\mathcal{G}}G$. To accomplish the latter, it suffices to apply the group generators to the candidate cycles a sufficient number of times (once for M since $M^2 = e$, and five times or fewer for C since $C^6 = e$) until all nodes and arcs are invariant under further applications of these generators.

Our example for $r = 1$ is trivially simple. We take the cycle $\tau^0\sigma_5$ and its M_a inverse $\tau^0\sigma_2$. These are an $M_a D$ pair. Repeated application of our generators gives the single simple cycle $\tau^0\sigma$ of ${}^{\mathcal{G}}G$, where the symbol σ here represents the single \mathcal{G} -invariant node in ${}^{\mathcal{G}}G$ representing all the σ_i states of the unreduced graph. Hence this D pair does not decompose; and there are many others. We can also easily find many D pairs at larger r , and so are confident that our conjecture concerning D pairs at all $r > r_{\min}$ is true for this problem.

We thus find that ideal kaolins are PNC with $r_{\min} = 1$. What about distortions from the ideal ML structure? We consider two forms of distortion: (a) distortions that preserve the LG symmetry; (b) those that do not.

(a) Our reasoning here is similar to that for micas. That is, distortions that preserve the LG symmetry but are not so large as to change the stacking rules have no effect on our analysis or conclusions.

(b) We are prompted to consider this case by experimental observations (Artioli *et al.*, 1995; Bookin *et al.*, 1989) that such distortions are measurable in kaolin samples. In particular, the specific kaolinite structure – which is a repeated $\sigma\tau$ pair – is

chiral (right- or left-handed) (Newnham, 1961; Bailey, 1963). It is observed (Artioli *et al.*, 1995; Bookin *et al.*, 1989) that this handedness gives rise to chiral distortions of the MLs. Such distortions of course do not preserve the mirror symmetry of the ideal kaolin ($C1m1$) ML. They are instead an example of the phenomenon [noted also in Zvyagin & Drits (1996)] that ML distortions are due not only to the interactions of subcomponents of a ML but also to the further environment, *i.e.* to the stacking sequence. This idea – which of course must be true in principle – is further supported by the experimental observation (Bookin *et al.*, 1989) that MLs in dickite are not chiral. Dickite is a period-4 (in units of spin components) kaolin crystal whose stacking sequence is nonchiral (Newnham, 1961).

At first glance, one might conclude that this kind of distortion simply cannot be dealt with by our formalism. After all, such distortions essentially redefine the spins in a way that is dependent upon stacking sequence. This seems like a hopeless complication.

We offer a tentative way of thinking about these distortions. The stacking sequence prescribes how one should stack ideal MLs (where here ‘ideal’ means ‘retaining the LG symmetries’). H_{1D} is then a recipe that tells (in principle) what *exact* energy results from such a stacking, *including* any distortions that relax the ML structures away from the ideal. That is, we suggest that stacking-dependent distortions do not redefine the spins in any useful way, and that their effects can be incorporated in the J 's for H_{1D} . This approach should be practical as long as the distortions are not so large as to alter the identity of the MLs – that is, as long as the model of the material as polytypic remains valid. It is in the same spirit as the idea (Cheng *et al.*, 1988; Engel, 1990) that the J 's can be thought of as functions of temperature (thus incorporating the effects of phonons *etc.*), in which case H_{1D} becomes a free energy. The approach still makes sense as long as the energetics justify the polytype picture – which reduces the configuration space of the constituent atoms to that small ‘slice’ defined by the ML definitions and the stacking rules. Thus we suggest that sequence-dependent distortions can be handled by incorporation into the couplings in H_{1D} – although we also feel that the question deserves further thought.

Finally, we consider the trioctahedral analogs of kaolins. These are called ‘cronstedtites’ by McLarnan and ‘serpentes’ by other sources (Brindley, 1980; Bailey, 1988), who reserve the term cronstedtite for a specific compound (but not structure!) in this group. That is, the term ‘cronstedtite’ refers to a whole set of polytypic structures of the same chemical composition. Hence we will use the term here as McLarnan does, to refer more generally to 1:1 (*i.e.* ML = TL + OL) trioctahedral polytypes.

The analysis of cronstedtites is simple, once the kaolins are understood. The trioctahedral occupation adds a threefold symmetry to the MLs and renders the LG $p31m$. The effect (McLarnan, 1981) on our analysis is that the σ variables now must obey $\sigma_0 = \sigma_2 = \sigma_4$ and $\sigma_1 = \sigma_3 = \sigma_5$, owing to the threefold symmetry. Hence we retain only σ_0 and σ_1 . The allowed τ 's remain unchanged. Hence we have $k_{\sigma} = 2$ while

$k_\tau = 9$; and the same extra stacking rule applies, such that $K = 12$. Because the τ spin components retain the same complex structure as for the kaolins, the group \mathcal{G} is the same for cronstedtites as for kaolins, *i.e.* $\mathcal{G} = C + M = 6mm$.

We also find $r_{\min} = 1$ for the cronstedtites. In fact, we can simply take the example $r = 1$ D pair from our kaolin discussion and appropriately relabel the σ 's. The result is still a pair of cycles related by M_σ , which are represented by one simple cycle $\tau^0\sigma$ in ${}^G G$ as before.

9. Summary and discussion

The crystal problem in one dimension has been addressed in various forms, with various results. The present work continues a thread of investigation involving (i) discrete configurations (' k -state spins') on a one-dimensional lattice, with (ii) finite-ranged interactions (of range r). Radin & Schulman (1983) and Teubner (1990) showed that the 'generic' problem of this class has a periodic ground state with vanishing entropy per spin, *i.e.* is crystalline. Canright & Watson (1996) (CW) then added *symmetry* to the problem, and showed that, in general, one no longer knows that even the 'generic' (but symmetric) problem has a crystalline ground state. More specifically, all problems in this class (one-dimensional, finite k , finite r) have a finite number of independent couplings in the Hamiltonian H_{1D} . Hence a *specific* Hamiltonian is a point in a finite-dimensional space. Radin & Schulman and Teubner showed that the set of points with nonperiodic ground states is of vanishing volume in the larger space of nonsymmetric Hamiltonians. CW showed that this same (nonperiodic) set is (for many values of k and r , and for many symmetries) of *finite* volume in the lower-dimensional subspace of symmetric Hamiltonians. Thus, in such a case (termed 'PNC' for 'possibly noncrystalline' here), if one has a symmetric Hamiltonian H_{1D} and chooses the couplings J by throwing a dart into the symmetric space, one has a finite probability of obtaining a set of J 's that has an uncountable number of disordered ground states.

Nature presumably does not throw darts; but we are still rather ignorant about how in fact nature almost invariably (Parsonage & Staveley, 1978) finds crystalline ground states for bulk matter. In this work, we have extended the finite- k , r thread considerably closer to real polytypes. It is known that such materials are well represented – especially at low temperature – as one-dimensional stacking problems falling into the class considered here. Here we have chosen a variety of polytype families, deduced the nature of the spins and the symmetry of the stacking Hamiltonian H_{1D} , and then asked and answered the following question: does each family have a finite (PNC) or vanishing (C for 'crystalline') subvolume of couplings giving disordered ground states?

We assume no knowledge about the couplings themselves, other than that they fall somewhere in the symmetric subspace. Thus, if nature has reasons to prefer crystalline ground states – reasons that are not embodied in our assumptions here – then she will perhaps not throw darts, but rather carefully aim such that real polytypes always land in a C

subvolume. We believe that we (following CW) have incorporated an important physical ingredient into our reasoning by including symmetry. But we recognize that there may be other ingredients, possibly arising from the quantum-mechanical origin of the effective classical couplings, which may be equally important, but are left out here. We have simply used those ingredients that are well known: the nature and symmetry of the layers, plus the stacking rules. With these ingredients, we have deduced the symmetry group \mathcal{G} of H_{1D} and then stated whether the polytype family is PNC or C .

Our results are a significant extension of the above-mentioned thread, and in particular of the work of CW, in two ways. For one, we have applied the general reasoning of CW to real materials, and found the interesting result that most of the families studied – in fact, all families but the SiC family – are PNC, *i.e.* cannot be assumed to be crystalline at $T = 0$. Secondly, we have discovered, and documented in this paper, that real materials exhibit a rich variety of kinds of spin, stacking rule, and symmetry group. Again excepting SiC, we have been required to study new spin types and/or new symmetries for each family studied.

This richness and the potential for noncrystalline ground states are summarized in Table 1. As discussed in the body of the paper, there is a minimum interaction range r_{\min} at and beyond which a family becomes PNC. (For a C family, $r_{\min} = \infty$.) We have included r_{\min} in Table 1; and in the cases where r_{\min} refers to interaction range in units of a fraction of a modular layer (because more than one spin component is required per ML, *i.e.* $D > 1$), we have also expressed this minimum interaction range in units of full MLs as R_{\min} . Besides these numbers, we have summarized a variety of information for each family in Table 1.

It is worthwhile repeating and clarifying what the answer PNC does and does not tell us. There is a 'P' in front because there is *no* problem in this class for which the ground state is disordered and degenerate for all values of the couplings. Hence our approach can never give a definite 'noncrystalline' answer. For that one must actually compute – or at least estimate – the true couplings, including their range, for a given material. However, our approach can do more than simply say 'possibly noncrystalline': it can also specify the precise range of J 's giving noncrystalline ground states (Watson *et al.*, 1997). Hence, even a rough estimate of the couplings may suffice to determine the nature of the ground state for a given material.

We know of two cases for which the J 's have been computed from first principles, namely, SiC (Cheng *et al.*, 1987, 1988; Heine, 1987; Shaw & Heine, 1990) and ZnS (Engel & Needs, 1990; Engel, 1990). Unfortunately, for each of these materials we predict nothing novel. They are in the same family and we find that this family has crystalline ground states for all values and ranges of the couplings.

Let us now try to assess how much promise there is, in the results of Table 1, of novel behavior (*i.e.* disorder at equilibrium at $T = 0$) in real materials. Certainly the PNC entries are numerous. And the R_{\min} values are not large. We may compare these with those found for SiC and for ZnS: the interactions for these materials extend to roughly three MLs

Table 1

We show here the results of our search for possible disordered ground states in real polytypic materials.

The only family of polytypes that must have a crystalline ground state is SiC. Using only the nature and symmetries of the modular layers and the stacking rules, we cannot exclude the possibility of disordered ground states for the other families, which receive the entry 'PNC'. Note that the kaolins and the cronstedtites have fewer ML configurations than might be expected from the possible configurations of each sublayer. This is due to the presence of constraints that prohibit some spin sequences.

Family	LG	D	k	\mathcal{G}	Crystallinity	r_{\min}	R_{\min}
SiC	$p\bar{3}m1$	1	2	S	C	∞	∞
CdI ₂	$p\bar{3}m1$	2	2, 2 = 4	$S + I$	PNC	6	3
GaSe	$p\bar{6}m2$	2	2, 2 = 4	$S + S_x I$	PNC	6	3
Micas	$C12/m1$	1	6	$S + I$	PNC	1	1
Kaolins	$C1m1$	2	6, 9 = 36	$C + M$	PNC	1	1
Cronstedtites	$p\bar{3}1m$	2	2, 9 = 12	$C + M$	PNC	1	1

and one ML, respectively. We have not computed the fraction of the coupling-parameter volume giving noncrystallinity; we have only shown that it is nonzero. This fraction could be obtained using the methods of Watson *et al.* (1997); however it is a tedious job and we are not sure the answer would be illuminating. We take the results of this study, as summarized in Table 1 with its many PNC entries, as saying that one cannot in general *assume* that the equilibrium low-temperature phase of a given polytype is crystalline. Instead one must look further; and the most promising approach is probably to compute or estimate the effective interlayer couplings for each specific polytype of interest.

We note that one does not obtain a clear picture from experimental observations either. Disorder is ubiquitous among real polytypes. And real polytypes suffer from the undoubted problem that most of the observed structures are metastable. We know this because there are so many observed structures for a single p and T – even for the cases such as SiC and ZnS, where we know the equilibrium structure is ordered – and because the activation energies for translating something as large as a modular layer are large. Hence we get no clear information about the equilibrium behavior of real polytypes from the observation that disordered structures are widespread.

We return, for the final time, to our own logic. Our reasoning is based on strong conditions such as the symmetry of MLs, stacking constraints, and the topology of cycles in graphs and their known relation to ground states of the one-dimensional Hamiltonian. Hence this reasoning is in most cases rigorous. However, it is not more reliable than its assumptions, which we will examine critically here. First, the symmetry. We take the ML symmetries to be exact. In some cases (micas and kaolins) we have discussed departures from the 'ideal' ML structure. Clearly such departures do not affect our reasoning or our results if the distortions from the ideal structure maintain the symmetry of the ML, *i.e.* if they do not change the layer group or the stacking rules. In the section on kaolins, we addressed a further possibility, namely distortions that *do* lower the ML symmetry. These in fact can (and do for kaolins) depend on the stacking sequence itself. This possibility – which is always present in principle – is clearly observed in kaolin polytypes; distortion is probably

pronounced for these materials because the hydrogen-bonding constraints are in fact difficult to satisfy. In any case, we have argued that such distortions also need not alter our logic or conclusions because they can be absorbed into the energetics of the couplings. We consider this argument to be only tentative. But regardless of the merit of this argument, our main line of reasoning should be 'nearly correct' if any distortions of the MLs are small. Here 'nearly correct' means that the distortions give rise at most to small changes

in the energetics of the material, such that it behaves as predicted by our logic except for small corrections due to small energy terms. If these corrections change the nature of the ground state from noncrystalline to crystalline (or *vice versa*), then the material will behave as if the corrections are zero until the temperature becomes of the same order as the small corrections – at which point metastability effects are likely to be very strong. [An example of this for a non-polytypic solid is water (Tajima *et al.*, 1982, 1984)].

The same comments apply to our other strict assumption, that the interlayer interactions are zero beyond some range r . They are of course not exactly zero for any r ; and, as discussed in CW, tiny terms at some larger range can make the domain-wall energy of a D pair nonzero instead of exactly zero. In such a case, a material will behave as if its domain-wall energy is zero down to some small temperature; and then (again) it must overcome activation barriers at low T in order to find the true crystalline ground state among the huge number of disordered structures specified by the D pair.

The present work (summarized in Table 1) shows how elementary symmetry considerations, plus some study of certain classes of directed graphs, can give interesting and nontrivial information about possible ground states of real polytypes. Our results say that the polytype families represented by CdI₂, GaSe, micas and kaolins/cronstedtites should not be assumed to have crystalline ground states – at least not without sufficient information about the nature of the interlayer couplings. Since the PNC entries are numerous, our results suggest the same conclusion for *any* polytype family of interest. We hope that these results inspire some new interest in and curiosity about the crystal problem – specifically, the crystal problem for the large number of solid materials that exhibit polytypism.

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References

- Artioli, G., Bellotto, M., Gualtieri, A. & Pavese, A. (1995). *Clays Clay Miner.* **43**, 438–445.
- Bailey, S.W. (1963). *Am. Mineral.* **48**, 1196–1209.

- Bailey, S.W. (1988). Editor. *Rev. Miner.* **19**.
- Blandin, A., Friedel, J. & Saada, G. (1966). *J. Phys. (Paris) Colloq.* **27**, C3-128–C3-136.
- Bookin, A. S., Drits, V. A., Plançon, A. & Tchoubar, C. (1989). *Clays Clay Miner.* **37**, 297–307.
- Brindley, G. W. (1946). *Mineral. Mag.* **27**, 242–253.
- Brindley, G. W. (1980). *Crystal Structures of Clay Minerals and their X-ray Identification*, edited by G. W. Brindley & G. Brown, ch. II. London: Mineralogical Society.
- Canright, G. S. & Watson, G. I. (1996). *J. Stat. Phys.* **84**, 1095–1131.
- Cheng, C., Needs, R. J. & Heine, V. (1988). *J. Phys. C*, **21**, 1049–1063.
- Cheng, C., Needs, R. J., Heine, V. & Churcher, N. (1987). *Europhys. Lett.* **3**, 475–479.
- Deer, W. A., Howie, R. A. & Zussman, J. (1962). *Rock Forming Miner.* **3**, 194–212.
- Engel, G. E. (1990). *J. Phys. Condens. Matter*, **2**, 6905–6919.
- Engel G. E. & Needs, R. J. (1990). *J. Phys. Condens. Matter*, **2**, 367–376.
- Goodman, P. (1984). *Acta Cryst.* **A40**, 635–642.
- Heine, V. (1987). In *Competing Interactions and Microstructures: Statics and Dynamics*, edited by R. LeSar, A. Bishop & R. Heffner. Berlin: Springer-Verlag.
- Kabra, V. K. & Pandey, D. (1988). *Phys. Rev. Lett.* **61**, 1493–1496.
- Krause, C. W. & Morris, J. W. Jr (1974). *Acta Metall.* **22**, 767–777.
- McLarnan, T. J. (1981). *Z. Kristallogr.* **155**, 247–268.
- Miękisz, J. & Radin, C. (1987). *Mod. Phys. Lett. B*, **1**, 61–66.
- Mogami, K., Nomura, K., Miyamoto, M., Takeda, H. & Sadanaga, R. (1978). *Can. Mineral.* **16**, 427–435.
- Newnham, R. E. (1961). *Mineral. Mag.* **32**, 683–704.
- O’Keeffe, M. & Navrotsky, A. (1981) Editors. *Structure and Bonding in Crystals II*, chs. 19–22. New York: Academic Press.
- Pandey, D. (1989). *Phase Transit.* **16/17**, 247–261.
- Pandey, D. & Krishna, P. (1982). *Current Topics in Materials Science*, Vol. 9, edited by E. Kaldis, ch. 2. Amsterdam: North-Holland.
- Parsonage, N. G. & Staveley, L. A. K. (1978). *Disorder in Crystals*. Oxford: Clarendon Press.
- Pauling, L. (1930). *Proc. Natl Acad. Sci. USA*, **16**, 123–129.
- Radin, C. & Schulman, L. S. (1983). *Phys. Rev. Lett.* **51**, 621–622.
- Sebastian, M. T. & Krishna, P. (1994). *Random, Non-Random and Periodic Faulting in Crystals*. New York: Gordon and Breach.
- Shaw, J. J. A. & Heine, V. (1990). *J. Phys. Condens. Matter*, **2**, 4351–4361.
- Shrestha, S. P. & Pandey, D. (1996). *Europhys. Lett.* **34**, 269–274.
- Shrestha, S. P. & Pandey, D. (1997). *Proc. R. Soc. London Ser. A*, **453**, 1311–1330.
- Tajima, Y., Matsuo, T. & Suga, H. (1982). *Nature (London)*, **299**, 810–812.
- Tajima, Y., Matsuo, T. & Suga, H. (1984). *J. Phys. Chem. Solids*, **45**, 1135–1144.
- Takeda, H. (1971). *Am. Mineral.* **56**, 1042–1056.
- Teubner, M. (1990). *Physica (Utrecht)*, **A169**, 407–420.
- Thompson, J. B. Jr (1981). *Structure and Bonding in Crystals II*, edited by M. O’Keeffe & A. Navrotsky, ch. 22. New York: Academic Press.
- Vainshtein, B. K. (1981). *Modern Crystallography I*. Berlin: Springer-Verlag.
- Verma, A. R. & Krishna, P. (1966). *Polymorphism and Polytypism in Crystals*. New York: John Wiley.
- Watson, G., Canright, G. S. & Somer, F. L. Jr (1997). *Phys. Rev. E*, **56**, 6459–6465.
- Yeomans, J. (1987). *Solid State Physics*, Vol. 41, edited by H. Ehrenreich & D. Turnbull. New York: Academic Press.
- Yi, J. & Canright, G. S. (1996). *Phys. Rev. B*, **53**, 5198–5210.
- Zvyagin, B. B. (1962). *Sov. Phys. Crystallogr.* **7**, 38–51.
- Zvyagin, B. B. & Drits, V. A. (1996). *Clays Clay Miner.* **44**, 297–303.