Frustration Driven Lattice Distortion in $Y_2Mo_2O_7$

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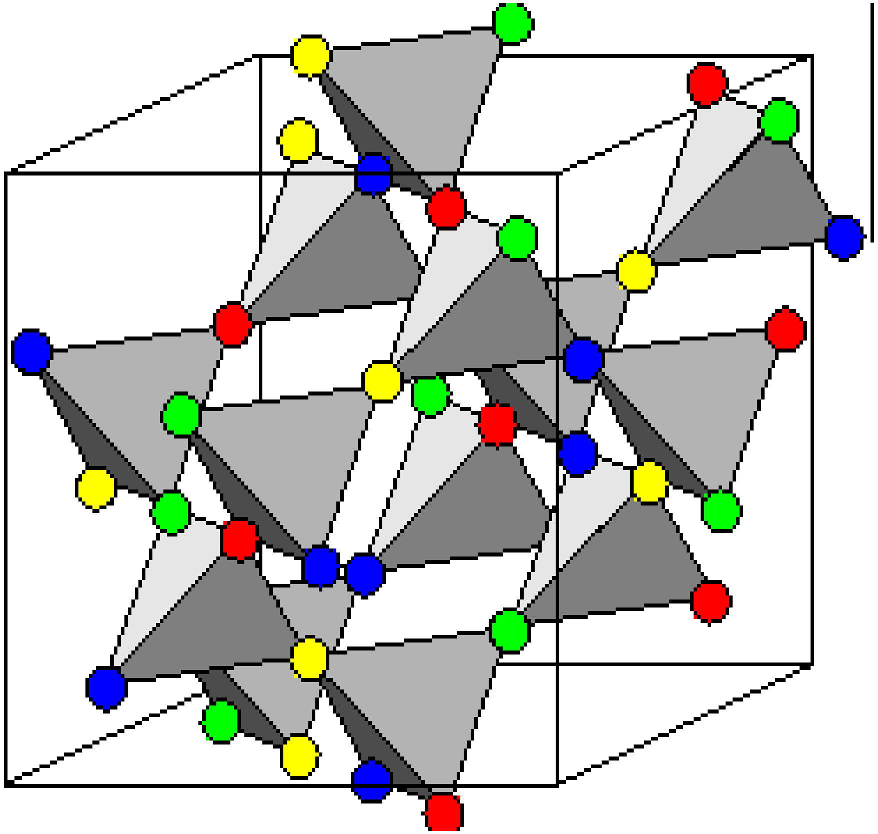
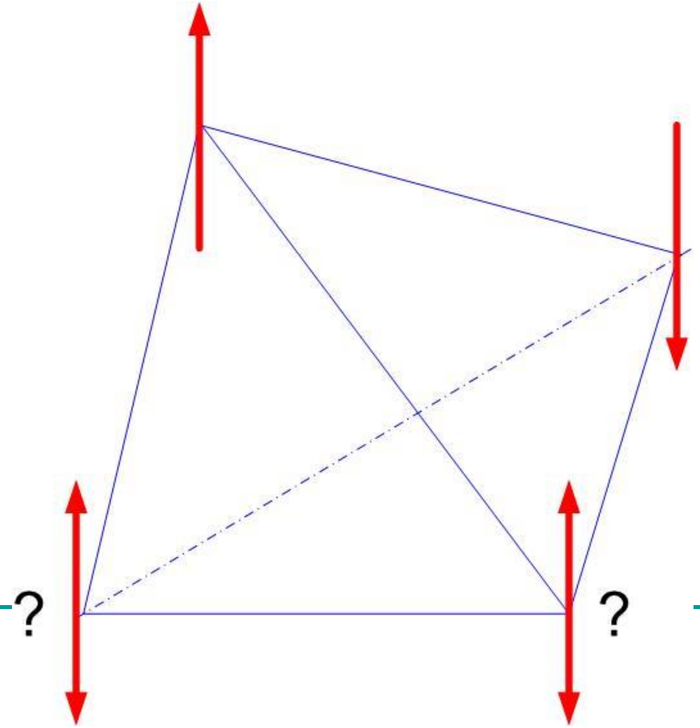
Outline

- What is frustration? Why is it interesting?
- Why $Y_2Mo_2O_7$?
- Experimental results.
- Computer simulations-no temperature.
- Computer simulations-crystal "melting".
- Conclusions.

Geometrical Frustration

- AF Hamiltonian and triangular geometry- not all near- neighbor spin interactions can be satisfied: FRUSTRATION.



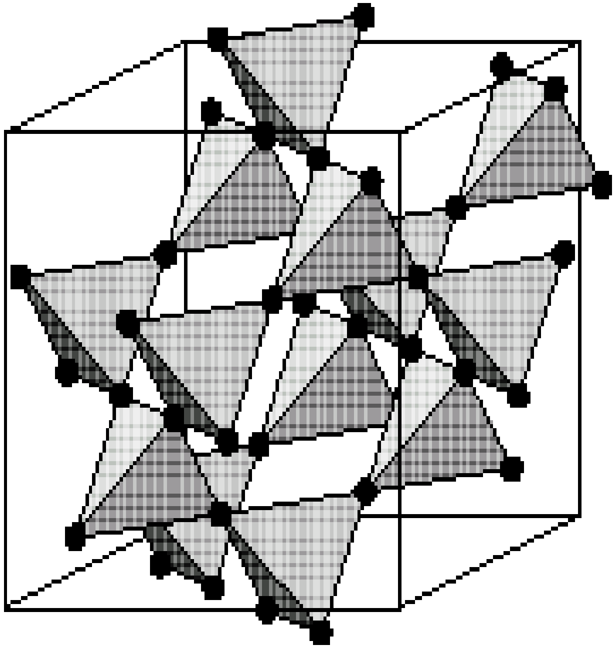


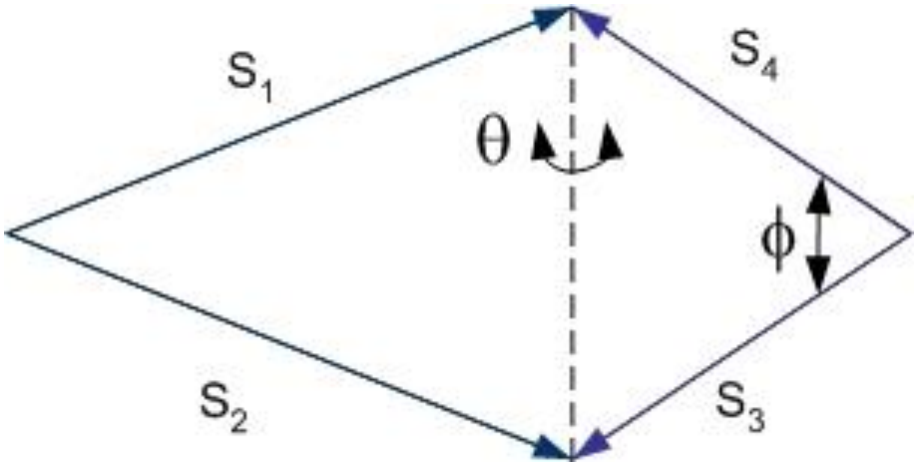
$$H = \sum_{i,j} J_{ij} S_i \cdot S_j$$

The Heisenberg Hamiltonian

$$H=\sum_{i,j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j=\frac{J}{2}\sum_{\nabla}\left(\sum_{i\in\nabla}\mathbf{S}_i\right)^2-\frac{J}{2}\sum_{\nabla}\sum_{i}(\mathbf{S}_i)^2.$$

- The only requirement for minimum of energy: $\sum_{i\in\nabla}\mathbf{S}_i=0.$
- The frustration is “shared” among bonds.





Heisenberg Hamiltonian on the Pyrochlore Lattice

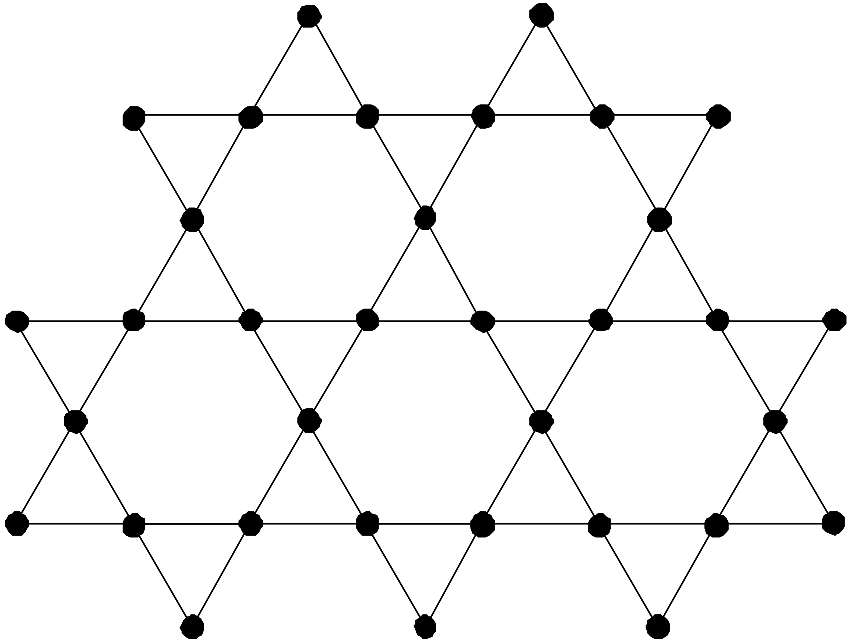
- Infinite set of mean field ground states with zero net spin on all tetrahedra.
- Each tetrahedron has an independent degree of freedom in the ground state!
- No barriers between mean field ground states.
- Infinite degeneracy, no single ground state can be selected by Heisenberg Hamiltonian- lower-order terms become significant.

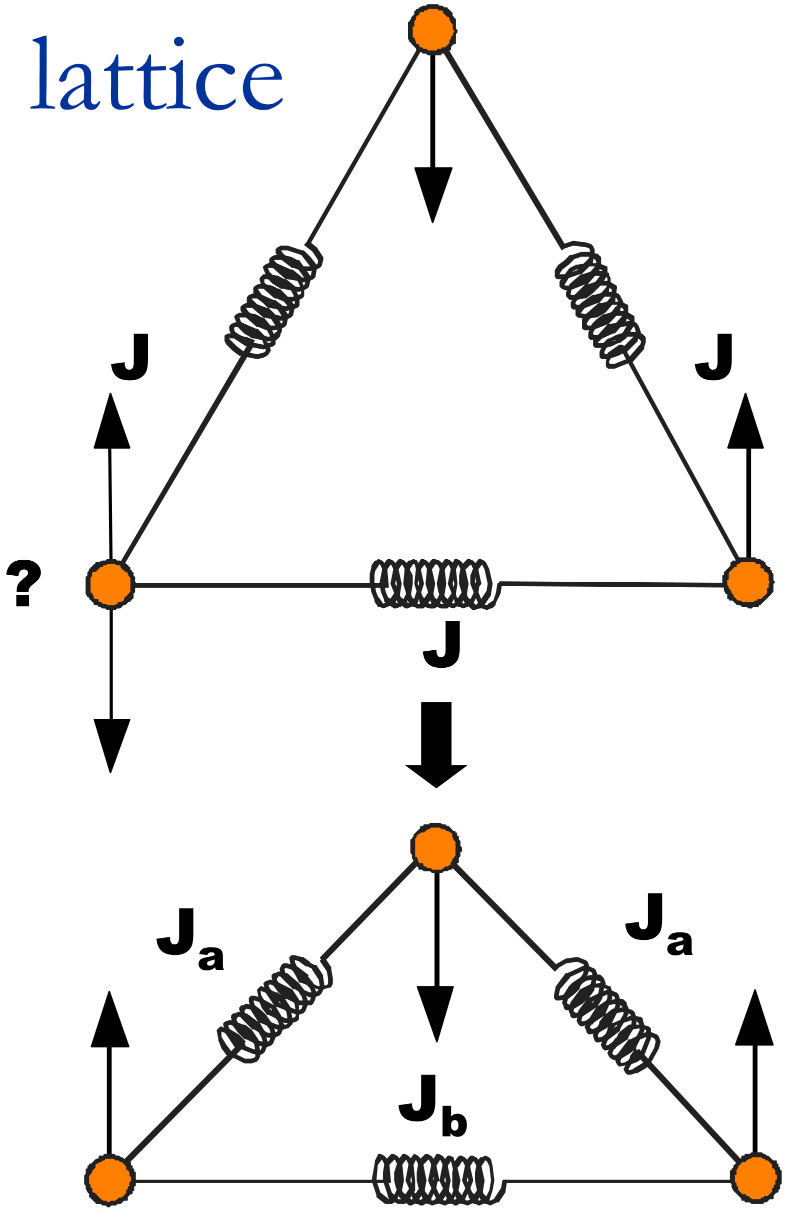
Is Exchange *Constant* ?

$$\mathrm{H} = \sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$$

- ❑ J_{ij} is controlled by higher energy physics that we like to consider irrelevant at low energies.
  - Atomic spacing
  - Orbital overlap
  - Orbital occupancy
  - Localized or itinerant electronic states
- ❑ These degrees of freedom can become relevant if H produces "degenerate" state.
- ❑ The lattice might distort, changing the value of the exchange, if the cost in elastic energy is smaller than the gain in magnetic energy.

Example- the kagome lattice





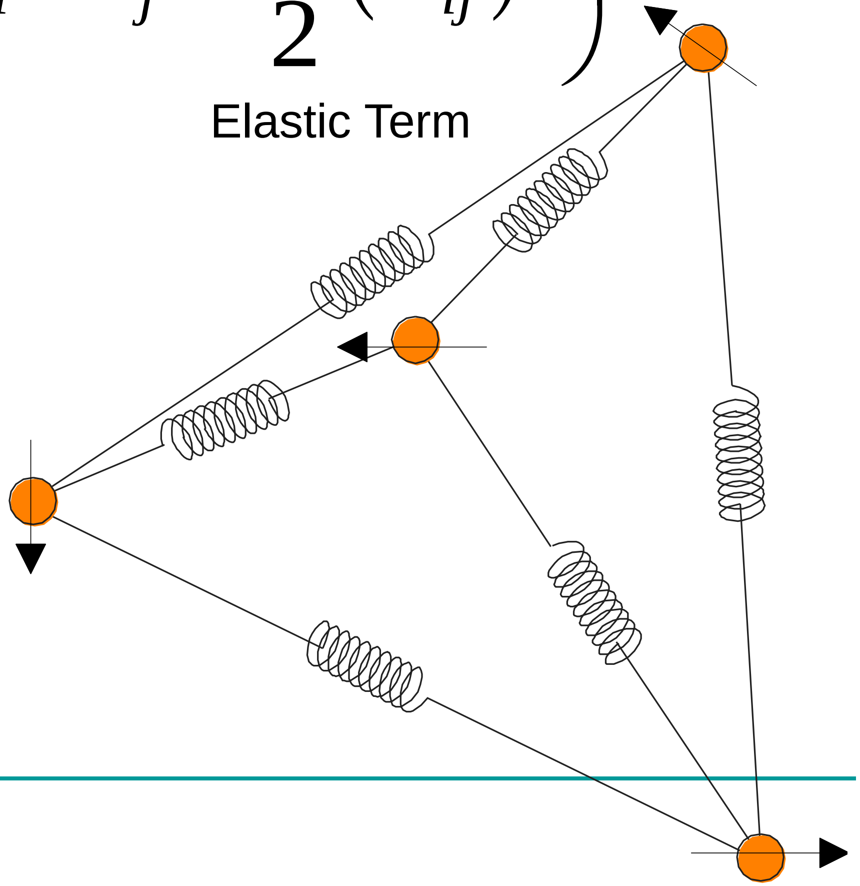
Suggestion for Relief of Degeneracy-Magnetoelastic Distortion

$$H = \sum_{i,j} \left(\left(J + J' \delta r_{ij} \right) S_i \cdot S_j + \frac{k}{2} \left(\delta r_{ij} \right)^2 \right)$$

Effective Exchange

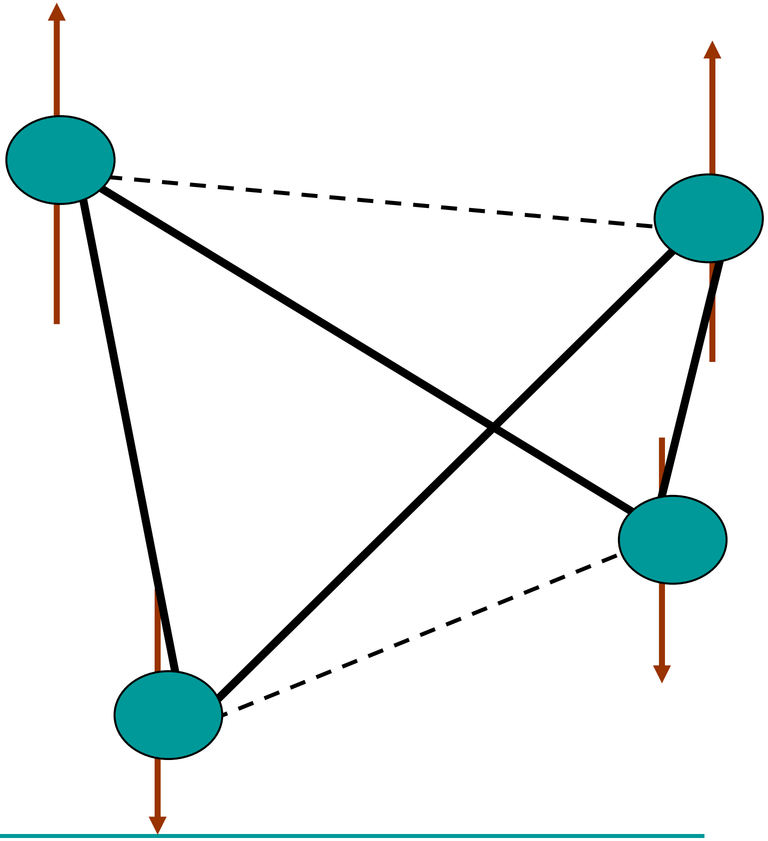
Elastic Term

- k models the electrostatic potential near its minimum.
- J' is the change in the exchange integral with change in interatomic distance.



Theoretical Ground State, T=0

$$H = \sum_{i,j}\left(\left(J + J'\delta r_{ij}\right)S_i \cdot S_j + \frac{k}{2}\left(\delta r_{ij}\right)^2\right)$$

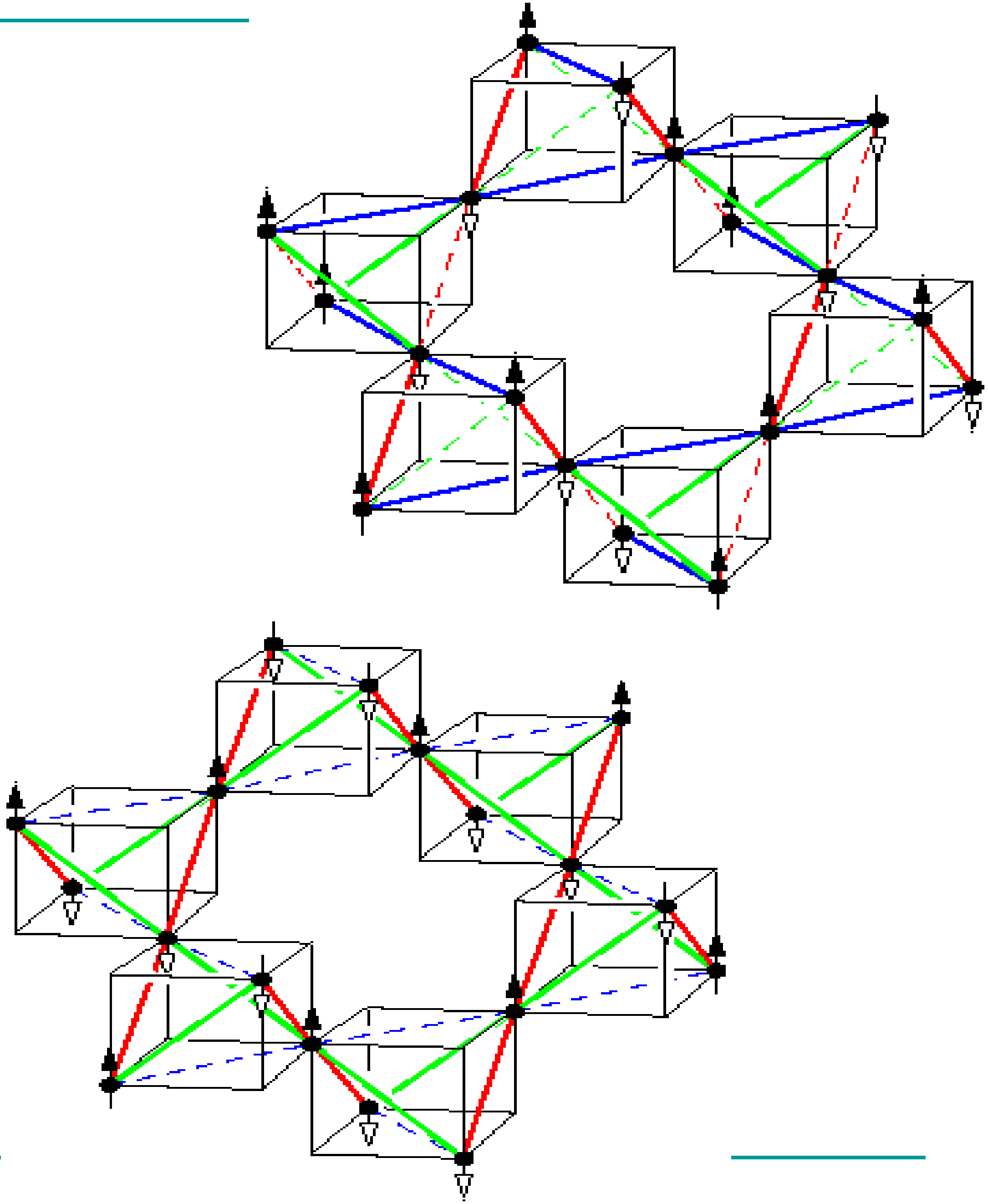


- Find minimal value of normal vibrational coordinates in the presence of magnetoelastic term $J'\delta r_{ij} S_i \cdot S_j$.
- Arrange distorted tetrahedrons on pyrochlore lattice.
- Net zero spin on each tetrahedron.

Tchernyshyov et al., PRB 66 (2002)

The q=0 State

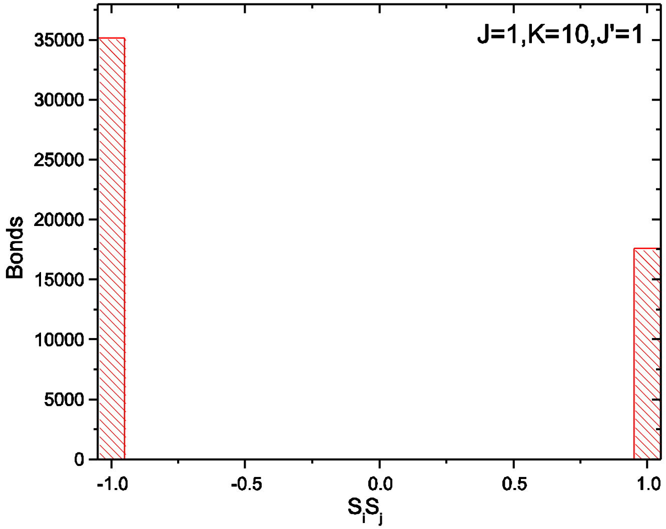
- The minimum energy state for a single tetrahedron can be arranged on the pyrochlore lattice in one of two q=0 configurations.
- The q=0 distortion: tetrahedrons with identical orientation distort the same way.

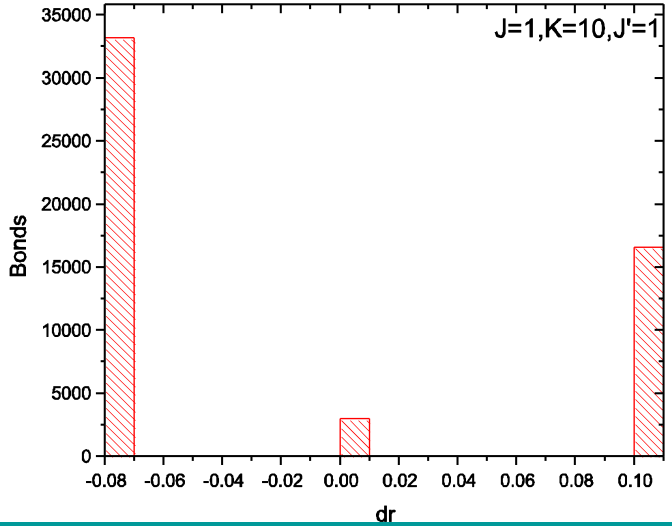


Tchernyshyov et al., PRB 66 (2002)

The q=0 State- Characteristics

- 2/3 strong (shortened) bonds,
- 1/3 weak (lengthened) bonds,
- collinear spins
- 2/3 bonds with antiparallel spins , 1/3 bonds with parallel spins.





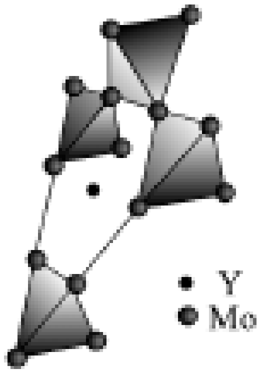
Searching for Frustration Driven Distortion

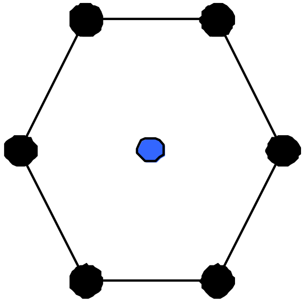
How will the system behave at $T \rightarrow 0$?

Material	spin type	spin value	Θ_{CW} (K)	T_c (K)	Low T phase	Ref.
MgV_2O_4	isotrop.	1	-750	45	LRO	Baltzer et al '66
ZnV_2O_4	isotrop.	1	-600	40	LRO	Ueda et al '97
$CdCr_2O_4$	isotrop.	3/2	-83	9	LRO	Baltzer et al '66
$MgCr_2O_4$	isotrop.	3/2	-350	15	LRO	Blasse and Fast '63
$ZnCr_2O_4$	isotrop.	3/2	-392	12.5	LRO	S.-H. Lee et al '99
FeF_3	isotrop.	5/2	-230	20	LRO	Ferey et al. '86
$Y_2Mo_2O_7$	isotrop.	1	-200	22.5	spin glass	Gingras et al. '97
$Y_2Mn_2O_7$	isotrop.	3/2		17	spin glass	Reimers et al '91
$Tb_2Mo_2O_7$	anisotr.	6 and 1		25	spin glass	Greedan et al '91
$Gd_2Ti_2O_7$	isotrop.	7/2	-10	1	LRO	Radu et al '99
$Er_2Ti_2O_7$	anisotr.		-25	1.25	LRO	Ramirez et al '99
$Tb_2Ti_2O_7$	anisotr.		-19		spin liquid?	Gardner et al '99
$Yb_2Ti_2O_7$	anisotr.		0	0.21	LRO	Ramirez et al '99
$Dy_2Ti_2O_7$	Ising	7.5 → 1/2	0.5	1.2	spin ice	Ramirez et al '99
$Ho_2Ti_2O_7$	Ising	8 → 1/2	1.9		spin ice	Harris et al "97

- We chose $Y_2Mo_2O_7$ as a candidate to look for frustration-driven distortion, since it is a spin glass, and we want to understand the origin of the disorder in this material.

$Y_2Mo_2O_7$ Characteristics

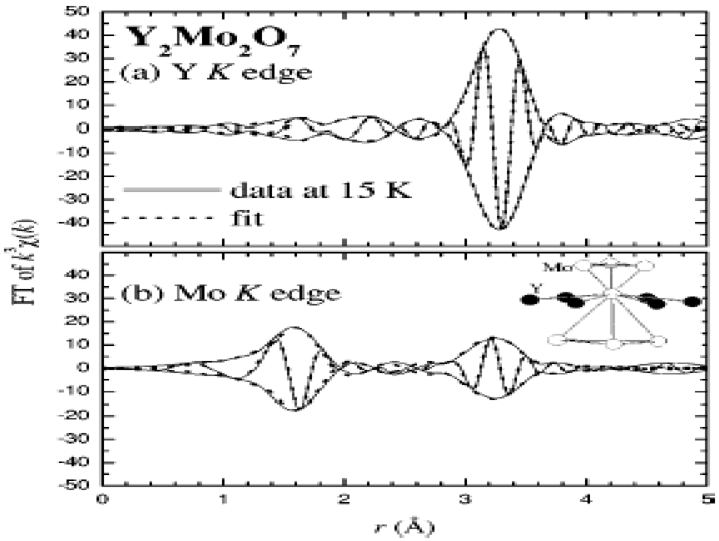


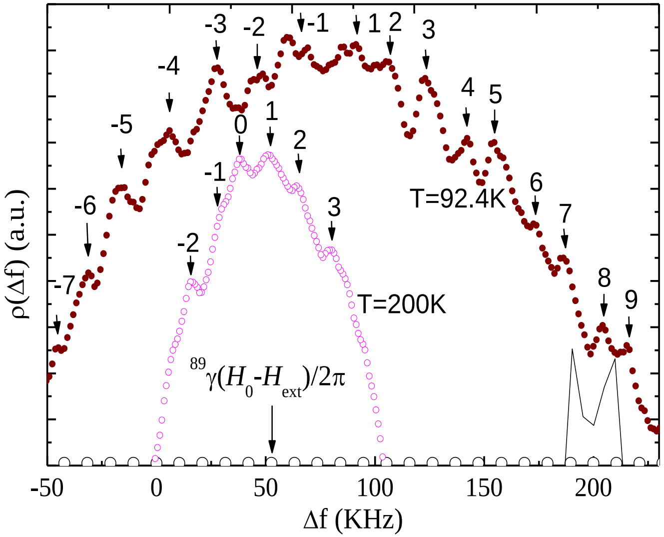


- Cubic pyrochlore $A_2B_2O_7$
- Magnetic ion Mo^{4+}, spin 1
- AF interaction, θ_{CW}=200K, J= $\theta_{CW}/z\sim$33K.
- Spin-Glass transition at 22.5K

Experimental Motivation: $Y_2Mo_2O_7$

- Booth et al.,XAFS: the Mo tetrahedra are in fact disordered from their ideal structure, with a relatively large amount of pair distance disorder, in the Mo-Mo pairs and perpendicular to the Y-Mo pairs (2000).
- Keren & Gardner, NMR: many nonequivalent ^{89}Y sites, possibly stemming from a lattice distortion (2001).



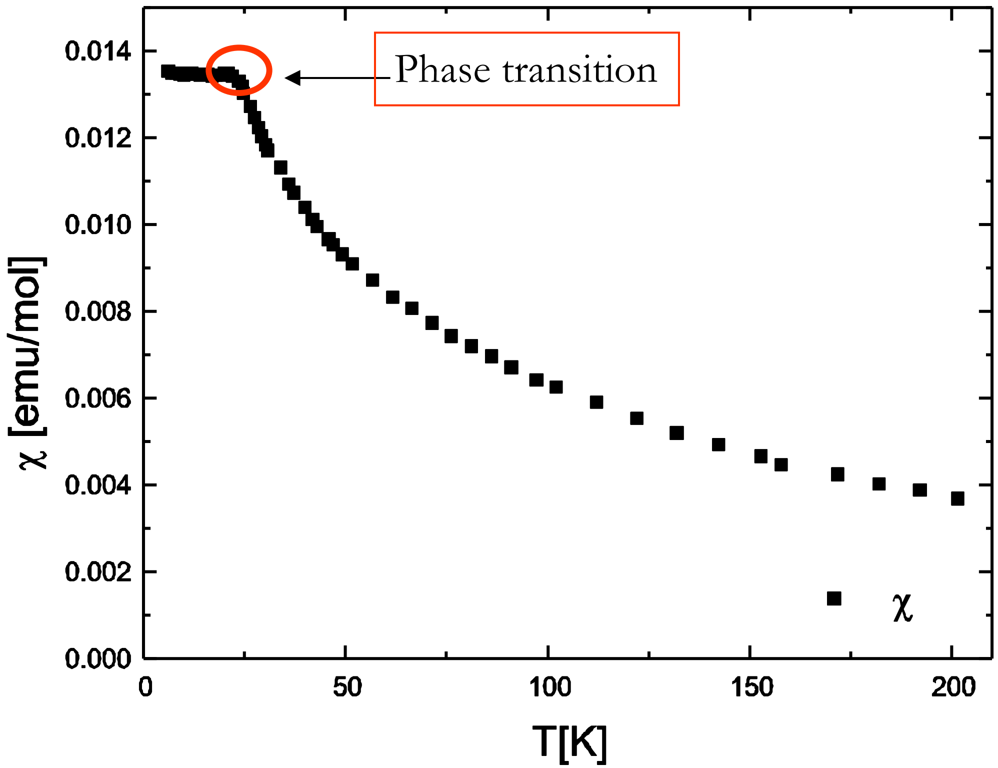


Experimental Data

- DC magnetization.
- μSR.
- High resolution neutron diffraction.

DC magnetization

- Measure sample magnetization with moving sample magnetometer.
- Observe phase transition to spin-glass.

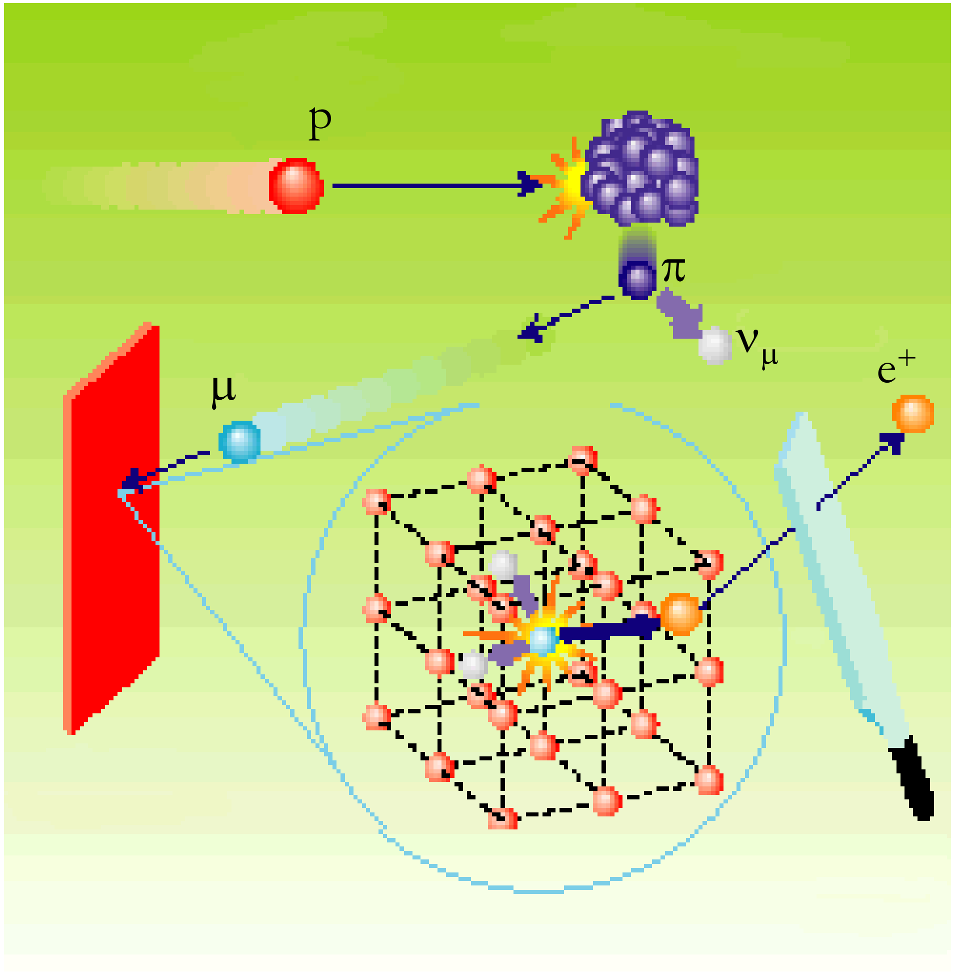


What is μSR?

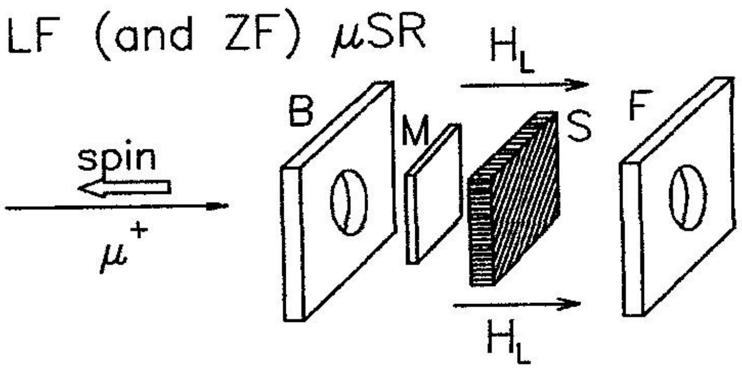
- 100% spin polarized muons.
- Muon life time :

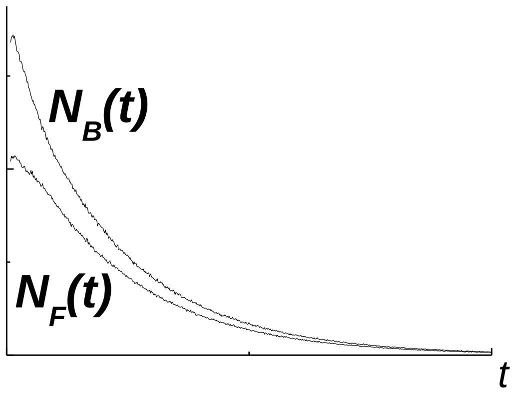
2.2μsec.

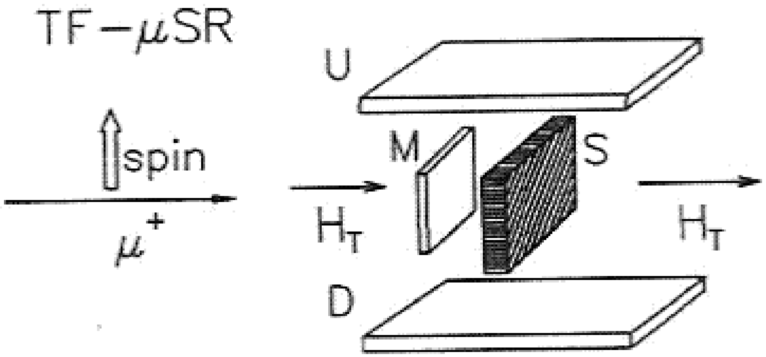
- Positron emitted preferentially in the muon spin direction.
- Collect positrons, obtain distribution of muon spin orientations.

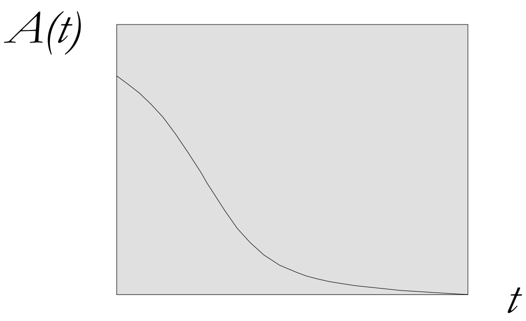


μSR





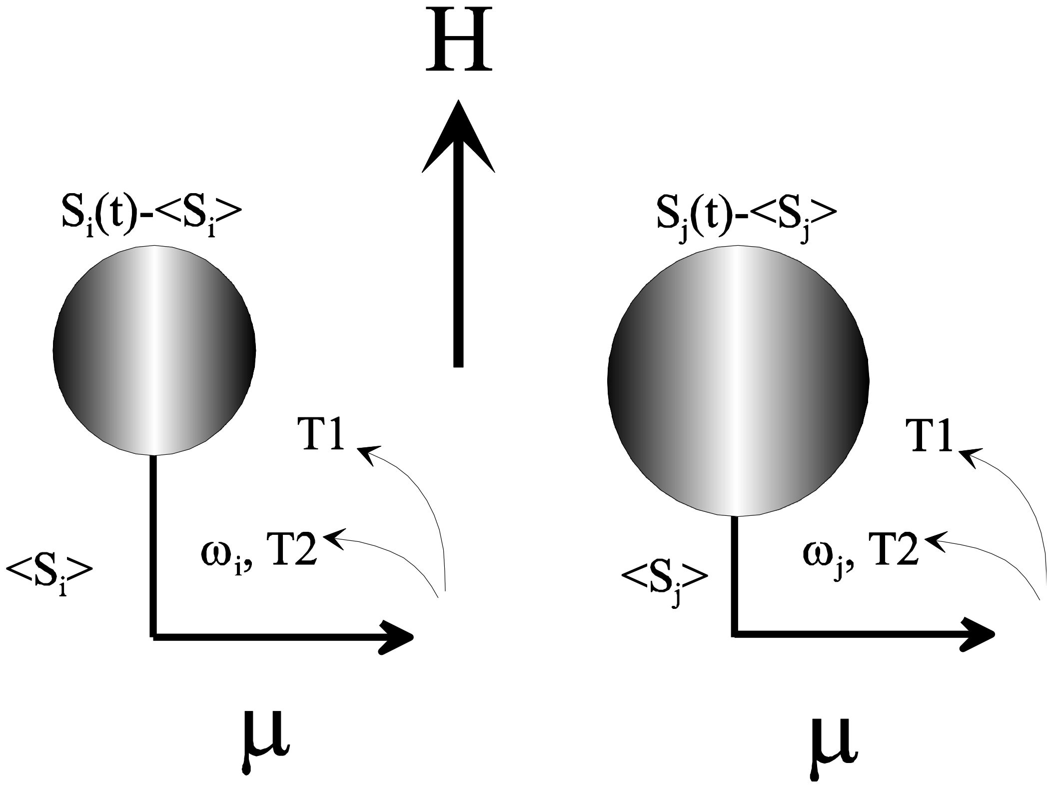




$$N(t) = Bg + N_0 e^{-t/\tau_\mu}\left[1 + A_0 P(t)\right]$$

Muon Relaxation Mechanisms

- Relaxation caused by dynamical field fluctuations, consists of both longitudinal relaxation caused by fluctuations in the xy plane, and dynamical transverse relaxation caused by fluctuations in the z direction.
- Static relaxation,which is reversible. It is caused by field inhomogeneities in the sample ΔB which are responsible for dephasing in the xy plane.



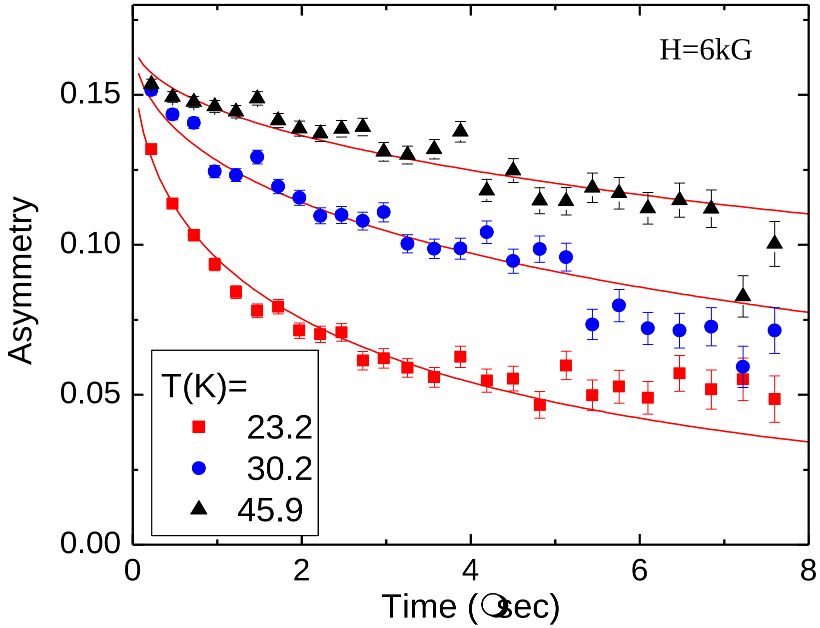
The μSR Experiment

- TF μSR: measure both static and dynamic relaxation.
- LF μSR: measure dynamic relaxation.
- Simultaneous TF and LF measurements, H=6000G, $20^0K<T<240^0K$.

- Subtract LF relaxation from TF relaxation- obtain relaxation from static fields only → compare to magnetization.

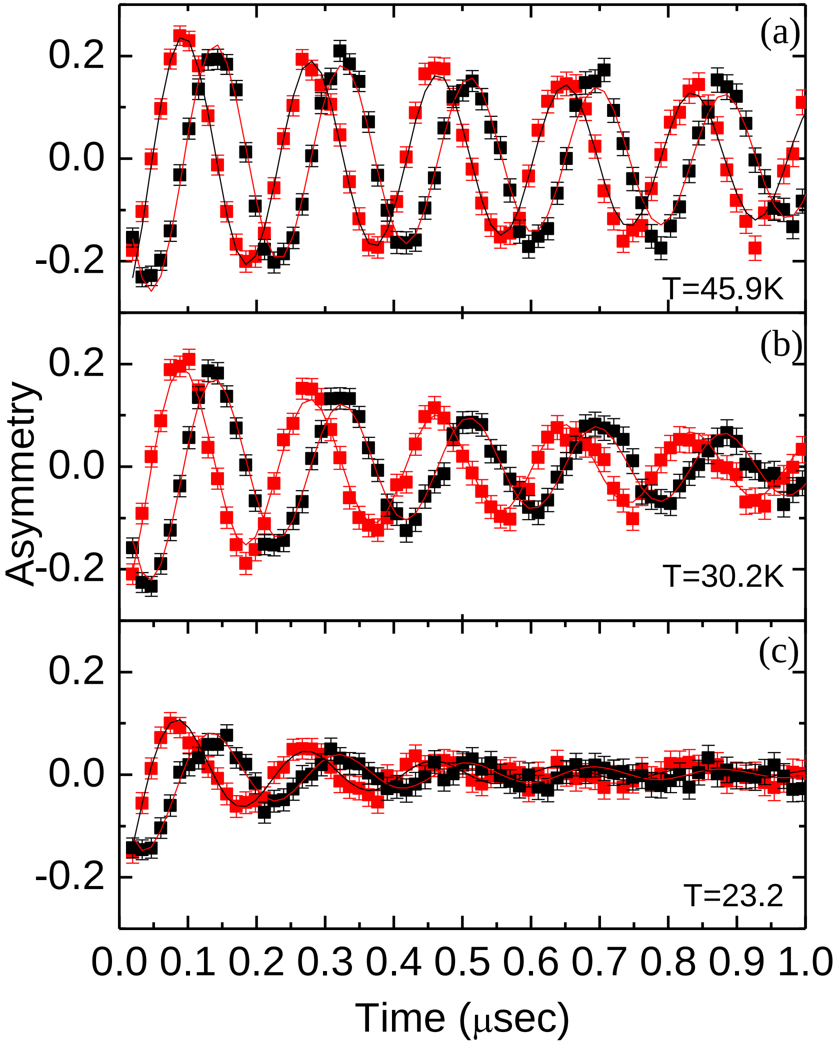
μSR Data

$$A(t) = A_0 \exp\left(-(R_{LF}t)^{1/2}\right) + Bg$$



- Relaxation increases as temperature is decreased.
- TF data displayed in rotating-reference-frame, H=5600G.

$$A(t) = A_0 \exp\left(-(R_{TF}t)^{1/2}\right)\cos(\omega t + \varphi) + Bg$$



μSR Data

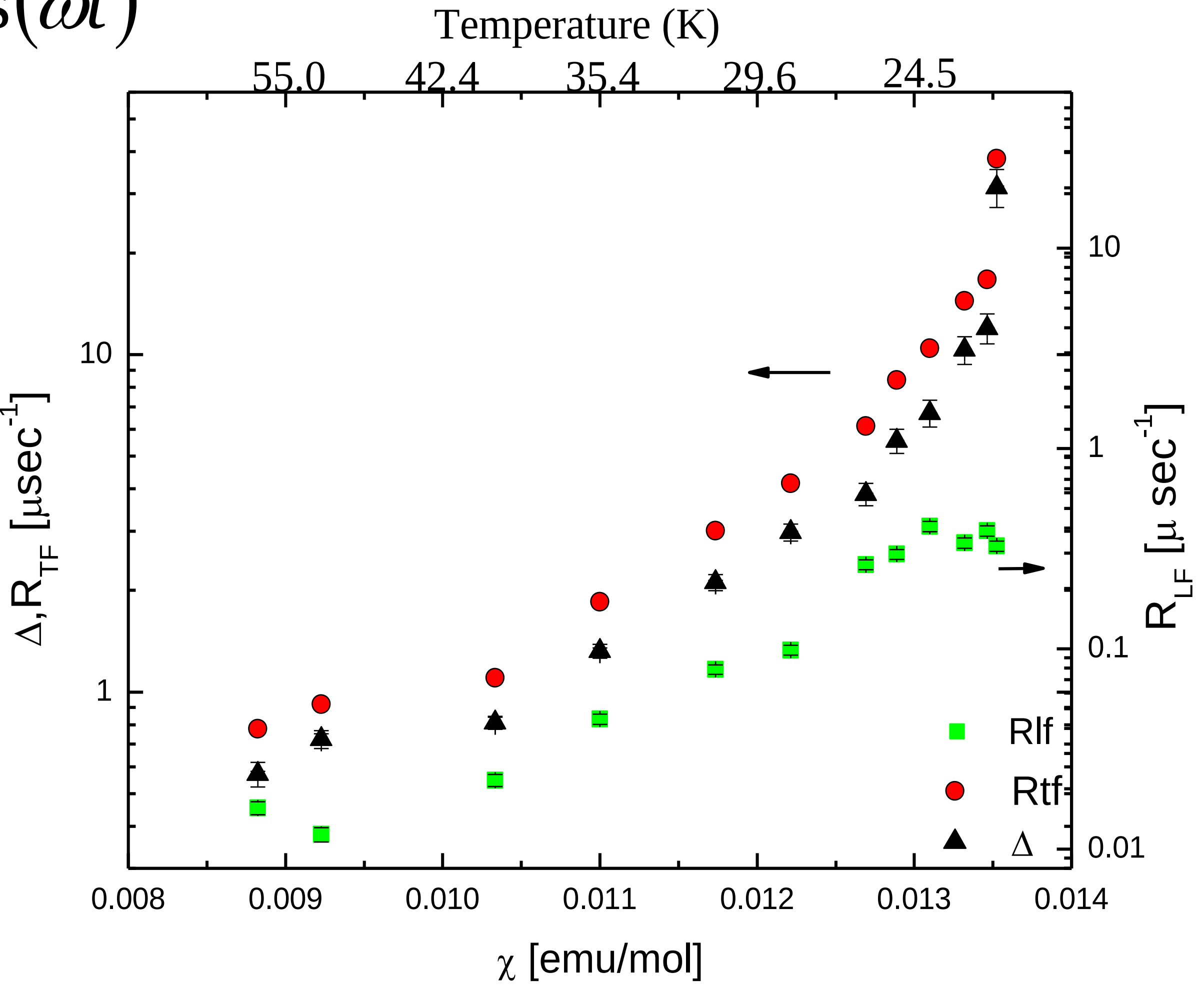
R_{TF} -transverse relaxation rate

R_{LF} -longitudinal relaxation rate

$$P_{static}(t) = P_0 e^{-(\Delta t)^{1/2}} \cos(\omega t)$$

$$\Delta = \left(R_{TF}^{1/2} - R_{LF}^{1/2}\right)^2$$

$$\omega = \gamma_\mu H_{TF}$$



- Δ increases exponentially fast with increasing χ.

What Does it Mean?

- The muon's Hamiltonian: $$\mathrm{H} = \gamma_\mu I \cdot \left(\mathrm{H}_{TF} + \mathrm{H}_{int}\right)$$
- Mean field: $$\mathrm{H}_{int} = A(r)S$$

$$\langle S \rangle = M = \chi \mathrm{H}$$

A - magnetic coupling
I - muon spin
S - electronic spin

- Relaxation function measured by μSR:

$$P(t) = \int P_0 \cos\left[\gamma_\mu (1 + A\chi)\mathrm{H}_{TF}\right]\rho(A)\,dA$$

Evolution of polarization of a single muon

Averaging over different muons

- We want the relation between what we measure in μSR and what happens in matter:

$$P(t) = P_0 e^{-(\Delta t)^{1/2}} \cos(\omega t)$$

$$\rho(A) = \frac{1}{|A|} f\left(\frac{\delta A}{|A|}\right)$$

$$e^{-(\Delta t)^{1/2}} = \int \cos\left(A \chi \gamma_{\mu} \mathrm{H}_{\mathrm{TF}} t\right) \rho(A) dA$$

$$\delta A = \left| \frac{\Delta}{\chi \gamma_{\mu} \mathrm{H}_{\mathrm{TF}}} \right|$$

δA represents the width of the distribution.

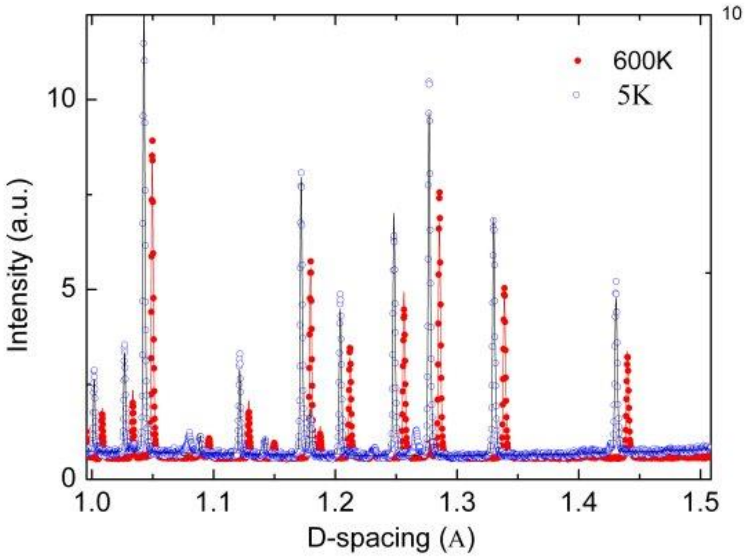
As the temperature is lowered, the ratio $\frac{\Delta}{\chi}$,and therefore δA, grows, and the distribution widens.

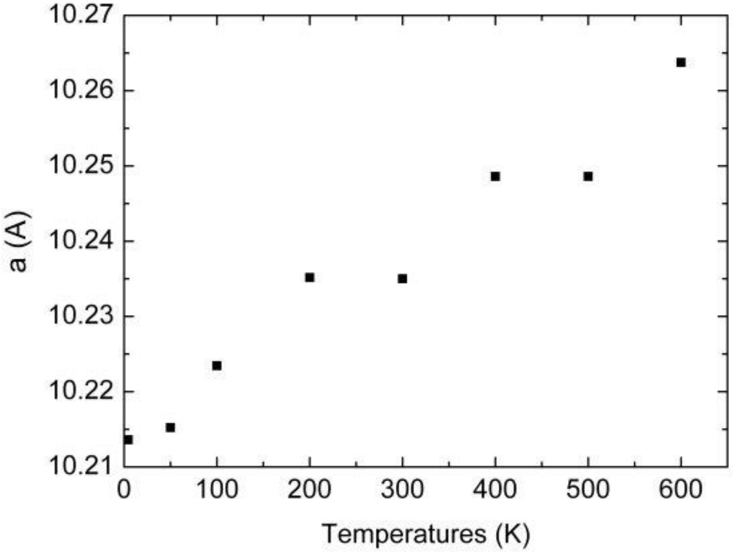
Conclusions from Magnetic Measurements:

⇒The change in the muon environment indicates that atoms shift!

⇒However…

High Resolution Neutron Diffraction



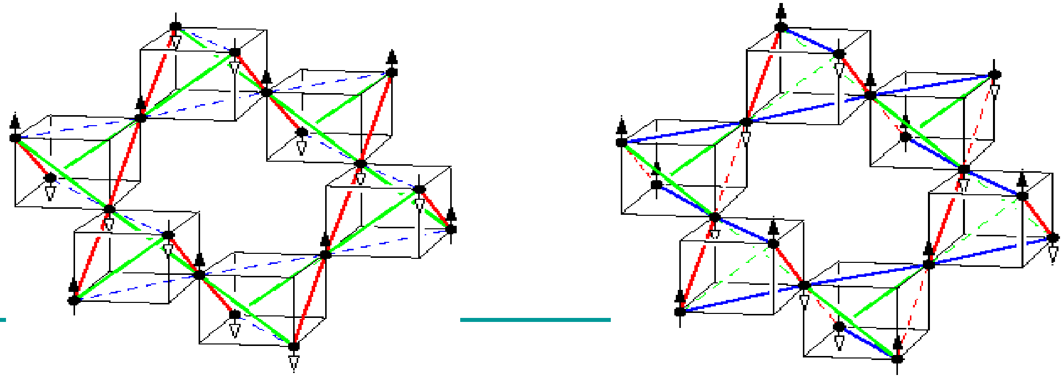


- No evidence for periodic rearrangement of the atoms, from μSR or neutrons .

- Neutron scattering data for $Y_2Mo_2O_7$ show uniform shrinking of the unit cell with decreasing temperature.

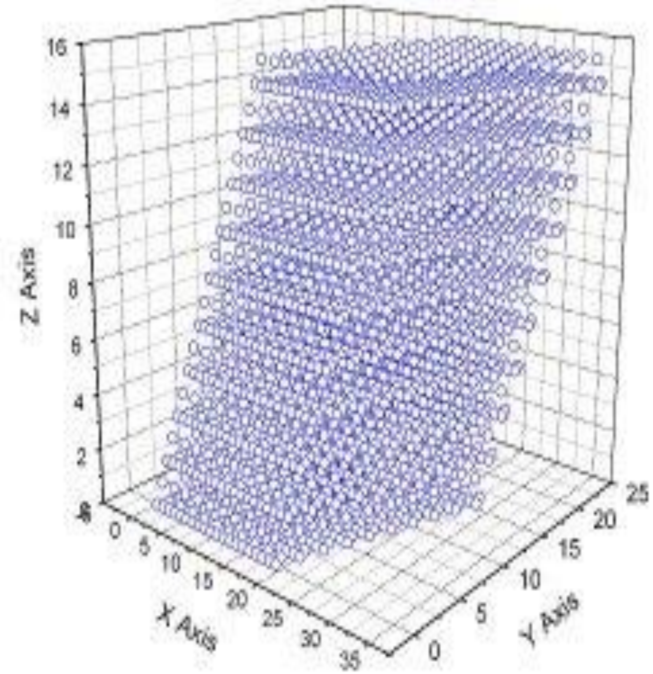
Is something wrong with theory?

- Valid only for T=0 ; we're not there yet…
- Only first order distortional terms were taken into account.
- Assumption of zero net spin on each tetrahedron ; not necessarily true in the presence of a magnetoelastic distortion.
- q=0 is guessed to be the ground state; the guess might be wrong…



Investigating Further- Computer Simulations

- Energy minimization at T=0.
- Periodic boundary conditions for the spins, open for the coordinates, to allow for non-volume-preserving change of the unit cell.
- Structure inspection by Fourier transform and virtual neutron scattering.
- Slow temperature increase from T=0 to inspect structure of excited states.

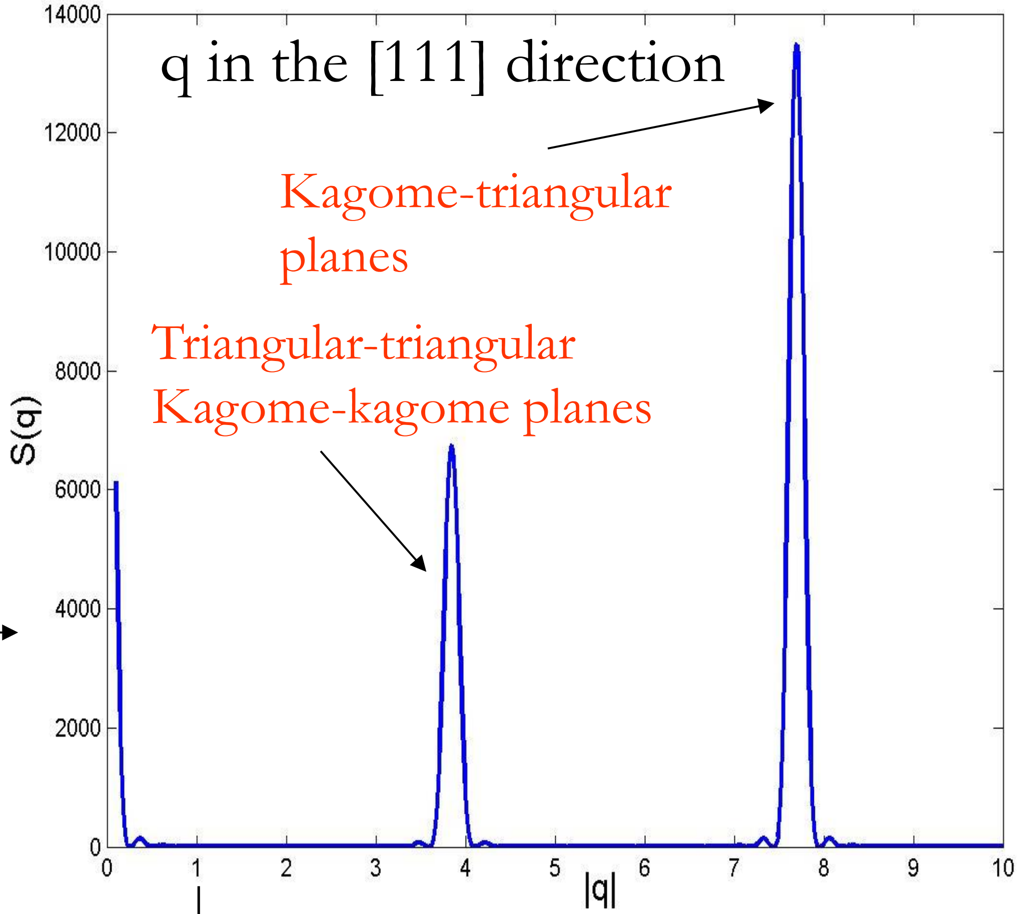


Structure investigation

- Fourier transform:

$$s(q) = \left| \sum_j e^{iq \cdot R_j} \right|$$

Undistorted pyrochlore lattice



q in the [111] direction

Kagome-triangular planes

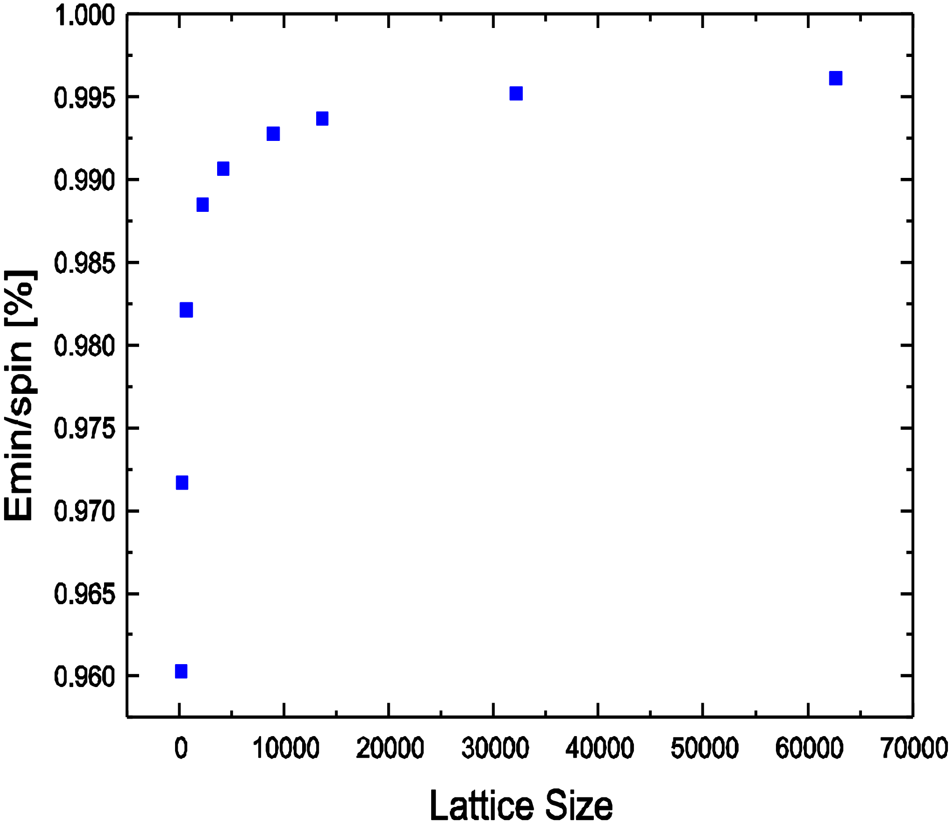
Triangular-triangular Kagome-kagome planes

- Magnetic neutron scattering:

$$S(q) = \left| \sum_{\alpha,\beta} \left(\delta_{\alpha\beta} - q_\alpha q_\beta \right) \sum_{i,j} S^i_\alpha S^j_\beta \cos\left(q\left(R_i - R_j \right) \right) \right|$$

Finite Size Effects

- Simulation lattice size ~ 10000 atoms << 10^{23} atoms in real crystals.
- Examine how characteristic output values of the simulation are affected by lattice size.
- Determine simulation error from finite size effects.



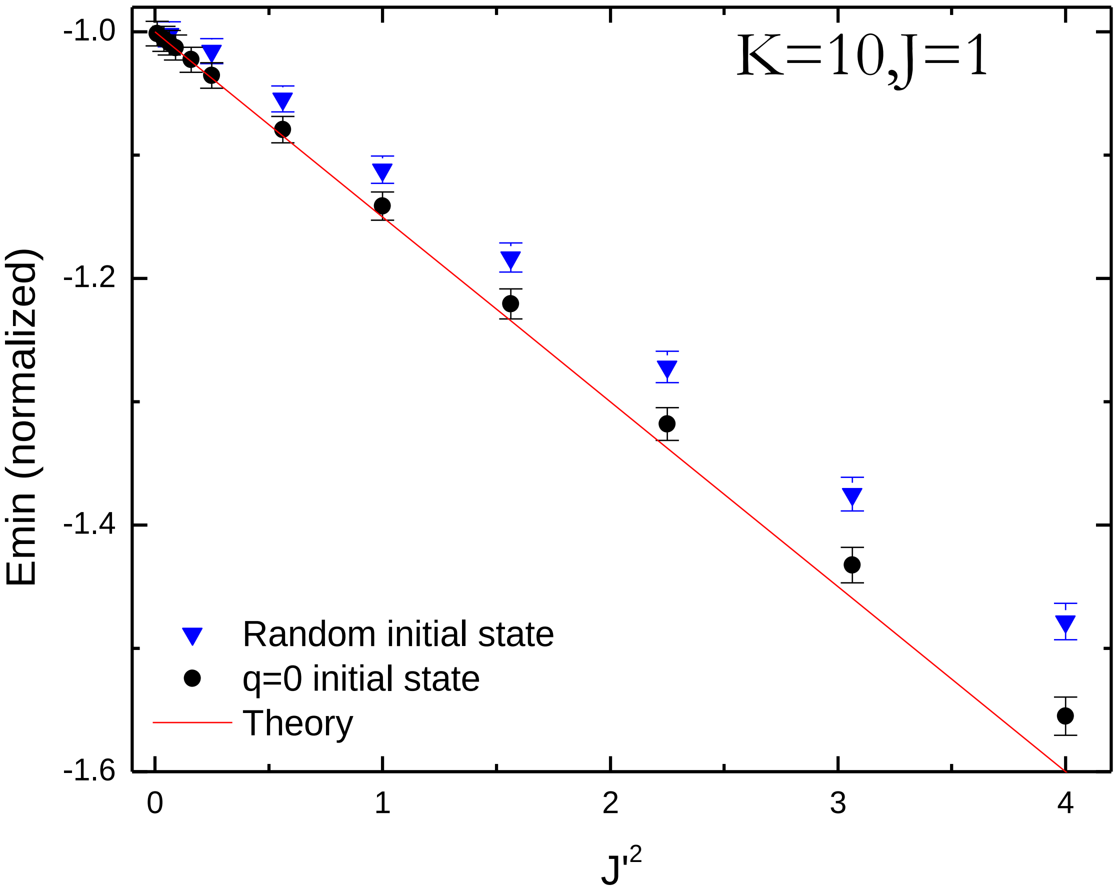
Initial Conditions

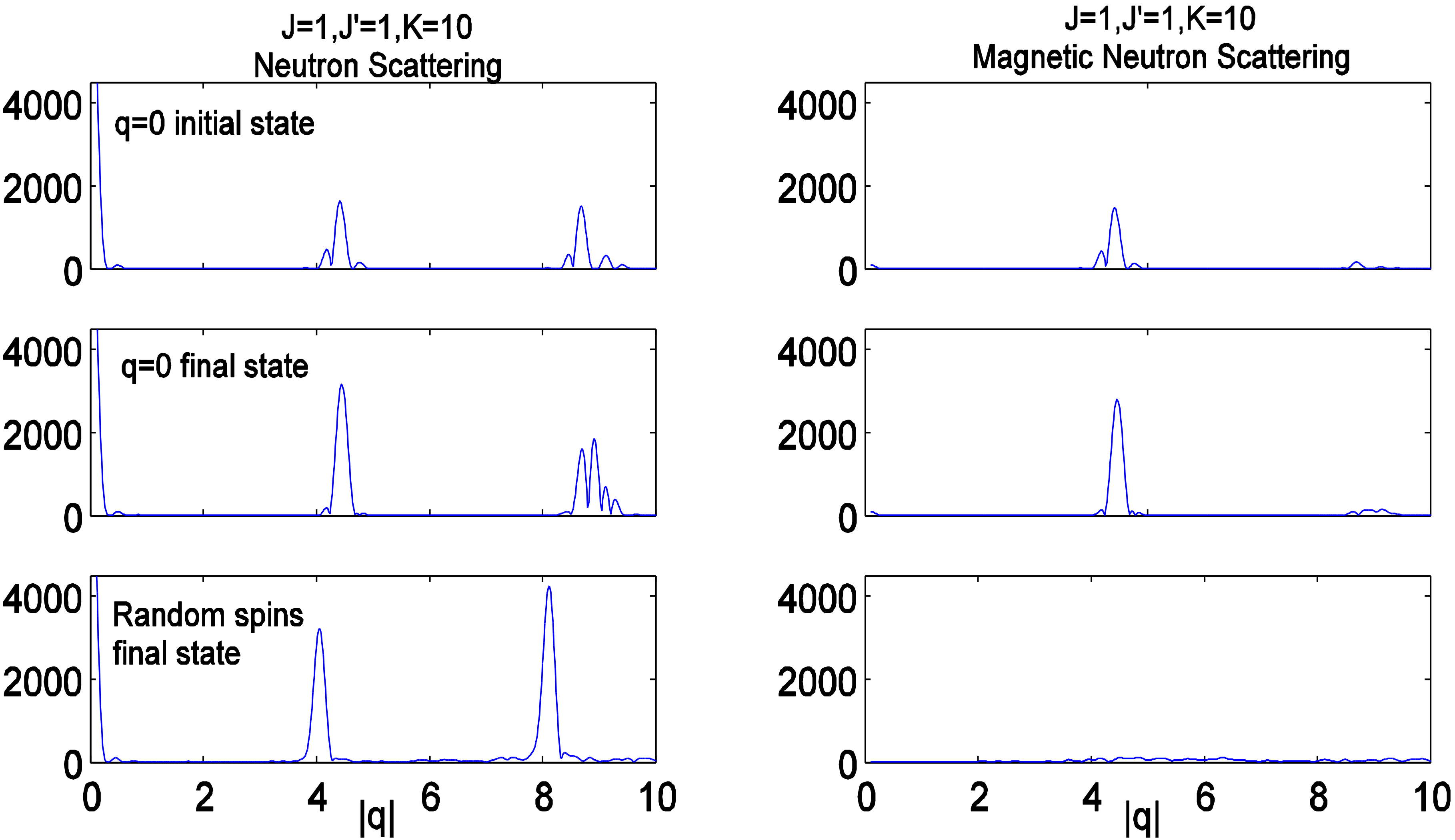
- q=0 state- is it stable against energy minimization, or can a lower energy state be found?.
- Undistorted lattice, random spin arrangement- what minimum energy state will be achieved?

Simulation Results

- The computer could not find a state with lower energy than the q=0 state.
- The divergence from linearity stems from non-harmonic effects.

$$E_{theory} = -\left(J + \frac{3}{2}\frac{J'^2}{k} \right)$$



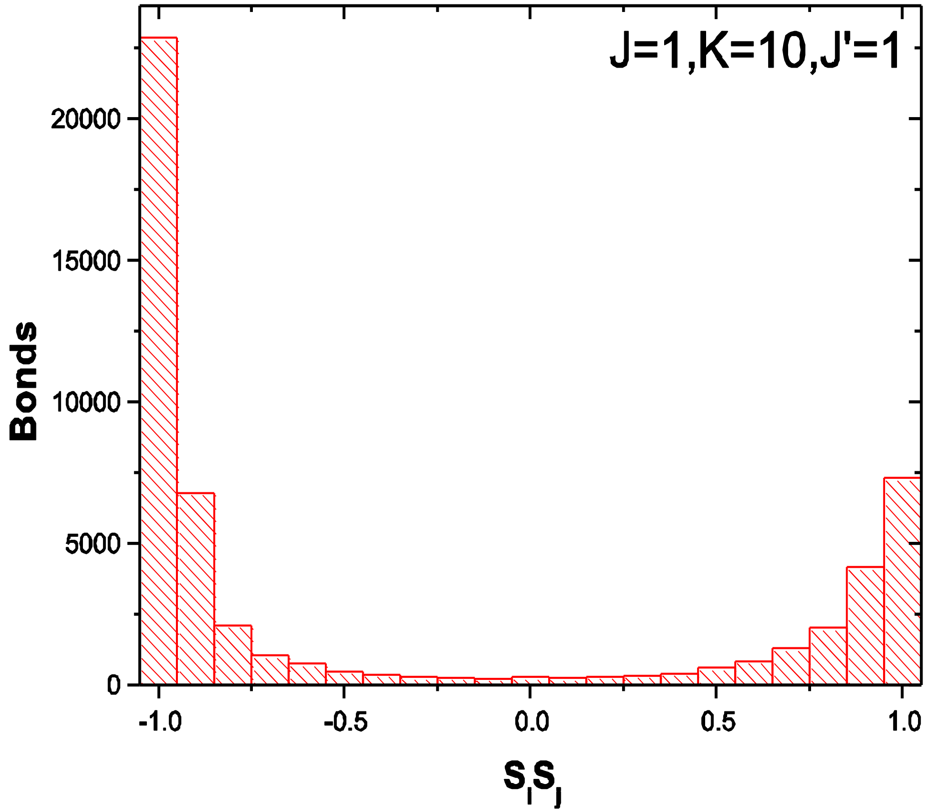

J=1,J'=1,K=10
Neutron Scattering
J=1,J'=1,K=10
Magnetic Neutron Scattering
q=0 initial state
q=0 final state
Random spins
final state
4000
2000
0
0
2
4
6
8
10
|q|

Magnetic and non-Magnetic Scattering-Conclusions

- The q=0 initial and final states exhibit scattering peaks which are shifted relative to the undistorted lattice peaks; this indicates a shrinking of the entire lattice.
- In the q=0 final state, we see a split in the peak corresponding to the kagome-triangular interplane distance, which shows that atoms have moved in and out of planes.
- The final state obtained from a random initial state does not exhibit long range spin correlations, as can be seen from the absence of magnetic scattering peaks.

Near-Neighbor Spin-Spin Correlations

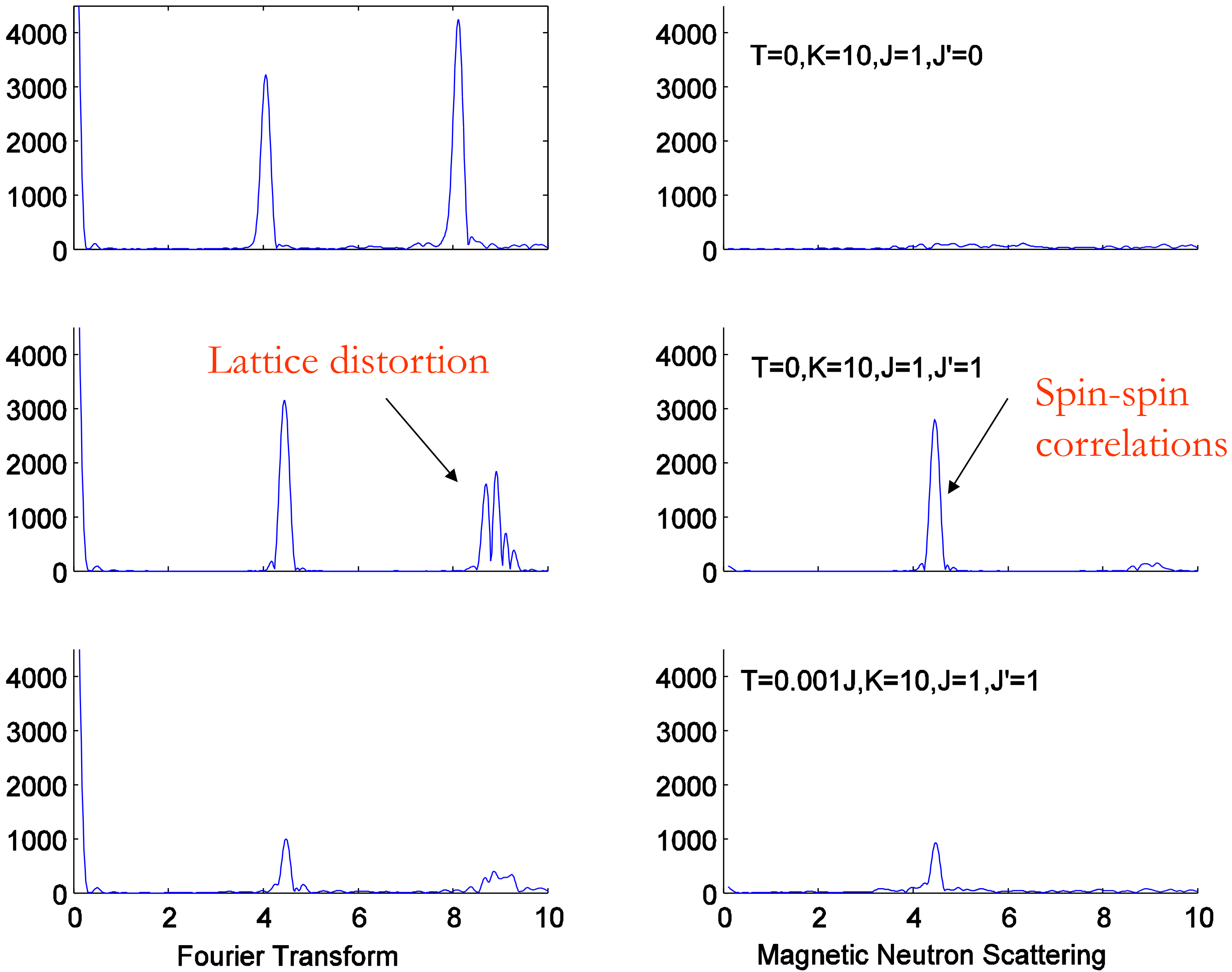
- The near-neighbor spin-spin correlations are similar to those characterizing the q=0 state.
- Zero net spin on each tetrahedron.



SiSj distribution-
initial random spin orientations.

Temperature

- Temperature was increased slowly from T=0.000001J to T=0.1J, starting from the q=0 initial state.
- Magnetoelastic term → long range spin-spin correlations, lattice distortion.
- At T=0.001J, splitting is no longer distinguishable, whereas magnetic correlations persist.
- Magnetic probes such as μSR and NMR are expected to be more sensitive to the presence of the magnetoelastic term than nonmagnetic probes.



Lattice distortion

Spin-spin correlations

Conclusions

- We looked for the ground state of the pyrochlore lattice with magnetoelastic Hamiltonian, with the aid of computer simulations. We could not find a state with lower energy than the q=0 state, for J'/k<<1.
- The computer simulation showed that for J'/k<<1 the theoretical assumptions hold: zero net spin on each tetrahedron, 2/3 strong (shortened) bonds,1/3 weak (lengthened) bonds, 2/3 bonds with antiparallel spins, 1/3 bonds with parallel spins.
- The simulation shows that the q=0 state is not distinguishable with non-magnetic probes above T=0.001J. For $Y_2Mo_2O_7$ this means T~0.03K.