1- Magnetic moments of U ions

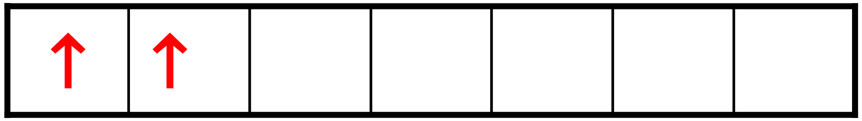
Many Uranium compounds are mixed valence systems: the valence state of U ions can be U^{3+}, U^{4+} or a mixture of both valence states. The atomic configurations are respectively $5f^3$ and $5f^2$.

-**What are the values of L, S and J for each ion**

-**If one measures a Curie-like susceptibility, what are the effctive moments in both cases?**

-**Conclusion: is it easy to deduce the valence state of U from the effective moment?**

U^{4+}



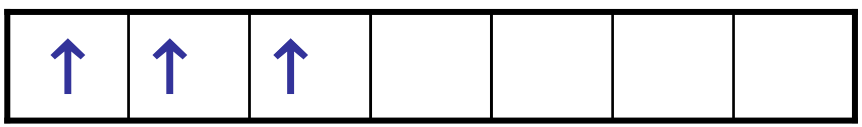
$$L_z = -3, -2, -1, 0, 1, 2, 3$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

S=1, L=5, J= L - S=4, g_J=4/5 (λ <0)

$$\mu_{eff} = g_J\sqrt{J(J+1)}\mu_B = 3.58\mu_B$$

U^{3+}



S=3/2, L=6, J= L-S=9/2, g_J=8/11

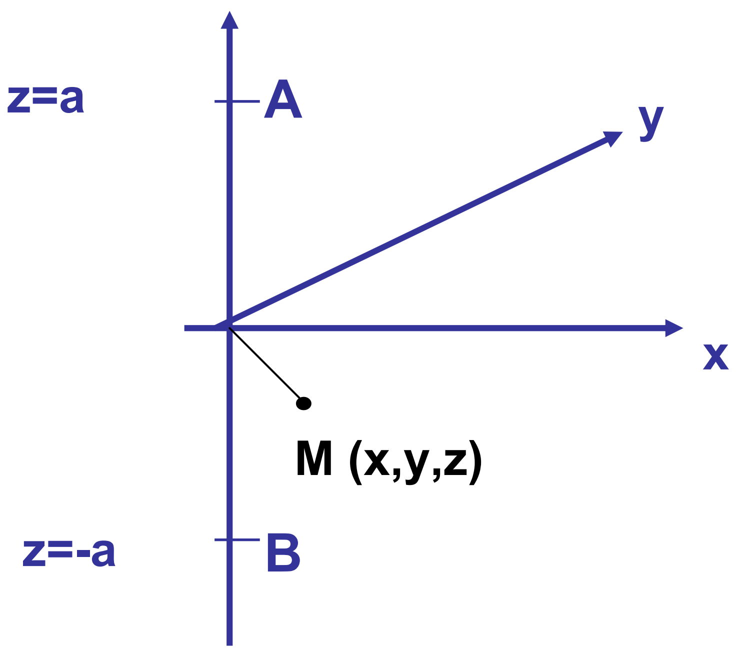
$$\mu_{eff} = g_J\sqrt{J(J+1)}\mu_B = 3.62\mu_B$$

Conclusion: difficult to distinguish!

2- One-dimensional crystal field

Let 2 identical charges q be located at $z = \pm$ aon the z-axis. Write the potential V(r) created by these 2 charges at a point M near the origin. Expand V(r) for $r/a \ll 1$ and show that it takes the form:

$$V(z,y,z) = Dz^2$$



$$V(r) = \frac{q}{|AM|} + \frac{q}{|BM|}$$

$$AM = \sqrt{x^2 + y^2 + (z - a)^2} \quad , BM = \sqrt{x^2 + y^2 + (z + a)^2}$$

$$z = r\cos\theta$$

$$\text{small x, y and z}: \frac{1}{AM} = \frac{1}{a}(1 + \frac{r}{a}\cos\theta + \frac{r^2}{2a^2}(3\cos^2\theta - 1))$$

$$V(r) = \frac{2q}{a} + \frac{qr^2}{a^2}(3\cos^2\theta - 1)$$

If q < 0 : potential is repulsive if the electron is on z-axis

attractive if the electron is in the x-y plane

$\Longrightarrow$ Planar orbitals are favored

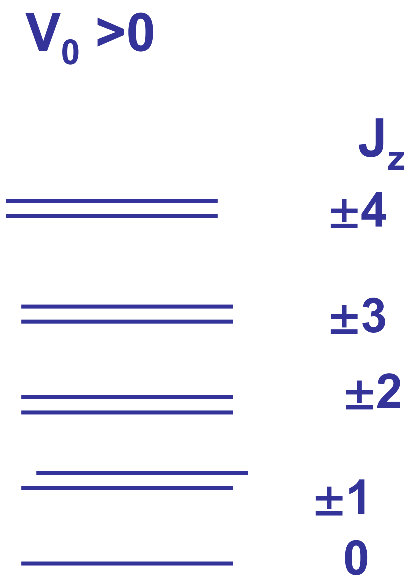
3 - The ground state of a Pr^{3+} ion ($4f^2$) is characterized by S=1, L=5, J=4

A uniaxial crystal field will partially remove the degeneracy of the ground state. The crystal field potential writes: $V_c=V_0 J_z^2$

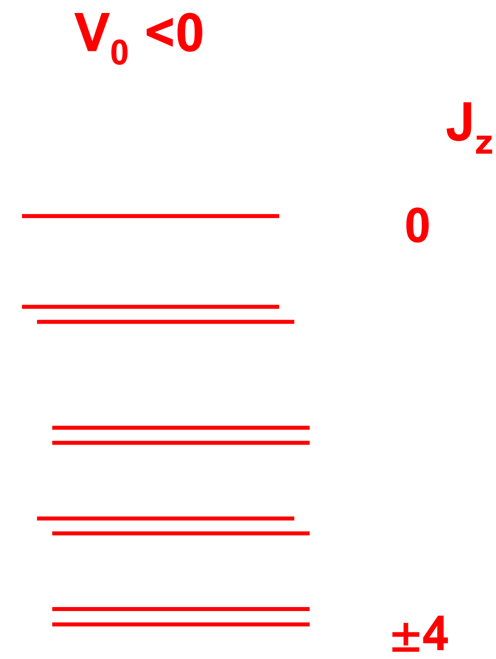
-How the energy levels are modified by the crystal field? What is the ground state if $V_0 > 0$? If $V_0 < 0$?

-When applying a magnetic field along z-axis, how these levels are modified in both cases?

-If $V_0 > 0$ show that the magnetic field can induce a transition from a non-magnetic GS ($J_z=0$) to a magnetic state ($J_z \neq 0$). What is the value of the critical field?



« Non-magnetic » ground state



« Ising-like »

In a magnetic field: Zeeman splitting

$$E(J_z) = V_0\, J_z^2 - g\mu_B H\, J_z$$

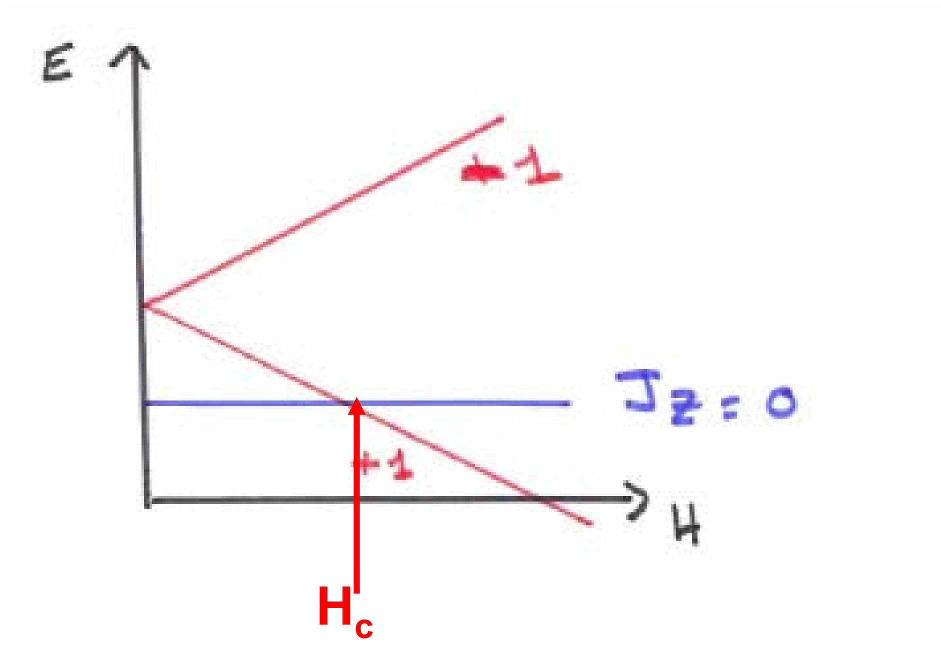
Degeneracy is lifted completely

Case $V_0 > 0$

Critical field H_c at which

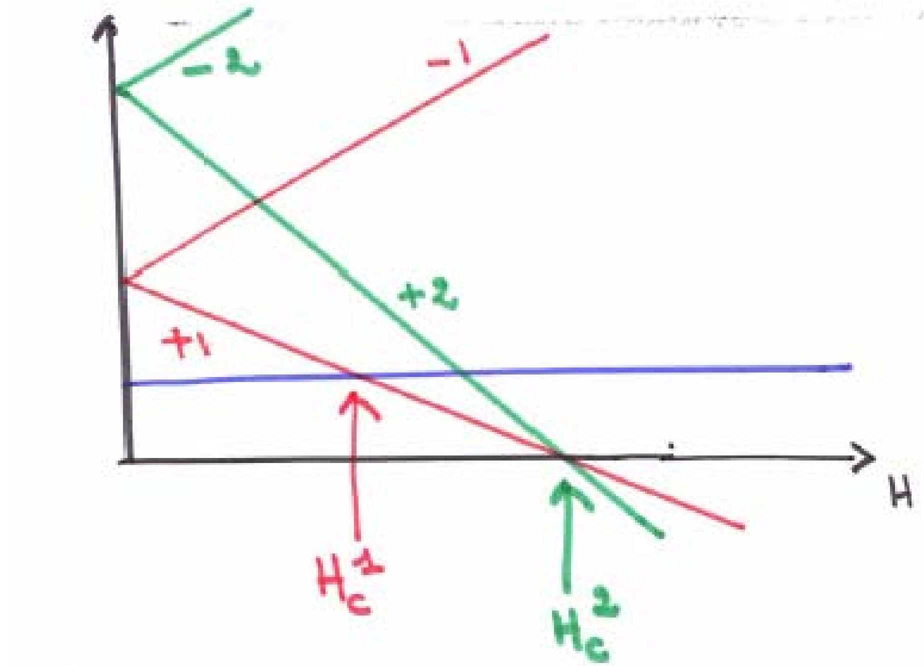
$E(J_z = 0) = E\,(J_z = 1)$

At H_c, the ground state becomes magnetic ($J_z = 1$)

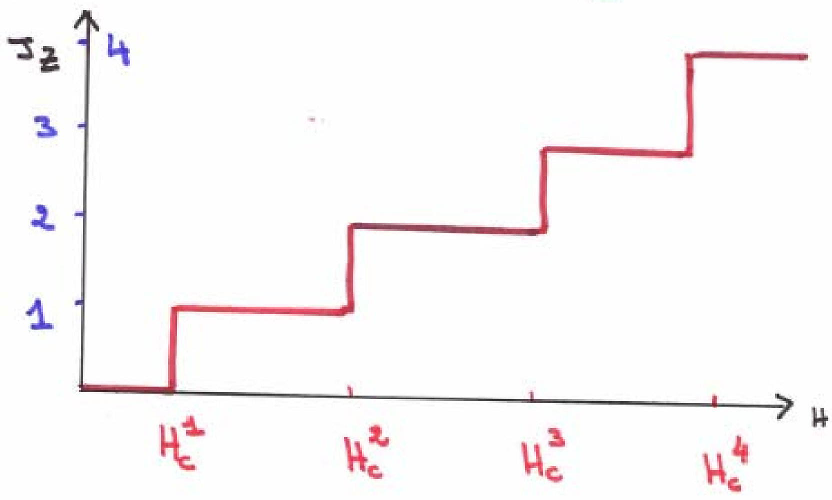


$$H_c = \frac{V_0}{g\mu_B}$$

At higher field: other transitions



At H_c^2 : $J_z = 2$ becomes the ground state

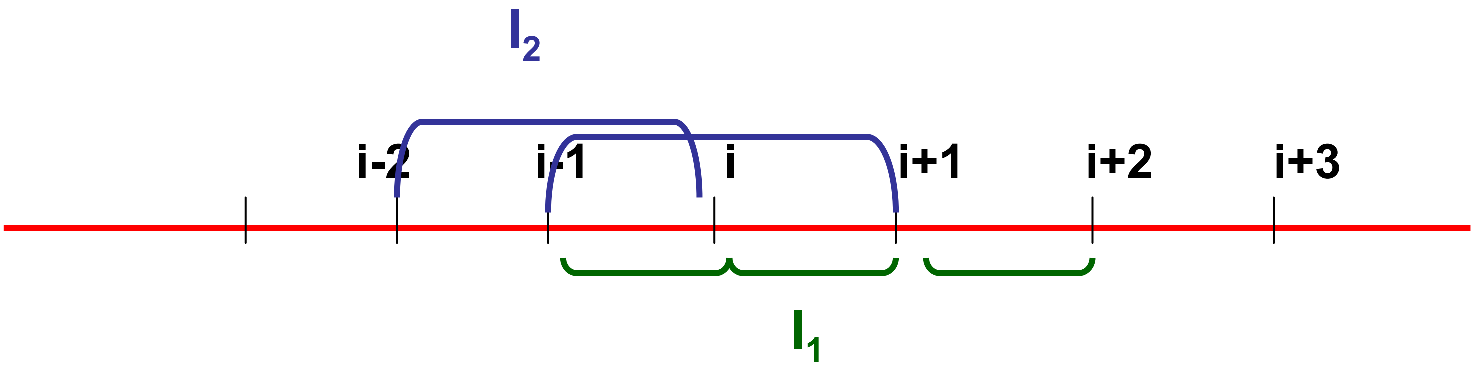


$$H_c^1 = \frac{V_0}{g\mu_B}, H_c^2 = \frac{3V_0}{g\mu_B},$$

$$H_c^3 = \frac{5V_0}{g\mu_B}, H_c^4 = \frac{7V_0}{g\mu_B}$$

4- Helimagnetism: a 1D example

Consider a chain of (classical) magnetic moments with 1st and 2nd neighbor exchange:



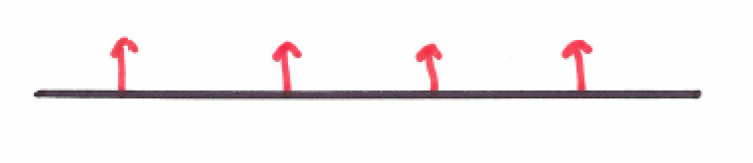
Energy:

$$E = -I_1 \sum_i \vec{S}_i \vec{S}_{i+1} - I_2 \sum_i \vec{S}_i \vec{S}_{i+2}$$

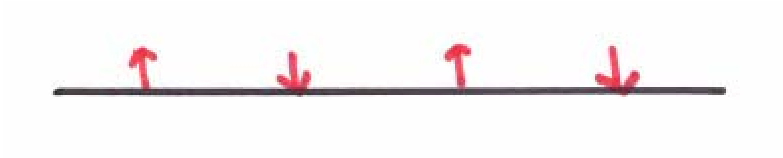
-Ground state for I_1 and $I_2 > 0$? For $I_1 < 0$ and $I_2 > 0$?

-General case : $\vec{S}_i = \vec{S}_q e^{iqR_i}$

I_1 and I_2 both >0: ferromagnetic state

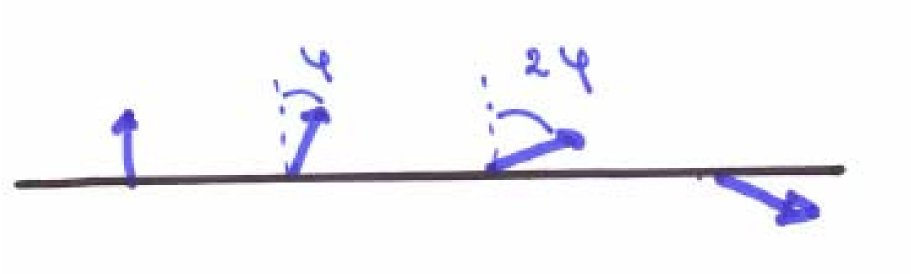


I_1 <0 and I_2 >0: antiferromagnetic state



No frustration, all interactions are satisfied

If I_2 <0, frustration is present: helimagnetic state
In helimagnet, each moment makes an angle φ with its neighbor



-By minimizing the energy, calculate the angle φ as a function of I_1 and I_2.
-Phase diagram on the plane(I_1, I_2)

Energy: $E = - I_1 \cos\varphi - I_2 \cos 2\varphi$

$\partial E / \partial\varphi = 0 \Longrightarrow \sin\varphi\,(I_1 + 4 I_2 \cos\varphi) = 0$

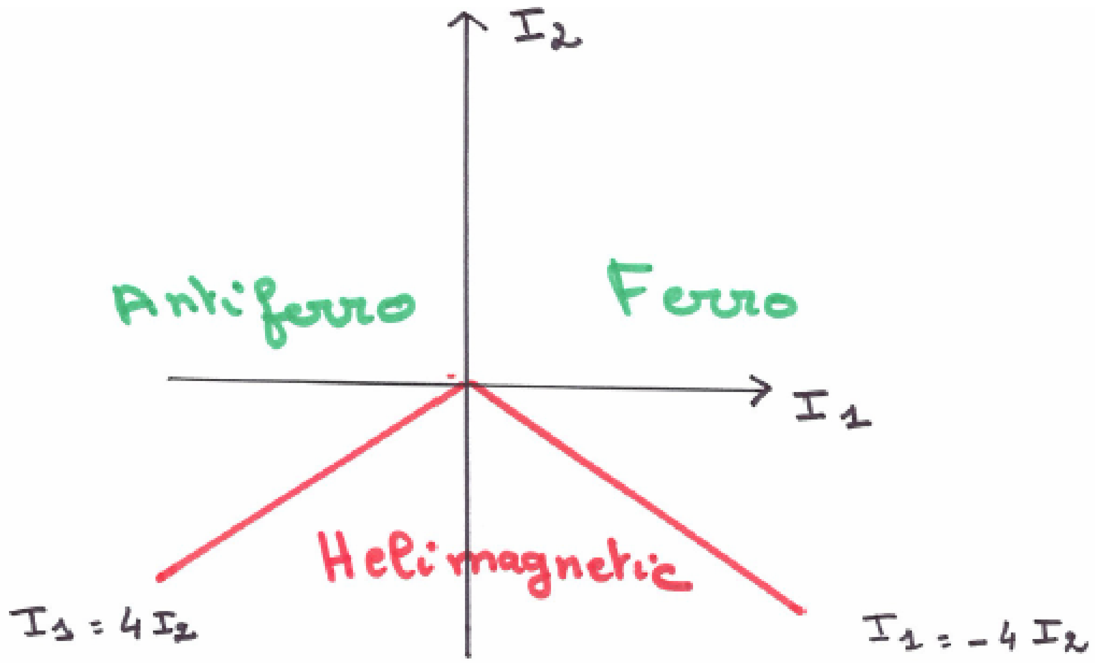
Solutions:

- $\varphi = 0 \longrightarrow$ ferro $E_F = -I_1 - I_2$
- $\varphi = \pi \longrightarrow$ antiferro $E_{AF} = I_1 - I_2$
- $\cos\varphi = - I_1/4I_2 \longrightarrow$ helicoidal $E_H = I_2 + 8I_1^2/8I_2$

    valid only if $|I_1/4I_2| \leq 1$

Phase diagram: comparison of the 3 energies

The phase diagram:



- The helimagnetic state is stabilized in the frustrated region ($J_2 < 0$)

- It is in general incommensurate with the lattice periodicity

General case: - interactions J_{ij} between 1st, 2nd, 3rd ….
- Any kind of Bravais lattice (1 magnetic site per unit cell)

$$H = -\sum_{ij} J_{ij} \vec{S}_i . \vec{S}_j$$

$$\text{Fourier transform}: S_i = \frac{1}{\sqrt{N}} \sum_q S_q \, e^{iqR_i} \;, \; Sq = \frac{1}{\sqrt{N}} \sum_i S_i \, e^{iqR_i}$$

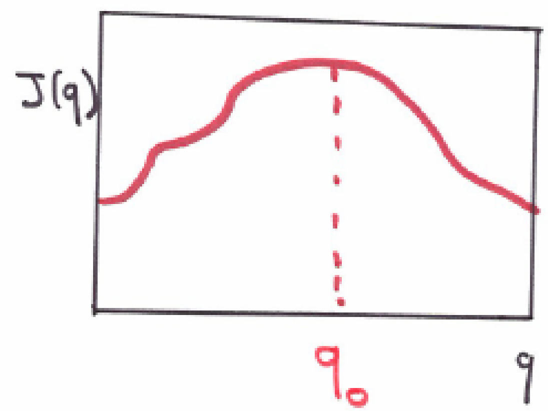
$$J(q) = \frac{1}{N} \sum_{ij} J_{ij} \, e^{iq(R_i - R_j)}$$

$$H = -\sum_q J(q)\, S_q S_{-q} = -\sum_q J(q) \left| S_q \right|^2$$

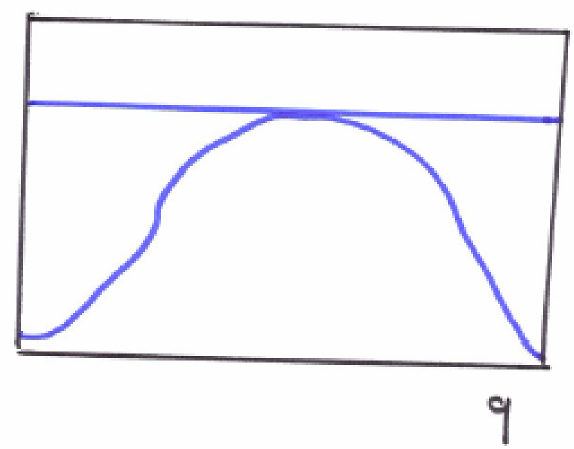
We restrict to solutions with only 1 q-vector (in fact at least q and –q): Energy is minimum at q_0 for which J(q) is maximum

For the 1D case : $J(q) = - I_1 \cos qa - I_2 \cos 2qa$. Show that the solution is similar to the one found previously

Generally, there is 1 q_0 (+ the equivalent vectors): the stable magnetic structure is well defined

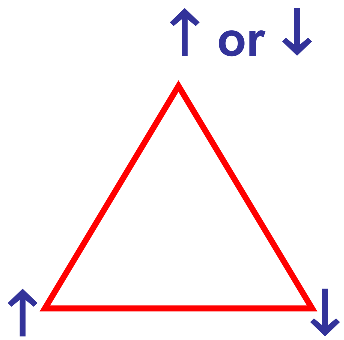


In frustrated systems (Kagome and pyrochlore): one « flat branch » + several dispersive branches

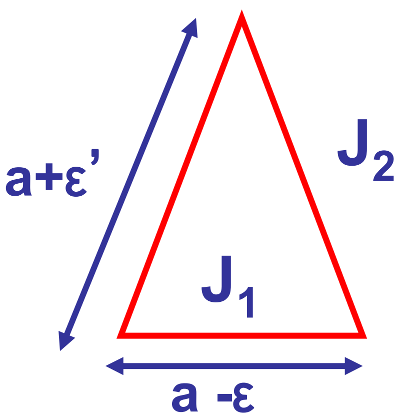


(when several atoms per unit cell: nb of branches = nb of magnetic sites in unit cell)

5- Magnetovolume effects: a simple model with 3 magnetic moments



Triangle with Ising spins
If J < 0, frustration: 6 equivalent states



If the triangle can deformed, the 3 exchange interactions are different:

$$J_1 = J_0 - \alpha\varepsilon \, , \; J_2 = J_0 + \alpha\varepsilon' \qquad \alpha = \frac{\partial J(r)}{\partial r}$$

Show that a deformation decrease the GS energy

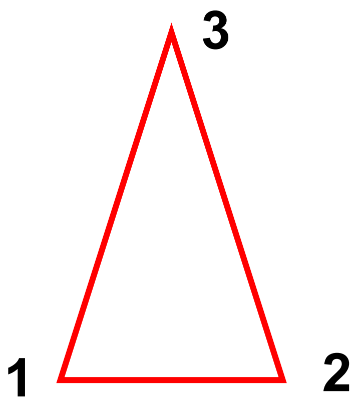
-Relation between ε and ε' in order to keep a constant « volume »

-Write the total energy: magnetic + elastic

-Show that the deformation partially supress the frustration

-Constant surface: $\varepsilon' = \varepsilon/2$

-Energy: $E = -J_1 S_1S_2 - J_2S_1S_3 - J_2 S_2S_3 + K(\varepsilon^2 + 2\varepsilon'^2)$



Energy : exchange + elastic

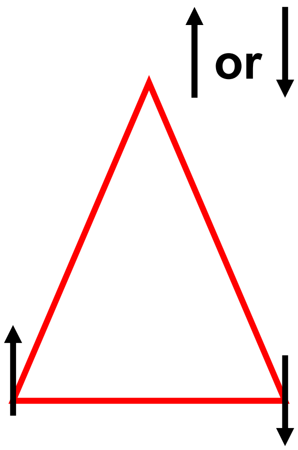
$$E = -(J_0 - \alpha\varepsilon)S_1S_2 - (J_0 + \frac{\alpha\varepsilon}{2})(S_1S_3 + S_2S_3) + \frac{3K}{2}\varepsilon^2$$

-1st case: $|J_1| > |J_2|$, i.e. $\alpha\varepsilon > 0$

To minimize E: satisfy J_1 first $\Longrightarrow S_1 = -1$, $S_2 = +1$

$$E = (J_0 - \alpha\varepsilon) + \frac{3K}{2}\varepsilon^2 \Rightarrow \text{mimimum for } \varepsilon = \frac{\alpha}{3K}$$

$$\Delta E = -\frac{\alpha^2}{6K}$$

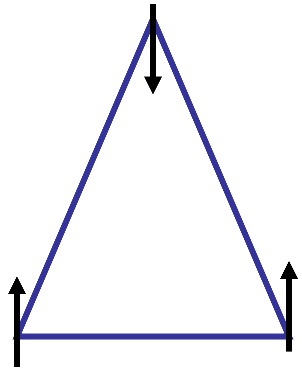


-2nd case: $|J_1| < |J_2|$, i.e. $\alpha\varepsilon < 0$

To minimize E: satisfy J_2 first: $S_1S_3 = S_2S_3 \Longrightarrow S_1 = S_2$

$$E = (J_0 + 2\alpha\varepsilon) + \frac{3K}{2}\varepsilon^2 \Rightarrow \text{mimimum for } \varepsilon = -\frac{2\alpha}{3K}$$

$$\Delta E = -\frac{2\alpha^2}{3K}$$



Stable configuration

(Same conclusion if no relation between ε and ε')

6 – **biquadratic interactions**

Consider a lattice of S = 1 spins which have both bilinear and biquadratic nearest neighbor interactions of the form:

$$H = -J\sum_{ij} S_i^z S_j^z - J_q \sum_{ij} ((S_i^z)^2 - 2/3)((S_j^z)^2 - 2/3) - H\sum_i S_i^z$$

This hamiltonian can model a system with quadrupolar interactions. At high T the 3 states S_z = 0, +1, -1 are equally populated; thus $\langle S^z \rangle = 0$ and $\langle (S^z)^2 \rangle = 2/3$, thus $\langle (S^z)^2 - 2/3 \rangle = 0$

Study this model in mean field approximation:

-What is the mean field hamiltonian acting on S^z and $(S^z)^2$

-Write the partition function

-Magnetic order occurs at T_c and quadrupolar ordering at T_Q. Calculate T_c if $T_c > T_Q$; calculate T_Q if $T_q > T_c$

-Susceptibilities above T_c and T_Q:

- **show that $Q \propto H^2$**
- **By an expansion in powers of H, M and Q, calculate χ_1, χ_3 and χ_Q defined as: $M = \chi_1 H + \chi_3 H^3$ and $Q = \chi_Q H^2$**
- **Discuss the results**

Introduce $Q_i = (S_i^z)^2 - 2/3$, $Q = \langle Q_i \rangle$ and $M = \langle S_i^z \rangle$

Mean-field hamiltonian :

$$H_{MF} = -\sum_i (H + zJM)\, S_i^z - \sum_i zJ_q Q\, ((S_i^z)^2 - 2/3)$$

For each site: 3 energy levels

$$S_i^z = 0 \Rightarrow E_0 = 2/3\, zJ_q\, Q$$

$$S_i^z = +1 \Rightarrow E_1 = -(H+zJM) - 1/3\, zJ_q\, Q$$

$$S_i^z = -1 \Rightarrow E_{-1} = +(H+zJM) - 1/3\, zJq\, Q$$

Partition function: $Z = (\exp(-\beta E_0) + \exp(-\beta E_1) + \exp(-\beta E_{-1}))^N = Z_0^N$

Magnetization:

$$\langle S_z \rangle = M = \frac{1}{Z}\left(\exp(-\beta E_1)\right) - \exp(-\beta E_{-1}))$$

Quadrupolar moment:

$$\langle Q \rangle = \frac{1}{Z}\left(-\frac{2}{3} \exp(-\beta E_0) + \frac{1}{3} \exp(-\beta E_1) + \frac{1}{3} \exp(-\beta E_{-1}) \right)$$

Calculation of ordering temperatures:

-If $T_c > T_Q$: Q = 0 at T_c; it is enough to make an expansion in M and H

$\Longrightarrow$ $T_c = 2/3\ zJ$

-If $T_Q > T_c$: M=0 at T_Q . Expansion in Q

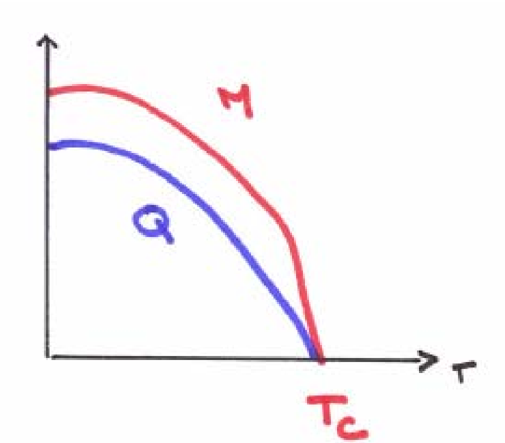
$\Longrightarrow$ $T_Q = 2/27\ zJ_q$

-If 2/3 zJ > 2/27 zJ_q , then magnetic ordering occurs at T_c, and eventually quadrupolar ordering at lower temperature

-If 2/3 zJ < 2/27 zJ_q , it is the contrary

1st case : $J > J_q/9$

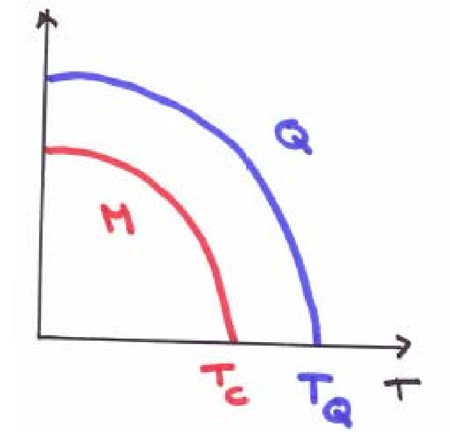
Magnetic ordering at T_c: $M \neq 0$, but then Q is also $\neq 0$



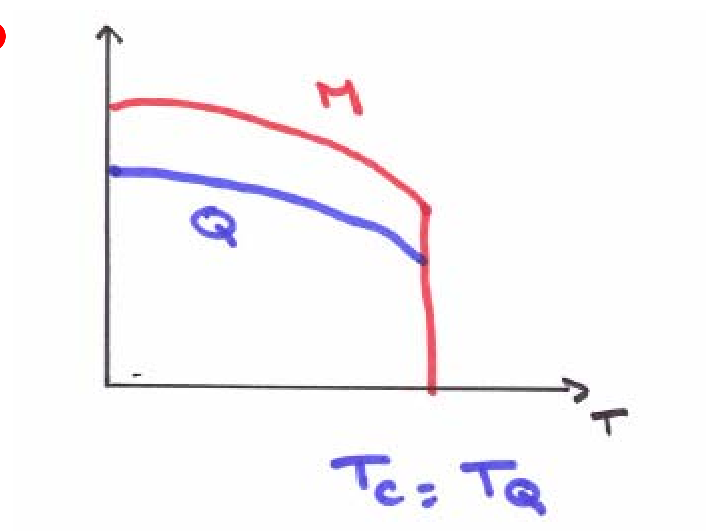
2^{nd} case: $J < J_q/9$

$Q \neq 0$ at T_Q, and $M \neq 0$ at $T_c < T_Q$

$$T_c \approx 2zJ \frac{1}{2 + \exp(-\beta z J_q Q(T_c))}$$



1st order transitions are also possible:



Susceptibility above the ordering temperatures:

$M = \chi_1 H + \chi_3 H^3 + \ldots \;, \; Q = \chi_Q H^2$

Expansion for small H:

$$\chi_1 = \frac{C}{T - T_c}, \quad \chi_3 = -\frac{C'T}{(T - T_c)^4}\left(1 + \frac{T_Q}{T - T_Q}\right)$$

$$\chi_Q = \frac{C''}{T - T_Q}\left(1 + \frac{a}{T - T_c}\right)$$

If no biquadratic interactions: $\chi_3 < 0$ and diverges at T_C. If $J_q \neq 0$, then χ_3 may change sign

If $T_Q > T_c$: quadrupolar ordering is signalle by a divergence of χ_3 , not of χ_1