Competing interactions, magnetic frustration, the “Devil’s Staircase”, and other exotic phenomena: How they become real in multiferroic compounds

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1. Commensurate, incommensurate, and other phases: A short overview

The definition of “commensurate” (CM) needs an underlying periodic structure as reference.

Various quantities. e.g. magnetic moments, lattice displacements, surface adsorbed ions, etc. can assume an ordered state that is commensurate (or not) with the periodic reference structure.

A commensurate modulation has a periodicity of $n/m^*b$, where $b$ is the fundamental length unit of the periodic reference structure.

Mathematical problem:
The rational numbers $(n/m)$ are dense, i.e. next to an irrational number there exist rational numbers arbitrary close.

Experimentally it is not possible to distinguish between truly incommensurate (ICM) or higher order CM periodicities.

It seems practical to restrict CM modulations to the lowest orders of $n/m$. e.g. 1/2, 1/3, 1/4, 2/3, ...

Incommensurate (ICM) modulations can than be defined as small deviations from the CM orders, the modulation vector given as $n/m \pm \delta$ ($\delta$ small)
Example: Atoms connected by harmonic forces (springs) in a periodic potential

\[ H = \sum_n \frac{1}{2b^2} (x_{n+1} - x_n - a_0)^2 + V \left( 1 - \cos \frac{2\pi}{b} x_n \right) \]

Characteristic cases:

**V=0:** Harmonic interactions favors a lattice constant \(a_0\) which is ICM with \(b\). Bragg spots in scattering experiments appear at \(Q = 2\pi N/a_0\), not coinciding with \(G = 2\pi N/b\) of the periodic potential.

**V large:** Atoms may settle into a CM structure with the average \(a\) being a simple fraction of \(b\). Diffraction pattern of substrate and adsorbed layer has infinite set of coinciding Bragg sheets.

CM, 2a=3b

ICM

chaotic

Frenkel & Kontorowa (1938),
Frank & Van der Merwe (1949)
$V > 0$, not too large:

Potential will modulate the chain, the average period, $a \neq a_0$, can be CM or ICM.

In the general ICM structure the $n^{th}$ atomic position is

$$x_n = na + \alpha + f(na + \alpha)$$

with $f$ a continuous and periodic function with period $b$.

Bragg sheets

Bragg spots for $N \neq 0$ form satellites around spots from the basic lattice (potential).

Note that the energy does not depend on the phase $\alpha$ and the chain is not “pinned”.

Chaotic states: (very strong potential, metastable)

Atoms are randomly distributed among the potential minima

Formation of CM chain sections with random length and domain wall distribution

Average period is in general ICM with the potential

Chaotic phase is “pinned” to the potential
How does the periodicity $a$ (or the wave vector $q=2\pi/a$) change if model parameters “$x$” (e.g. $a_0$, $V$, $b$, $T$) are tuned?

If $x$ goes from $x_1$ to $x_2$, $q$ goes from $q_1$ to $q_2$ - but how?

$$H = \sum_n \frac{1}{2b^2} (x_{n+1} - x_n - a_0)^2 + V\left(1 - \cos\frac{2\pi}{b} x_n\right)$$

Typical Examples

**The floating phase:**

$q$ varies continuously with $x$ passing through an infinity of CM (ICM) values without locking into specific CM phases. (may occur in 2 dimensions)

**The harmless staircase:**

$q$ assumes a finite number of CM values, the periodicity is locked in intervals of $x$
The incomplete devil’s staircase:

$q/2\pi$ locks in at an **infinity** of finite intervals of $x$, it remains constant and rational in these intervals, however, there exist **floating phases** between the CM intervals.

The complete devil’s staircase:

The **infinity** of locked CM portions fills the whole interval of $x$.

Experimentally it is nearly impossible to distinguish different cases, however, hysteresis effects can be observed (they are expected in the harmless and complete devils staircase).
Most examples of CM and ICM phases have been found in magnetic systems:

Temperature dependence of the wave vector of the magnetic structure of Er

Note the CM → ICM transition at 24 K

Most “devilish” staircase in the sinusoidal magnetic structure of CeSb. $q$ jumps between different (up to 7) CM values.

Habenschuss et al., 1974

Fischer et al., 1978
Other examples in condensed-matter physics:

1) Adsorption of rare-gas monolayers (Krypton) on graphite (2-dimensional realization)

(a) CM $\sqrt{3}$ structure with Kr occupying 1/3 of the graphite honeycomb cells
(b) Incommensurate phase (higher density)
Due to the layered structure of graphite the intercalation of metal atoms between the honeycomb carbon planes is easily achievable.

Within one layer CM and ICM structures are realized, additional order along the c-axis results in “staging” orders of the metal layers.

3-D system as compared to 2-D for surface adsorption.

2) Staging in graphite intercalation compounds

ICM order is a periodic distortion of the lattice due to competing short-range forces (in insulators) or due to the formation of a charge density wave, “Peierls effect”, in metals (e.g. TaSe$_2$, NbSe$_3$).

In many magnetic ICM systems the lattice exhibits a similar ICM distortion with

$$q_{latt} = 2 q_{mag}$$

because of strong spin-lattice coupling.

3) Displacive incommensurability
2. The CM \( \rightarrow \) ICM transition in the Frank & Van der Merwe model

\[
H = \sum_n \frac{1}{2b^2} (x_{n+1} - x_n - a_0)^2 + V \left( 1 - \cos \frac{2\pi}{b} x_n \right)
\]

Continuum limit:

\[
x_n = nb + \frac{b}{2\pi} \phi_n, \quad \phi_n - \phi_{n-1} = \frac{d\phi}{dn}
\]

\[
H = \int \left[ \frac{1}{2} \left( \frac{d\phi}{dn} - \delta \right)^2 + V(1 - \cos p\phi) \right] dn
\]

\( \delta = (2\pi/b) (a_0 - b) \) is the “natural misfit”, and \( p = 1 \)

\( \varphi(n) = 0 \) describes the commensurate phase, \( \varphi(n) = \delta n \) is the unperturbed ICM phase

The ground state is defined by the minimum of \( H \), i.e. by:

\[
\frac{d^2\varphi}{dn^2} = pV \sin p\varphi
\]

1-D sine-Gordon equation
One of the solutions of the sine-Gordon equation is the single soliton:

\[ \varphi(n) = \frac{4}{p} \tan^{-1} \exp(p\sqrt{V} n) \]

The soliton is a domain wall at \( n=0 \) separating two CM regions with 
\( \varphi = 0 \) and \( \varphi = \frac{2\pi}{p} \)

The more general solution is a “soliton lattice”:

Regularly spaced domain walls (solitons) separate the commensurate regions

The distance \( l \) is related to the average misfit \( <q> = \frac{2\pi}{b} (a - b) \) by

\[ <q> = \frac{2\pi}{pl} \quad \text{(soliton density)} \]
The energy density near the CM phase (\( <q> \ll 1 \)) is:

\[
E = \left( \frac{4\sqrt{V}}{\pi} - \delta \right) \langle q \rangle + \frac{16\sqrt{V}}{\pi} \langle q \rangle \exp\left( -\frac{2\pi\sqrt{V}}{\langle q \rangle} \right)
\]

- soliton energy
- effective soliton repulsion

The CM → ICM transition takes place when E changes sign from \( E > 0 \) (CM) to \( E < 0 \) (ICM, soliton phase), i.e.

\[
V_c = \frac{\pi^2}{16} \delta^2
\]

Note:
The soliton-like modulation is strongly anharmonic giving rise to high order harmonics in scattering experiments (in contrast to the sinusoidal modulation for \( V = 0 \)).
3. Incommensurate magnetic phases: The anisotropic Ising model with competing interactions

ANNNI model: (Elliot, 1961)

Ising spins with ferromagnetic nearest-neighbor ($J_1$) and antiferromagnetic next-nearest-neighbor ($J_2$) interactions along one particular axis.

$$ H = -J_1 \sum_{i,j}^{(NN)} S_i S_j + J_2 \sum_{i,j}^{(NNN)} S_i S_j $$

Ground state solution:

Phase transition from FM ($q = 0$) to ↑↑↓↓ ($q = 1/4$) at $J_1 = 2 J_2$

At $J_1 = 2 J_2$ the ground state is degenerated and consists of successive ↑↑↑... and ↓↓↓... domains (formation of domain wall does not cost any energy!)

No exact solution for $T > 0$!
High-temperature (series expansion) solution  (Redner & Stanley, 1977)

Three regions in the phase diagram (T/J₁ vs. J₂/J₁):

(i) Disordered paramagnetic phase at high T
(ii) Ferromagnetic phase for J₂/J₁ < 0.5
(iii) “Modulated” phase with periodic modulation of the wave vector \( q = 2\pi(0,0,q) \)

All three phases meet at a Lifshitz point, P

q = 0 at the left side of P, but increases continuously to \( \frac{1}{4} \) for J₂/J₁ → 0.⁰.

At T=0: q = \( \frac{1}{4} \) for all J₂/J₁ > 0.5

How does the periodicity (q) in the modulated phase change if the temperature is lowered?
Mean-field theory (for the modulated phase): (Bak & von Boehm, 1980; Rasmussen & Knak-Jensen, 1981)

\[ H = -J_1 \sum_{i,j} S_i S_j + J_2 \sum_{i,j} S_i S_j \]

Mean-field approximation – neglect second order fluctuations

\[ S_i S_j = S_i \langle S_j \rangle + \langle S_i \rangle S_j - \langle S_i \rangle \langle S_j \rangle + (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \]

With this approximation the free energy can be expressed as: \( \langle S_i \rangle \equiv M_i \)

\[ F = \sum_{i,j} J_{ij} M_i M_j - T \sum_{i=1}^{M} \int_0^{\infty} \tanh^{-1} \sigma \ d\sigma \]

The stability of the \( q = 1/4 \) CM (↑↑↓↓) phase can be estimated using a trial function for the \( M_i \):

\[ M(r) = A \exp(i \varphi(z)) \exp \left( 2\pi i \frac{z}{4} \right) + CC \]

This trial Ansatz for \( M \) keeps the amplitude of \( M \) constant and allows for a variation of the phase \( \varphi \) with the coordinate \( z \)

In the CM phase: \( \varphi = \text{const.} \) in the ICM phase: \( \varphi = 2\pi \delta z \) \( \rightarrow q = \frac{1}{4} + \delta \)
In the continuum limit and expanding $F$ to fourth order in $M$:

$$F = -4J_2A^2 \int \left[ \frac{1}{2} \left( \frac{d\phi}{dz} - \delta \right)^2 + v(\cos 4\phi + 1) \right] dz$$

Note the similarity with the Frank & Van der Merve model!

The phase function $\phi(z)$ minimizing the free energy is the soliton lattice.

Near the CM phase boundary the free energy is:

$$F \sim \left[ \left( \frac{4\sqrt{v}}{\pi} - \delta \right) + \frac{16\sqrt{v}}{\pi} \exp \left( -\frac{2\pi\sqrt{v}}{\langle q \rangle} \right) \right] \langle q \rangle , \quad \langle q \rangle = \langle \frac{d\phi}{dz} \rangle$$

How does the soliton solution look like?

The domain wall has the structure:

↓↓↑↑↓↓↑↑↓↓↑↑↓↓
The (approximate) analytic solution results in a continuous function $q(T)$, however, the numerical solution of the mean-field model reveals the staircase behavior:

A sequence of “locked” commensurate phases is realized with increasing temperature, ICM phases appear closer to $T_c$ in between high-order CM phases.

The global Mean-field phase diagram is constructed from numerical calculations:

The dark areas of the “Devil’s Tree” represent high-order CM phases and ICM phases in between → Incomplete Devil’s Staircase

Near $T=0$ and $J_1=2J_2$ there is a multicritical point where an infinity of CM phases exist (Villain & Gordon, 1980) with CM modulations of $q=l/2(2l+1)$ (Fisher & Selke, 1980)

This point is highly unstable with respect to perturbations
4. Helical (non-collinear) magnetic phases: The Heisenberg model with frustration and anisotropy

The Ising model (by definition) cannot describe any non-collinear spin structures, as observed in the ferroelectric phases of some multiferroics.

Extension to Heisenberg model, for example:

\[
H = J_1 \sum_n \mathbf{S}_n \cdot \mathbf{S}_{n+1} + J_2 \sum_n \mathbf{S}_n \cdot \mathbf{S}_{n+2} - K \sum_n (S_n^z)^2 - \bar{H} \sum_n \mathbf{S}_n
\]

\(J_1 < 0, \quad J_2 > 0, \quad K > 0, \quad \text{spin } S = 1\)

\(J_1 < 0\) is the nearest neighbor ferromagnetic exchange interaction

\(J_2 > 0\) is the next-nearest neighbor AFM exchange

\(K\) is the uniaxial anisotropy, and \(\bar{H}\) is the external magnetic field.

This model, although too simple to be applied to “real” multiferroic compounds, has a wealth of solutions describing different magnetic orders, including collinear CM and ICM structures as well as non-collinear (helical) spin orders.

First reports of helical magnetic orders as solutions of the Heisenberg model by Kaplan (1959), Villain (1959), and Yoshimori (1959).
Early solutions reveal a global phase diagram with a Lifshitz point:

(Hornreich, 1975; Redner & Stanley, 1977)

(i) The transition across “1 − 2” \( (T_\lambda) \) is a second order phase transition with conventional critical behavior

(ii) The critical behavior changes dramatically near the Lifshitz point “L”, where the three phases meet

(iii) The modulation vector “k” is zero (FM) between “1” and “L” but it continuously changes from “L” towards “2”

(iv) The control parameter “P” can be pressure, composition, or the ratio of competing exchange coupling parameters

Redner & Stanley derived the corresponding phase diagram for the Heisenberg model with competing NN and NNN exchange:

\[
\mathcal{H} = -J_{xy} \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_z \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J'_{zz} \sum_{\langle i j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j
\]

High-temperature series expansion provide small corrections to the mean-field theory

Despite the small corrections, the mean-field theory seems to be an adequate description.
Ground state of the isotropic Heisenberg model

\[ E = -\sum_{i,j} J(\vec{r}_{ij}) \vec{S}_i \vec{S}_j , \quad \vec{r}_{ij} = \vec{r}_i - \vec{r}_j \]

Note: \( S_i \) is classical spin vector (for simplicity)
J is not limited to nearest neighbors

Fourier transformation into reciprocal space:

\[ J(\vec{q}) = \sum_n J(\vec{r}_n) e^{-i\vec{q}\vec{r}_n} , \quad \vec{S}_q = N^{-1/2} \sum_n \vec{S}_n e^{-i\vec{q}\vec{r}_n} \]
\[ E = -\sum_{\vec{q}} J(\vec{q}) \vec{S}_\vec{q} \vec{S}_{-\vec{q}} \]

The ground state is defined by the minimum of energy, with the condition

\[ \vec{S}_n^2 = \text{const.} = S^2 , \quad \sum_n \vec{S}_n^2 = \text{const.} , \quad \sum_{\vec{q}} \vec{S}_{\vec{q}} \vec{S}_{-\vec{q}} = \text{const.} \]

The minimum of E is obtained for the \( q = \pm Q \) that maximizes the coupling \( J(q) \):

\[ E = -J(Q)(\vec{S}_\vec{Q} \vec{S}_{-\vec{Q}} + \vec{S}_{-\vec{Q}} \vec{S}_\vec{Q}) \]
In real space:

\[
\vec{S}_n = N^{-1/2} \left[ \vec{S}_Q e^{i\vec{Q}\vec{r}_n} + \vec{S}_{-Q} e^{-i\vec{Q}\vec{r}_n} \right], \quad \vec{S}_{-Q} = \vec{S}_Q^* \\
S_{nx} = A \cos(\vec{Q}\vec{r}_n + \alpha) \\
S_{ny} = B \cos(\vec{Q}\vec{r}_n + \beta) \\
S_{nz} = C \cos(\vec{Q}\vec{r}_n + \gamma)
\]

The equations above describe an elliptic helical order of spins with wave vector Q, which is circular for the condition $S_n^2 = \text{const}$. We may choose $z \perp$ plane of circle:

\[
S_{nx} = S \cos(\vec{Q}\vec{r}_n + \alpha) \\
S_{ny} = S \sin(\vec{Q}\vec{r}_n + \alpha) \\
S_{nx} = 0 \\
E = -NS^2 J(\vec{Q})
\]

“Screw structure” (Yoshimori)

Orientation of magnetization plane and Q not always perpendicular.

“Proper screw”: $S \perp Q$

“Cycloidal screw”: $S \parallel Q$ (breaks spatial inversion symmetry !)

The magnitude of Q is solely determined by the exchange coupling constants and is therefore in general incommensurate with the lattice!
Example: A spin system consisting of layers with $Q$ perpendicular to the layers ($\text{WMnO}_4$)

- $J_0 = \text{sum of } J(r_{ij}) \text{ over all sites in one layer containing site } j$
- $J_1 = \text{sum over all } J(r_{ij}) \text{ of site } i \text{ and all sites of the neighboring layer}$
- $J_2$ similar for second neighbor layer
- ...
- $d$ distance between planes

\[
J(q) = \sum_{\nu} J_{\nu} e^{-i\nu dq} = J_0 + 2J_1 \cos(dq) + 2J_2 \cos(2dq) + ...
\]

Limiting the interaction to next-nearest neighbors ($J_2$), $J(q)$ is maximized by:

\[
\left[J_1 + 4J_2 \cos(dQ)\right] \sin(dQ) = 0
\]

This equation has three solutions for $0 \leq dQ < 2\pi$:

(i) $Q = 0$ \hspace{1cm} \text{ferromagnetic spin order}

(ii) $Q = \pi/d$ \hspace{1cm} \text{antiferromagnetic order}

(iii) $\cos(dQ) = -J_1 / 4J_2$ \hspace{1cm} \text{Helical arrangement with ICM, for } |J_1| < |4 J_2|$
Ground state energy:

(i) \( Q = 0 \) : \( J(Q) = J_0 + 2J_1 + 2 J_2 \) \( E = - N S^2 J(Q) \)

(ii) \( Q = \pi/d \) : \( J(Q) = J_0 - 2 J_1 + 2 J_2 \)

(iii) \( Q = d^{-1} \arccos(-J_1/4J_2) \) \( J(Q) = J_0 - (J_1^2/4J_2) - 2 J_2 \) \( |J_1| < |4 J_2| \)

If \( J_2 > 0 \) (FM NNN coupling), the ground state is FM (for \( J_1 > 0 \)) or AFM (for \( J_1 < 0 \))

If \( J_2 < 0 \) (AFM coupling), the helical state has lowest energy for \( |J_1| < |4 J_2| \).

Note the difference to the ANNNI model:

Only two commensurate phases exist at \( T=0 \) in the ANNNI model:

FM (AFM) for \( |J_1| > |2 J_2| \), and the CM ↑↑↓↓ solution otherwise.

The FM (AFM) states of the isotropic (Heisenberg) model becomes unstable at much lower \( |J_2| = |J_1| / 4 \) (instead of \( |J_1| / 2 \) in the ANNNI model)
5. Can these simple models describe real multiferroics?

Example: MnWO₄ and Mn₁₋ₓFeₓWO₄

Taniguchi et al., 2006; Arkenbout et al., 2006

Phase sequence:
PM → SIN (incommens., collinear)
→ Helical (incommens., non-collin.)
→ E-type (commensurate, collinear)

In ICM phases: \( Q \sim 0.22 \)

The spiral phase is ferroelectric!

Competing exchange interactions:
FM nearest neighbor \( (J_1) \)
AFM next nearest neighbor \( (J_2) \)
Strong uniaxial anisotropy \( (K) \)
Strong magnetic field effect (if oriented along the easy axis)
The observed phase sequence \text{SIN (collinear)} \rightarrow \text{Helical} \rightarrow \uparrow \uparrow \downarrow \downarrow \text{ cannot be obtained from either the ANNNI or the isotropic Heisenberg model.}

The \uparrow \uparrow \downarrow \downarrow \text{ order in the ground state suggests a strong uniaxial anisotropy.}

The Heisenberg model with uniaxial anisotropy does interpolate between the isotropic limit and the ANNNI model:

\begin{align*}
H &= J_1 \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{[i,j]} \vec{S}_i \cdot \vec{S}_j - K \sum_i (S_i^z)^2 - \tilde{H} \sum_i \vec{S}_i \\
J_1 < 0, \quad J_2 > 0, \quad K > 0, \quad \text{spin} \quad S = 1
\end{align*}

\( K > 0 \) favors the alignment of spins along one axis (z)
\( K < 0 \) would favor the in-plane anisotropy (x-y plane)
For \( K \gg J_1, J_2 \) the spins are forced into one direction = ANNNI model
\( K = 0 \) results in the isotropic Heisenberg model
The effects of substitutions — Why Mn$_{1-x}$Fe$_x$WO$_4$?

(i) The end members, MnWO$_4$ and FeWO$_4$, are isostructural and a solid solution does exist

(ii) Both end members have different magnetic structures

(iii) Replacing Mn with Fe does allow for the control of exchange coupling and anisotropy parameters

(iv) Our main interest is the stability of the helical (ferroelectric) phase

Synthesis of large single crystals of Mn$_{1-x}$Fe$_x$WO$_4$
A small concentration of Fe (4%) destroys the helical (FE) phase completely at $H = 0$:

(Chaudhury et al., 2008)

The helical, ferroelectric phase covers a very small region in the phase diagram.

The suppression by this little Fe content indicates how fragile and susceptible this phase is as may be expected for frustrated spin systems.
The recovery of the helical (ferroelectric) phase in magnetic fields : (Chaudhury et al., 2008)

In magnetic fields along the easy axis the FE phase of Mn$_{0.9}$Fe$_{0.1}$WO$_4$ is completely restored.

Magnetic data reflect the field-induced FE transition and prove that it is associated with a major change of the magnetic structure.

From the dielectric and magnetic measurements we conclude that the external field restores the helical spin phase that allows for the ferroelectric displacements via the spin-lattice coupling.

This needs to be proven by the detailed investigation of the magnetic structure, e.g. by neutron scattering experiments.
Magnetic field induced ferroelectric phase should be helical with ICM spin modulation. This needs to be confirmed by neutron scattering experiments.
Can these complex physical phenomena be qualitatively described by a simple model?

The minimum requirements:

(i) Heisenberg-type spins and exchange interactions to allow for non-collinear order

(ii) Competing nearest (FM) and next-nearest (AFM) neighbor interactions

(iii) Strong uniaxial anisotropy to come close enough to the Ising (ANNNI) limit to describe the \( \uparrow \uparrow \downarrow \downarrow \) - type ground state.

(iv) External magnetic field (to be oriented along the easy axis of the spins)

Evaluation of the model in the ground state, at finite temperatures, and in magnetic fields.
Heisenberg model with (competing) nearest neighbor (FM) and next-nearest neighbor (AFM) interactions, uniaxial anisotropy, and external magnetic fields

$$H = J_1 \sum_n \vec{S}_n \cdot \vec{S}_{n+1} + J_2 \sum_n \vec{S}_n \cdot \vec{S}_{n+2} - K \sum_n (S_n^z)^2 - \vec{H} \sum_n \vec{S}_n$$

$$J_1 < 0, \quad J_2 > 0, \quad K > 0, \quad \text{spin } S = 1$$

Mean field approximation:

$$\vec{S}_n \cdot \vec{S}_{n+k} = (\vec{S}_n - \langle \vec{S}_n \rangle)(\vec{S}_{n+k} - \langle \vec{S}_{n+k} \rangle) + \langle \vec{S}_{n+k} \rangle \vec{S}_n + \langle \vec{S}_n \rangle \vec{S}_{n+k} - \langle \vec{S}_n \rangle \langle \vec{S}_{n+k} \rangle$$

$$H_{MF} = \sum_n \vec{h}_n \cdot \vec{S}_n - K \sum_n (S_n^z)^2 + E_{MF}$$

$$E_{MF} = -J_1 \sum_n \langle \vec{S}_n \rangle \langle \vec{S}_{n+1} \rangle - J_2 \sum_n \langle \vec{S}_n \rangle \langle \vec{S}_{n+2} \rangle$$

$$\vec{h}_n = -\vec{H} + J_1 \left( \langle \vec{S}_{n-1} \rangle + \langle \vec{S}_{n+1} \rangle \right) + J_2 \left( \langle \vec{S}_{n-2} \rangle + \langle \vec{S}_{n+2} \rangle \right)$$
For spin 1, eigenfunctions $|{-1}\rangle$, $|0\rangle$, $|1\rangle$ (i.e. $m = -1, 0, +1$)

$$H(n) = \sum_n \tilde{h}_n \tilde{S}_n - K \sum_n (S_n^z)^2$$

$$\langle m \pm 1 | S^x | m \rangle = \frac{1}{2}\sqrt{(1 \mp m)(2 \pm m)}, \quad \langle m \pm 1 | S^y | m \rangle = \mp \frac{i}{2}\sqrt{(1 \mp m)(2 \pm m)}, \quad \langle m | S^z | m \rangle = m$$

$$H_{ij}(n) = \begin{pmatrix}
-K + h^z_n & \frac{1}{\sqrt{2}}(h^x_n - ih^y_n) & 0 \\
\frac{1}{\sqrt{2}}(h^x_n + ih^y_n) & 0 & \frac{1}{\sqrt{2}}(h^x_n + ih^y_n) \\
0 & \frac{1}{\sqrt{2}}(h^x_n - ih^y_n) & -K - h^z_n
\end{pmatrix}$$

Eigenvalues $\lambda_i(n)$:

$$\lambda_i(n)\left[(\lambda_i(n) + K)^2 - (h^z_n)^2\right] - (\lambda_i(n) + K)(h^x_n)^2 + (h^y_n)^2 = 0$$

**Note:** This equation has to be solved for each single spin at location $n$.

The internal fields $h_n$ couple the solution to the neighboring spins at $n \pm 1$, $n \pm 2$.
Partition function and free energy:

\[
Z_{MF} = \text{Tr} \left( e^{-\beta H_{MF}} \right) = e^{-\beta E_{MF}} \prod_n \text{Tr}_n e^{-\beta H(n)}
\]

\[
F_{MF} = -\frac{1}{\beta} \ln Z_{MF} = E_{MF} - \frac{1}{\beta} \sum_n \ln \left\{ \text{Tr}_n e^{-\beta H(n)} \right\} = E_{MF} - \frac{1}{\beta} \sum_n \ln \left\{ e^{-\beta \lambda_1(n)} + e^{-\beta \lambda_2(n)} + e^{-\beta \lambda_3(n)} \right\}
\]

Mean field equations (self consistency equations for \(<S_n>\) :)

\[
\langle S_n^\alpha \rangle = \frac{\text{Tr} \left( S_n^\alpha e^{-\beta H_{MF}} \right)}{\text{Tr} \left( e^{-\beta H_{MF}} \right)}, \quad \alpha = x, y, z
\]

\[
\langle S_n^\alpha \rangle = \frac{\partial F_{MF}}{\partial h_n^\alpha} = -\frac{1}{\beta} \frac{\partial}{\partial h_n^\alpha} \ln \left\{ e^{-\beta \lambda_1(n)} + e^{-\beta \lambda_2(n)} + e^{-\beta \lambda_3(n)} \right\}
\]

\[
\frac{\partial \lambda_1(n)}{\partial h_n^\alpha} e^{-\beta \lambda_1(n)} + \frac{\partial \lambda_2(n)}{\partial h_n^\alpha} e^{-\beta \lambda_2(n)} + \frac{\partial \lambda_3(n)}{\partial h_n^\alpha} e^{-\beta \lambda_3(n)} =
\]

\[
= \frac{e^{-\beta \lambda_1(n)} + e^{-\beta \lambda_2(n)} + e^{-\beta \lambda_3(n)}}{e^{-\beta \lambda_1(n)} + e^{-\beta \lambda_2(n)} + e^{-\beta \lambda_3(n)}}
\]
Remember!

since \( h_n \) depend on \( <S_{n\pm 1}> \) and \( <S_{n\pm 2}> \) the self consistency equations for \( <S_n> \) cannot be solved easily for arbitrary spin orders.

Some special cases:

Ferromagnetic order, FM

\[
\langle S_n^z \rangle = S, \quad \langle S_n^y \rangle = 0, \quad \langle S_n^x \rangle = 0, \quad \text{for all } n
\]

\[
h_n^z = h^z = -H^z + 2S(J_1 + J_2)
\]

\[
\lambda_1 = 0, \quad \lambda_2 = -K + h^z, \quad \lambda_3 = -K - h^z
\]

\[
S = -\frac{2 \sinh \beta [2S(J_1 + J_2) - H^z]}{e^{-\beta K} + 2 \cosh \beta [2S(J_1 + J_2) - H^z]}
\]

\[
F / N = -(J_1 + J_2)S^2 - \frac{1}{\beta} \ln \left[ 1 + 2e^{\beta K} \cosh \beta [2S(J_1 + J_2) - H^z] \right]
\]
Antiferromagnetic order (AFM, two sublattices A, B):

\[
\langle S_n^x \rangle = \langle S_n^y \rangle = 0, \quad \langle S_n^z \rangle = S_A \quad (n \text{ even}), \quad \langle S_n^z \rangle = S_B \quad (n \text{ odd})
\]

\[
h_n^z = h_A = -H^z + 2J_1 S_B + 2J_2 S_A \quad (n \text{ even})
\]

\[
h_n^z = h_B = -H^z + 2J_1 S_A + 2J_2 S_B \quad (n \text{ odd})
\]

\[
S_A = -\frac{2 \sinh \beta (2J_1 S_B + 2J_2 S_A - H^z)}{e^{-\beta K} + 2 \cosh \beta (2J_1 S_B + 2J_2 S_A - H^z)}
\]

\[
S_B = -\frac{2 \sinh \beta (2J_1 S_A + 2J_2 S_B - H^z)}{e^{-\beta K} + 2 \cosh \beta (2J_1 S_A + 2J_2 S_B - H^z)}
\]

\[
F / N = -J_1 S_A S_B - \frac{1}{2} J_2 (S_A^2 + S_B^2) + \frac{1}{2} (f_A + f_B)
\]

\[
f_{A,B} = -\frac{1}{\beta} \ln \left\{ 1 + 2e^{\beta K} \cosh \beta (2J_1 S_{B,A} + 2J_2 S_{A,B} - H^z) \right\}
\]
Sinusoidal or arbitrary collinear order, spins $|| z$:

$$\langle S^x_n \rangle = \langle S^y_n \rangle = 0$$

$$\lambda_1(n) = 0, \quad \lambda_2(n) = -K + h^z_n, \quad \lambda_3(n) = -K - h^z_n$$

$$h^z_n = -H^z + J_1 \left( \langle S^z_{n-1} \rangle + \langle S^z_{n+1} \rangle \right) + J_2 \left( \langle S^z_{n-2} \rangle + \langle S^z_{n+2} \rangle \right)$$

$$\langle S^z_n \rangle = -\frac{2 \sinh \beta h^z_n}{e^{-\beta K} + 2 \cosh \beta h^z_n}$$

$$F / N = \frac{1}{N} \sum_n \left\{ -J_1 \langle S^z_n \rangle \langle S^z_{n+1} \rangle - J_2 \langle S^z_n \rangle \langle S^z_{n+2} \rangle - \frac{1}{\beta} \ln \left[ 1 + 2 e^{\beta K} \cosh \beta h^z_n \right] \right\}$$

This is (in general) a system of $N$ coupled equations that have to be solve simultaneously.

Can be done numerically!
Problems with the numerical solution:

(i) Iterative solution for N (up to 100) coupled equations, one for each $\langle S_n \rangle$, convergence sometimes slow, use $> 500$ iterative steps

(ii) Free energy of N variables may have many local minima => difficult to find the absolute minimum in the first run
Solved by repeating iteration many times with random initial spin configurations

Ground state phase diagram ($J_1 < 0$, $J_2 > 0$, $K > 0$):
For “A” the phase sequence is : E-type => helix => SIN => PM  (MnWO₄)
For “B” it is : E-type => SIN => PM , no helical phase ! (Mn₀.₉Fe₀.₁WO₄)
Since only “helix” can induce ferroelectricity, there is no FE in the latter compound.
Magnetic field may stabilize the helical magnetic structure ??
In a frustrated system many states are very close in energy, this explains their sensitivity to external fields or perturbations.

Example:

\[ J_1 = -1, \quad J_2 = 0.8, \quad K = 0.9 \quad (\rightarrow \text{ path "A" in the phase diagram}) \]

The transition \((\uparrow\uparrow\downarrow\downarrow) \rightarrow \text{helical}\) is a first order phase transition.

The next transition \(\text{helical} \rightarrow \text{sinusoidal}\) is of second order (\(<S_x>\) continuously approaches zero).

The transition into the paramagnetic phase is second order (\(<S_z>\) continuously approaches zero).
J1 = -1,  J2 = 0.8 ,  K = 1.2  ( ➔ path “B” in the phase diagram)

The helical phase is metastable, the transition from the (↑↑↓↓) phase proceeds directly into the sinusoidal phase. The transition is a first order phase transition.

In all cases, the FM phase is never stable (for the parameters chosen).
Question:

Can a magnetic field applied along the easy axis induce a non-collinear magnetic order?

YES!

For example, for $J_2 = 1$, $K = 0.8$, and $T = 0.8$,

- E-type order is stable for $H^z < 0.45$
- Transition to helical structure takes place at $H^z = 0.45$
Field – temperature phase diagram of the model for two characteristic sets of parameters

Note that the helical (ferroelectric) phase becomes unstable at high field due to the parallel alignment of the spins enforced by the magnetic field. The high-field transition into a paraelectric phase was indeed observed in MnWO$_4$. 
The high-field phase diagram of MnWO$_4$ is surprisingly similar to the numerical results.

A number of features seem to be reproduced at least qualitatively:

(i) Field-induced transition from the $\uparrow\uparrow\downarrow\downarrow$ phase to the helical (FE) phase at low $T$

(ii) Paraelectric high-field phase above 12 T

(iii) Suppression of the SIN phase at moderate field values.

The chosen model provides a reasonable description of the complex physics of magnetic states in substituted Mn$_{1-x}$Fe$_x$WO$_4$. 
Other examples of field-induced ferroelectric phases:

Delafossite CuFeO$_2$ (Kimura et al., 2006)

The ground state at H=0 is the $↑↑↓↓$ modulated CM state ($Q = 0.25$)

Magnetic fields induce a non-collinear ICM phase and ferroelectricity

At higher fields the stable phase is collinear again with an $↑↑↑↓↓$ ($Q = 0.2$) modulation

Other collinear phases are observed at higher fields (Mitamura et al., 2007)
The effect of substitution (Al for Fe) is opposite to MnWO$_4$; it induces a helical (FE) phase (Seki et al., 2007; Nakajima et al., 2008).

The spin wave excitations in CuFeO$_2$ have been measured and fitted to the Heisenberg model with uniaxial anisotropy (Ye et al., 2007)

$$H = - \sum_{i,j} J_{i,j}^{\perp} \vec{S}_i \cdot \vec{S}_j - \sum_{i,j} J_{i,j}^{\parallel} \vec{S}_i \cdot \vec{S}_j - D \sum_i S_{i,z}$$

The phases denoted PD and OPD are collinear sinusoidal magnetic structures, they are all paraelectric.
Nickel Vanadate $\text{Ni}_3\text{V}_2\text{O}_8$ (Lawes et al., 2005)

LTI phase is ferroelectric $\rightarrow$ for $H \parallel a$
the FE phase is induced by $H$ at low $T$