Spin Hamiltonian and Order out of Coulomb Phase in Pyrochlore Structure of FeF_3

Farhad Shahbazi
in collaboration with
Azam Sadeghi (IUT)
Mojtaba Alaei (IUT)
Michel J. P. Gingras (UWaterloo)

arXiv: 1407.0849

Outline

- Experimental observation on Pyr-FeF3
- Derivation of an effective spin Hamiltonian using *ab initio* DFT method
- Monte Carlo Simulation
- Conclusion

Experimental Observations

Structures of FeF3

G.Ferey et al, Revue de Chimie minerale 23, 474 (1986)

- Rhombohedral (R-FeF3)

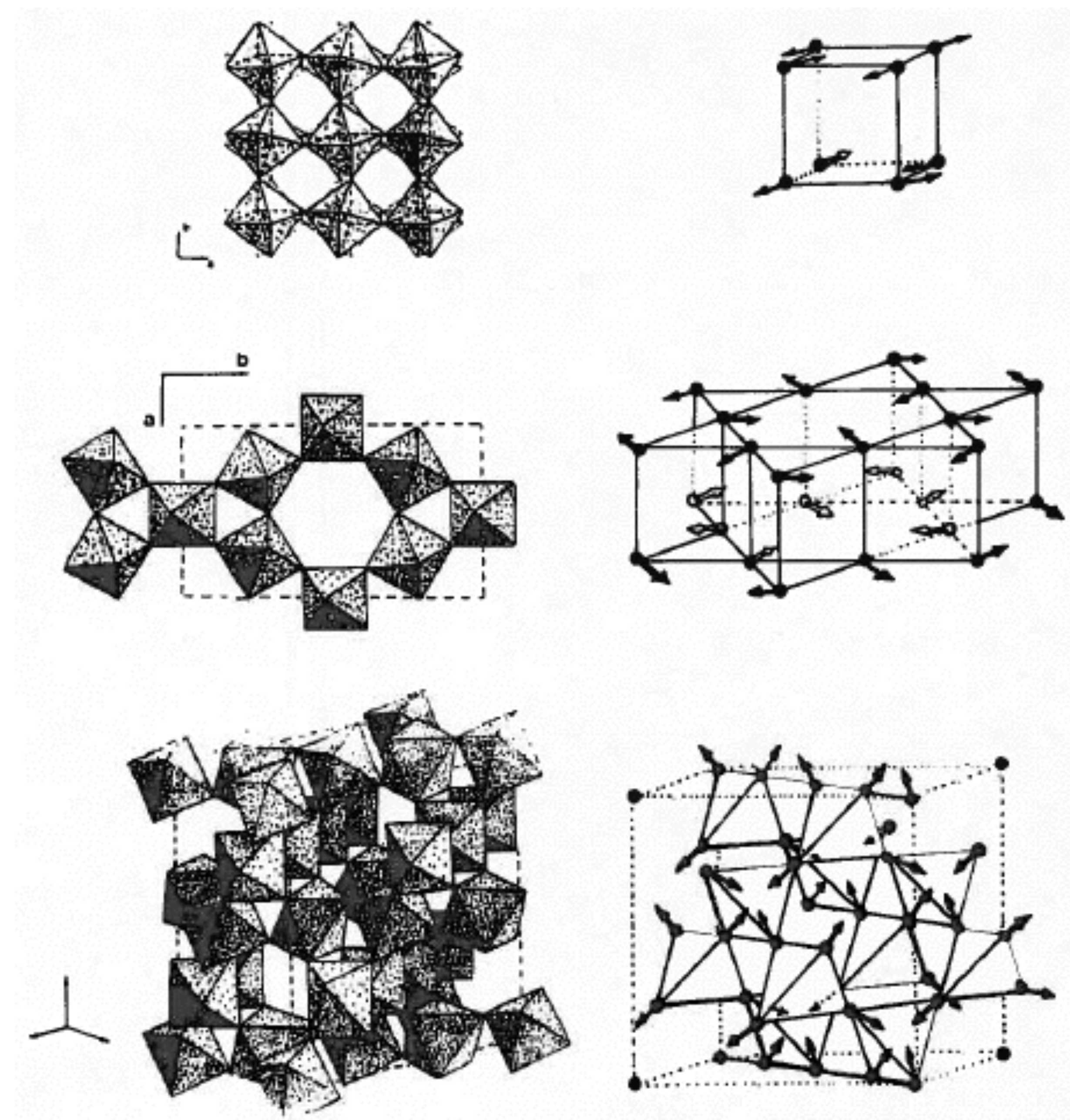
$$Fe - F - Fe = 142.3^{\circ}$$
$$T_N = 110K$$
$$\mu = 4.45\mu_B$$

- Hexagonal Tungsten Bronze (HTB-FeF3)

$$Fe - F - Fe = 152.15^{\circ}$$
$$T_N = 365K$$
$$\mu = 4.07\mu_B$$

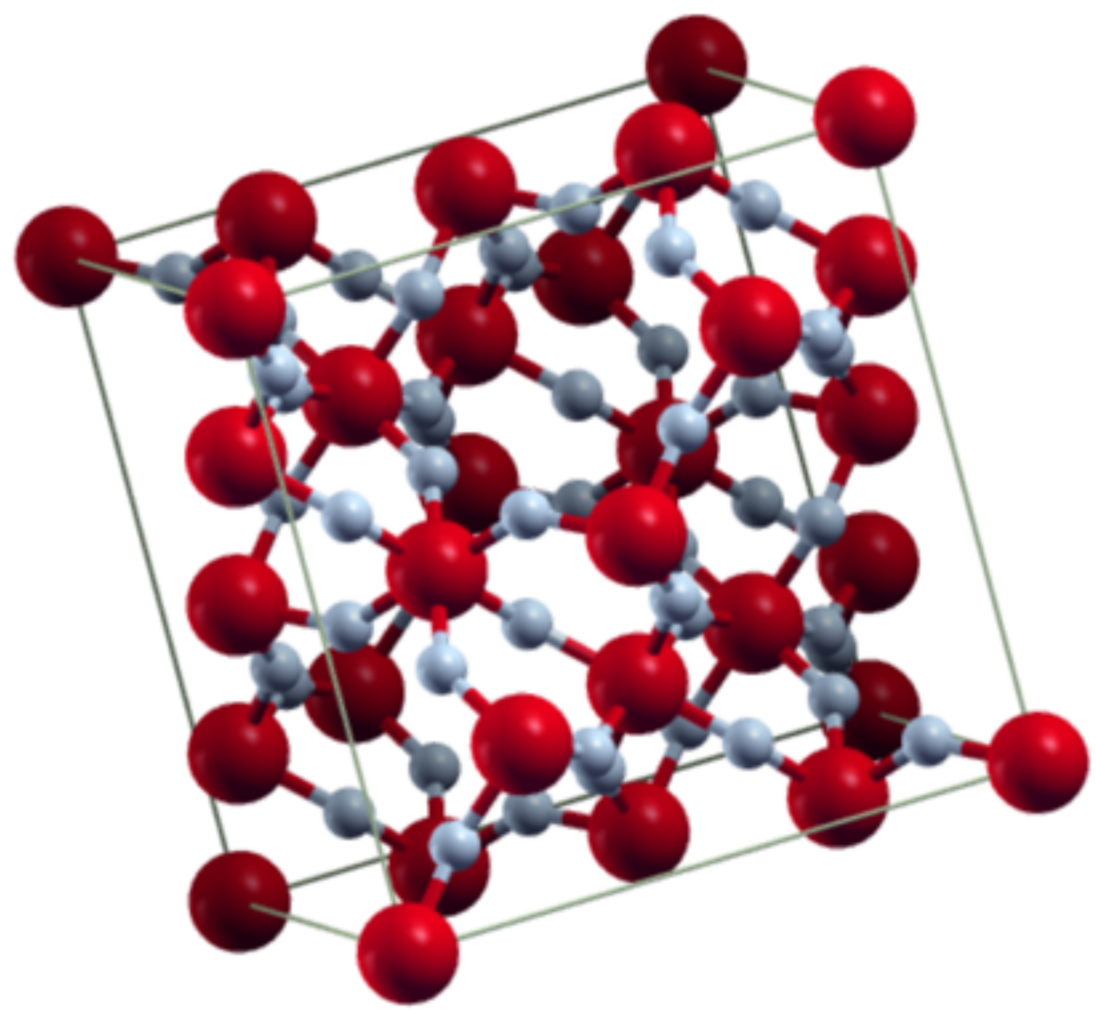
- Pyrochlore (Pyr- FeF3)

$$Fe - F - Fe = 141.65^{\circ}$$
$$T_N = 20 \pm 2K$$
$$\mu = 3.32\mu_B$$



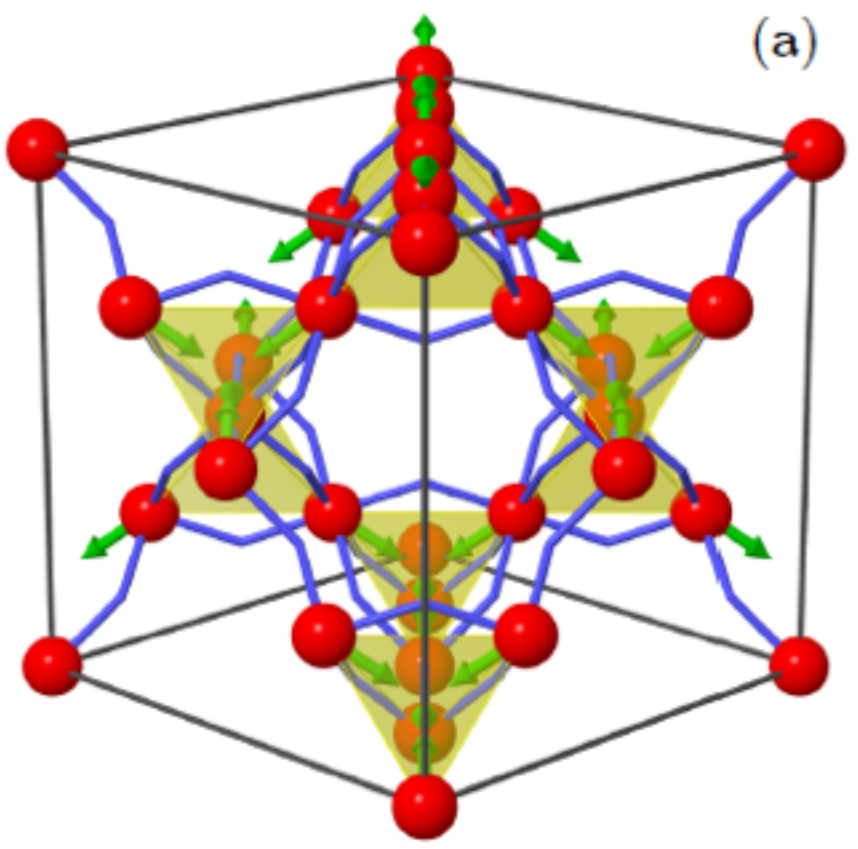
$$Fe^{+3} : 3d^5$$
$$\mu_{free-ion} = 5\mu_B$$

Pyr-FeF3



Pyrochlore Structure

- Corner sharing array of tetrahedra
- Fcc Bravais lattice+ 4 lattice point basis
- In Pyr-FeF3, Fe^{+3} ions reside on the corners of the tetrahedra
- The ground state has all-in/all-out (AIAO) ordering

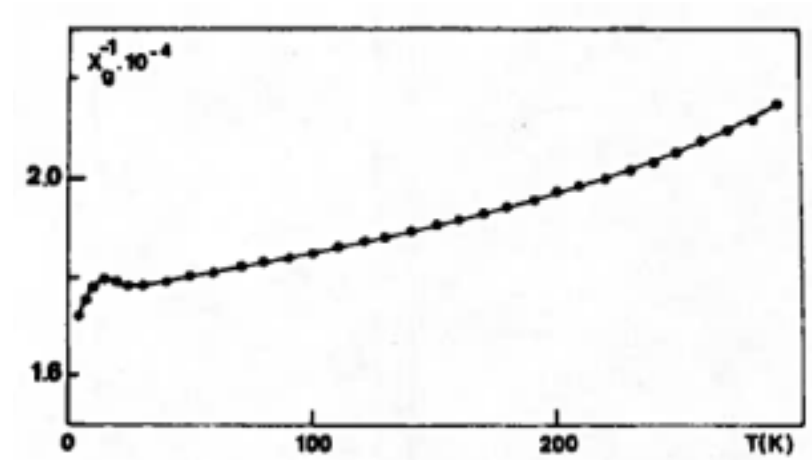


Measurements

- Magnetic Susceptibility

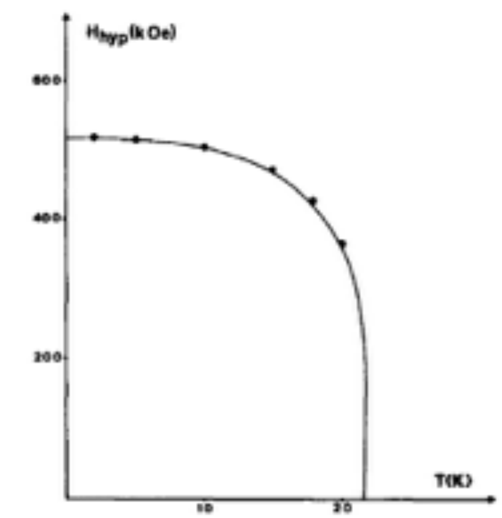
  G. Ferey, *et al*, Revue de Chimie minerale 23, 474 (1986)

  Results: Deviation from Curie-Weiss law even at T=300K.
  sign of transition at T~20K



- Mossbauer Study

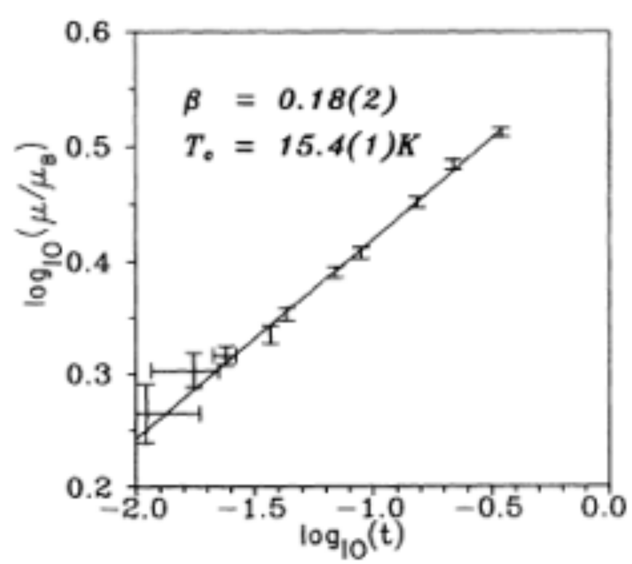
  Y. Calage, *et al*, Journal of Solid State Chemistry 69, 197 (1987)



- Neutron Diffraction

  J.N. Reimers, *et al*, Phys. Rev. B, 5692 (1991);

  Phys. Rev. B 45, 7295 (1992)



Questions

- Why the transition temperature is too small in Pyr-FeF3?
- What is the origin of non-coplanar “AIAO” ordering?
- What is the universality class of transition?

* Why the transition temperature is too small in Pyr-FeF3?

- Geometric frustration

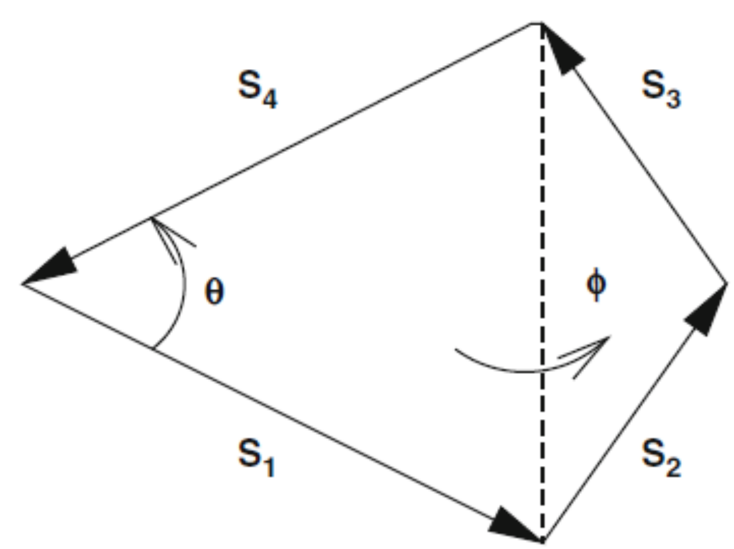
- The ground state of nearest neighbour classical Heisenberg Anti-ferromagnet is highly degenerate on pyrochlore lattice. This model remains disordered down to zero kelvin.

R. Moessner, and J. T Chalker, Phys. Rev Lett 80, 2929; Phys. Rev. B 58, 12049 (1998)

$$\mathcal{H} = J \sum_{\text{pairs}} \mathbf{S}_i \cdot \mathbf{S}_j \equiv \frac{J}{2}|\mathbf{L}|^2 + c$$

with

$$\mathbf{L} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4$$

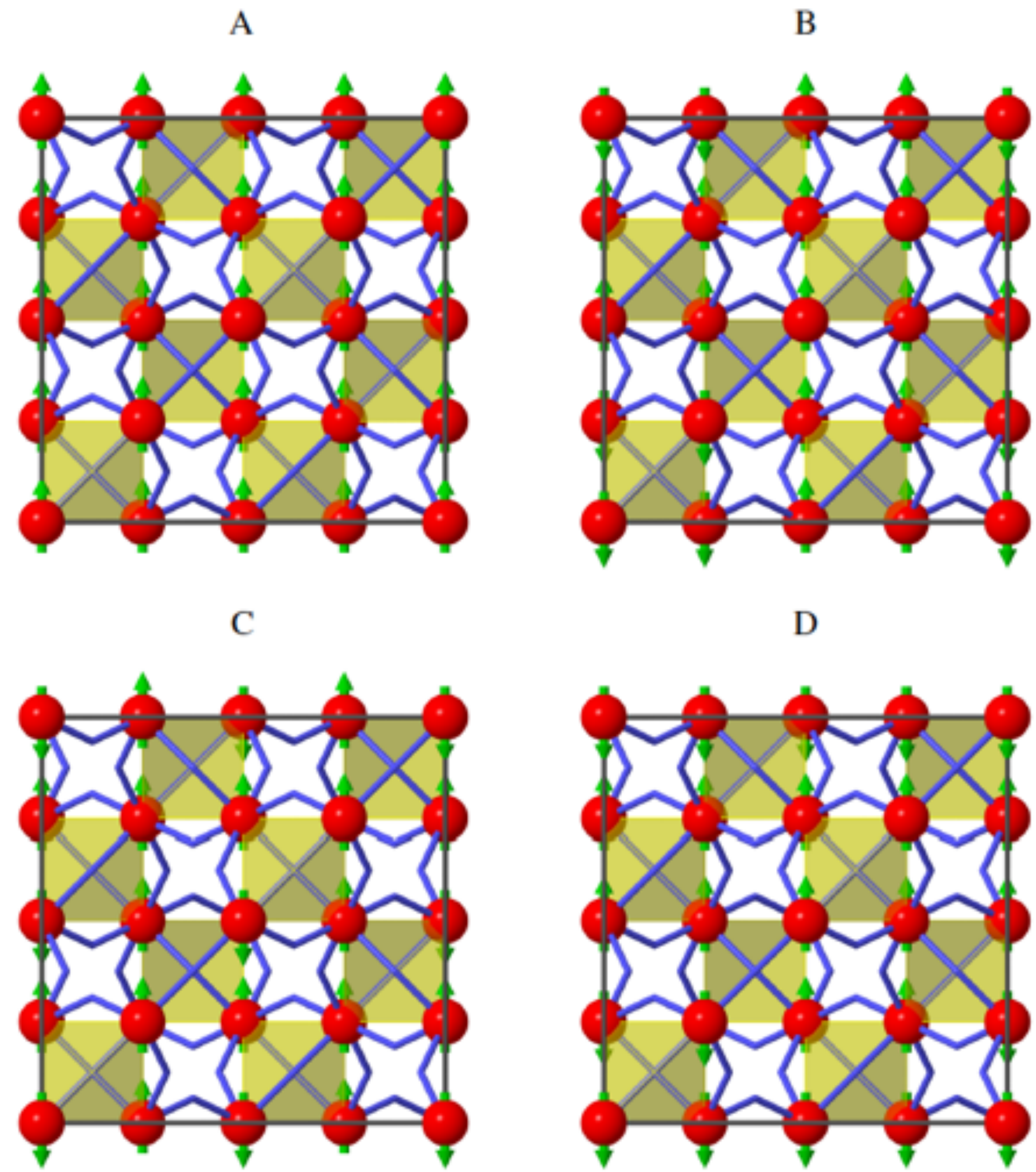


* What is the origin of non-coplanar “AIAO” ordering?

- Spin anisotropy due to spin-orbit coupling
- But the angular momentum of iron ion is zero, then where does the spin-obit coupling may come from?

Abinitio DFT Calculation

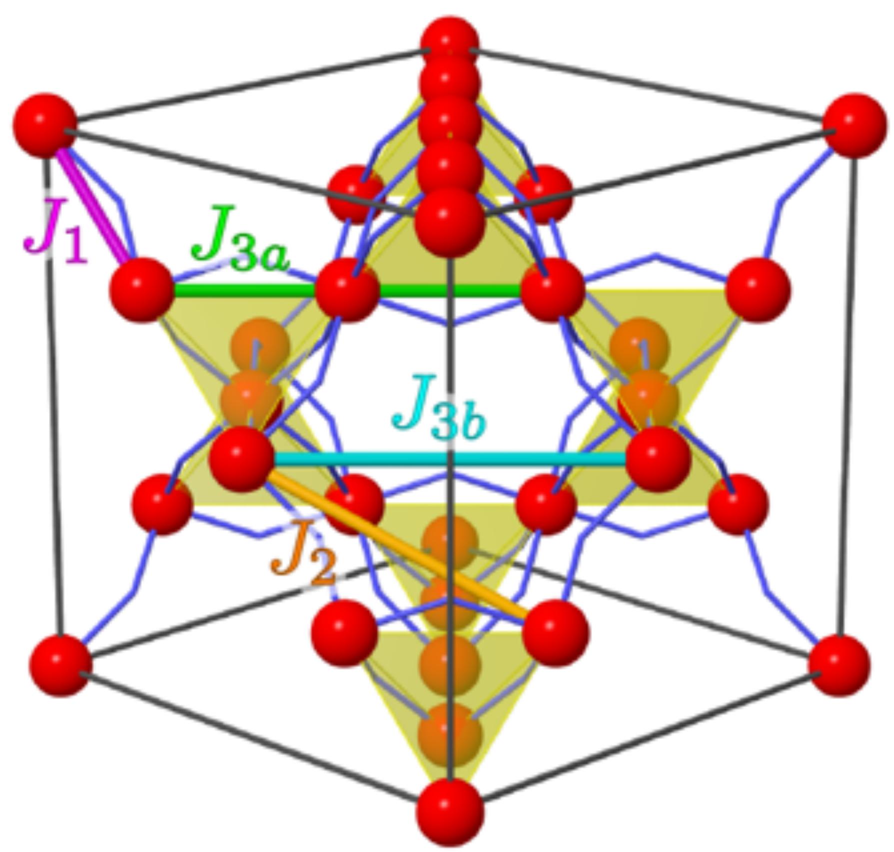
$$
\begin{aligned}
E_{\rm A} &= 48J_1 + 96J_2 + 48J_{3,a} + 48J_{3,b} \\
E_{\rm B} &= 24J_1 \\
E_{\rm C} &= 48J_{3,a} + 48J_{3,b} \\
E_{\rm D} &= 12J_1 - 16J_2 - 8J_{3,a} - 8J_{3,b}.
\end{aligned}
$$



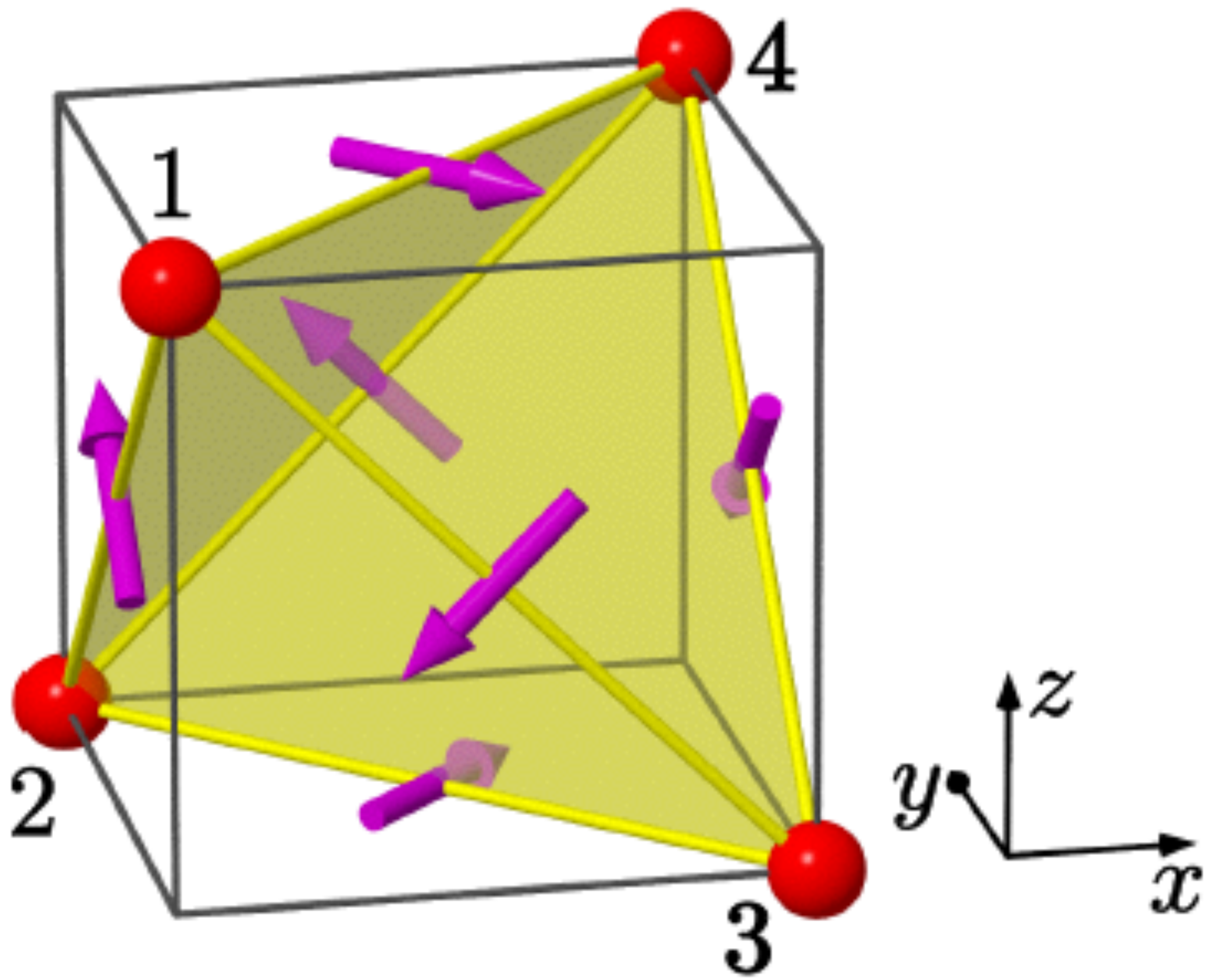
Microscopic Spin Hamiltonian

$$\mathcal{H}_{\text{eff}} = \frac{J_1}{2} \sum_{\langle i,j \rangle} \sum_{a \neq b} \mathbf{n}_i^a \cdot \mathbf{n}_j^b + \frac{B}{2} \sum_{\langle i,j \rangle} \sum_{a \neq b} (\mathbf{n}_i^a \cdot \mathbf{n}_j^b)^2 + \frac{D}{2} \sum_{\langle i,j \rangle} \sum_{a \neq b} \hat{\mathbf{D}}^{ab} \cdot (\mathbf{n}_i^a \times \mathbf{n}_j^b)$$

Exchange parameters (meV)	J_1	J_2	J_{3a}	B	D	J_2/J_1	J_{3a}/J_1	B/J_1	D/J_1
LDA+SOC	54.1	1.6	2.6	4.7	2.5	0.029	0.048	0.087	0.046
LDA+U+SOC ($U_{eff} = 2.8$ eV)	32.7	0.6	0.5	1.0	0.6	0.018	0.015	0.030	0.018



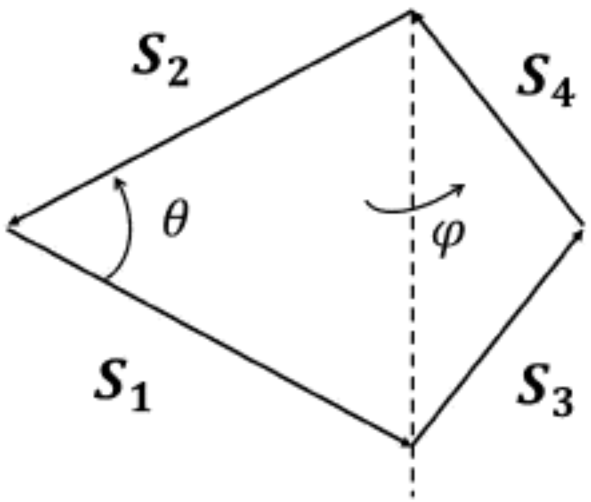
Direct DM vectors



M. Elhajal, *et al*, Phys. Rev. B 71, 094420 (2005)

Energy Landscape of biquadratic term for Single Tetrahedron

$$Q = \sum_{<i,j>} (\mathbf{S}_i.\mathbf{S}_j)^2 = B(1 - 2\sin^2\phi\cos\theta + (3+\cos^2\phi)\cos^2\theta + \cos^2\phi).$$



- Minimum locates at

$$\phi = \pi/2, \theta = \cos^{-1}(1/3)$$

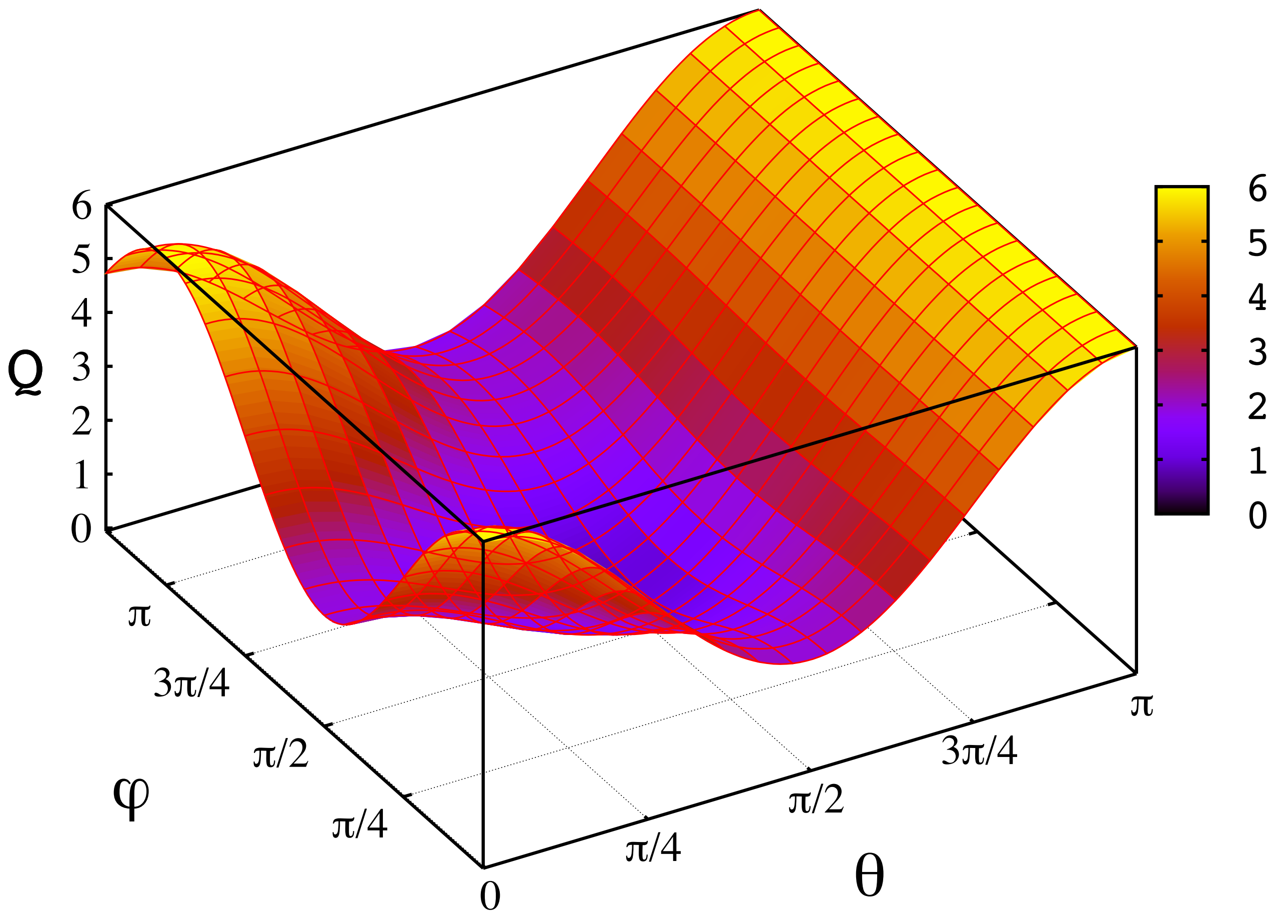
- corresponding to a non-collinear state. DM interaction fixes this state to the all-in or all-out directions.

The location of the saddle point is

$$\phi = 0, \pi; \theta = \pi/2$$

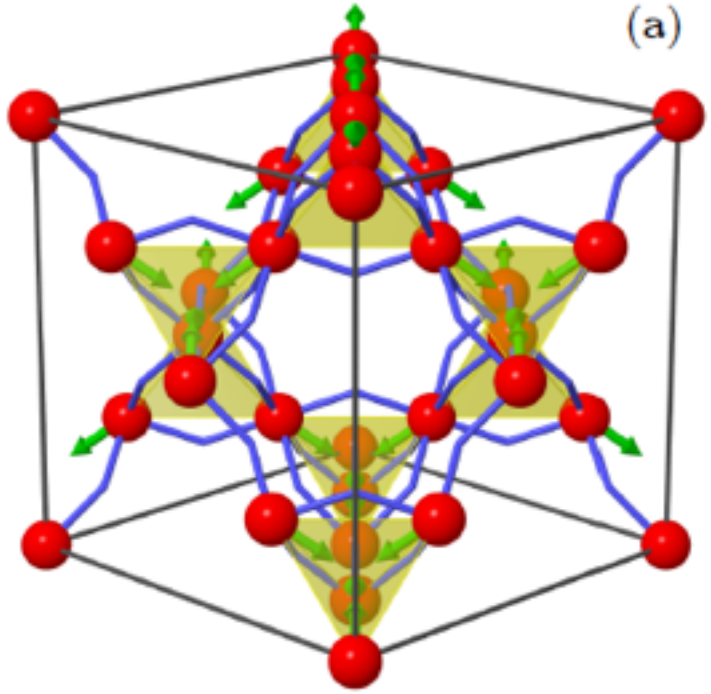
$$\phi = \pi/2; \theta = 0$$

- corresponding to co-planar states which have triple degeneracy. DM interaction fixes these states to xy, xz or yz planes, depending which two spins are collinear.

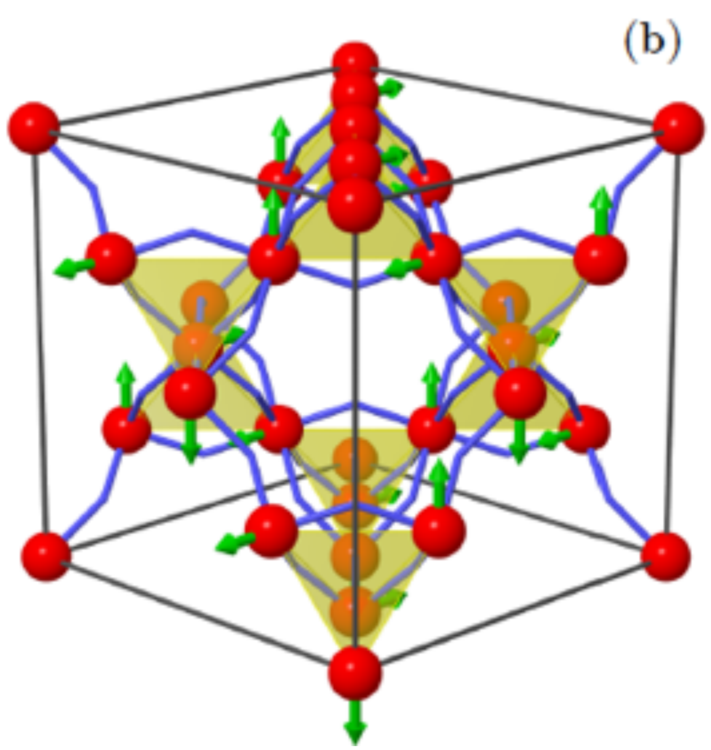


Coplanar vs AIAO state

$$E_{\mathrm{AIAO}}/N = -J_1 + B/3 - 2\sqrt{2}D$$

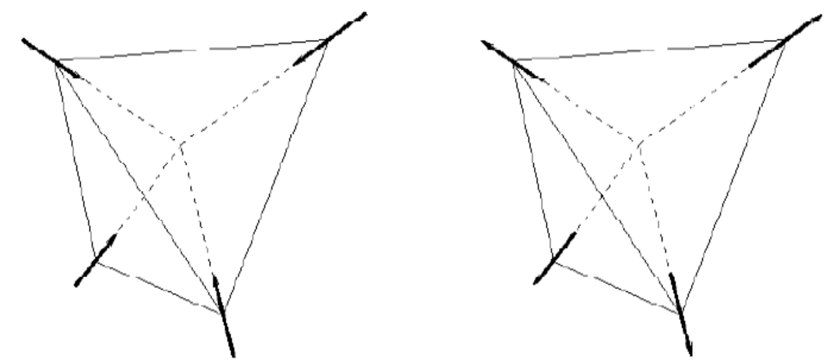


$$E_{\mathrm{coplanar}}/N = -J_1 + B - \sqrt{2}D$$



What is the universality class of transition?

- Monte Carlo simulation



AIAO order parameter

$$M = \langle m \rangle_T$$

$$m = \Sigma_{i,a} \mathbf{S}_i^a . \hat{\mathbf{d}}^a / N$$

Order parameter Binder's cumulant

$$U_m(T) = 1 - \frac{1}{3} \frac{< m^4 >}{< m^2 >^2}$$

Finite size scaling

$$M = L^{-\beta/\nu} \mathcal{M}(tL^{1/\nu})$$

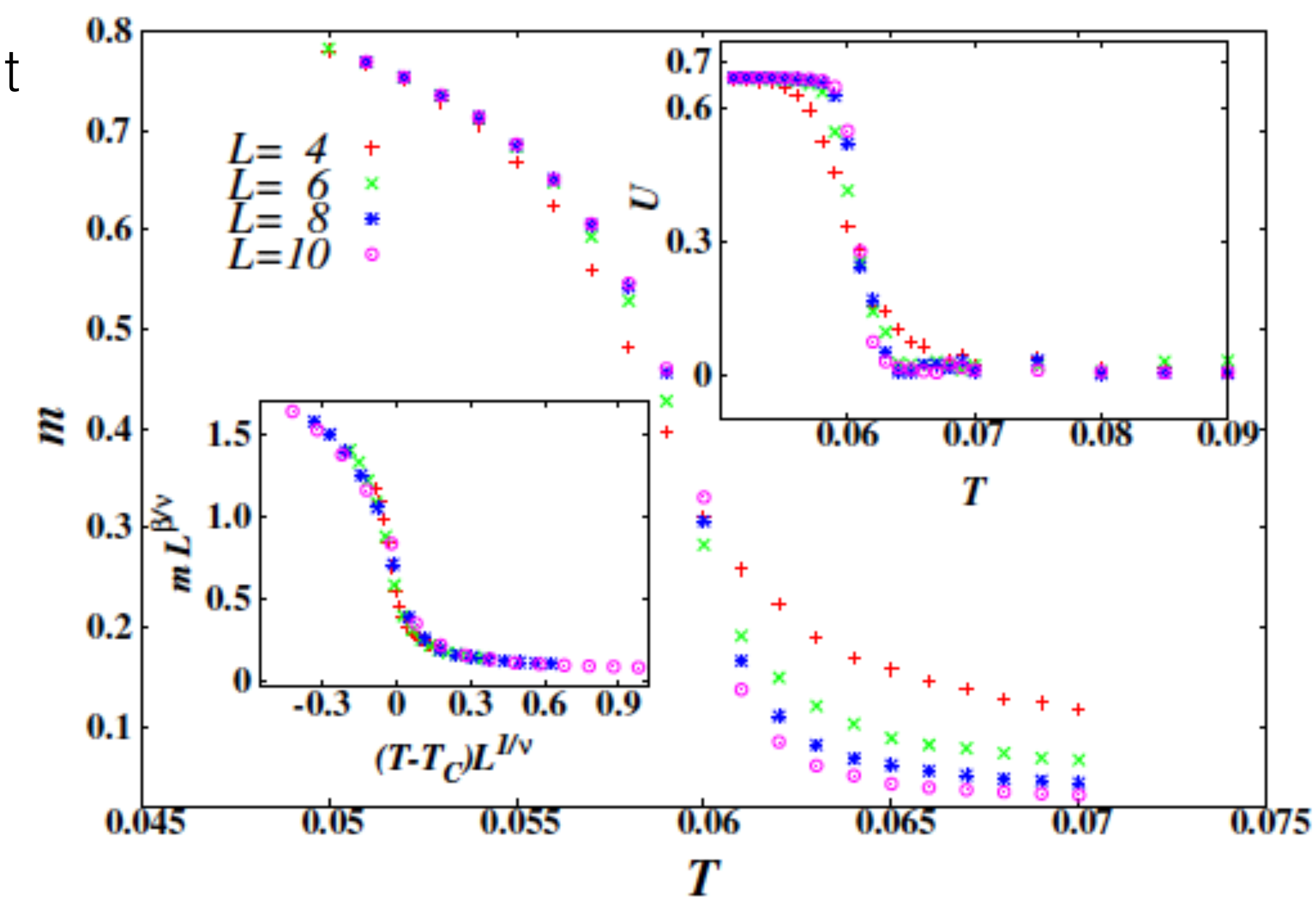
Results

$$T_c/J_1 = 0.0601(2)$$

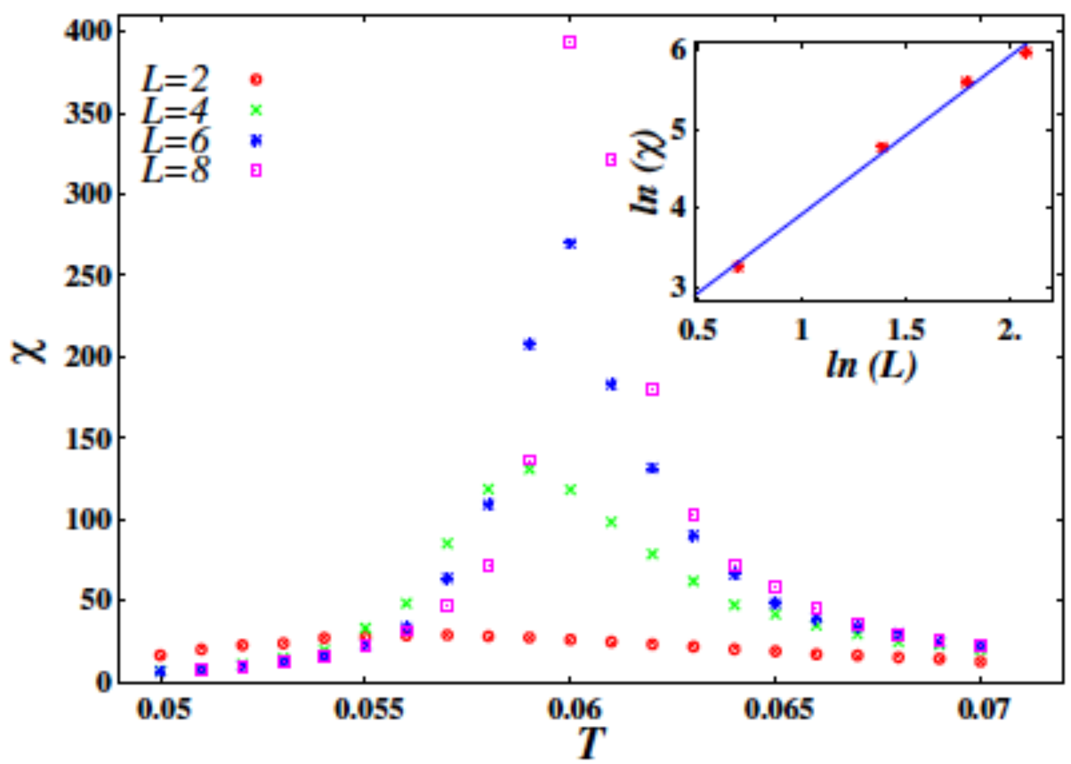
$$\beta = 0.18(2)$$

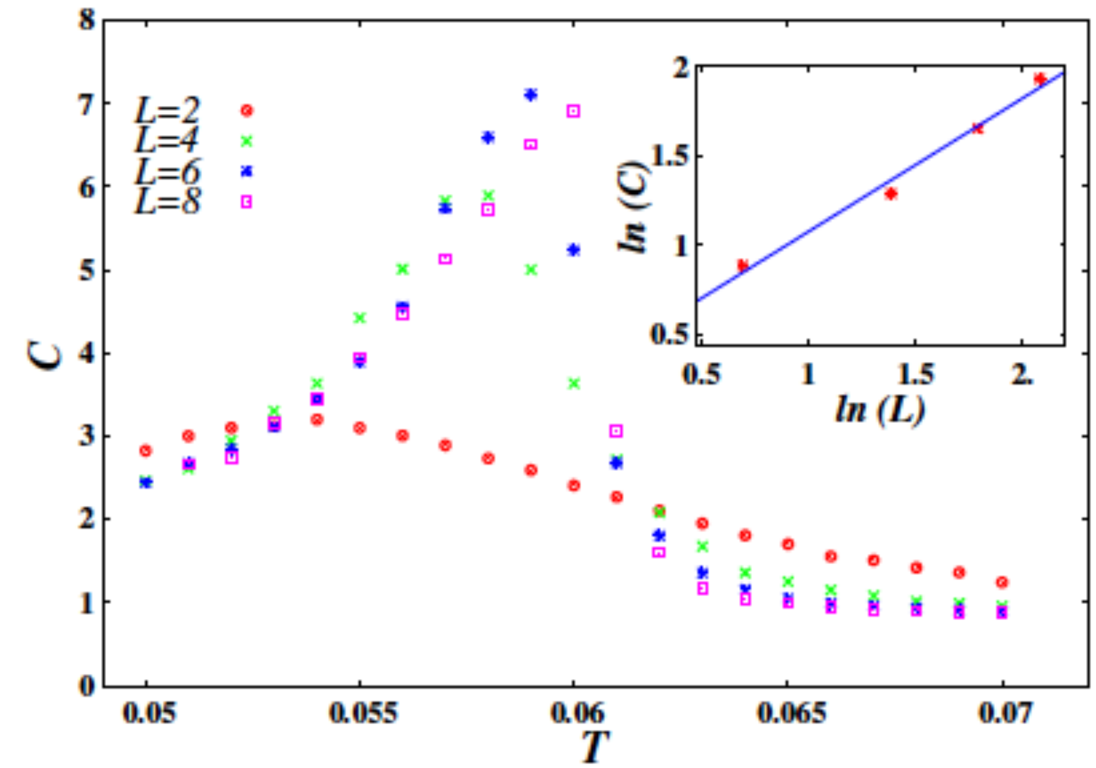
$$\nu = 0.60(2)$$

$$J_1 = 32.7eV \rightarrow T_c =\approx 22K$$



The critical exponents of specific heat and AIAO susceptibility





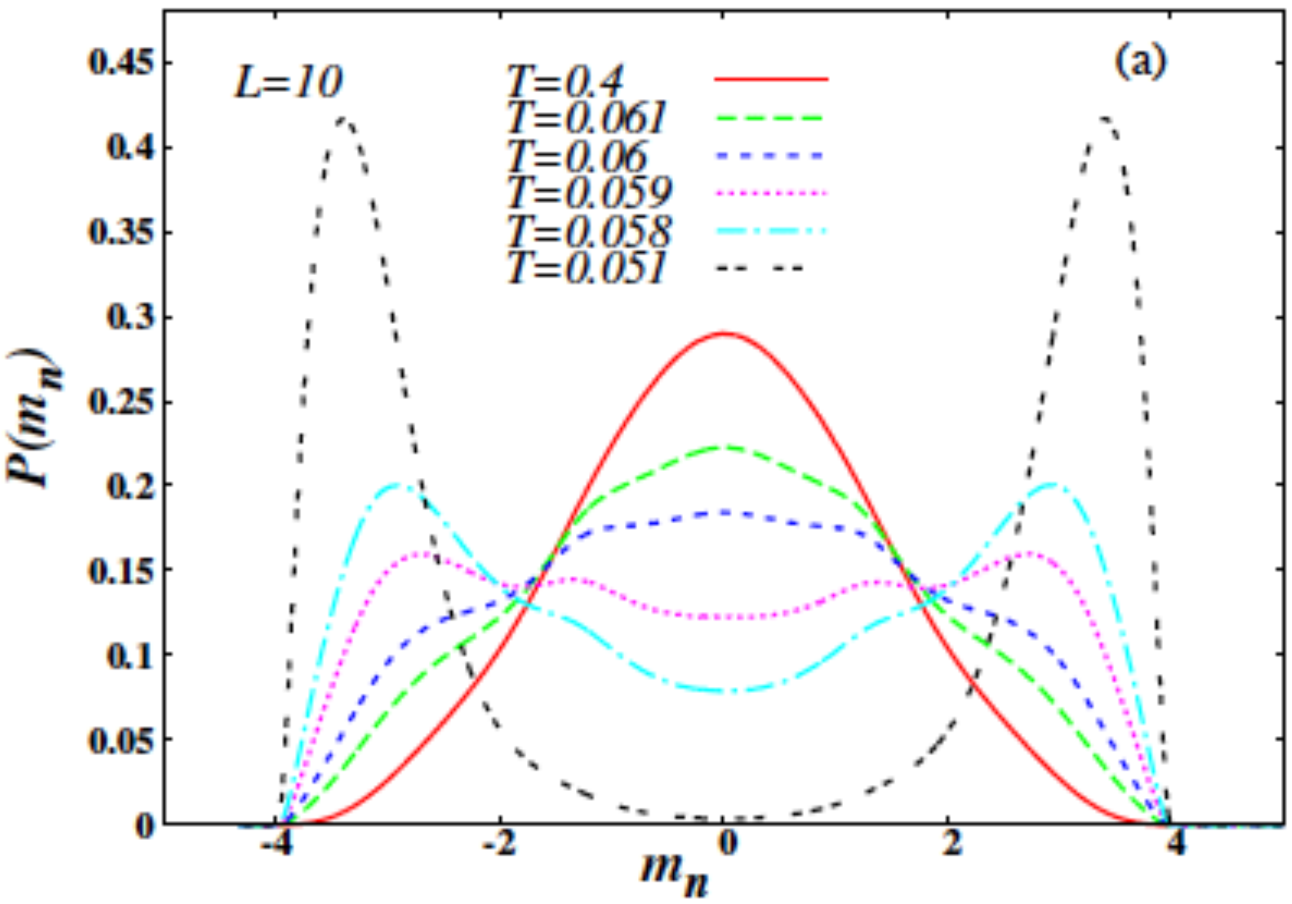
$$\alpha = 0.44(3), \chi = 1.20(3)$$

$$\alpha + 2\beta + \chi = 2.0(1)$$

Deeper Look for the order of transition

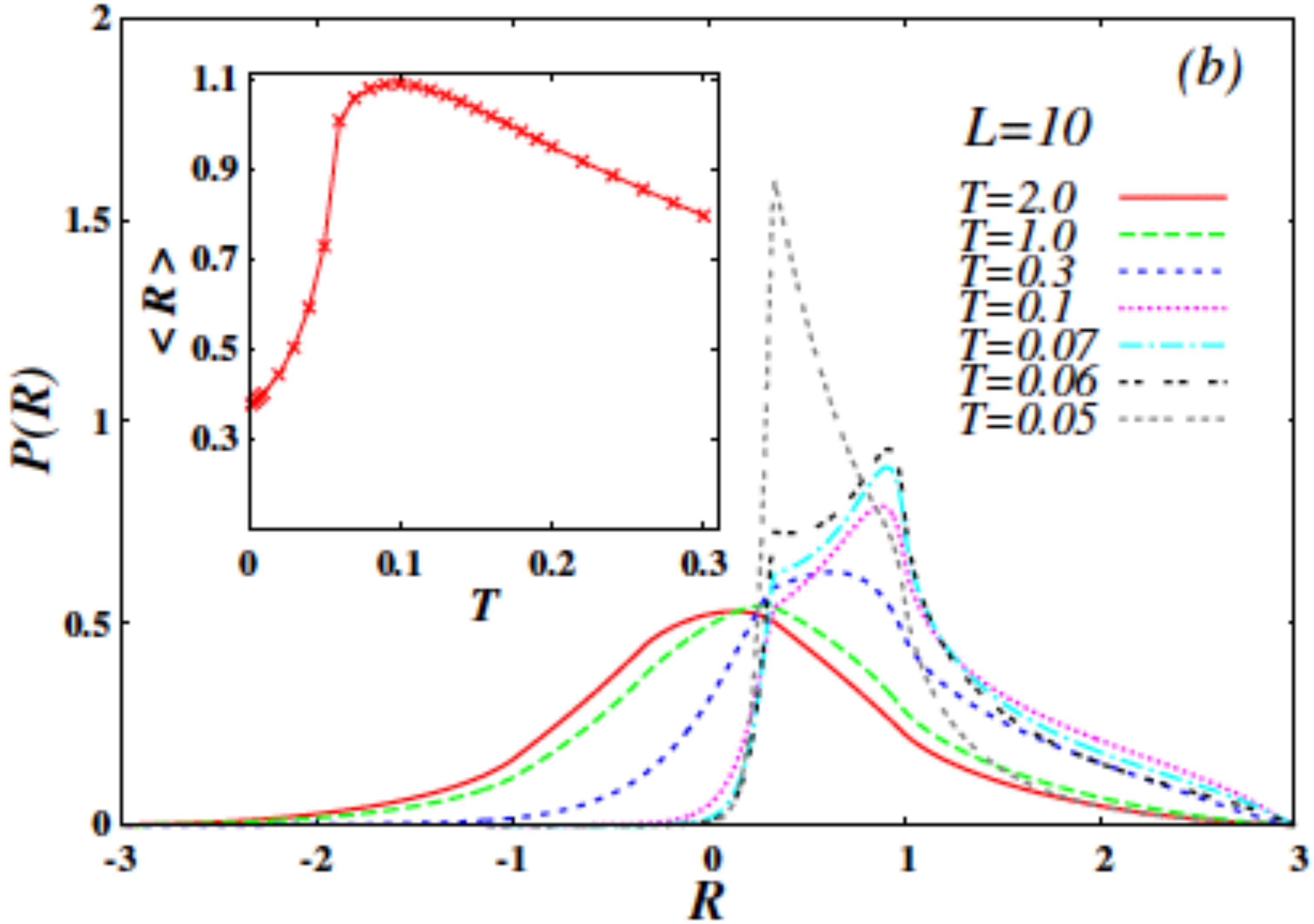
- Probability density of the AIAO order parameter in a tetrahedron

$$m_n = \sum_{a=1}^{4} \mathbf{S}^a \cdot \mathbf{d}^a$$

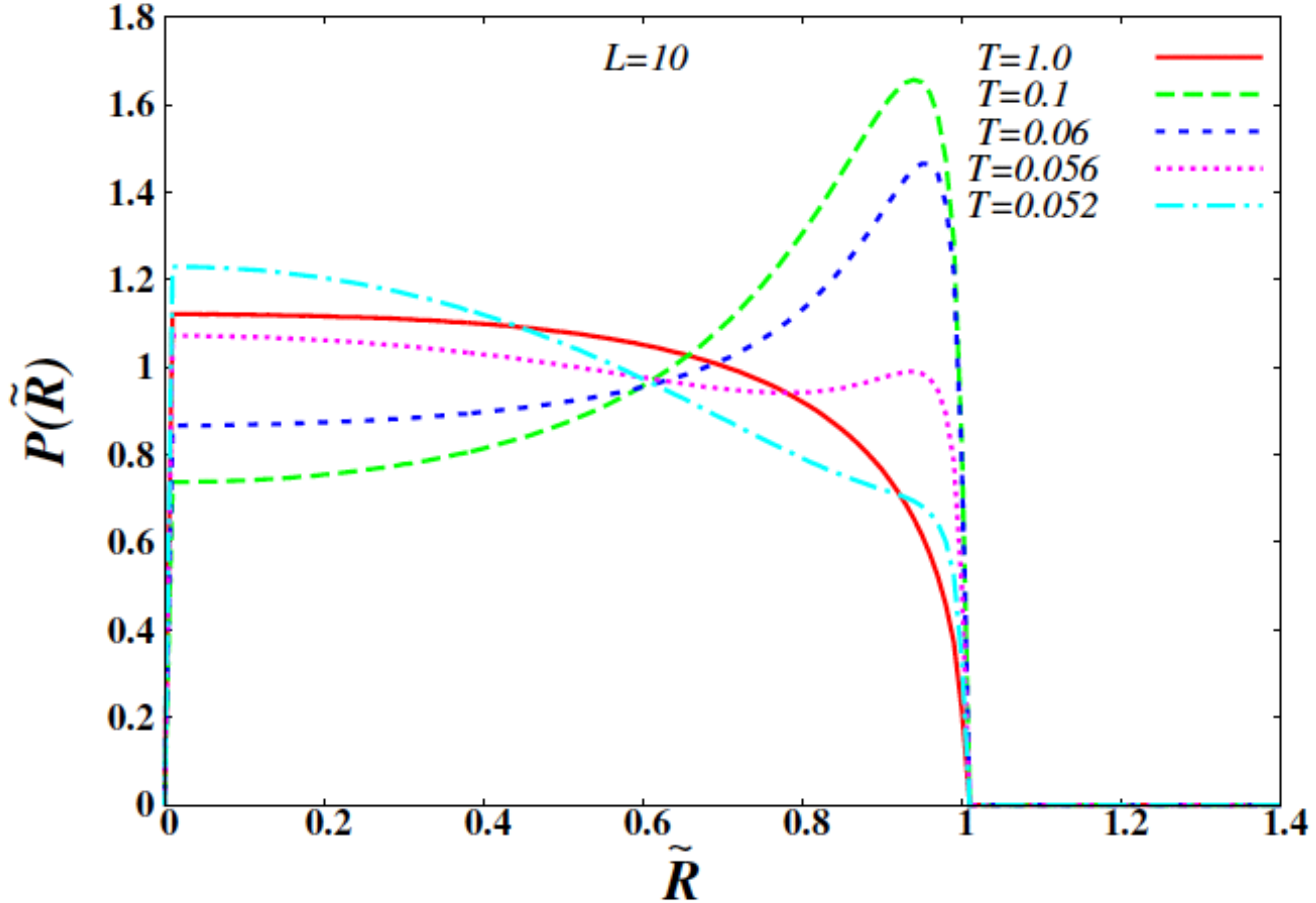


- Probability density of Four-spin correlation

$$R = \langle (\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_3 \cdot \mathbf{S}_4) + (\mathbf{S}_1 \cdot \mathbf{S}_3)(\mathbf{S}_2 \cdot \mathbf{S}_4) + (\mathbf{S}_1 \cdot \mathbf{S}_4)(\mathbf{S}_2 \cdot \mathbf{S}_3) \rangle$$



$$\tilde{R} \equiv |(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_3 \cdot \mathbf{S}_4) - (\mathbf{S}_1 \cdot \mathbf{S}_3)(\mathbf{S}_2 \cdot \mathbf{S}_4) + (\mathbf{S}_1 \cdot \mathbf{S}_4)(\mathbf{S}_2 \cdot \mathbf{S}_3)|$$

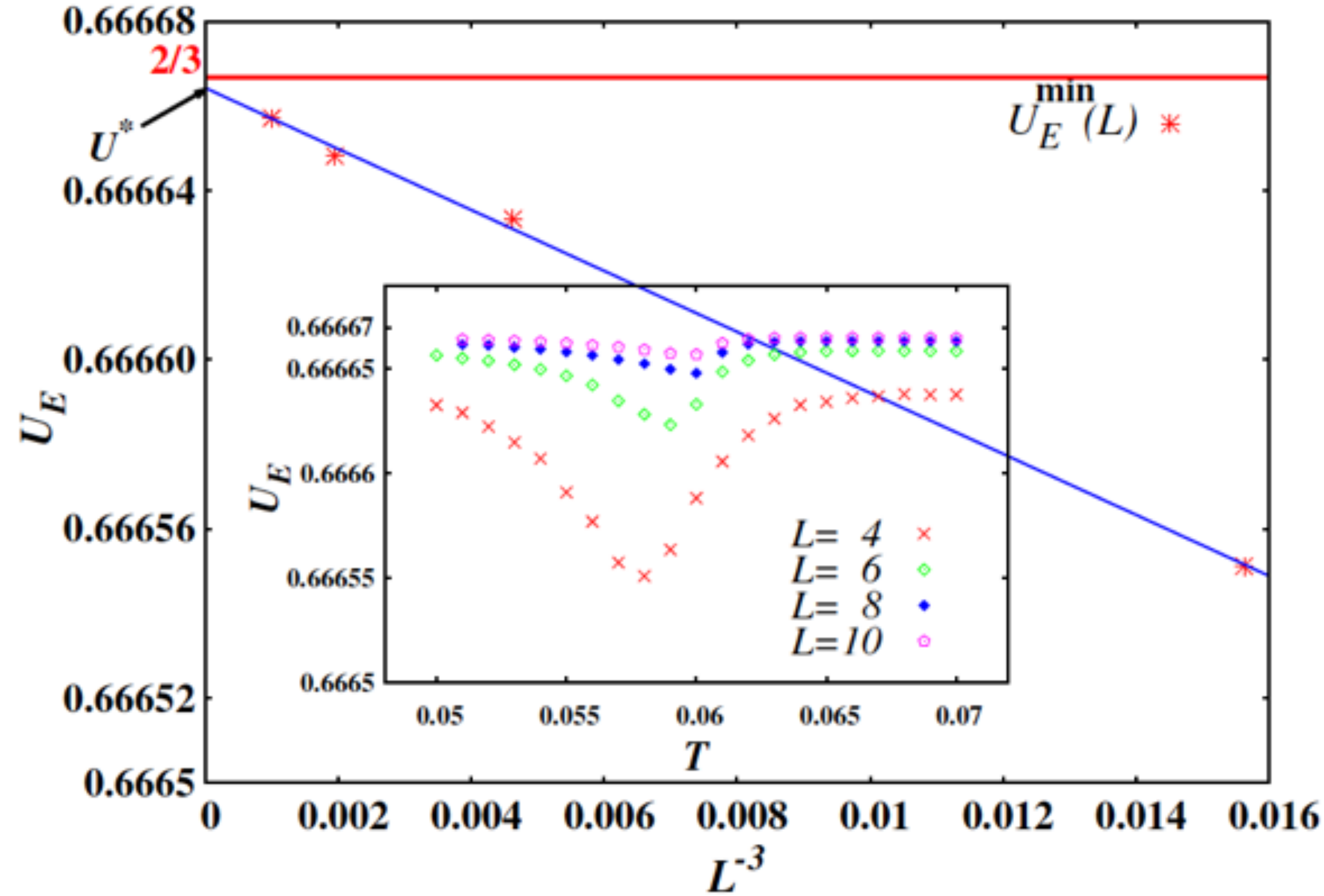


Binder Forth energy cumulant

D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics* (Cambridge University Press, Cambridge, 2000)

$$U_E(T) \equiv 1 - \frac{1}{3}\frac{\langle E^4 \rangle}{\langle E^2 \rangle^2}$$

$$U_E^{\min}(L) = U^* + AL^{-d} + \mathcal{O}(L^{-2d})$$



Proof of coplanarity above transition temperature

$$R = \frac{1}{2}\left[1 - 2\sin^2\phi\cos\theta + (3 + \cos^2\phi)\cos^2\theta + \cos^2\phi\right]$$

$$\tilde{R} = |1 - \sin^2\theta(1 + \cos\phi)|$$

$$R = \tilde{R} = 1 \Rightarrow \begin{cases} \phi = 0, \pi; \theta = \pi/2 \\ \phi = \pi/2; \theta = 0 \end{cases}$$

Irreducible representations of tetrahedron group

N. Shannon, K. Penc, and Y. Motome, Phys. Rev. B 81, 184409 (2010)

$$\Lambda_{\mathbf{E},1} \equiv \frac{1}{\sqrt{3}}\Big[(\mathbf{S}_1 \cdot \mathbf{S}_2) - \frac{1}{2}(\mathbf{S}_1 \cdot \mathbf{S}_3) - \frac{1}{2}(\mathbf{S}_1 \cdot \mathbf{S}_4) - \frac{1}{2}(\mathbf{S}_2 \cdot \mathbf{S}_3) - \frac{1}{2}(\mathbf{S}_2 \cdot \mathbf{S}_4) + (\mathbf{S}_3 \cdot \mathbf{S}_4)\Big]$$

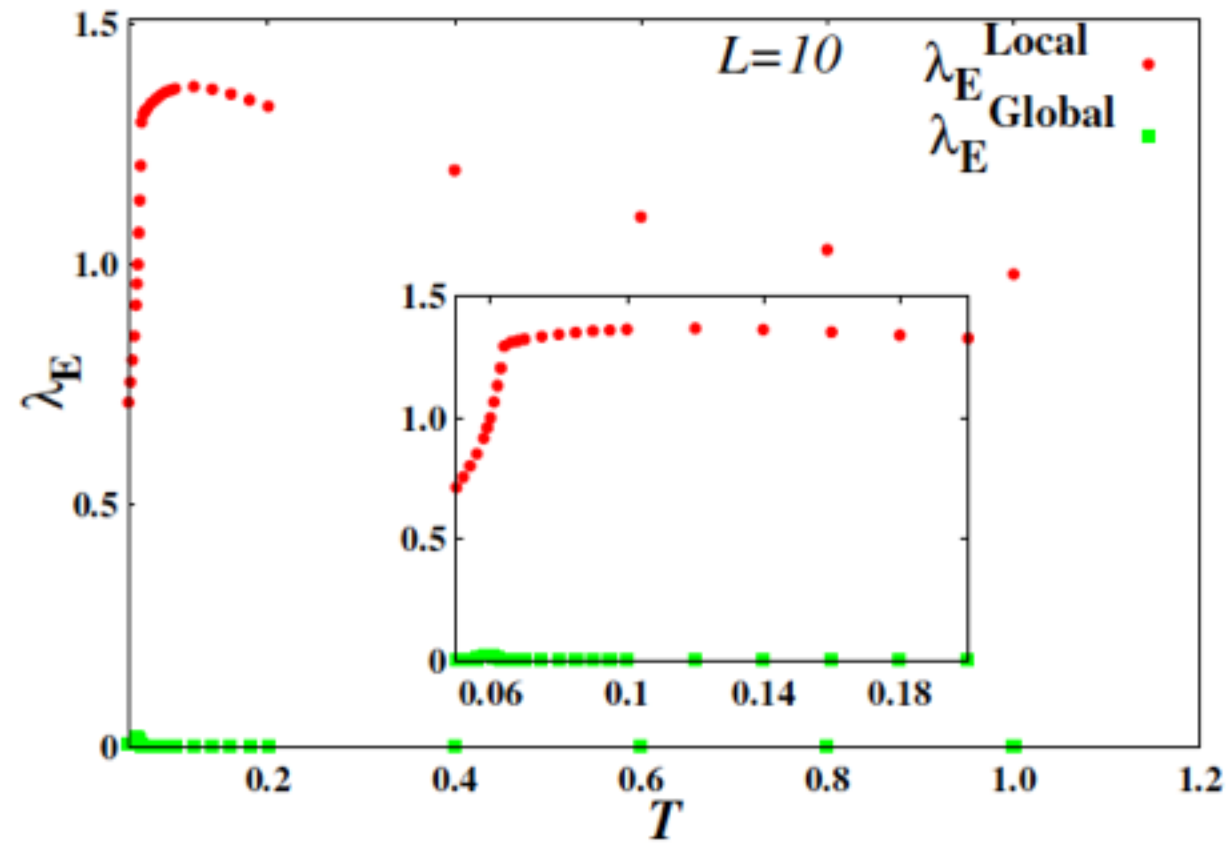
$$\Lambda_{\mathbf{E},2} \equiv \frac{1}{2}\Big[(\mathbf{S}_1 \cdot \mathbf{S}_3) - (\mathbf{S}_1 \cdot \mathbf{S}_4) - (\mathbf{S}_2 \cdot \mathbf{S}_3) + (\mathbf{S}_2 \cdot \mathbf{S}_4)\Big]$$

$$\lambda_{\mathbf{E}}^{\mathbf{Global}} = \frac{4}{N}\left[\Big(\sum_{\text{tetra}} \Lambda_{\mathbf{E},1}\Big)^2 + \Big(\sum_{\text{tetra}} \Lambda_{\mathbf{E},2}\Big)^2\right]$$

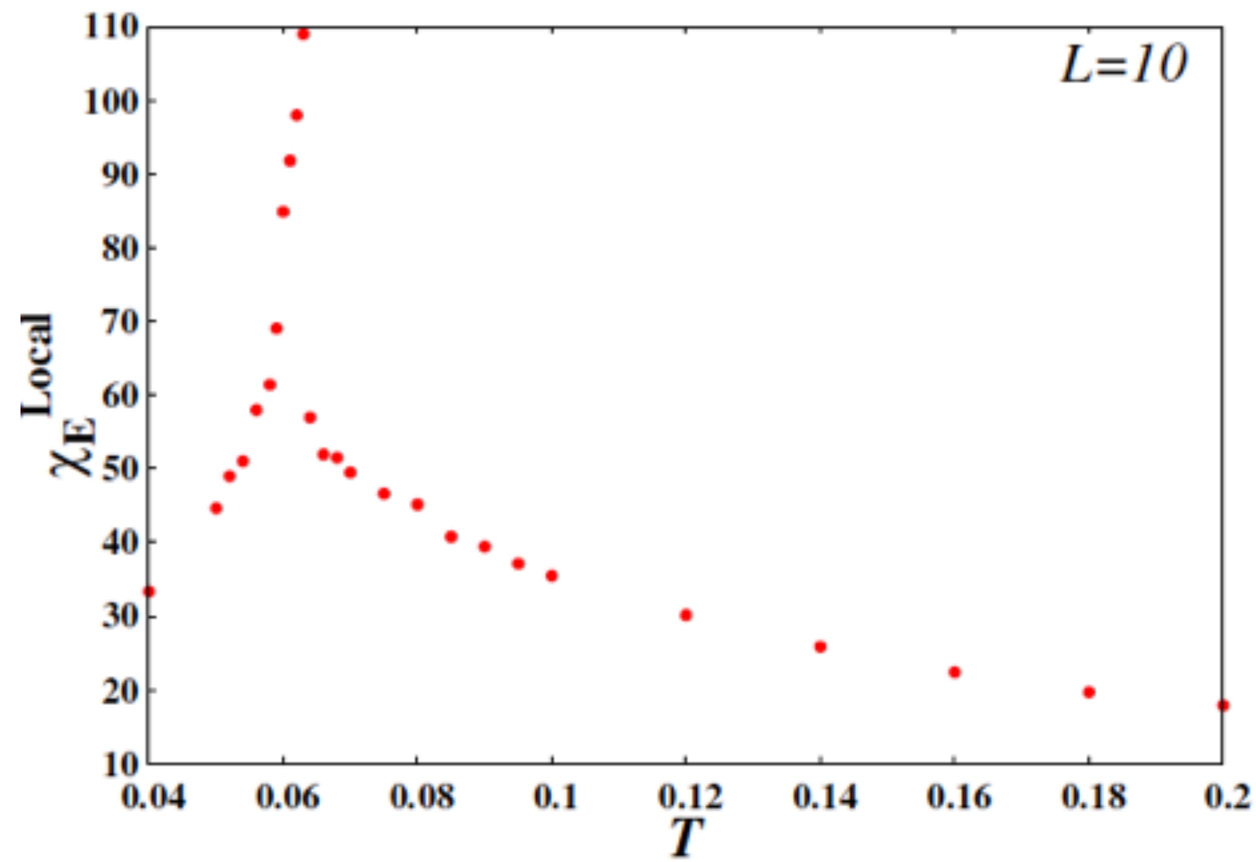
$$\lambda_{\mathbf{E}}^{\mathbf{Local}} = \frac{4}{N}\left[\sum_{\text{tetra}} \left(\Lambda_{\mathbf{E},1}^2 + \Lambda_{\mathbf{E},2}^2\right)\right]$$

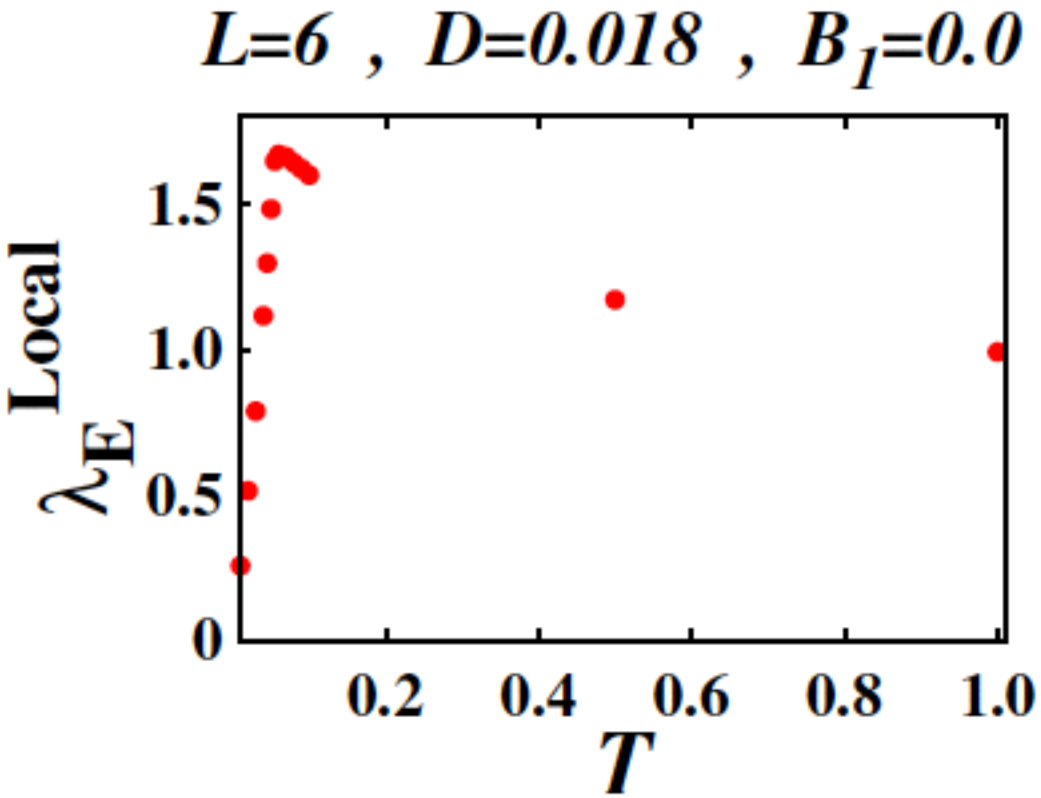
$$\lambda_{\mathbf{E}}^{\mathbf{Global}} = \frac{4}{N}\left[\Big(\sum_{\text{tetra}} \Lambda_{\mathbf{E},1}\Big)^2 + \Big(\sum_{\text{tetra}} \Lambda_{\mathbf{E},2}\Big)^2\right]$$

$$\lambda_{\mathbf{E}}^{\mathbf{Local}} = \frac{4}{N}\left[\sum_{\text{tetra}} \left(\Lambda_{\mathbf{E},1}^2 + \Lambda_{\mathbf{E},2}^2\right)\right]$$

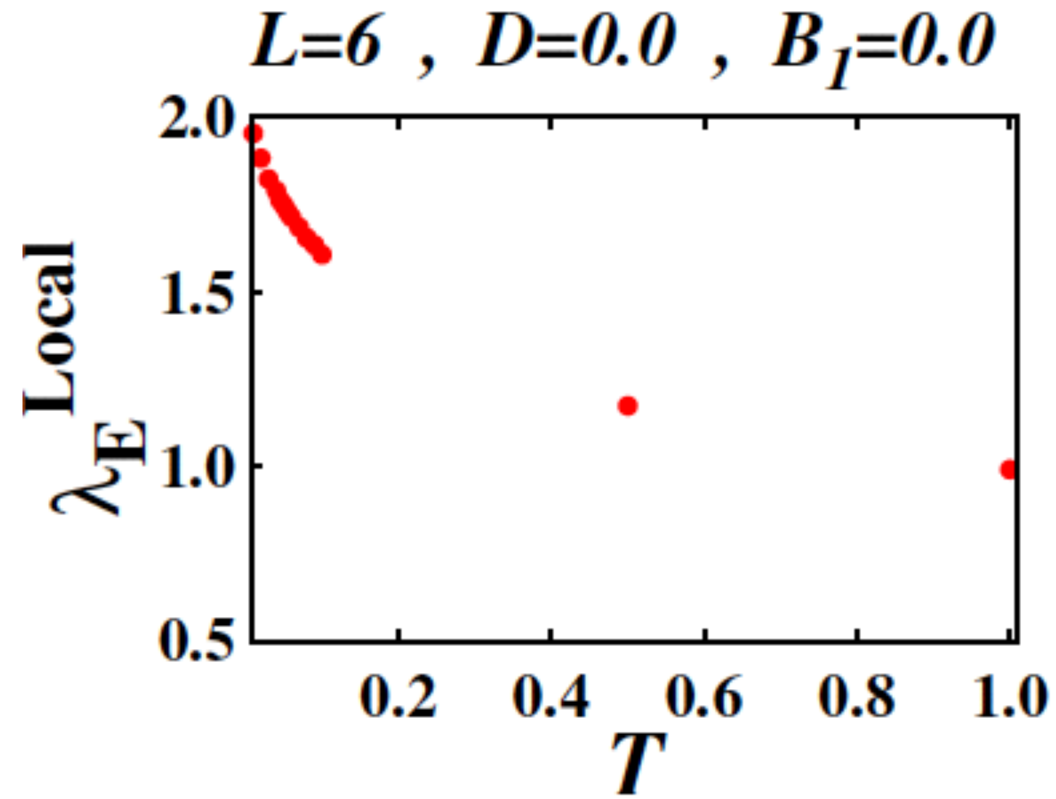


$$\chi_{\mathbf{E}}^{\mathbf{Local}} = \frac{N}{T}\left[\langle(\lambda_{\mathbf{E}}^{\mathbf{Local}})^2\rangle - \langle\lambda_{\mathbf{E}}^{\mathbf{Local}}\rangle^2\right]$$

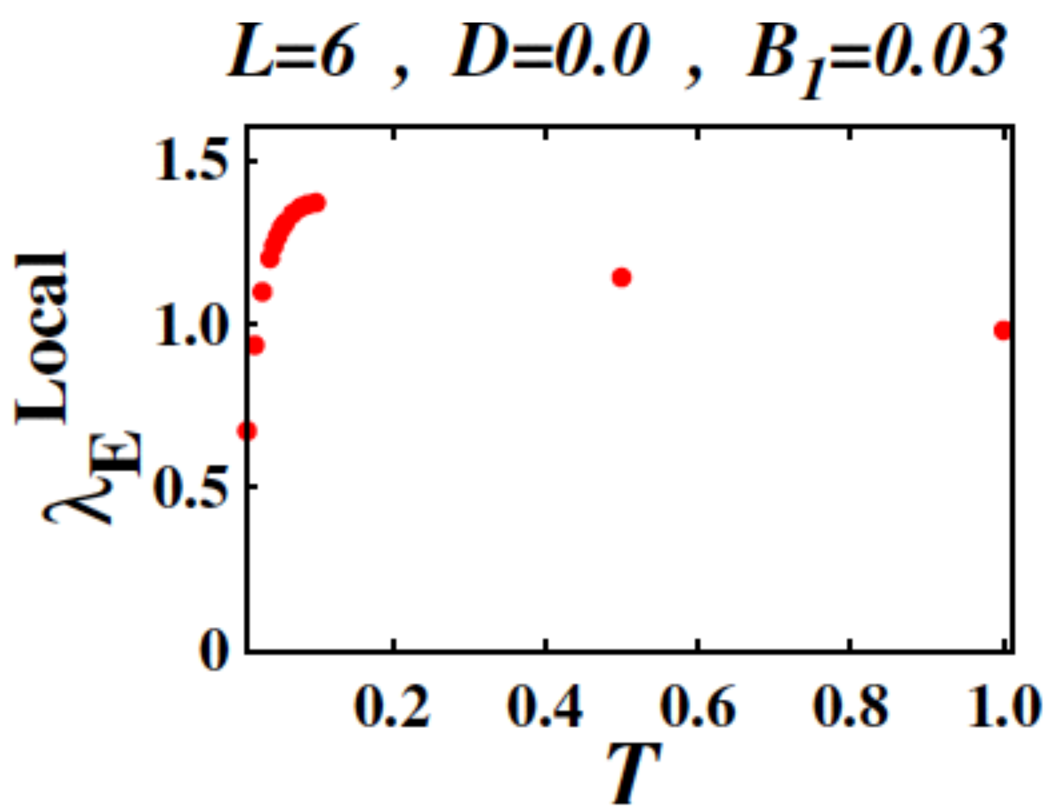




L=6 , D=0.018 , B1=0.0
λE Local
T
0
0.5
1.0
1.5
0.2
0.4
0.6
0.8
1.0



L=6 , D=0.0 , B1=0.0
λE Local
T
0.5
1.0
1.5
2.0
0.2
0.4
0.6
0.8
1.0



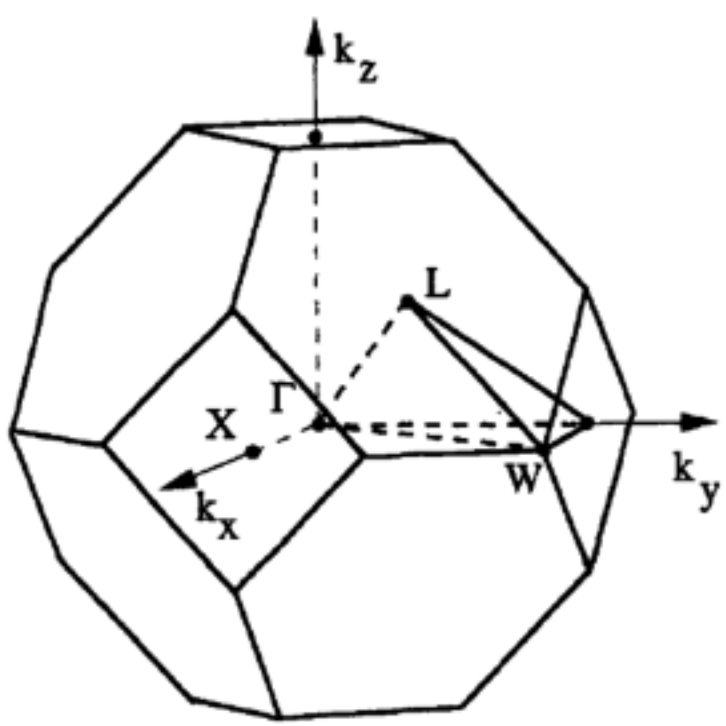
L=6 , D=0.0 , B1=0.03
λE Local
T
0
0.5
1.0
1.5
0.2
0.4
0.6
0.8
1.0

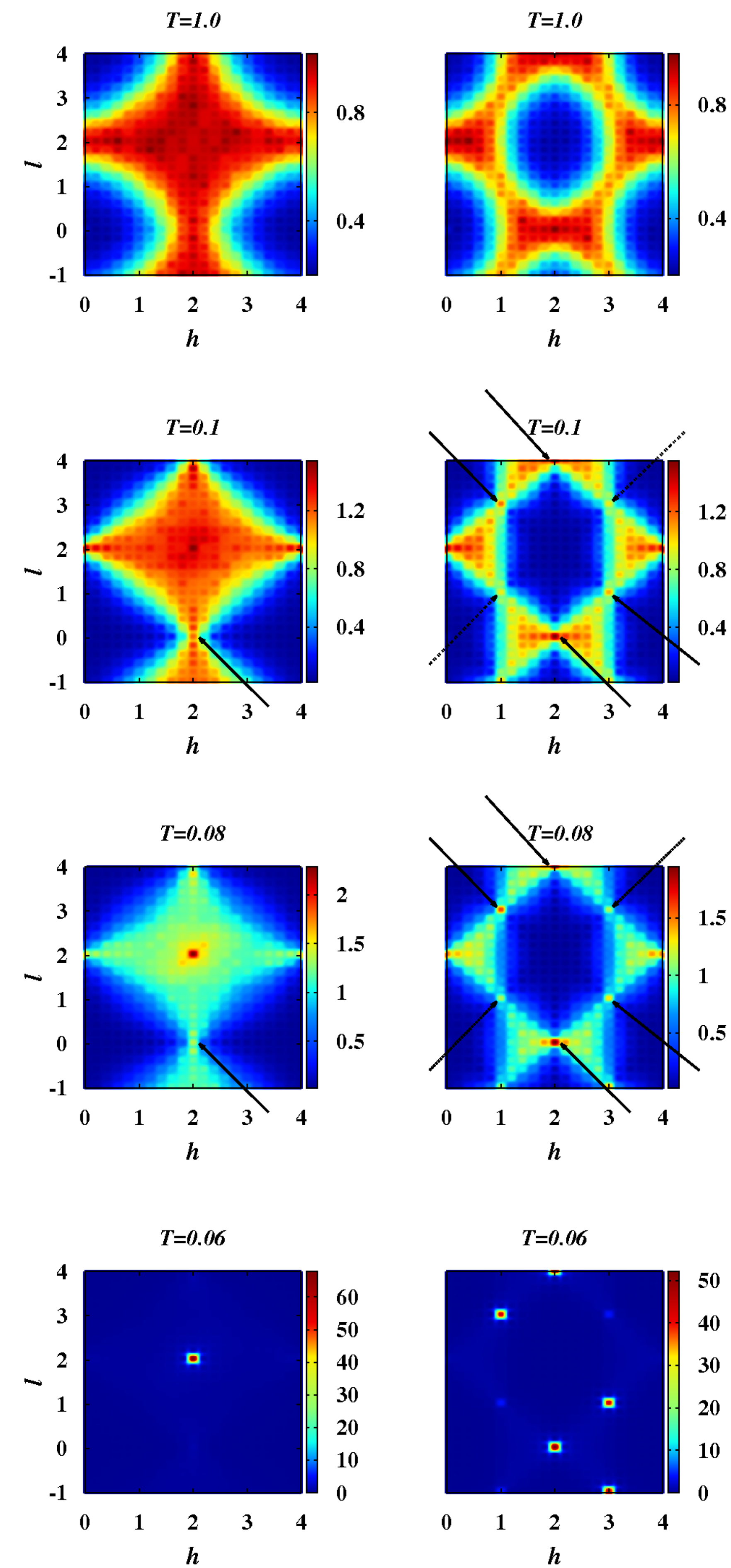
Neutron Structure Function

$$f(q) = \langle |\mathbf{S}^{\perp}(\mathbf{q})|^2 \rangle$$

$$\mathbf{S}^{\perp}(\mathbf{q}) = \mathbf{S} - \mathbf{S}\cdot\mathbf{q}/\mathbf{q^2}$$

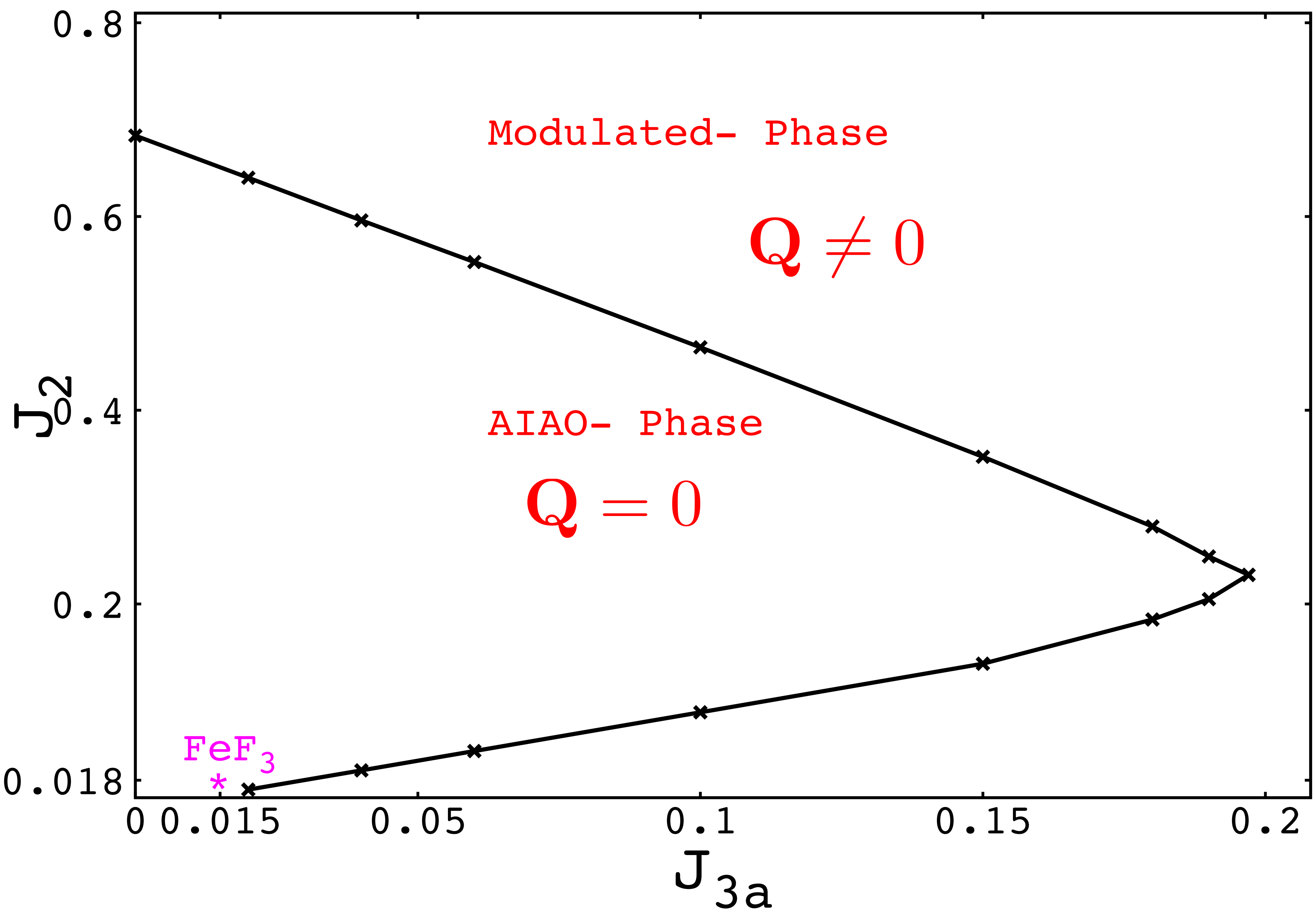
$$S(\mathbf{q}) = \sum_{\mathbf{r}_i} \mathbf{S}_i \exp(i\mathbf{q}\cdot\mathbf{r}_i)$$





The effect of second and third neighbor exchange interactions

The mean field phase diagram



Conclusion

- An effective spin Hamiltonian containing nearest neighbour AF Heisenberg, biquadratic and DM interactions, precisely describes the magnetic properties of Pyr-FeF3.

- The transition to from disordered to AIAO is weakly first order.

- Possible tricritical or Lifshitz universality class.

- A coulomb phase comprised of short-range coplanar states is proposed above transition temperature.

Thanks for your attention