Critical properties of pyrochlore-$\mathrm{FeF_3}$

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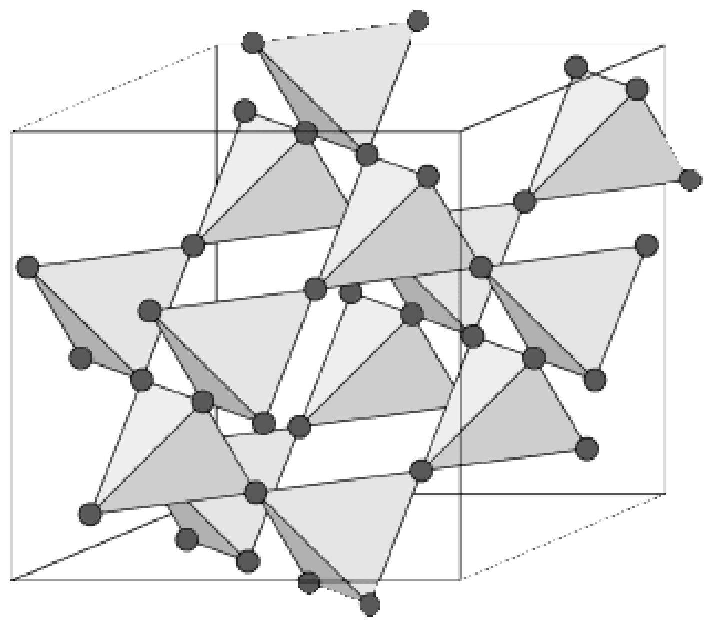
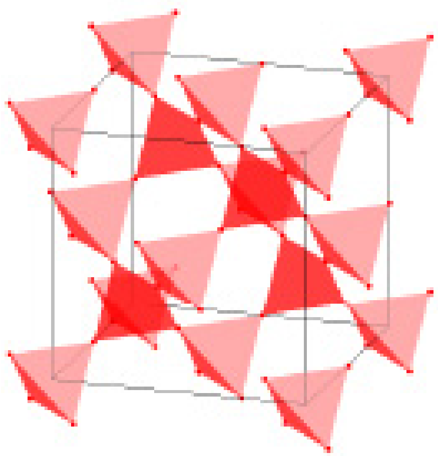
What is pyrochlore structure?

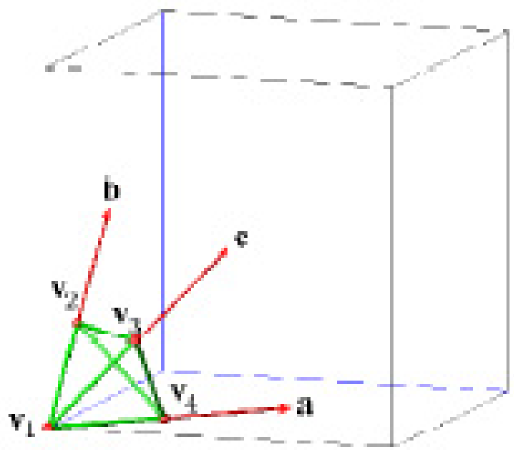
- An infinite three dimensional lattice of corner-sharing tetrahedra



Structure

- faced center cubic Bravais lattice + 4 basis
- Magnetic Fe^{+3} ions are located in the corners of the tetrahedra

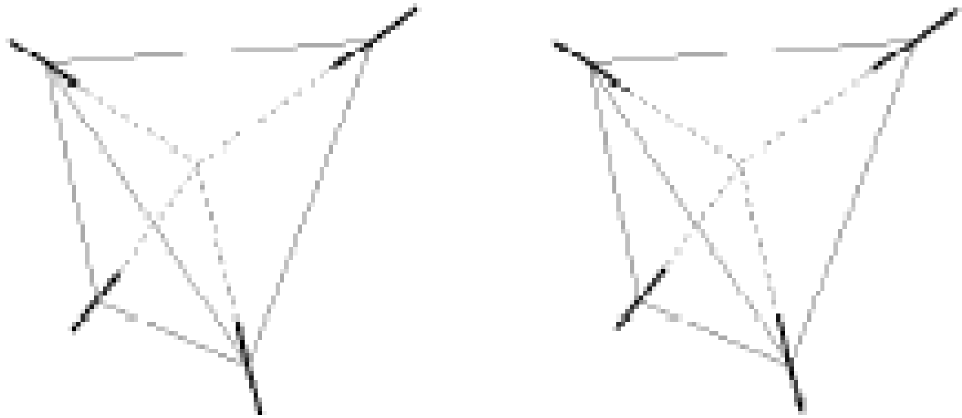




Magnetic properties of FeF3

- The Magnetic Fe^{+3} ions are in d^5 electronic configuration with a totally symmetric ground state with no net angular momentum.
- Anti-ferromagnetic exchange interactions between nearest neighbors
- System is highly frustrated, hence any small amount of anisotropy will be important in determining the ground state of the system
- The observed low-temperature phase consists of four sublattices oriented along four [111] directions (All-in All-out state)

All-in All-out state



Experiment

J. N. Reimers, J. E. Greedan, C. V. Stager and M. Bjorgvinssen (McMaster university), Phys . Rev B, **43**, 5692(1991)

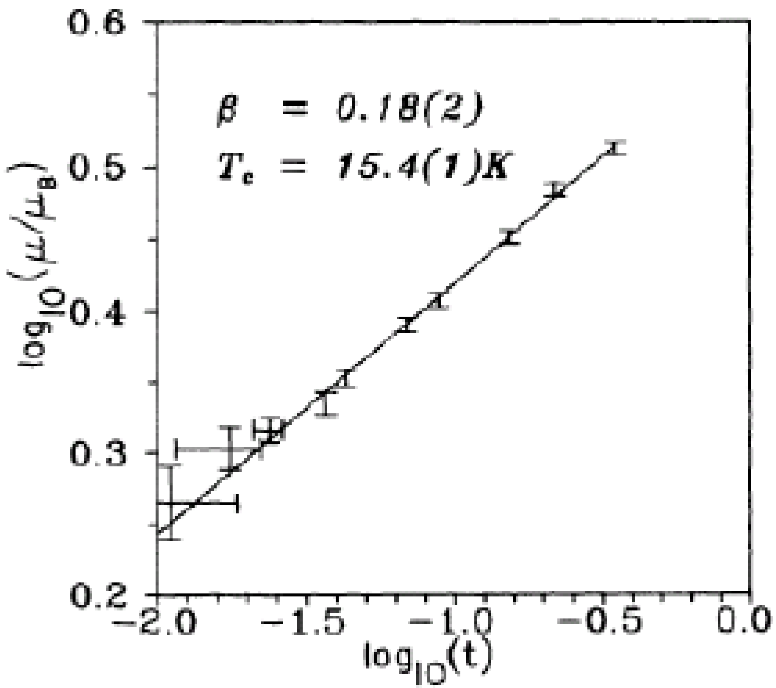


FIG. 2. log-log plot of the measured magnetic moment in pyr-FeF_3 vs reduced temperature, $t=(T_c-T)/T_c$, giving $\beta=0.18(2)$ and $T_c=15.4(1)$ K.

Phase transitions

Generally, there are two types of phase transitions:

- Discontinues transitions(first order transitions): The first derivatives of the free energy are discontinues at the transition points; the order parameter changes discontinuesly.
- Continuous transitions: Higher order derivatives of the free energy might be discontinues or singular; the order parameter changes continuesly at the transition point (Critical points).

Aspects of the Critical point

Near critical points, some thermodynamic quantities such as order parameter, specific heat, susceptibility, compressibility, correlation length and also the equation of state obey a power law relation (scaling). *i.e*

$$
\begin{aligned}
c \approx A^{\pm}|t|^{-\alpha} \quad & t \rightarrow 0\pm \\
\kappa \approx C^{\pm}|t|^{-\gamma} \quad & t \rightarrow 0\pm \\
M \approx B(-t)^{\beta} \quad & t \rightarrow 0-, h = 0 \\
M \approx D h^{1/\delta} \quad & t = 0 \\
\xi \approx |t|^{-\nu} \quad & t \rightarrow 0\pm
\end{aligned}
$$

where $t = \frac{T-T_c}{T_c}$.

Magnetic model

It is possible to model the magnetic properties of FeF3 by the Heisenberg spins with nearest neighbors anti-ferromagnetic interaction on a Pyrochlore lattice under easy-axes anisotropy:

$$H = -\frac{J}{2}\sum_{i,j}\sum_{a,b}\mathbf{S}_i^a\cdot\mathbf{S}_j^b - D\sum_i\sum_a(\mathbf{S}_i^a\cdot\hat{z}^a)^2,$$

$$\begin{aligned}\hat{z}^1 &= \frac{1}{\sqrt{3}}(1,1,1), \hat{z}^2 = \frac{1}{\sqrt{3}}(-1,1,1)\\ \hat{z}^3 &= \frac{1}{\sqrt{3}}(1,-1,1), \hat{z}^4 = \frac{1}{\sqrt{3}}(1,1,-1),\end{aligned}$$

Frustration

Consider a tetrahedron and isotropic case ($D = 0$), the Hamiltonian is:

$$
\begin{aligned}
H &= -\frac{J}{2}\sum_{i,j}\mathbf{S}_i \cdot \mathbf{S}_j \\
&= -\frac{J}{4}[(\sum_{i=1}^{4}\mathbf{S}_i)^2 - \sum_{i=1}^{4}\mathbf{S}_i^2] = -\frac{J}{4}[(\sum_{i=1}^{4}\mathbf{S}_i)^2] + J
\end{aligned}
$$

for the ground state of an anti-ferromagnetic system ($J < 0$), the sum of spins in a tetrahedron should vanish, *i.e* $\sum_{i=1}^{4}\mathbf{S}_i = 0$

Number of equations=3

number of components=8

Total degrees of freedom=5

Internal degrees of freedom=5-3=2

Mean-field approximation

To apply the mean-field approximation, we define the average magnetization as $\mathbf{M_i^a} = \langle \mathbf{S_i^a} \rangle$ and deviation from mean magnetization $\delta \mathbf{S}_i^a = \mathbf{S_i^a} - \mathbf{M_i^a}$, such that to order $O(\delta S^2)$, we can write the Hamiltonian as the following linear form:

$$\begin{aligned} H &= \frac{J}{2} \sum_{i,j} \sum_{a,b} \mathbf{M}_i^a \cdot \mathbf{M}_j^b + D \sum_i \sum_a (\mathbf{M}_i^a \cdot \hat{z}^a)^2 \\ &- J \sum_{i,a} \sum_{j,b} \mathbf{M}_j^b \cdot \mathbf{S}_i^a - 2D \sum_{i,a} (\mathbf{S}_i^a \cdot \hat{z}^a)(\mathbf{M}_i^a \cdot \hat{z}^a) \end{aligned}$$

Partition function

The mean-field partition function can be written as:

$$Z = e^{-\beta\left(\frac{J}{2}\sum_{i,j}\sum_{a,b}\mathbf{M}_i^a\cdot\mathbf{M}_j^b + D\sum_i\sum_a(\mathbf{M}_i^a\cdot\hat{z}^a)^2\right)}\Pi_{i,a}\int e^{\beta\mathbf{B}_i^a\cdot\mathbf{S}_i^a}d\mathbf{S}_i^a, \tag{1}$$

where

$$\mathbf{B}_i^a = J\sum_{j\neq i}\sum_{b\neq a}\mathbf{M}_j^b + 2D(\mathbf{M}_i^a\cdot\hat{z}^a)\hat{z}^a, \tag{2}$$

in which the summation is over the nearest neighbors.

$$\int e^{\beta\mathbf{B}_i^a\cdot\mathbf{S}_i^a}d\mathbf{S}_i^a = 2\pi\int_0^\pi e^{\beta B_i^a\cos(\theta)}\sin(\theta)d\theta = 4\pi\frac{T}{B_i^a}\sinh(\frac{B_i^a}{T}), \tag{3}$$

where $B_i^a = |\mathbf{B}_i^a|$.

Free energy

$$G = \quad -T \ln Z = \\ \frac{J}{2}\sum_{i,j}\sum_{a,b}\mathbf{M}_i^a \cdot \mathbf{M}_j^b + D\sum_i\sum_a(\mathbf{M}_i^a \cdot \hat{z}^a)^2 \\ -T\sum_{i,a}\ln\left(4\pi\frac{T}{B_i^a}\sinh(\frac{B_i^a}{T})\right)$$

from The mean-field free energy obtained above one can calculate the magnetization as:

$$\mathbf{M}_i^a = -\nabla_B G = -\frac{\partial G}{\partial B_i^a}\hat{B}_i^a = \left(\coth(\frac{B_i^a}{T}) - \frac{T}{B_i^a}\right)\hat{B}_i^a. \qquad (4)$$

For small values of B fields one can expand Eq.(9) as:

$$M_i^a = \frac{1}{3}\frac{B_i^a}{T} - \frac{1}{45}\frac{B_i^{a3}}{T^3} + \frac{2}{945}\frac{B_i^{a5}}{T^5} + O(B^6), \qquad (5)$$

reversing the above series one gets:

$$B_i^a = 3TM_i^a + \frac{9}{5}TM_i^{a3} + \frac{297}{175}M_i^{a5} + O(M^6), \qquad (6)$$

Legender transformation

$$
\begin{aligned}
F &= G - \sum_i^a \mathbf{M}_i^a \mathbf{B}_i^a \\
&= -4NT\ln(4\pi) - \frac{J}{2}\sum_{i,j}\sum_{a,b}\mathbf{M}_i^a \cdot \mathbf{M}_j^b - D\sum_{i,a}(\mathbf{M}_i^a \cdot \hat{z}^a)^2 \\
&+ T\sum_{i,a}\left(\frac{3}{2}M_i^{a2} + \frac{9}{20}M_i^{a4} + \frac{99}{350}M_i^{a6} + O(M^7)\right)
\end{aligned}
$$

Fourier modes

$$\mathbf{M}_i^a = \sum_q \mathbf{M}_{\mathbf{q}}^a \exp(i\mathbf{q}\cdot\mathbf{R}_i^a)$$

$$J_{\mathbf{q}}^{ab} = \sum_{j\neq i}\sum_{b\neq a} J \exp\left(i\mathbf{q}\cdot(\mathbf{R}_i^a - \mathbf{R}_j^b)\right)$$

$$
\begin{aligned}
f(T,J,D) &= \frac{F(T,J,D)}{N} = -4T\ln(4\pi) \\
&+\frac{1}{2}\sum_{q}\sum_{ab}\mathbf{M}^a_{\mathbf{q}}\mathbf{M}^b_{-\mathbf{q}}(3T\delta^{ab}-J^{ab}_{\mathbf{q}}) \\
&-D\sum_{q}\sum_{a}(\mathbf{M}^{\mathbf{a}}_{\mathbf{q}}\cdot\hat{z}^a)(\mathbf{M}^{\mathbf{a}}_{-\mathbf{q}}\cdot\hat{z}^a) \\
&+\frac{9}{20}T\sum_{a}\sum_{\{\mathbf{q}\}}{}^{\prime}(\mathbf{M}^a_{\mathbf{q1}}\cdot\mathbf{M}^a_{\mathbf{q2}})(\mathbf{M}^a_{\mathbf{q3}}\cdot\mathbf{M}^a_{\mathbf{q4}}) \\
&+\frac{99}{350}T\sum_{a}\sum_{\{\mathbf{q}\}}{}^{\prime}(\mathbf{M}^a_{\mathbf{q1}}\cdot\mathbf{M}^a_{\mathbf{q2}})(\mathbf{M}^a_{\mathbf{q3}}\cdot\mathbf{M}^a_{\mathbf{q4}})(\mathbf{M}^a_{\mathbf{q5}}\cdot\mathbf{M}^a_{\mathbf{q6}}) \\
&+O(M^7)
\end{aligned}
$$

$\sum'_{\{\mathbf{q}\}} = \sum_{\{\mathbf{q}\}}\delta(\sum_i \mathbf{qi})$.

In terms of cartesian components of $\mathbf{M}^a_{\mathbf{q}} = (m^{a,1}_{\mathbf{q}}, m^{a,2}_{\mathbf{q}}, m^{a,3}_{\mathbf{q}})$, the free energy can be rewritten as:

$$
\begin{aligned}
& f(T,J,D) = -4T\ln(4\pi) \\
& +\frac{1}{2}\sum_{q}\sum_{ab}\sum_{\alpha\beta}(3T\delta^{ab}\delta^{\alpha\beta} - J^{ab}_{\mathbf{q}}\delta^{\alpha\beta} - \frac{2}{3}D^{a}_{\alpha\beta}\delta^{\alpha\beta})m^{a,\alpha}_{\mathbf{q}}m^{b,\beta}_{-\mathbf{q}} \\
+ \quad & \frac{9}{20}T\sum_{a}\sum_{\alpha\beta}\sum_{\{\mathbf{q}\}}{}^{'}(m^{a,\alpha}_{\mathbf{q1}}m^{a,\alpha}_{\mathbf{q2}})(m^{a,\beta}_{\mathbf{q3}}m^{a,\beta}_{\mathbf{q4}}) \\
+ \quad & \frac{99}{350}T\sum_{a}\sum_{\alpha\beta\gamma}\sum_{\{\mathbf{q}\}}{}^{'}(m^{a,\alpha}_{\mathbf{q1}}m^{a,\alpha}_{\mathbf{q2}})(m^{a,\beta}_{\mathbf{q3}}m^{a,\beta}_{\mathbf{q4}})(m^{a,\gamma}_{\mathbf{q5}}m^{a,\gamma}_{\mathbf{q6}}) + O(M^7)
\end{aligned}
$$

where α, β, γ take the values $1, 2, 3$.

The 3×3 matrices D^a are given by:

$$D^1 = D \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}, D^2 = D \begin{pmatrix} 1 & 1 & -1 \\ 1 & 1 & -1 \\ -1 & -1 & 1 \end{pmatrix},$$

$$D^3 = D \begin{pmatrix} 1 & -1 & 1 \\ -1 & 1 & -1 \\ 1 & -1 & 1 \end{pmatrix}, D^4 = D \begin{pmatrix} 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & 1 \end{pmatrix}$$

Quadratic term of the free energy

defining a new set of indices $s = 1 \cdot \cdot 12$ and the 12 component magnetization vector:

$$\mathbf{M_q} = (m_{\mathbf{q}}^{1,1}, m_{\mathbf{q}}^{1,2}, m_{\mathbf{q}}^{1,3}, \cdot \cdot \cdot m_{\mathbf{q}}^{4,3}) = (m_{\mathbf{q}}^{1}, m_{\mathbf{q}}^{2}, \cdot \cdot \cdot m_{\mathbf{q}}^{12}),$$

the quadratic term in free energy can be written as:

$$f^{(2)} = \sum_{\mathbf{q}} \mathbf{M_q}.\tilde{J}_q.\mathbf{M}_{\mathbf{q}}^T.$$

Quadratic coupling matrix

$$\tilde{J}_{\mathbf{q}} = \begin{pmatrix} \frac{2}{3}D^1 & J^{12}_{\mathbf{q}} & J^{13}_{\mathbf{q}} & J^{14}_{\mathbf{q}} \\ J^{12}_{\mathbf{q}} & \frac{2}{3}D^2 & J^{23}_{\mathbf{q}} & J^{24}_{\mathbf{q}} \\ J^{13}_{\mathbf{q}} & J^{23}_{\mathbf{q}} & \frac{2}{3}D^3 & J^{34}_{\mathbf{q}} \\ J^{14}_{\mathbf{q}} & J^{24}_{\mathbf{q}} & J^{34}_{\mathbf{q}} & \frac{2}{3}D^4 \end{pmatrix}$$

$$\begin{aligned} J^{12}_{\mathbf{q}} &= 2J\cos(\frac{q_x+q_z}{4})I_{3\times3},\ J^{13}_{\mathbf{q}} = 2J\cos(\frac{q_y+q_z}{4})I_{3\times3} \\ J^{14}_{\mathbf{q}} &= 2J\cos(\frac{q_x+q_y}{4})I_{3\times3},\ J^{23}_{\mathbf{q}} = 2J\cos(\frac{q_x-q_y}{4})I_{3\times3} \\ J^{24}_{\mathbf{q}} &= 2J\cos(\frac{q_y-q_z}{4})I_{3\times3},\ J^{34}_{\mathbf{q}} = 2J\cos(\frac{q_x-q_z}{4})I_{3\times3} \end{aligned}$$

Normal modes

Diagonalizing the quadratic term requires transforming to the normal modes $\Phi_{\mathbf{q}}$:

$$m_{\mathbf{q}}^{s} = \sum_{i=1}^{12} U_{\mathbf{q}}^{si} \phi_{\mathbf{q}}^{j}$$

for $s = 1, 2, \cdots 12$. $U_{\mathbf{q}}$ is the unitary matrix that diagonalize the coupling matrix $\tilde{J}_{\mathbf{q}}$ with eigenvalues $\lambda_{\mathbf{q}}^{i}$:

$$\sum_{b} \tilde{J}_{\mathbf{q}}^{ab} U_{\mathbf{q}}^{bi} = \lambda_{\mathbf{q}}^{i} U_{\mathbf{q}}^{ai}$$

in which, unitarity condition requires:

$$\sum_{a} U_{\mathbf{q}}^{ai} U_{-\mathbf{q}}^{aj} = \delta^{ij}$$

In terms of the normal modes, the free energy can be written as:

$$f(T,J,D) = -4T\ln(4\pi) + \frac{1}{2}\sum_{q}\sum_{i=1}^{12}(3T-\lambda^i_{\mathbf{q}})\phi^i_{\mathbf{q}}\phi^i_{-\mathbf{q}}$$

$$+\frac{9}{20}T\sum_{s=1}^{12}\sum_{ijkl}\sum_{\{\mathbf{q}\}}^{\prime} U^{si}_{\mathbf{q1}}U^{sj}_{\mathbf{q2}}U^{sk}_{\mathbf{q3}}U^{sl}_{\mathbf{q4}}\phi^i_{\mathbf{q1}}\phi^j_{\mathbf{q2}}\phi^k_{\mathbf{q3}}\phi^l_{\mathbf{q4}}$$

$$+\frac{99}{350}T\sum_{s=1}^{12}\sum_{\{\mathbf{q}\}}^{\prime} U^{si}_{\mathbf{q1}}U^{sj}_{\mathbf{q2}}U^{sk}_{\mathbf{q3}}U^{sl}_{\mathbf{q4}}U^{sm}_{\mathbf{q5}}U^{sn}_{\mathbf{q6}}\phi^i_{\mathbf{q1}}\phi^j_{\mathbf{q2}}\phi^k_{\mathbf{q3}}\phi^l_{\mathbf{q4}}\phi^m_{\mathbf{q5}}\phi^n_{\mathbf{q6}}$$

The first state with broken symmetry, corresponds to the wave vector for which λ is maximum and the transition temperature is given by $T_c = \frac{1}{3}\mathbf{max}_{\mathbf{q},i}\{\lambda^i_{\mathbf{q}}\}$

The isotropic case($D = 0$)

In this case the eigenvalues of the matrix $\tilde{J}$ with $J = -1$, can be derived analytically as:

$$
\begin{aligned}
\lambda_{\mathbf{q}}^{i} &= 2, & i = 1 \ldots 6 \\
\lambda_{\mathbf{q}}^{i} &= -2(1 - \sqrt{1+Q}) & i = 7, 8, 9 \\
\lambda_{\mathbf{q}}^{i} &= -2(1 + \sqrt{1+Q}) & i = 10, 11, 12
\end{aligned}
$$

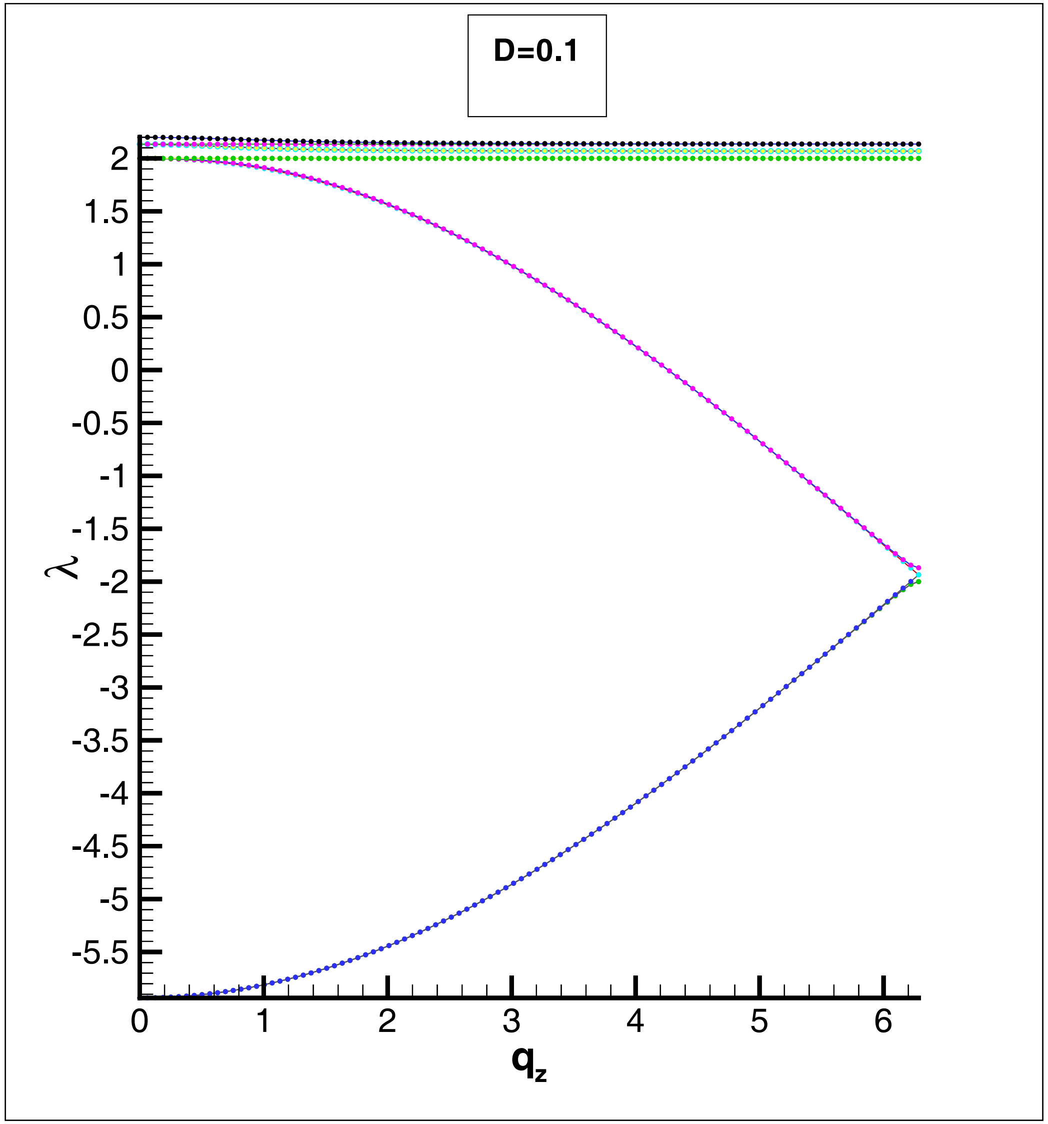
where

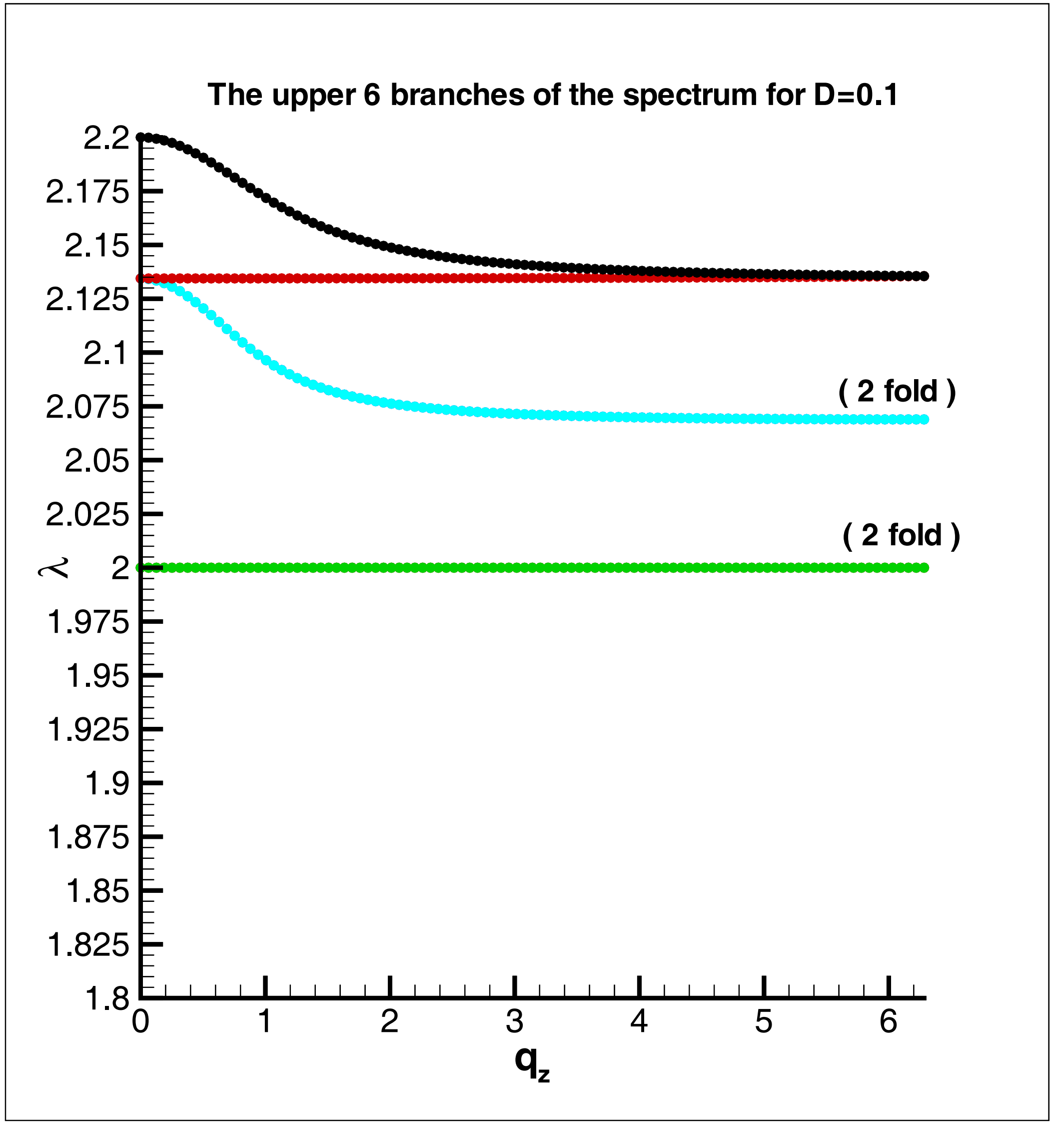
$$
\begin{aligned}
Q &= \frac{1}{2}\{\cos(\frac{q_x + q_y}{2}) + \cos(\frac{q_x + q_z}{2}) + \cos(\frac{q_y + q_z}{2}) \\
&\quad + \cos(\frac{q_x - q_y}{2}) + \cos(\frac{q_x - q_z}{2}) + \cos(\frac{q_y - q_y}{2})\}
\end{aligned}
$$

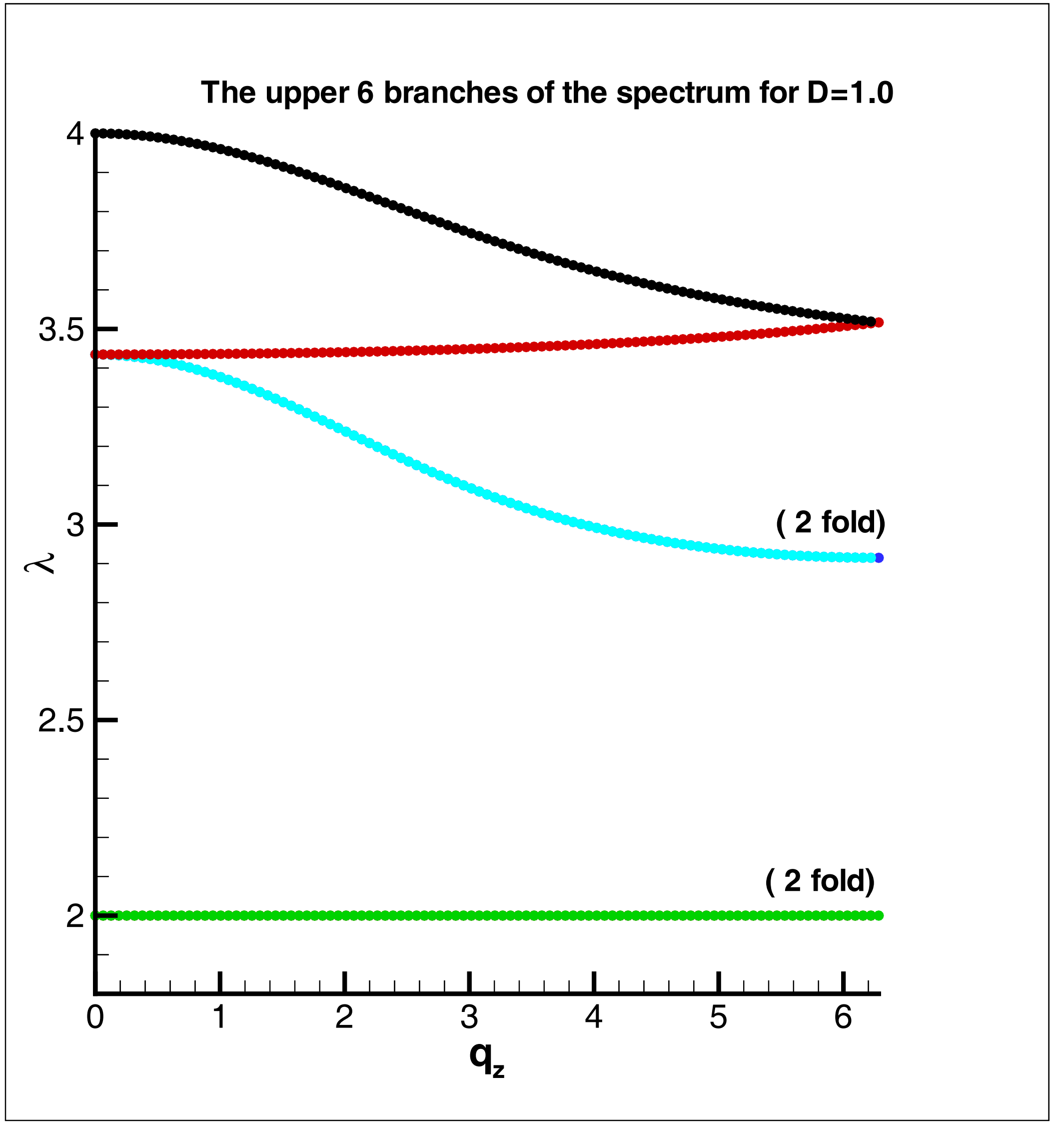
The system is highly frustrated

The easy-axes anisotropy

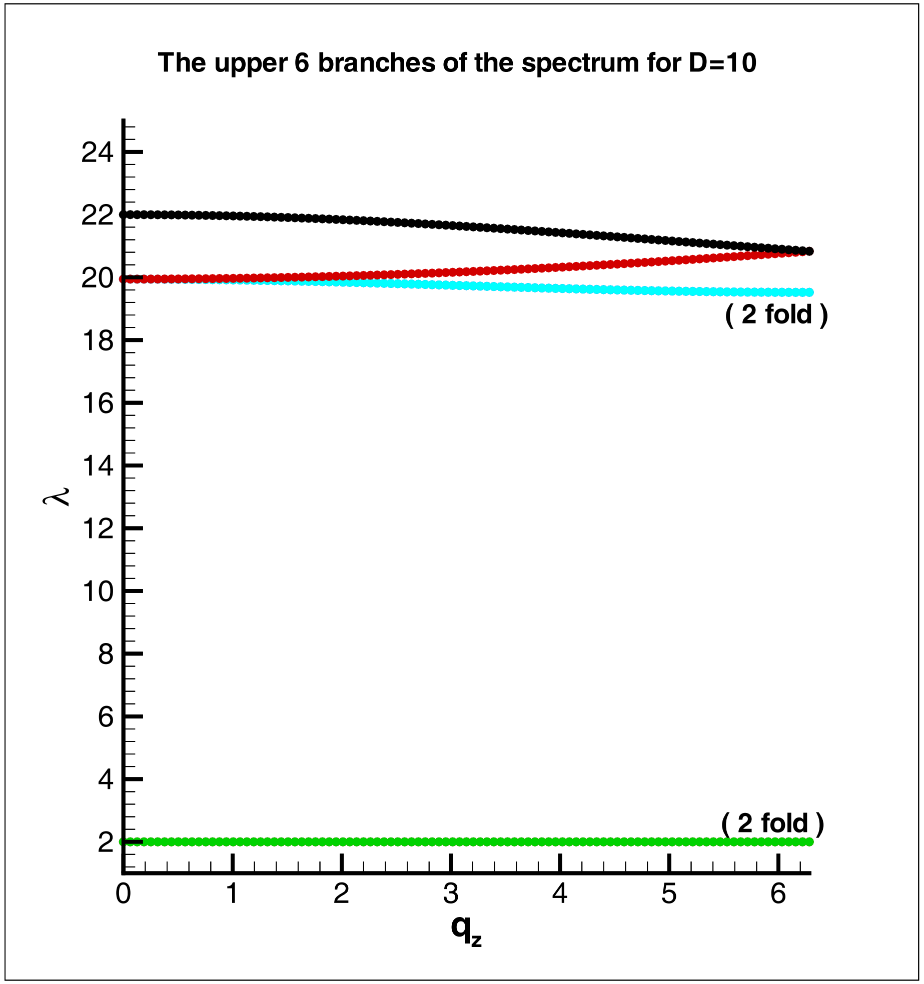
In this case the eigenvalues of $\tilde{J}$ can be calculated numerically.




The upper 6 branches of the spectrum for D=0.1
2.2
2.175
2.15
2.125
2.1
2.075
2.05
2.025
λ
2
1.975
1.95
1.925
1.9
1.875
1.85
1.825
1.8
0
1
2
3
4
5
6
q_z
(2 fold)
(2 fold)


The upper 6 branches of the spectrum for D=1.0
4
3.5
3
2.5
2
λ
(2 fold)
(2 fold)
0
1
2
3
4
5
6
q_z

The largest mode at $q = 0$ corresponds to all-in all-out state



Effective free energy in Gaussian approximation

Integrating out the non-dispersive modes, one reaches the following expression for the effective free energy in Gaussian level:

$$f(T,D) = -4T\ln(4\pi) + \frac{1}{2}(3T-2-2D)(\phi_{\mathbf{0}}^1)^2$$
$$+\frac{3T}{80}(\phi_{\mathbf{0}}^1)^4 + \frac{11T}{5600}(\phi_{\mathbf{0}}^1)^6$$
$$+T\ln\left(3T-2+\frac{9T}{20}(\phi_{\mathbf{0}}^1)^2+\frac{33T}{560}(\phi_{\mathbf{0}}^1)^4+\frac{57T}{8000}(\phi_{\mathbf{0}}^1)^6\right).$$

By expanding the effective free energy in terms of $\phi_{\mathbf{0}}^1$ we get:

$$f(T,D) = U_2(T,D)(\phi_{\mathbf{0}}^1)^2 + U_4(T,D)(\phi_{\mathbf{0}}^1)^4 + U_6(T,D)(\phi_{\mathbf{0}}^1)^6.$$

The coefficients of the effective free energy

$$U_2(T,D) = \frac{3T-2-2D}{2} + \frac{9T^2}{20(3T-2)}$$

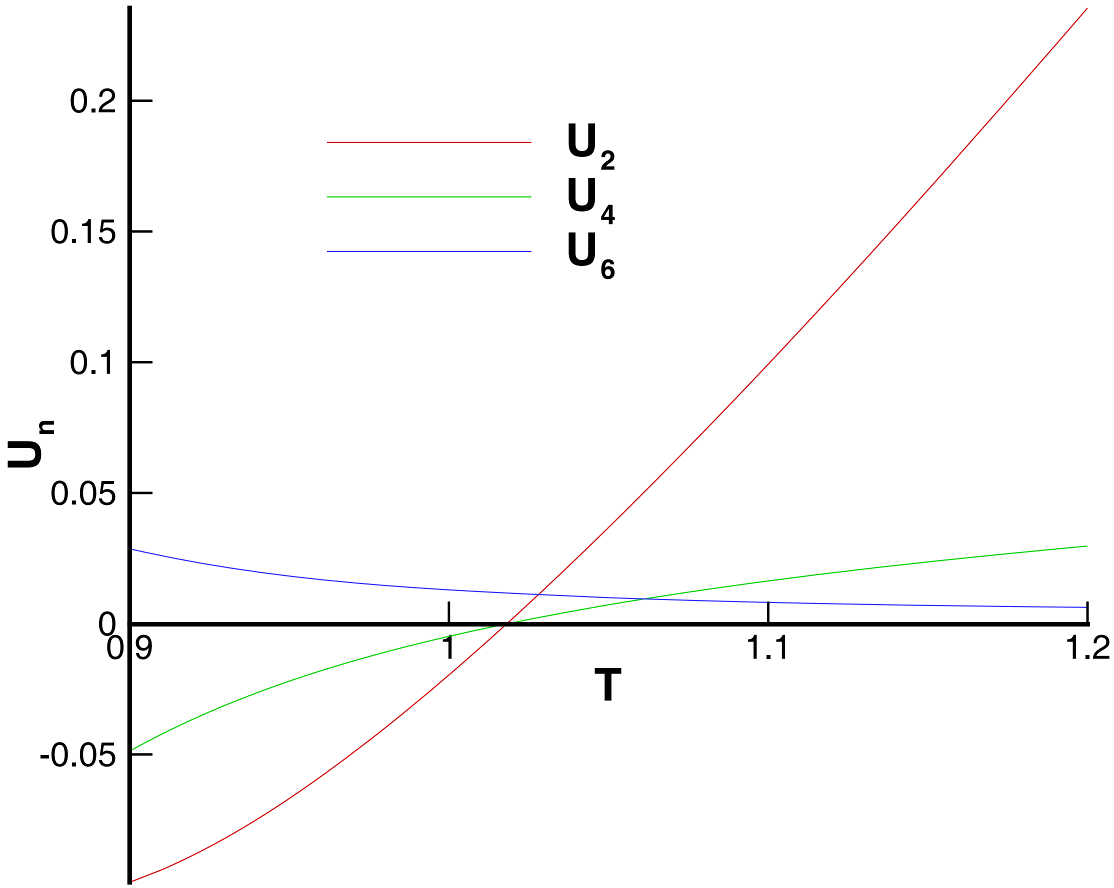
$$U_4(T,D) = \frac{3T(771T^2-1060T+280)}{5600(3T-2)^2}$$

$$U_6(T,D) = \frac{T(3807T^3-7758T^2+5556T-880)}{56000(3T-2)^3}$$

1-$U_2(T, D)$ can change sign only for $D\rangle 0.8633$, such that for less than this value, hence first order transitions would be expected.
2-For $0.8633\langle D\langle 0.9696$ the sign of U_2 changes at a critical temperature, but U_4 is negative for this range of temperatures. Therefore the transition is again first order. The critical temperature corresponding to $D = 0.9696$ is $T_t = 1.018$.
3-U_4 is negative for $T\langle 1.018$ and positive for $T\rangle 1.018$. So this system exhibit a tricritical transition at $T_t = 1.018$ and $D = 0.9696$.

4-U_6 is always positive and decreases monotonically.

Temperature dependence of the coefficients at the tricritical point $D_t = 0.9696$



Tetracritical hypothesis

U_6 is very small at the tricritical point $U_6(T_t) \sim 0.006$. This suggests that the transition might be in a crossover region from tricritical to tetracritical behaviour, and so justify the value of order parameter critical exponent $\beta \sim 0.18(2)$ obtained in the experiments and simulations.

Thanks for your attention