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

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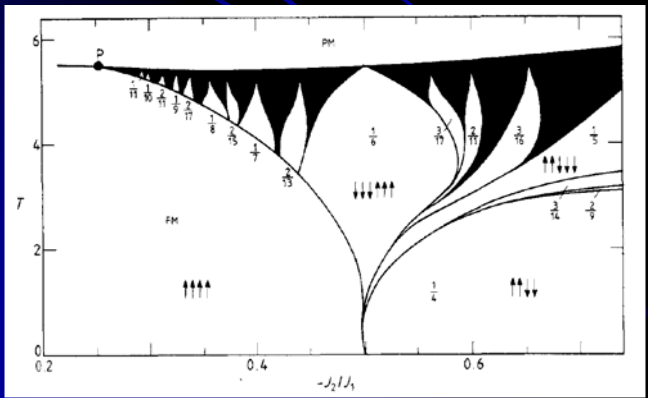

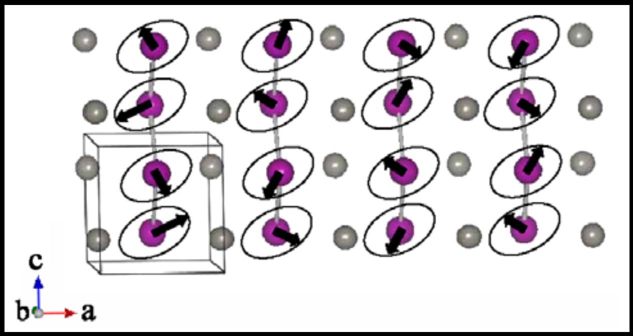

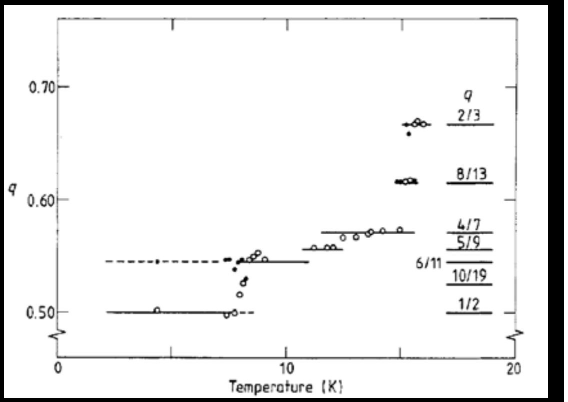

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1. Commensurate, incommensurate, and other phases: A short overview

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.

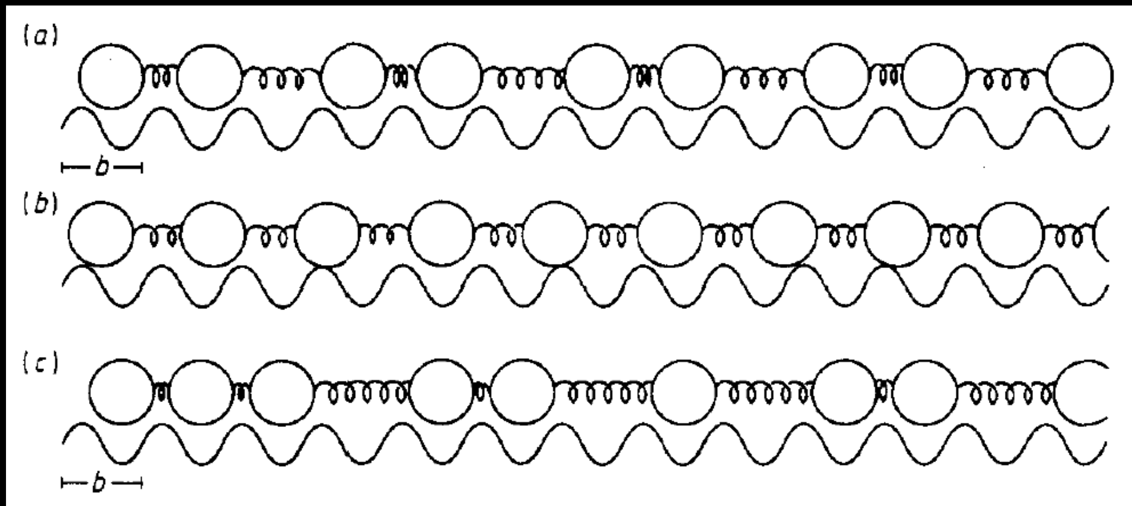
Mathematical problem:
The rational numbers (n/m) are dense, i.e. next to an irrational number there exist rational numbers arbitrary close.

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 $\pm\,\delta$ (δ small)

Example: Atoms connected by harmonic forces (springs) in a periodic potential



CM, 2a=3b

ICM

chaotic

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

Frenkel & Kontorowa (1938),

Frank & Van der Merwe (1949)

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

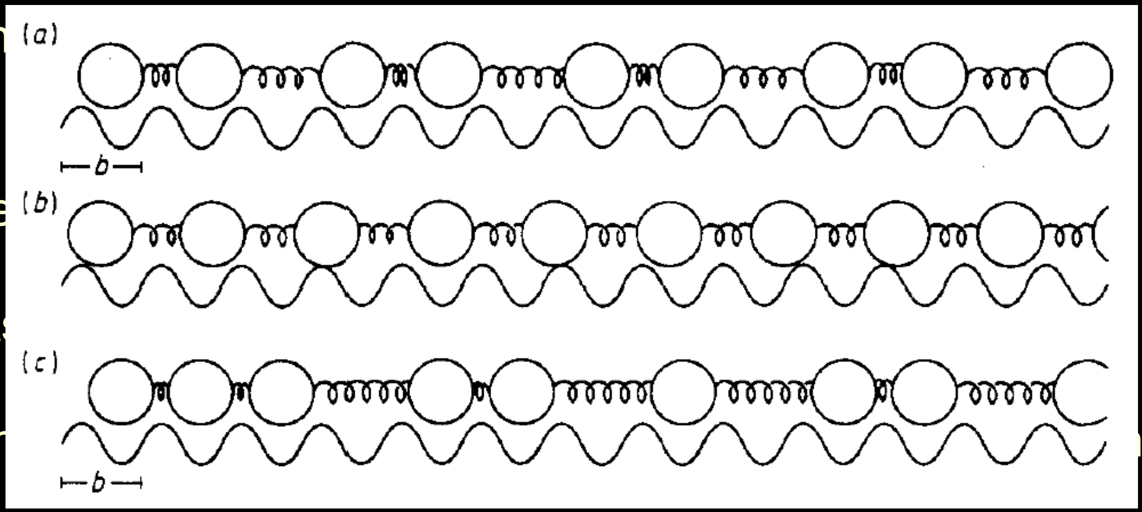
V large: Atoms may settle into a CM structure with the average a being a simple fraction of b. Diffraction pattern of substrate and adsorbed layer has infinite set of coinciding Bragg sheets.

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 con



Bragg shee

Bragg spot lattice (potential).

Note that th ain 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 ?

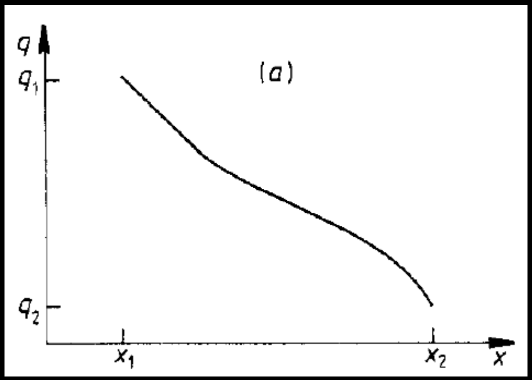
If *x* goes from x_1 to x_2, *q* goes from q_1 to q_2 - but how ?

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

Typical Examples

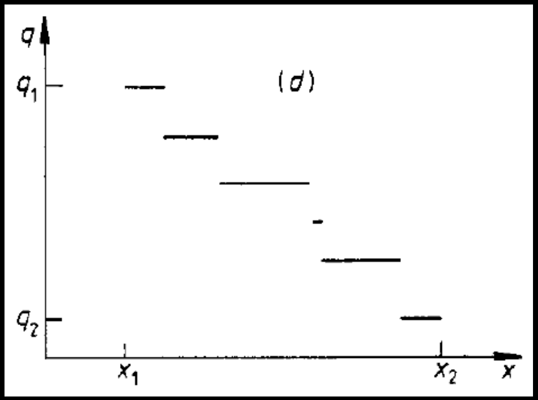
The floating phase:

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:

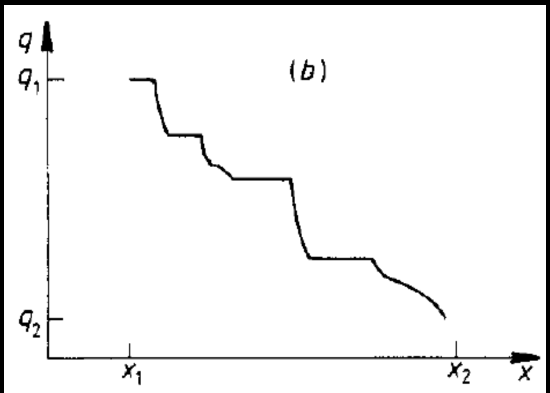
q assumes a finite number of CM values, the periodicity is locked in intervals of *x*



The incomplete devil's staircase :

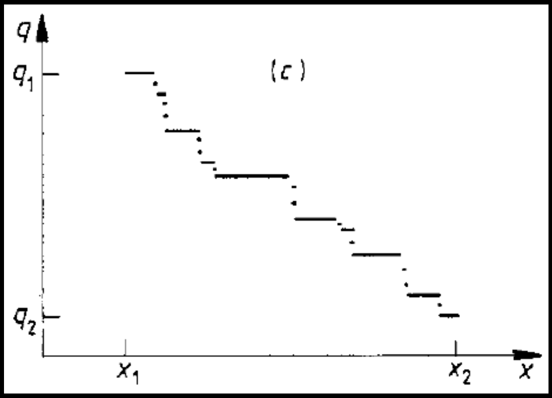
$q/2\pi$ locks in at an infinity of finite intervals of x, it remains constant and rational in these intervals,

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

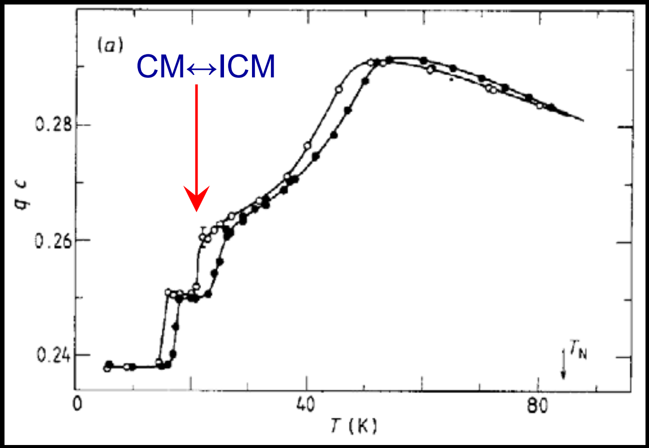


Experimentally it is nearly impossible to distinguish different cases, however, hysteresis effects can be observed (they are expected in the harmless and complete devils staircase).

Most examples of CM and ICM phases have been found in magnetic systems :

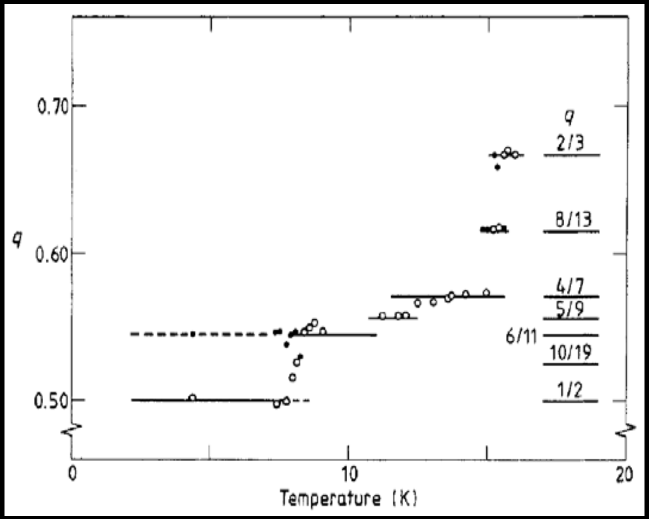
Temperature dependence of the wave vector of the magnetic structure of Er

Note the CM → ICM transition at 24 K



Habenschuss et al., 1974

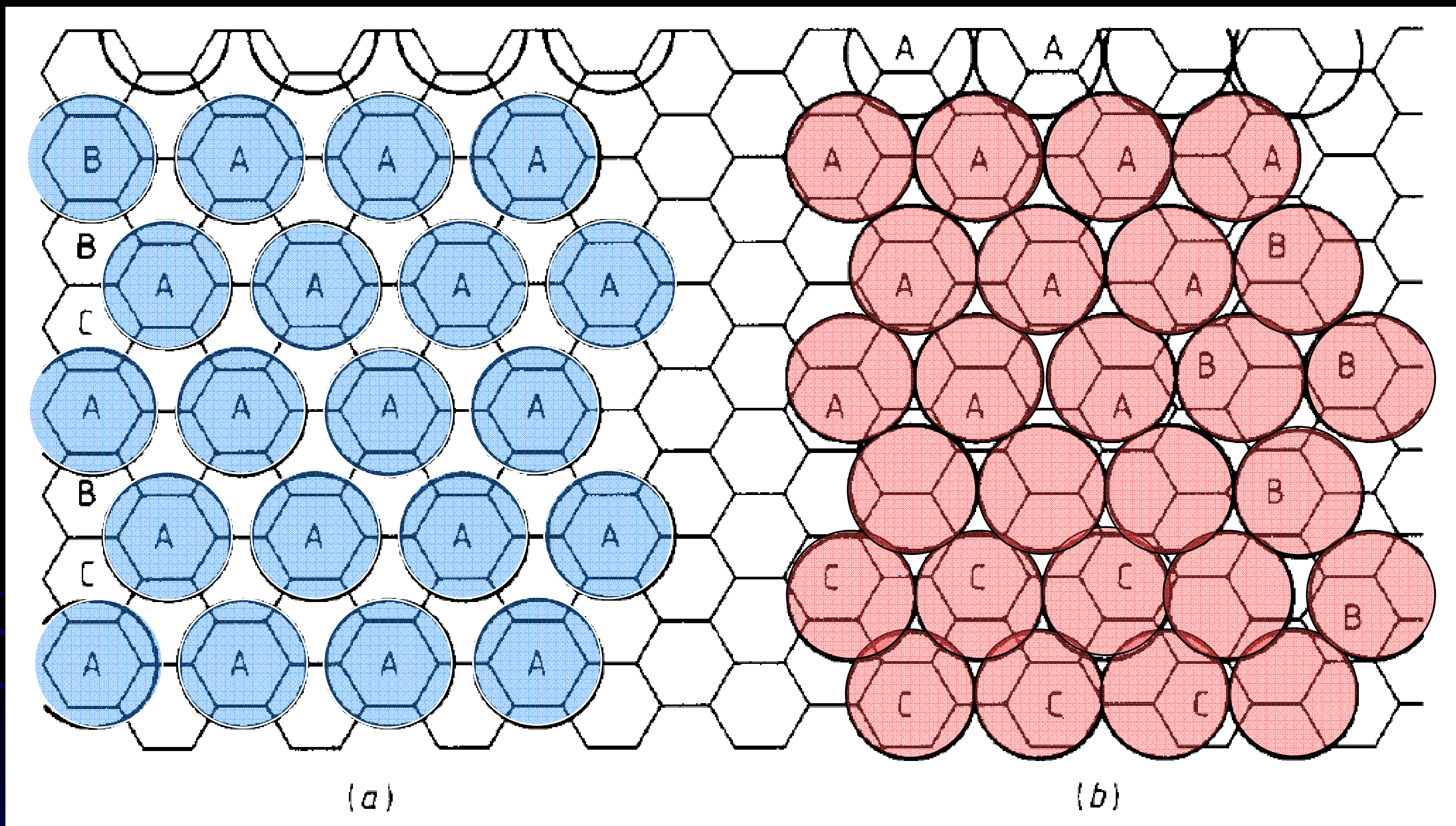
Most “devilish” staircase in the sinusoidal magnetic structure of CeSb.
q jumps between different (up to 7) CM values.



Fischer et al., 1978

Other examples in condensed-matter physics :

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



(a) CM "√3 structure" with Kr occupying 1/3 of the graphite honeycomb cells

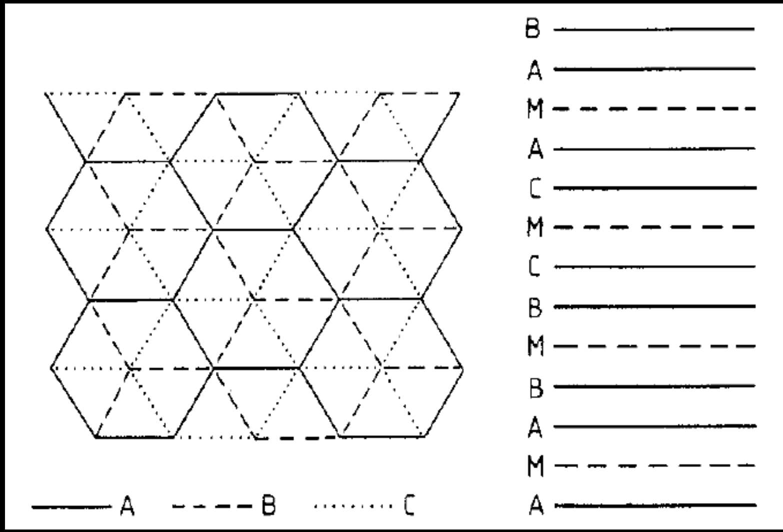
(b) Incommensurate phase (higher density)

2) Staging in graphite intercalation compounds

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.



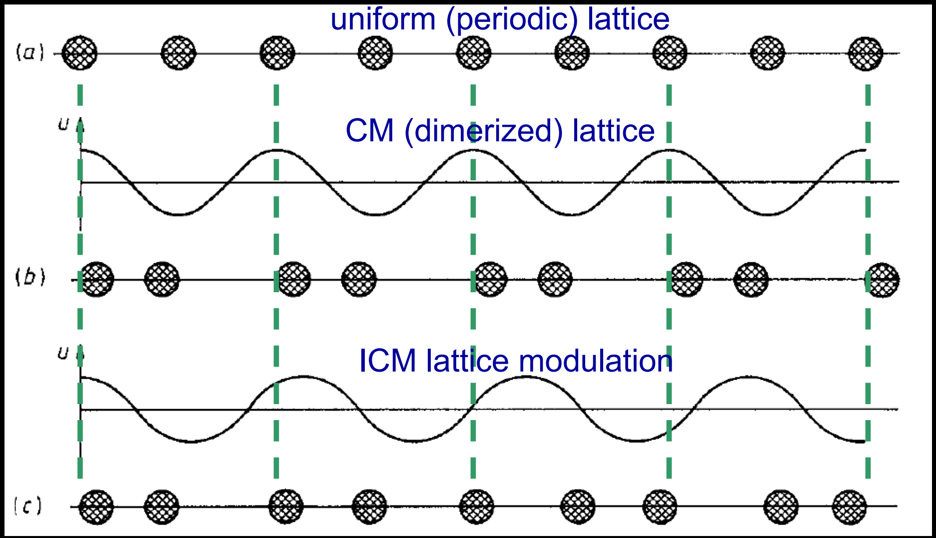
3) Displacive incommensurability

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. $TaSe_2$, $NbSe_3$).

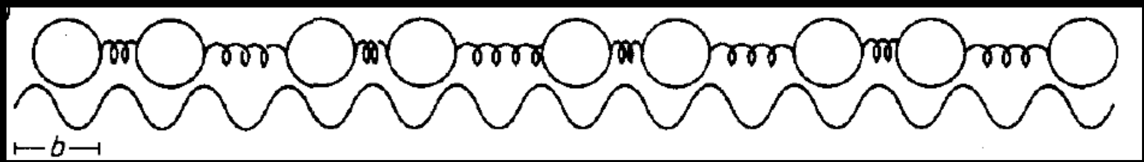
In many magnetic ICM systems the lattice exhibits a similar ICM distortion with

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

because of strong spin-lattice coupling



2. The CM → ICM transition in the Frank & Van der Merwe model



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

Continuum limit :

$$x_n = nb + \frac{b}{2\pi}\varphi_n\,, \qquad \varphi_n - \varphi_{n-1} = \frac{d\varphi}{dn}$$

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

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

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

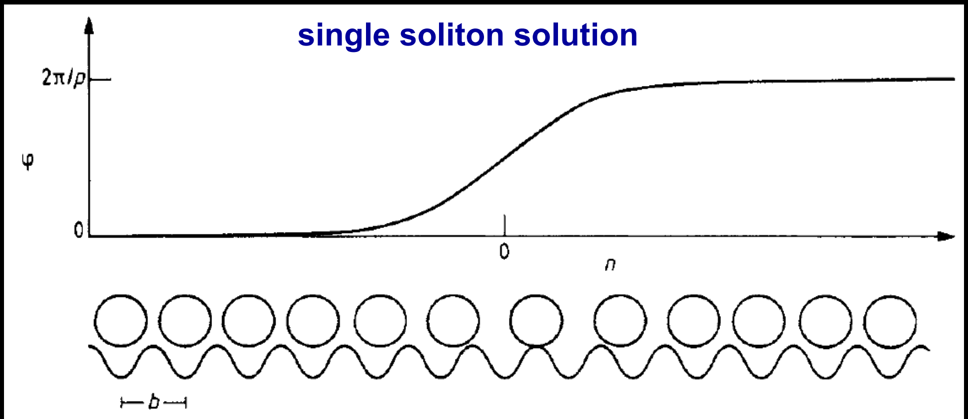
The ground state is defined by the minimum of H, i.e. by:

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

1-D sine-Gordon equation

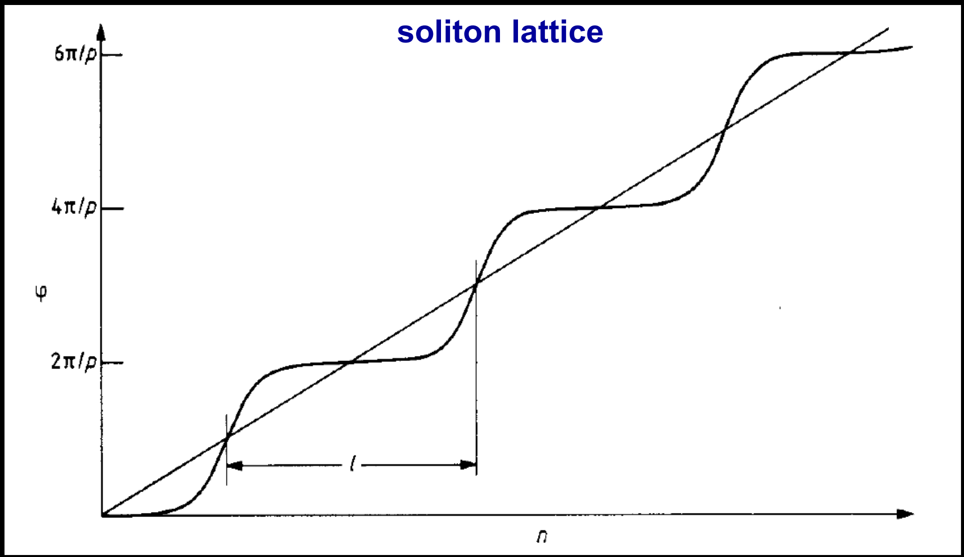
One of the solutions of the sine-Gordon equation is the single soliton :

$$\varphi(n) = \frac{4}{p}\tan^{-1}\exp\left(p\sqrt{V}\,n\right)$$



The soliton is a domain wall at n=0 separating two CM regions with $\varphi = 0$ and $\varphi = 2\pi/p$

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 $\langle q\rangle = (2\pi/b)\,(a - b)$ by

$\langle q\rangle = 2\pi/pl$ (soliton density)

The energy density near the CM phase (<q> << 1) is : (Bak & Emery, 1976)

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

soliton energy

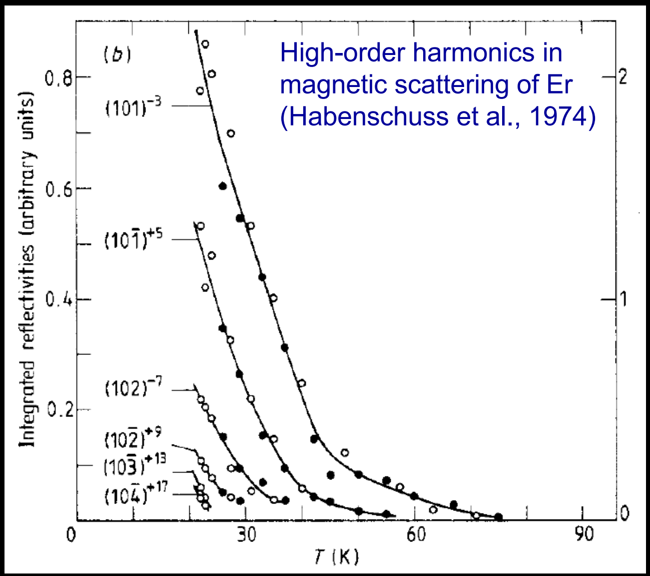
effective soliton repulsion

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

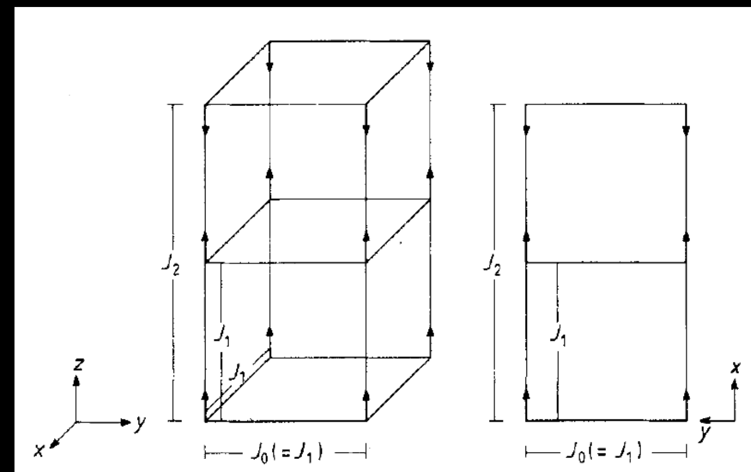
$$V_c = \frac{\pi^2}{16}\delta^2$$

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.

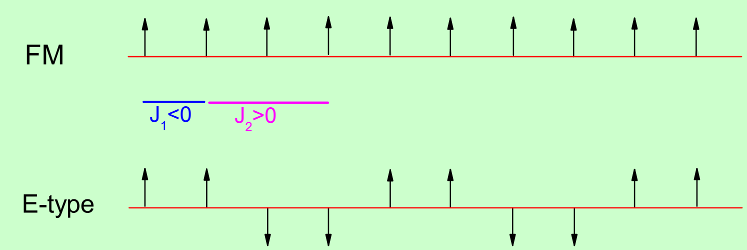
$$H = -J_1 \sum_{i,j}^{(NN)} S_i S_j + J_2 \sum_{i,j}^{(NNN)_z} S_i S_j$$

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 !



Ground state energy (Ising limit):

FM: $N (J_2 - |J_1|)$

E-type: $- N J_2$

Transition from FM to E-type at $|J_1| = 2 J_2$

Same arguments hold for $J_1 > 0$ (AFM to E-type)

High-temperature (series expansion) solution (Redner & Stanley, 1977)

Three regions in the phase diagram (T/J_1 vs. J_2/J_1) :

(i) Disordered paramagnetic phase at high T

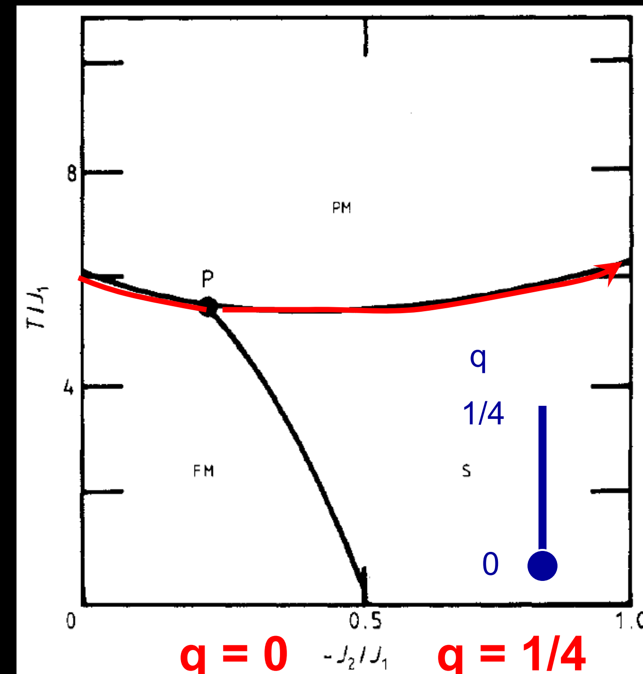
(ii) Ferromagnetic phase for $J_2/J_1 < 0.5$

(iii) “Modulated” phase with periodic modulation of the wave vector $\boldsymbol{q} = 2\pi(0,0,q)$

All three phases meet at a Lifshitz point, P

q = 0 at the left side of P, but increases continuously to ¼ for $J_2/J_1 \to$ ◎ .

At T=0 : q = ¼ for all $J_2/J_1 > 0.5$



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)

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

Mean-field approximation – neglect second order fluctuations

$$S_i S_j = S_i \langle S_j \rangle + \langle S_i \rangle S_j - \langle S_i \rangle \langle S_j \rangle + \cancel{\left(S_i - \langle S_i \rangle\right)\left(S_j - \langle S_j \rangle\right)}$$

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

$$F = \sum_{i,j} J_{ij} M_i M_j - T \sum_i \int_0^{M_i} \tanh^{-1} \sigma \, d\sigma$$

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 φ with the coordinate z

In the CM phase: φ = const., in the ICM phase: φ = 2πδz (→ q = ¼ + δ)

In the continuum limit $\varphi(z)-\varphi(z-1)=d\varphi/dz$ and expanding F to fourth order in M :

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

$$\delta=J_1/4J_2\,,\quad v=-TA^2/96J_2$$
$$A^2=3(4J_1+2J_2-T)/T)$$

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

The phase function φ(z) minimizing the free energy is the soliton lattice.

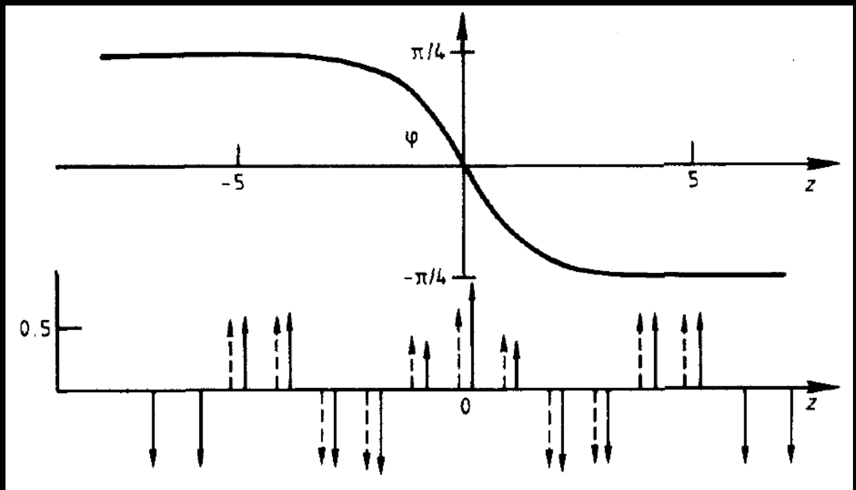
Near the CM phase boundary the free energy is:

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

How does the soliton solution look like ?

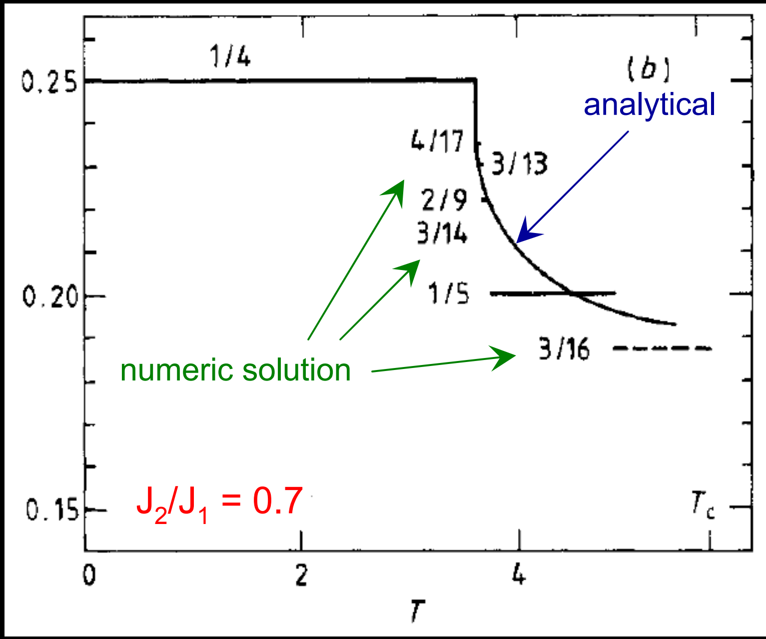
The domain wall has the structure

↓ ↓ ↑ ↑ ↓ ↓ ↑ ↑ ↑ ↓ ↓ ↑ ↑ ↓ ↓



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.

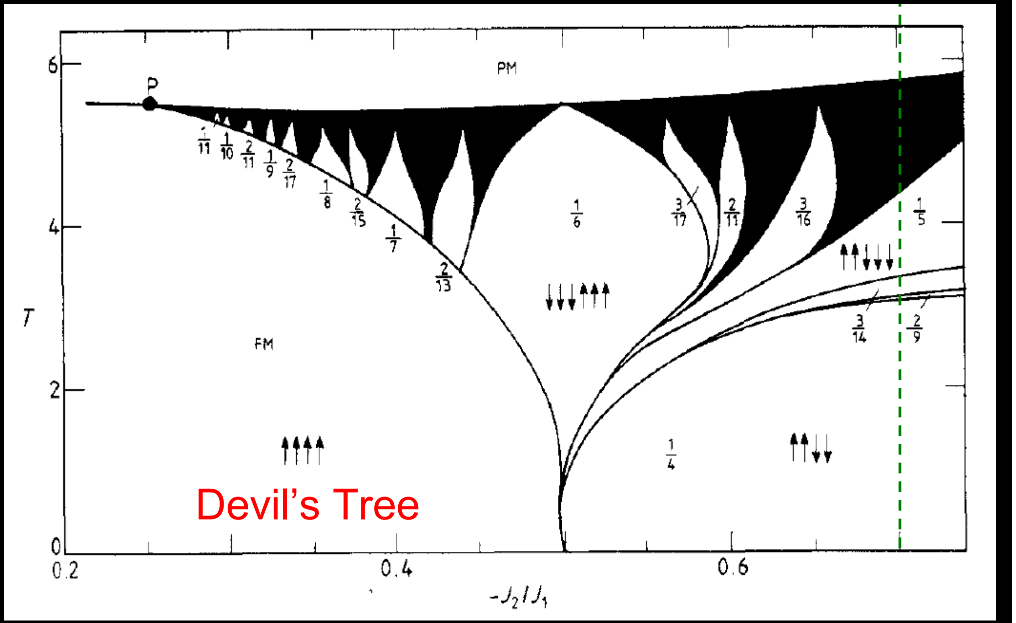


The global Mean-field phase diagram is constructed from numerical calculations:

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:

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

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

$J_1 < 0$ is the nearest neighbor ferromagnetic exchange interaction

$J_2 > 0$ is the next-nearest neighbor AFM exchange

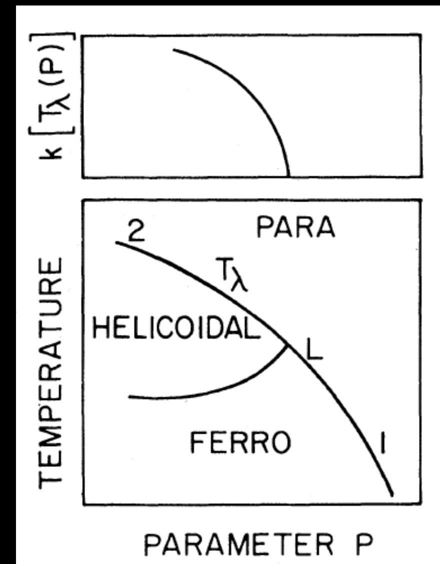
K is the uniaxial anisotropy, and H is the external magnetic field

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)



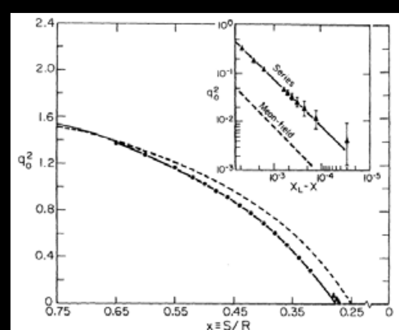
(i) The transition across "1 – 2" (T_λ) is a second order phase transition with conventional critical behavior
(ii) The critical behavior changes dramatically near the Lifshitz point "L", where the three phases meet
(iii) The modulation vector "k" is zero (FM) between "1" and "L" but it continuously changes from "L" towards "2"
(iv) The control parameter "P" can be pressure, composition, or the ratio of competing exchange coupling parameters

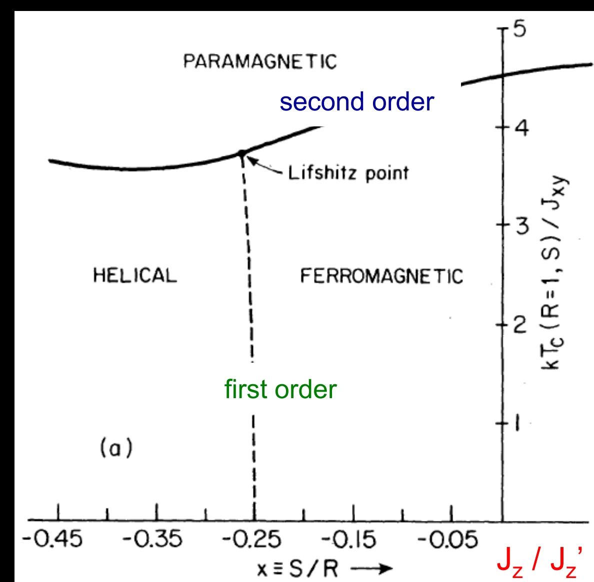
Redner & Stanley derived the corresponding phase diagram for the Heisenberg model with competing NN and NNN exchange :

$$\mathcal{H} = -J_{xy}\sum_{\langle ij\rangle}^{xy} \vec{S}_i\cdot\vec{S}_j - J_z\sum_{\langle ij\rangle}^{z} \vec{S}_i\cdot\vec{S}_j - J'_z\sum_{[ij]}^{2z} \vec{S}_i\cdot\vec{S}_j$$

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

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

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

Fourier transformation into reciprocal space:

$$J(\vec{q}) = \sum_n J(\vec{r}_n)e^{-i\vec{q}\vec{r}_n} \quad , \qquad \vec{S}_{\vec{q}} = N^{-1/2}\sum_n \vec{S}_n e^{-i\vec{q}\vec{r}_n}$$

$$E = -\sum_{\vec{q}} J(\vec{q})\vec{S}_{\vec{q}}\vec{S}_{-\vec{q}}$$

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

$$\vec{S}_n^2 = const. = S^2 \quad , \qquad \sum_n \vec{S}_n^2 = const. \quad , \qquad \sum_{\vec{q}} \vec{S}_{\vec{q}}\vec{S}_{-\vec{q}} = const.$$

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

$$E = -J(\vec{Q})(\vec{S}_{\vec{Q}}\vec{S}_{-\vec{Q}} + \vec{S}_{-\vec{Q}}\vec{S}_{\vec{Q}})$$

In real space:

$$\vec{S}_n = N^{-1/2}\left[\vec{S}_{\vec{Q}} e^{i\vec{Q}\vec{r}_n} + \vec{S}_{-\vec{Q}} e^{-i\vec{Q}\vec{r}_n}\right] \quad , \qquad \vec{S}_{-\vec{Q}} = \vec{S}^{*}_{\vec{Q}}$$

$$S_{nx} = A\cos\left(\vec{Q}\vec{r}_n + \alpha\right)$$

$$S_{ny} = B\cos\left(\vec{Q}\vec{r}_n + \beta\right)$$

$$S_{nz} = C\cos\left(\vec{Q}\vec{r}_n + \gamma\right)$$

The equations above describe an elliptic helical order of spins with wave vector Q, which is circular for the condition S_n^2 = 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 || 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 ($WMnO_4$)

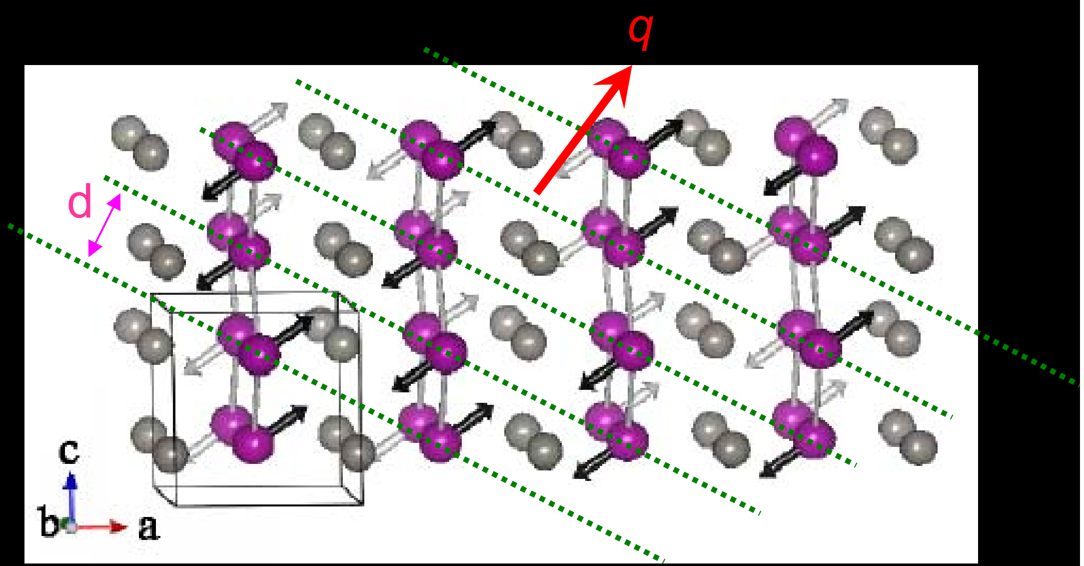
J_0 = sum of $J(r_{ij})$ over all sites in one layer containing site j

J_1 = sum over all $J(r_{ij})$ of site i and all sites of the neighboring layer

J_2 similar for second neighbor layer

...

d distance between planes



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

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 $0 \le dQ < 2\pi$:

(i) $Q = 0$ ferromagnetic spin order

(ii) $Q = \pi/d$ antiferromagnetic order

(iii) $\cos(dQ) = -J_1/4J_2$ Helical arrangement with ICM, for $|J_1| < |4 J_2|$

Ground state energy:

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

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

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

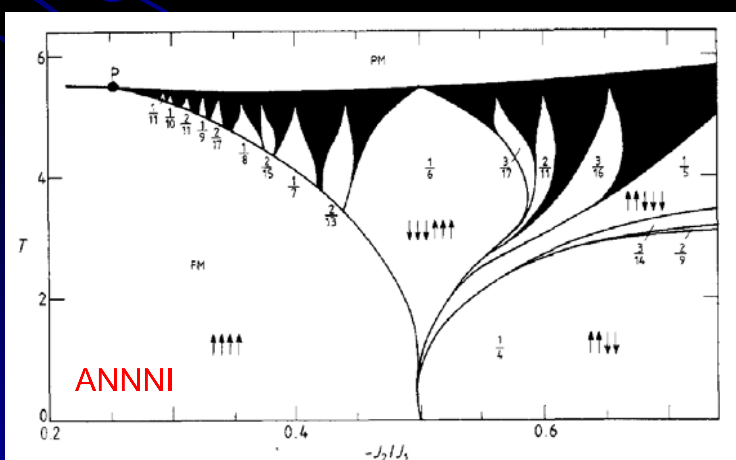
If $J_2 > 0$ (FM NNN coupling), the ground state is FM (for $J_1 > 0$) or AFM (for $J_1 < 0$)
If $J_2 < 0$ (AFM coupling), the helical state has lowest energy for $|J_1| < |4\,J_2|$.

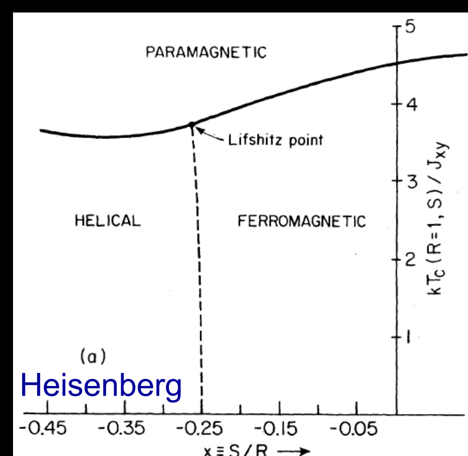
Note the difference to the ANNNI model:

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)

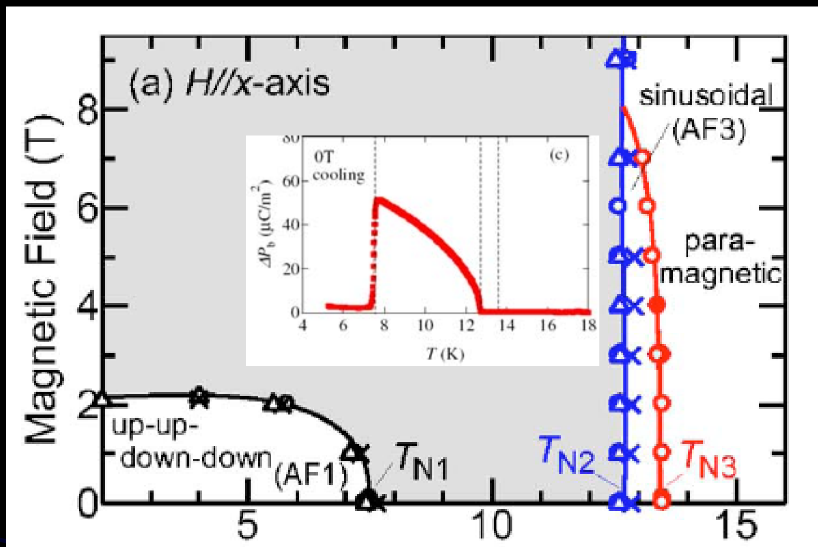


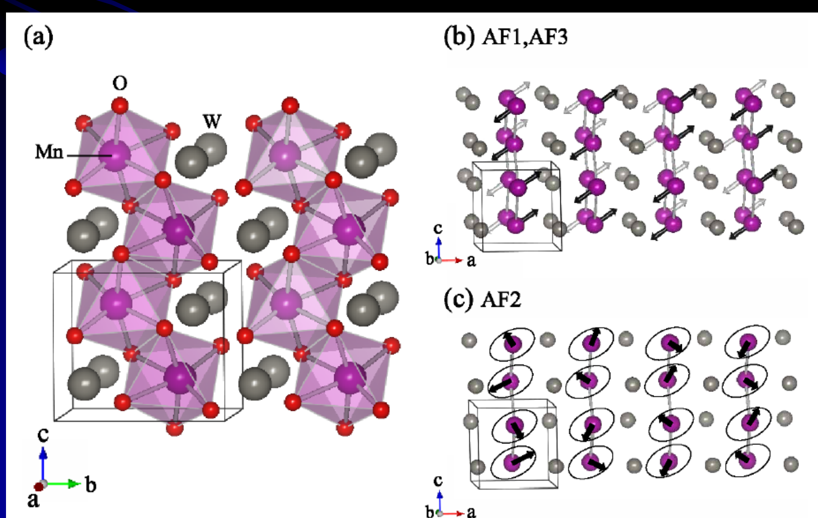


5. Can these simple models describe real multiferroics ?

Example: $MnWO_4$ and $Mn_{1-x}Fe_xWO_4$

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





$MnWO_4$

Phase sequence:

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

In ICM phases: Q ~ 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 SIN (collinear) → Helical → ↑↑↓↓ cannot be obtained from either the ANNNI or the isotropic Heisenberg model

The ↑↑↓↓ 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 :

$$H = J_1 \sum_{<i,j>} \vec{S}_i \vec{S}_j + J_2 \sum_{[i,j]} \vec{S}_i \vec{S}_j - K \sum_i (S_i^z)^2 - \vec{H} \sum_i \vec{S}_i$$

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

$K > 0$ favors the alignment of spins along one axis (z)

$K < 0$ would favor the in-plane anisotropy (x-y plane)

For $K >> J_1$, J_2 the spins are forced into one direction = ANNNI model

$K = 0$ results in the isotropic Heisenberg model

The effects of substitutions — Why $Mn_{1-x}Fe_xWO_4$?

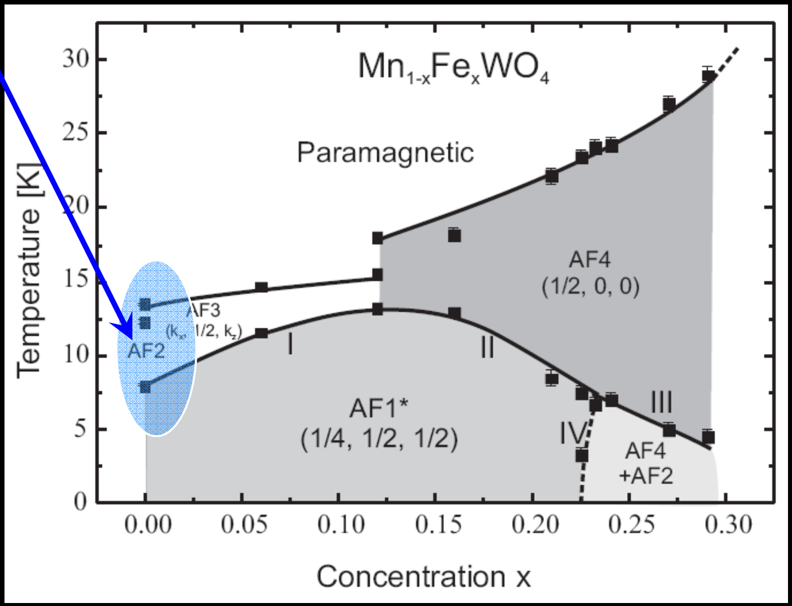
(i) The end members, $MnWO_4$ and $FeWO_4$, are isostructural and a solid solution does exist

(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

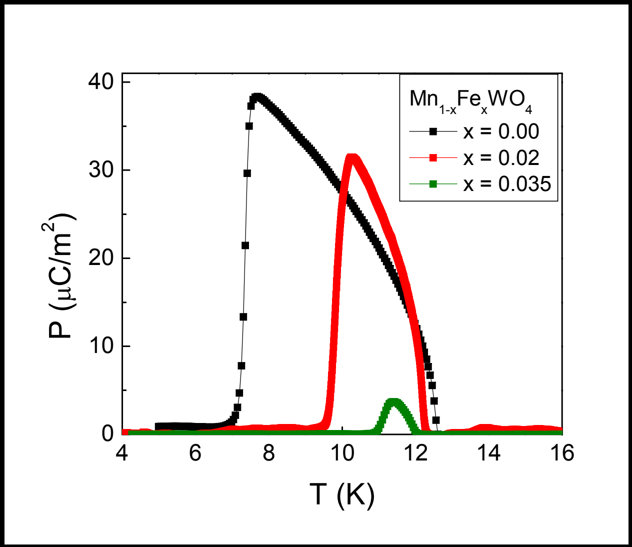
Garcia_Matres et al., 2003

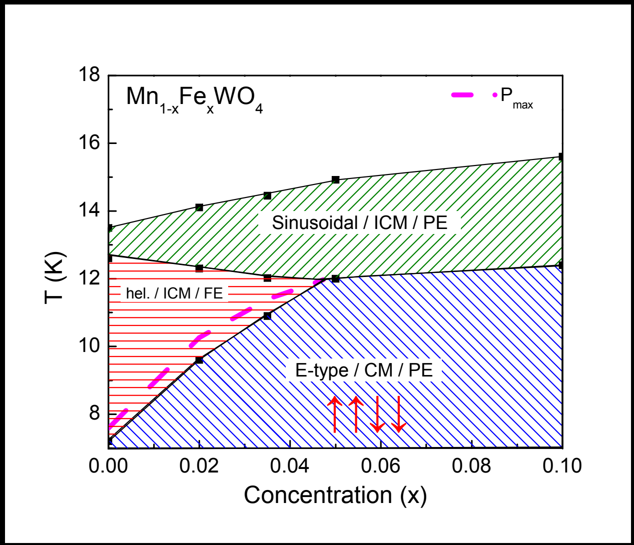


Synthesis of large single crystals of $Mn_{1-x}Fe_xWO_4$

A small concentration of Fe (4 %) destroys the helical (FE) phase completely at H = 0 :

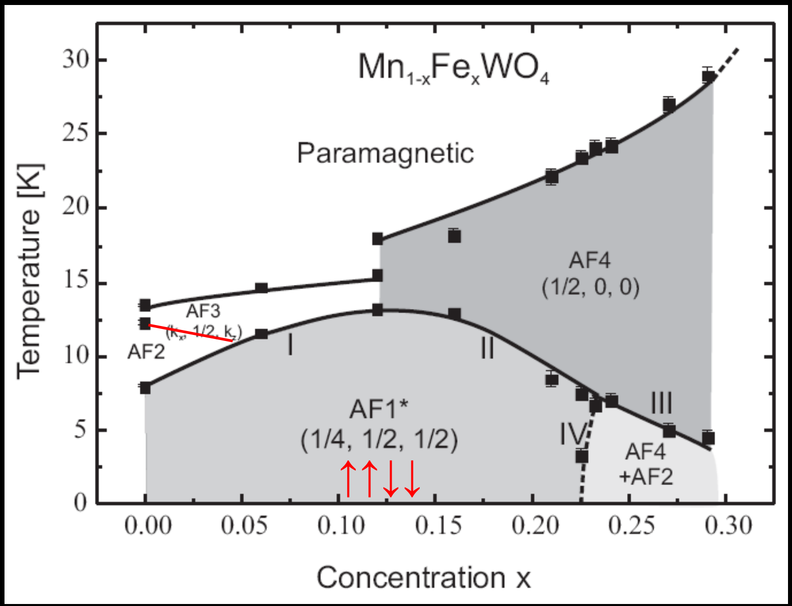
(Chaudhury et al., 2008)





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

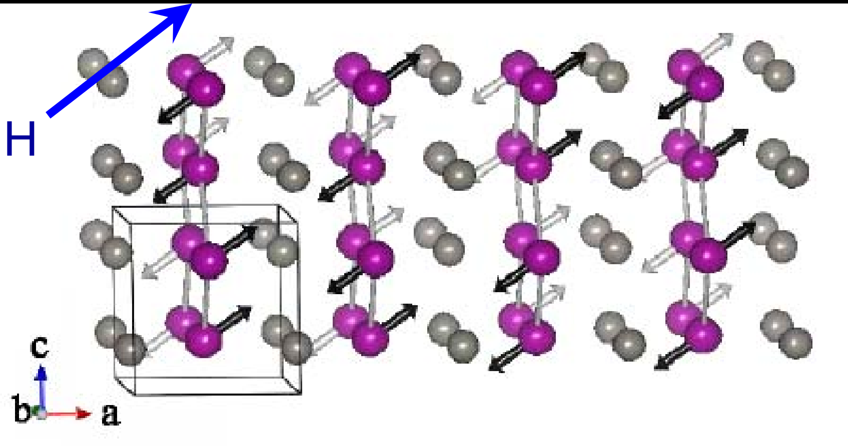
The suppression by this little Fe content indicates how fragile and susceptible this phase is as may be expected for frustrated spin systems

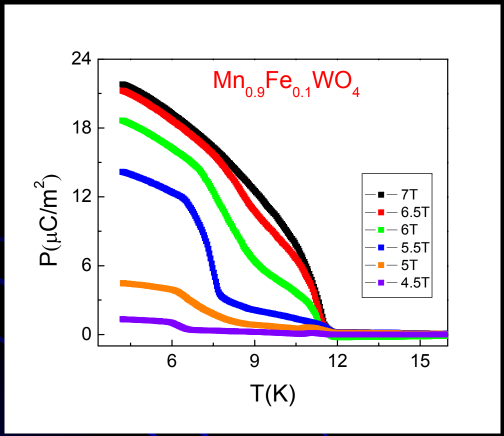


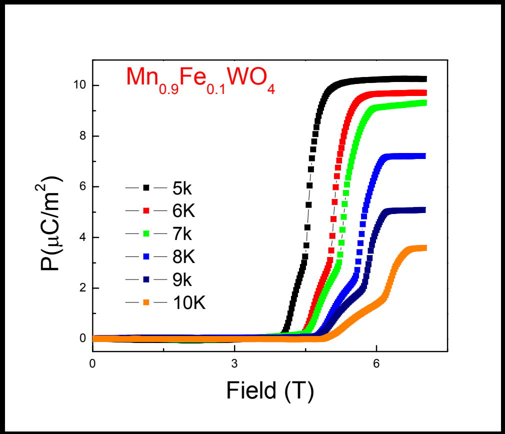
The recovery of the helical (ferroelectric) phase in magnetic fields : (Chaudhury et al., 2008)

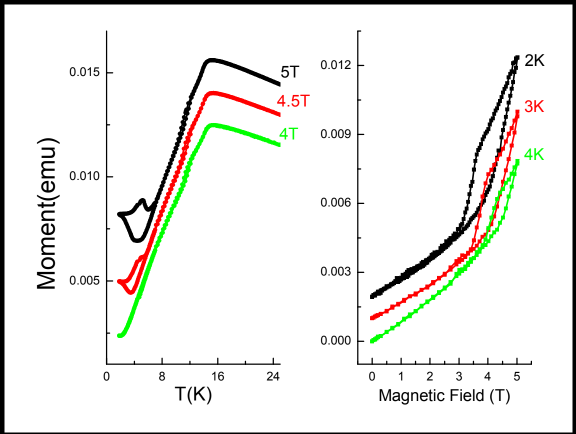
In magnetic fields along the easy axis the FE phase of $Mn_{0.9}Fe_{0.1}WO_4$ is completely restored.

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





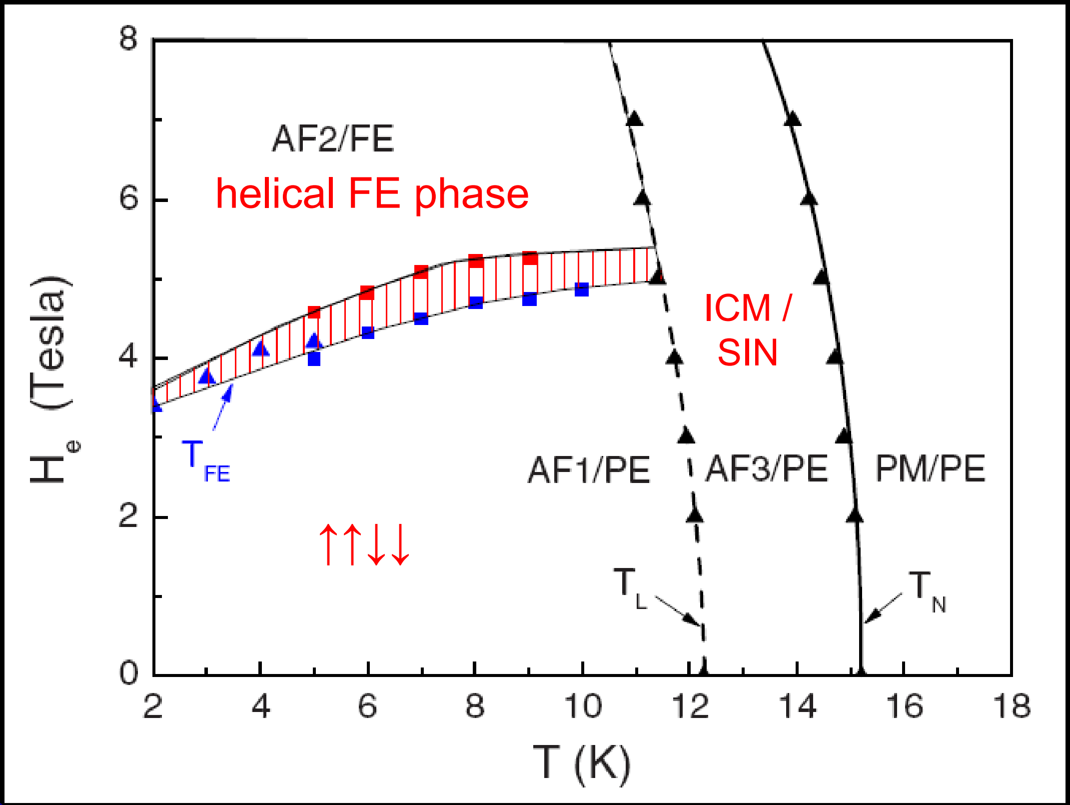




From the dielectric and magnetic measurements we conclude that the external field restores the helical spin phase that allows for the ferroelectric displacements via the spin-lattice coupling.

This needs to be proven by the detailed investigation of the magnetic structure, e.g. by neutron scattering experiments.

Magnetic and ferroelectric phase diagram of $Mn_{0.9}Fe_{0.1}WO_4$ (Chaudhury et al., PRB 2008)



Magnetic field induced ferroelectric phase shoud 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

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

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

Mean field approximation:

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

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

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

$$\vec{h}_n = -\vec{H} + J_1 \left(\left\langle \vec{S}_{n-1} \right\rangle + \left\langle \vec{S}_{n+1} \right\rangle \right) + J_2 \left(\left\langle \vec{S}_{n-2} \right\rangle + \left\langle \vec{S}_{n+2} \right\rangle \right)$$

Solve quantum mechanical problem

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

For spin 1, eigenfunctions |-1>, |0>, |1>
(i.e. m = -1, 0, +1)

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

$$H_{ij}(n) = \begin{pmatrix} -K + h_n^z & \frac{1}{\sqrt{2}}\left(h_n^x - ih_n^y\right) & 0 \\ \frac{1}{\sqrt{2}}\left(h_n^x + ih_n^y\right) & 0 & \frac{1}{\sqrt{2}}\left(h_n^x + ih_n^y\right) \\ 0 & \frac{1}{\sqrt{2}}\left(h_n^x - ih_n^y\right) & -K - h_n^z \end{pmatrix}$$

Eigenvalues $\lambda_i(n)$:

$$\lambda_i(n)\left[\left(\lambda_i(n) + K\right)^2 - \left(h_n^z\right)^2\right] - \left(\lambda_i(n) + K\right)\left(\left(h_n^x\right)^2 + \left(h_n^y\right)^2\right) = 0$$

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:

$$Z_{MF} = Tr\, e^{-\beta H_{MF}} = e^{-\beta E_{MF}} \prod_n \left\{ Tr_n\, e^{-\beta H(n)} \right\}$$

$$F_{MF} = -\frac{1}{\beta} \ln Z_{MF} = E_{MF} - \frac{1}{\beta} \sum_n \ln\left\{ Tr_n\, e^{-\beta H(n)} \right\} = E_{MF} - \frac{1}{\beta} \sum_n \ln\left\{ e^{-\beta\lambda_1(n)} + e^{-\beta\lambda_2(n)} + e^{-\beta\lambda_3(n)} \right\}$$

Mean field equations (self consistency equations for $\langle S_n \rangle$:

$$\left\langle S_n^\alpha \right\rangle = Tr\left(S_n^\alpha e^{-\beta H_{MF}}\right) \Big/ Tr\left(e^{-\beta H_{MF}}\right), \quad \alpha = x, y, z$$

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

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

Remember !

since h_n depend on $\langle S_{n\pm1}\rangle$ and $\langle S_{n\pm2}\rangle$ the self consistency equations for $\langle S_n\rangle$ cannot be solved easily for arbitrary spin orders.

Some special cases:

Ferromagnetic order, FM

$$\langle S_n^z\rangle = S, \quad \langle S_n^y\rangle = 0, \quad \langle S_n^x\rangle = 0, \quad \textit{for all } n$$

$$h_n^z = h^z = -H^z + 2S(J_1 + J_2)$$

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

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

$$F/N = -(J_1+J_2)S^2 - \frac{1}{\beta}\ln\left\{1 + 2e^{\beta K}\cosh\beta\left[2S(J_1+J_2) - H^z\right]\right\}$$

Antiferromagnetic order (AFM, two sublattices A, B):

$$\langle S_n^x \rangle = \langle S_n^y \rangle = 0, \quad \langle S_n^z \rangle = S_A \quad (n\ even), \quad \langle S_n^z \rangle = S_B \quad (n\ odd)$$

$$h_n^z = h_A = -H^z + 2J_1 S_B + 2J_2 S_A \quad (n\ even)$$

$$h_n^z = h_B = -H^z + 2J_1 S_A + 2J_2 S_B \quad (n\ odd)$$

$$S_A = -\frac{2\sinh\beta\left(2J_1S_B + 2J_2S_A - H^z\right)}{e^{-\beta K} + 2\cosh\beta\left(2J_1S_B + 2J_2S_A - H^z\right)}$$

$$S_B = -\frac{2\sinh\beta\left(2J_1S_A + 2J_2S_B - H^z\right)}{e^{-\beta K} + 2\cosh\beta\left(2J_1S_A + 2J_2S_B - H^z\right)}$$

$$F/N = -J_1S_AS_B - \frac{1}{2}J_2(S_A^2 + S_B^2) + \frac{1}{2}(f_A + f_B)$$

$$f_{A,B} = -\frac{1}{\beta}\ln\left\{1 + 2e^{\beta K}\cosh\beta\left(2J_1S_{B,A} + 2J_2S_{A,B} - H^z\right)\right\}$$

Sinusoidal or arbitrary collinear order, spins || z :

$$\langle S_n^x \rangle = \langle S_n^y \rangle = 0$$

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

$$h_n^z = -H^z + J_1\left(\langle S_{n-1}^z \rangle + \langle S_{n+1}^z \rangle\right) + J_2\left(\langle S_{n-2}^z \rangle + \langle S_{n+2}^z \rangle\right)$$

$$\langle S_n^z \rangle = -\frac{2\sinh \beta h_n^z}{e^{-\beta K} + 2\cosh \beta h_n^z}$$

$$F/N = \frac{1}{N}\sum_n \left\{ -J_1 \langle S_n^z \rangle \langle S_{n+1}^z \rangle - J_2 \langle S_n^z \rangle \langle S_{n+2}^z \rangle - \frac{1}{\beta} \ln\left[1 + 2e^{\beta K} \cosh \beta h_n^z\right] \right\}$$

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

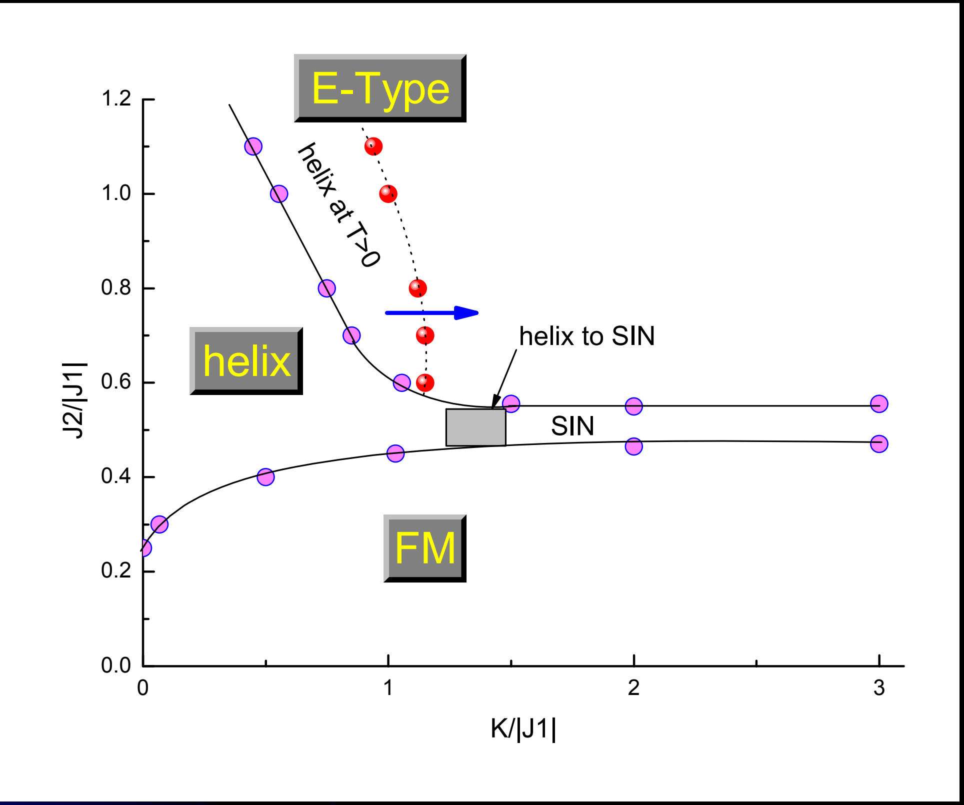
Can be done numerically !

Problems with the numerical solution:

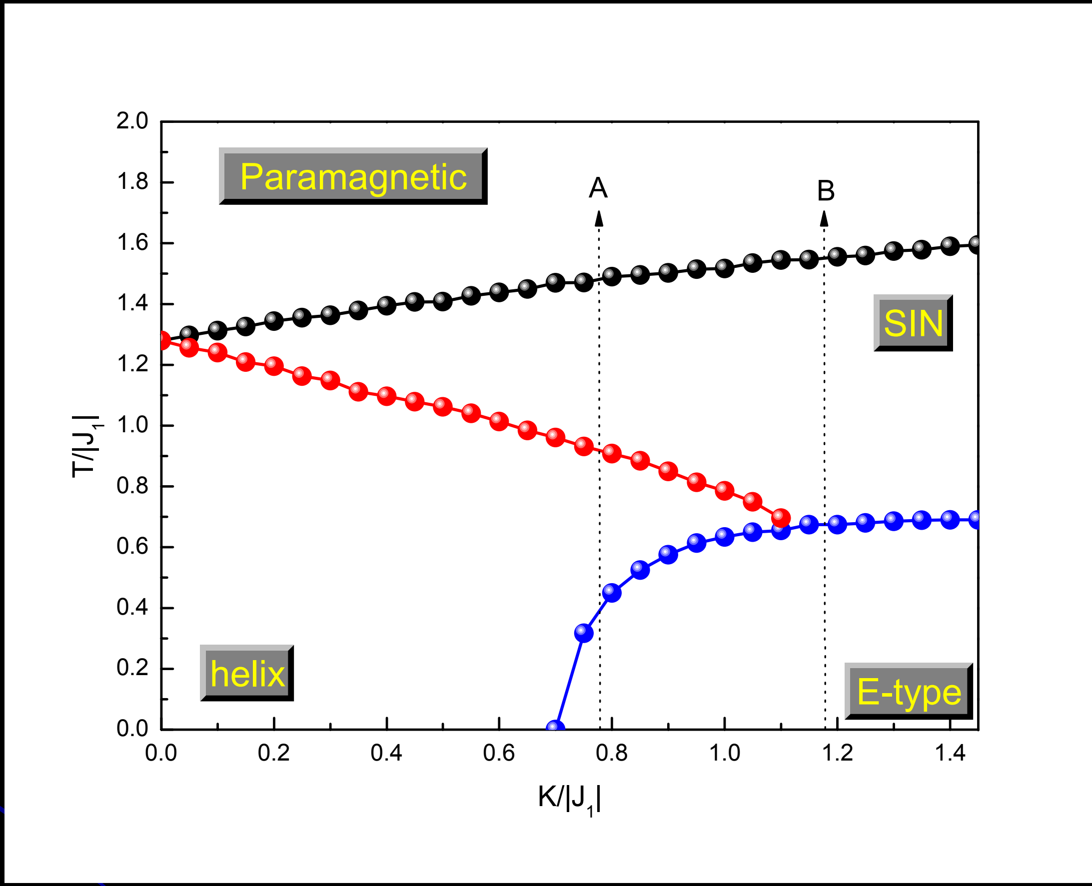
(i) Iterative solution for N (up to 100) coupled equations, one for each $\langle S_n \rangle$, Convergence sometimes slow, use > 500 iterative steps

(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 ($J_1 < 0$, $J_2 > 0$, $K > 0$) :



K – T phase diagram (for $J_2 = 0.8$) :



For “A” the phase sequence is : E-type => helix => SIN => PM ($MnWO_4$)

For “B” it is : E-type => SIN => PM , no helical phase ! ($Mn_{0.9}Fe_{0.1}WO_4$)

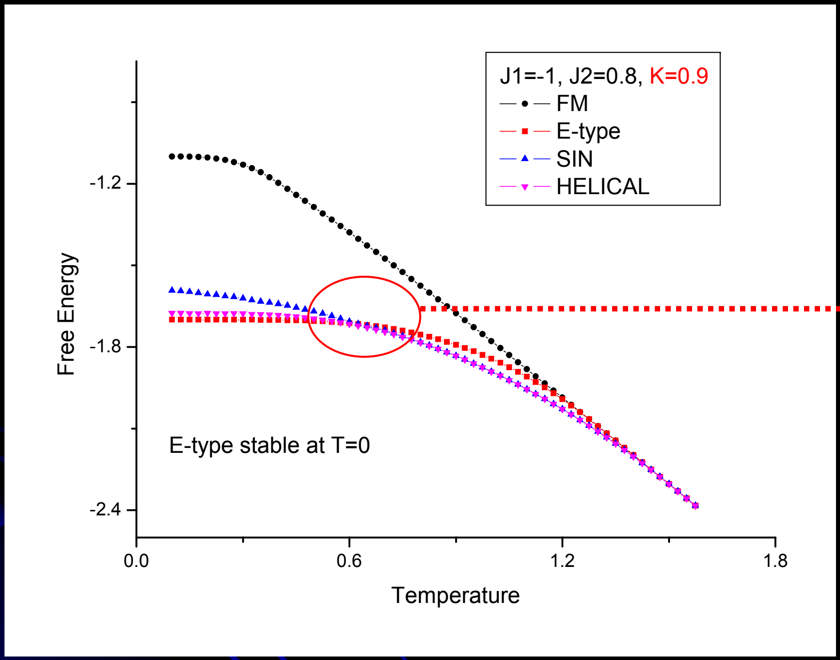
Since only “helix” can induce ferroelectricity, there is no FE in the latter compound.

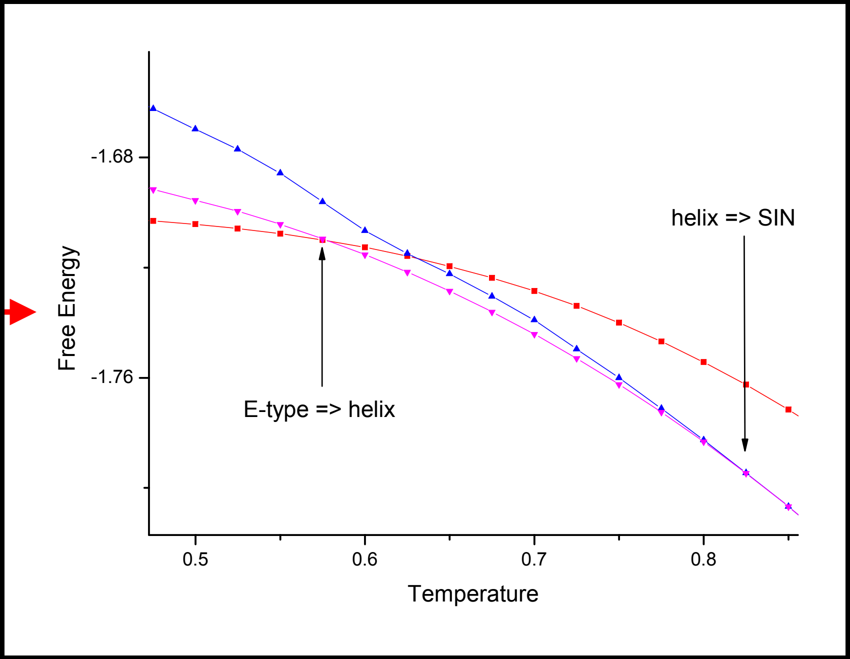
Magnetic field may stabilize the helical magnetic structure ???

In a frustrated system many states are very close in energy, this explains their sensitivity to external fields or perturbations.

Example:

$J_1 = -1$, $J_2 = 0.8$, $K = 0.9$ (➔ path "A" in the phase diagram)



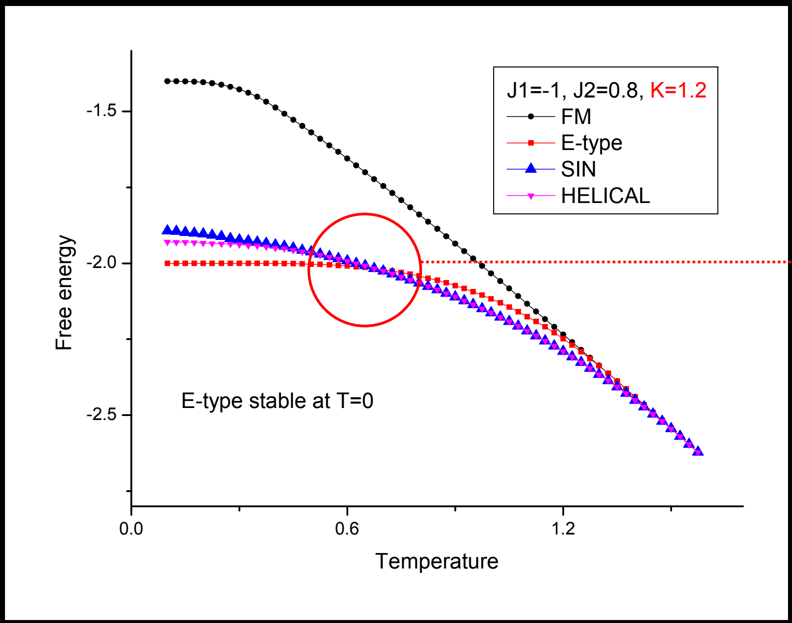


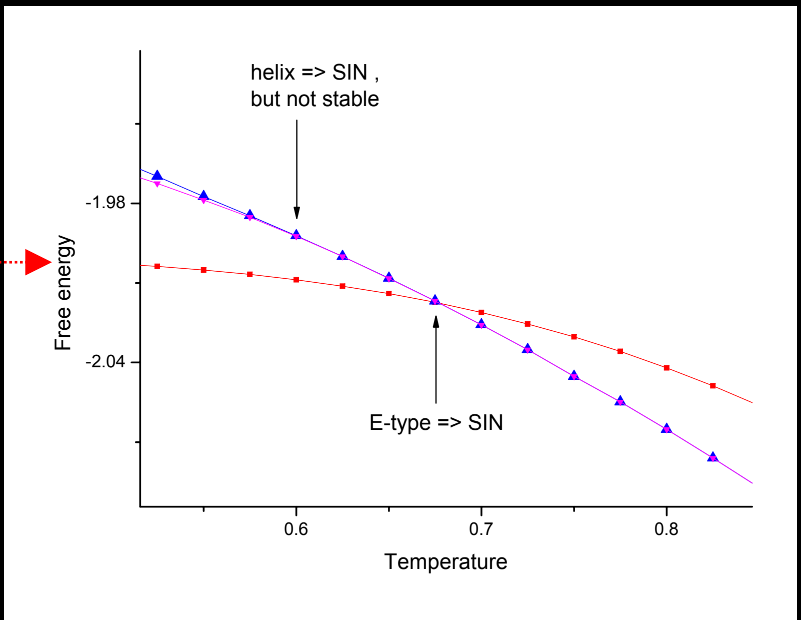
The transition (↑↑↓↓) → helical is a first order phase transition.

The next transition helical → sinusoidal is of second order ($\langle S_x \rangle$ continuously approaches zero).

The transition into the paramagnetic phase is second order ($\langle S_z \rangle$ 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 ?

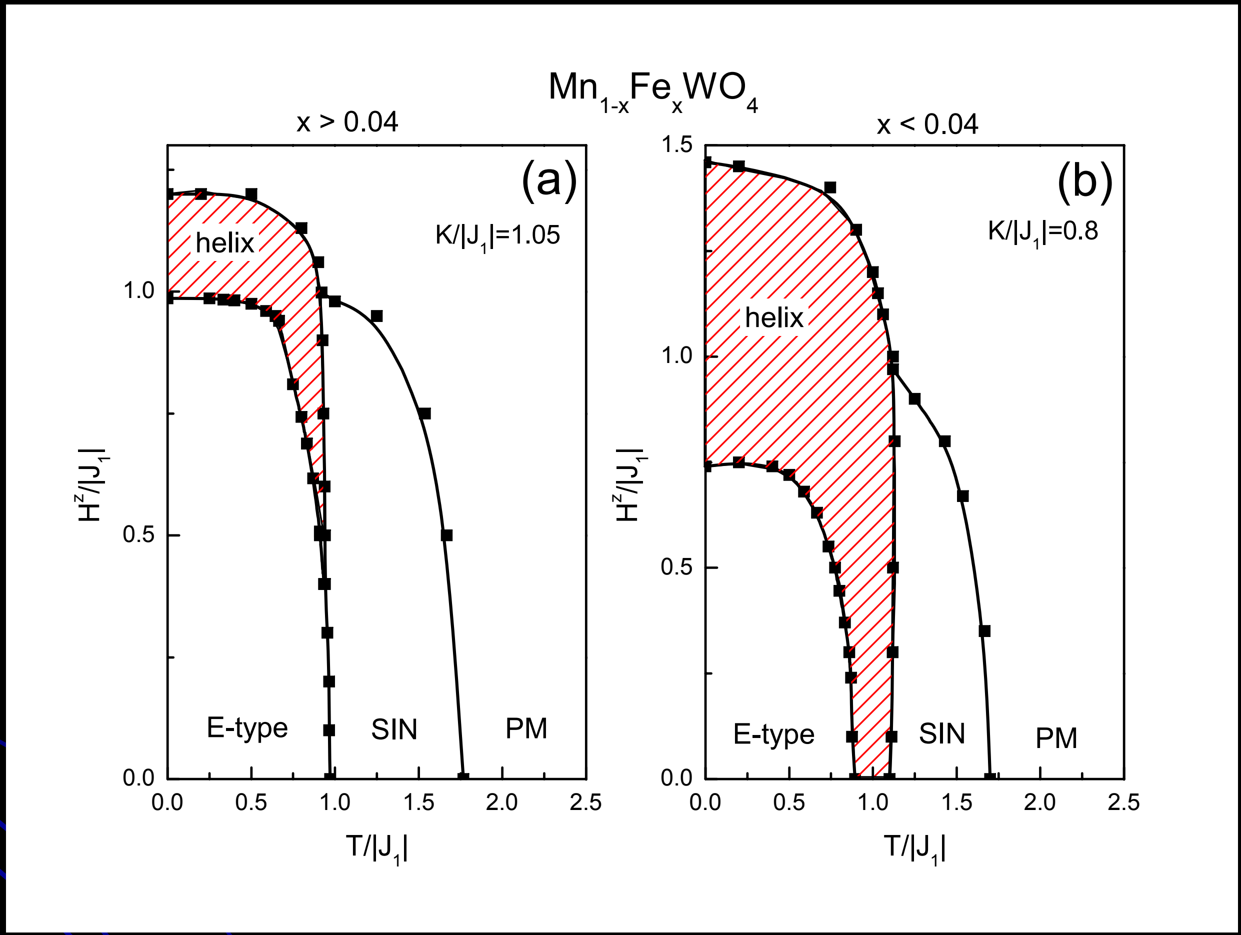
YES !

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

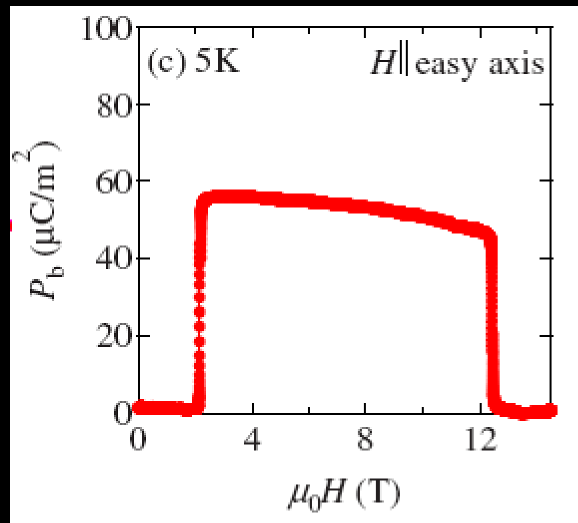


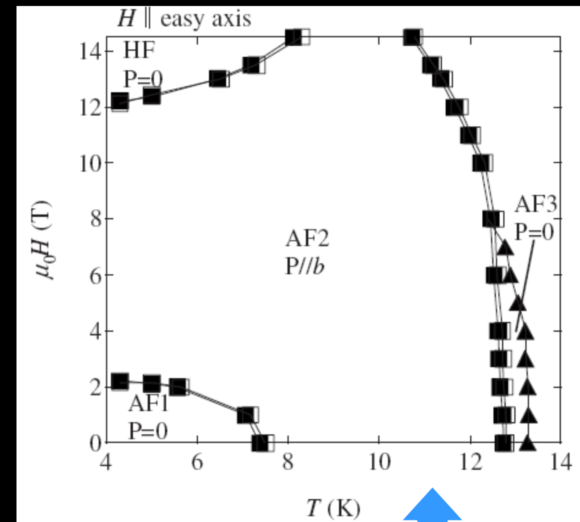
Note that The helical (ferroelectric) phase becomes unstable at high field due to the parallel alignment of the spins enforced by the magnetic field.

The high-field transition into a paraelectric phase was indeed observed in $MnWO_4$.

Taniguchi et al., PRB 2008

The high-field phase diagram of $MnWO_4$ is surprisingly similar to the numerical results.



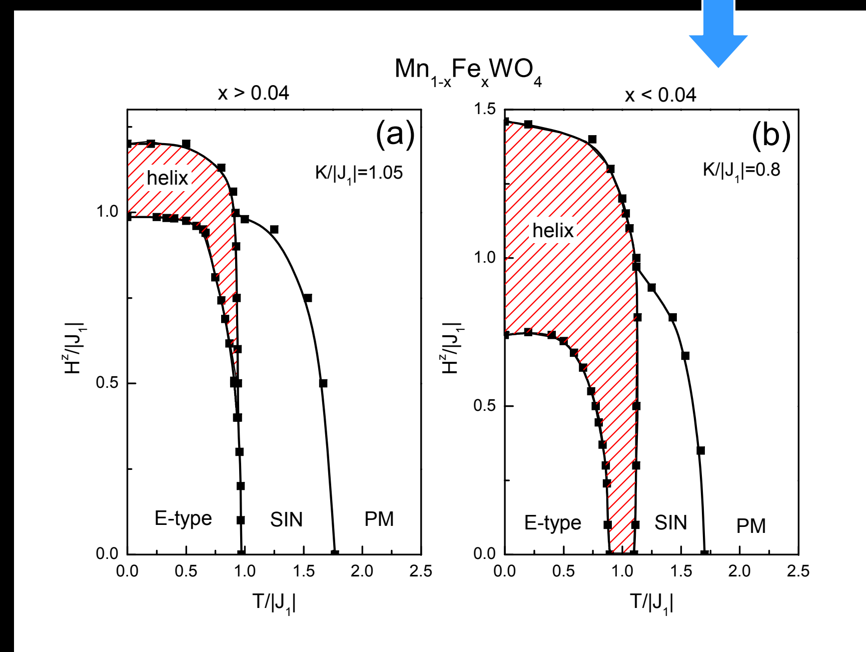


A number of features seem to be reproduced at least qualitatively:

(i) Field-induced transition from the (↑↑↓↓) phase to the helical (FE) phase at low T

(ii) Paraelectric high-field phase above 12 T

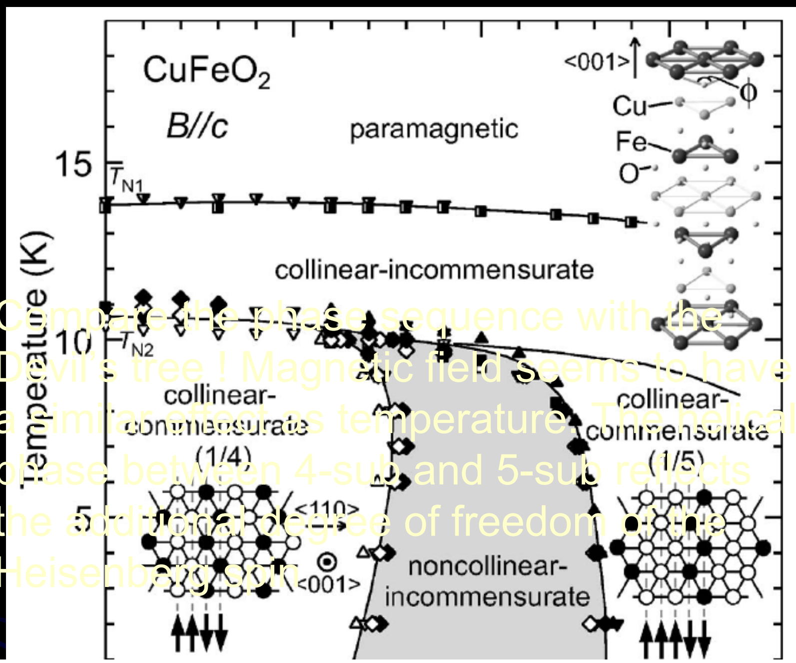
(iii) Suppression of the SIN phase at moderate field values.



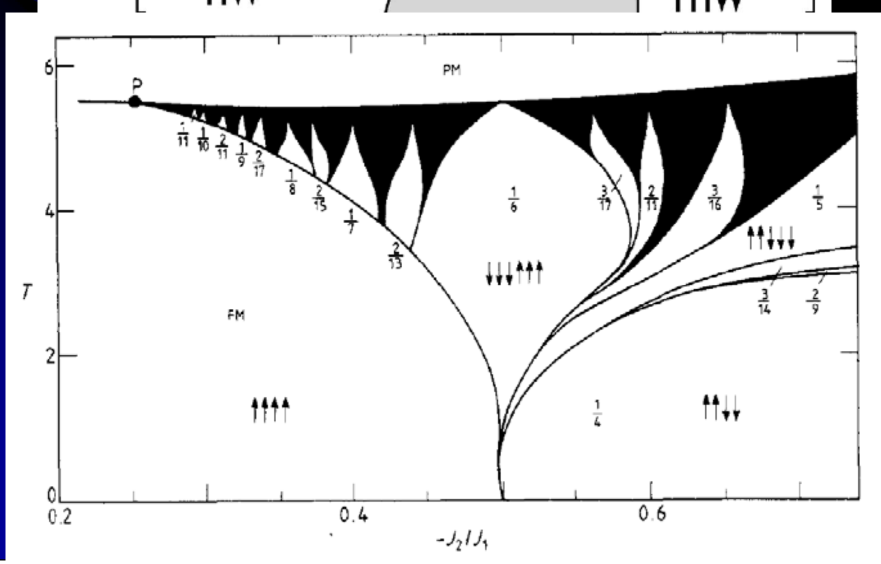
The chosen model provides a reasonable description of the complex physics of magnetic states in substituted $Mn_{1-x}Fe_xWO_4$.

Other examples of field-induced ferroelectric phases:

Delafossite $CuFeO_2$ (Kimura et al., 2006)



Compare the phase sequence with the Devil's tree ! Magnetic field seems to have a similar effect as temperature. The helical phase between 4-sub and 5-sub reflects the additional degree of freedom of the Heisenberg spin

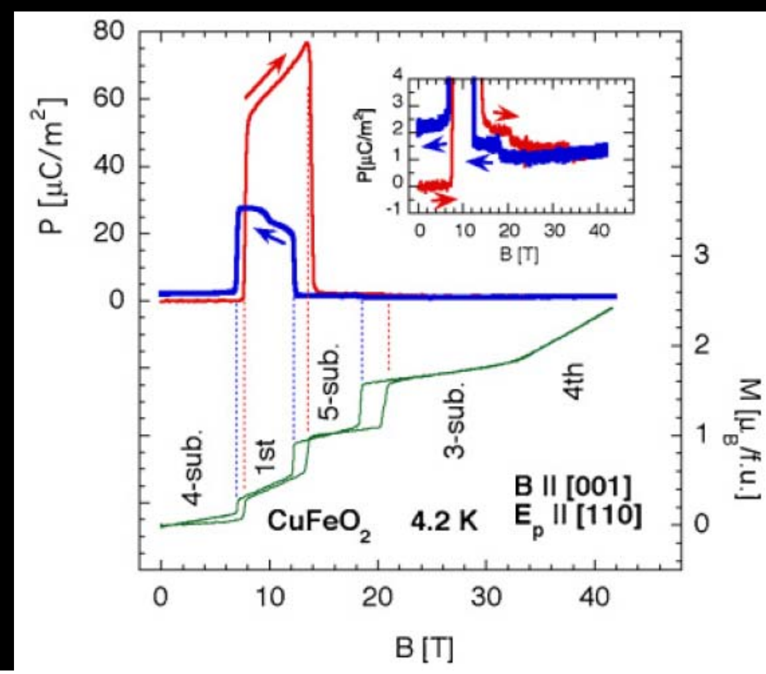


The ground state at H=0 is the ↑↑↓↓ modulated CM state (Q = 0.25)

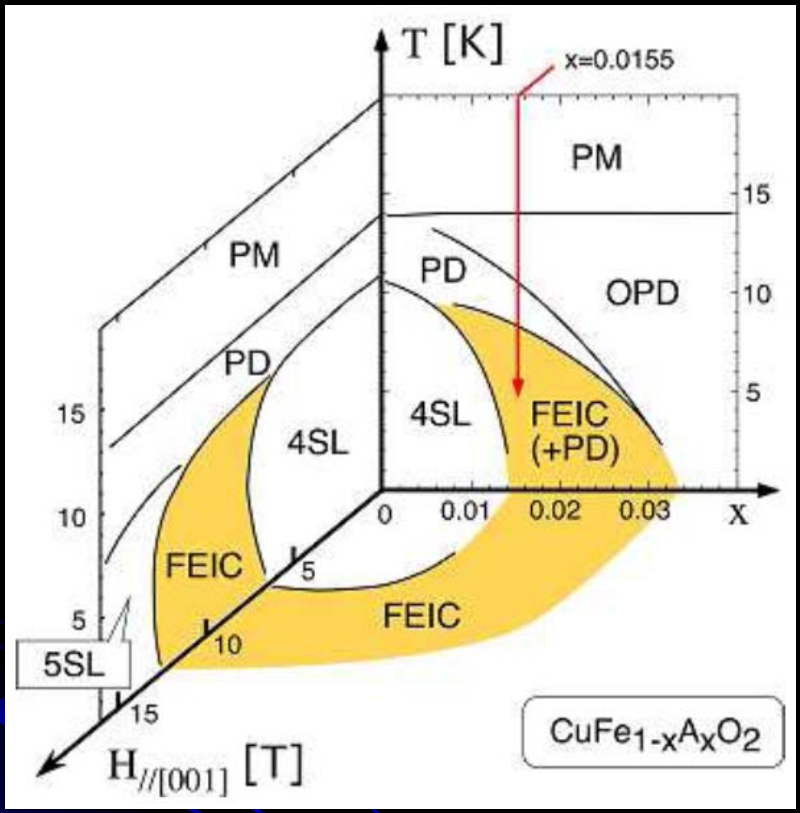
Magnetic fields induce a non-collinear ICM phase and ferroelectricity

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)



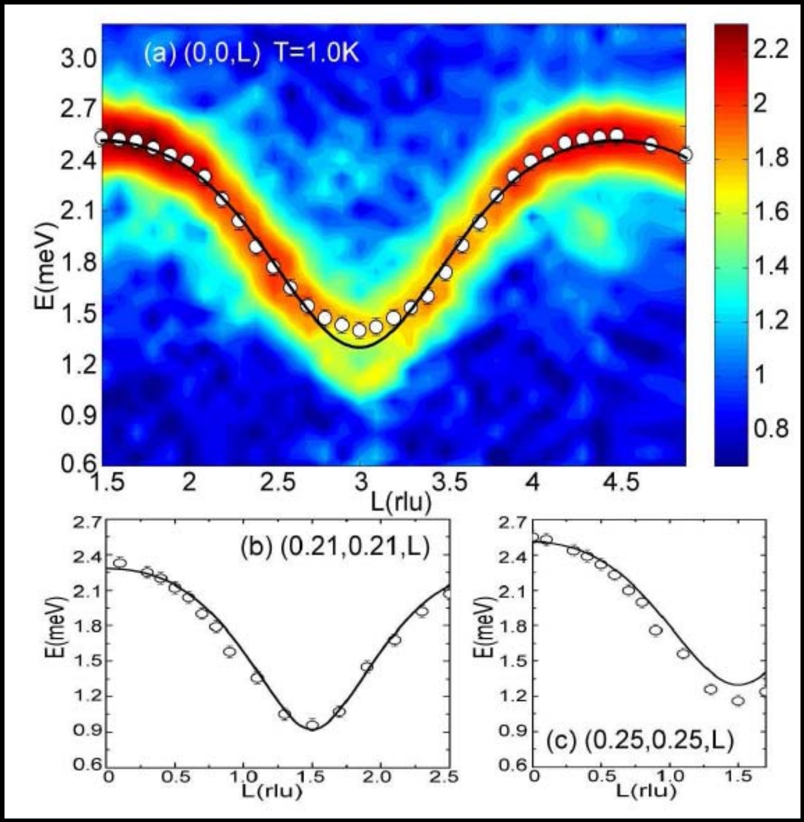
The effect of substitution (Al for Fe) is opposite to $MnWO_4$:   It induces a helical (FE) phase
(Seki et al., 2007; Nakajima et al., 2008)



The phases denoted PD and OPD are collinear sinusoidal magnetic structures, they are all paraelectric.

The spin wave excitations in $CuFeO_2$ have been measured and fitted to the Heisenberg model with uniaxial anisotropy (Ye et al., 2007)

$$H = -\sum_{i,j} J^{\parallel}_{i,j}\vec{S}_i\cdot\vec{S}_j - \sum_{i,j} J^{\perp}_{i,j}\vec{S}_i\cdot\vec{S}_j - D\sum_i S^2_{iz}$$



Nickel Vanadate $Ni_3V_2O_8$ (Lawes et al., 2005)

LTI phase is ferroelectric → for H || a
the FE phase is induced by H at low T