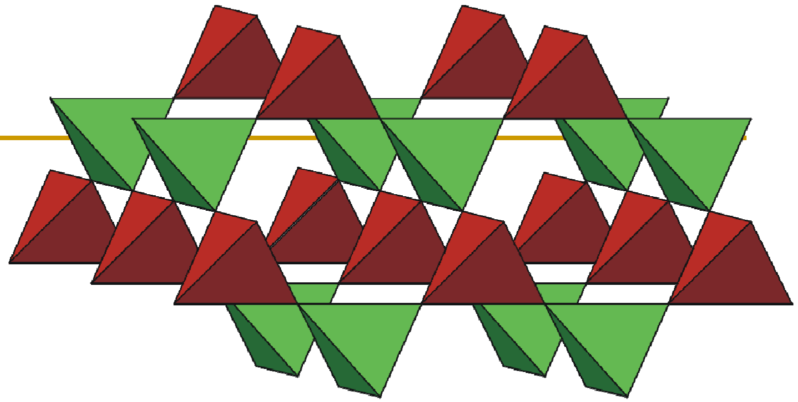
Order by Distortion and Chiral Magnetism in $CdCr_2O_4$



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Collaborators

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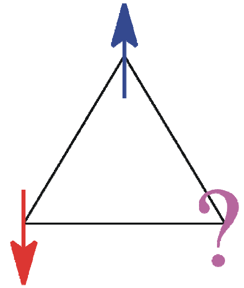
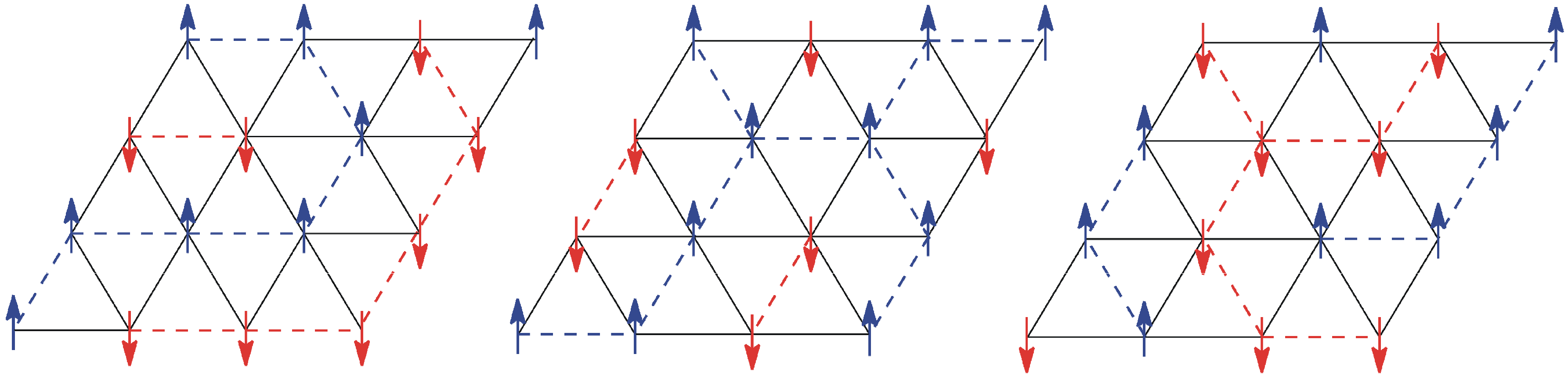
Outline

- Geometrical frustration. Pyrochlore antiferromagnet.
- Spin-lattice coupling and Jahn-Teller instability.
- Spin-Peierls phases in pyrochlore antiferromagnet.
- The case of $\mathrm{CdCr_2O_4}$:
  - Lattice distortion: Broken parity.
  - Chiral ground state: Spiral magnetic order.
- Theoretical model for the magnetic spirals.
- Summary and open questions.

Geometrical frustration



Triangular Ising antiferromagnet

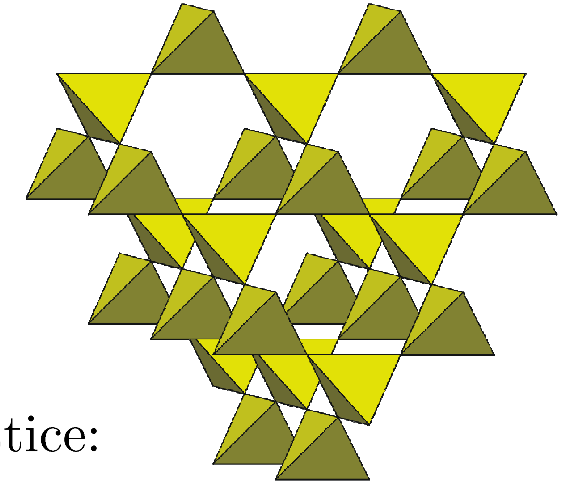


- One frustrated bond on each $\triangle$.
- Infinitely many ground state.
- Finite entropy density: $S = 0.323$ per spin at $T = 0$.
- No spin order. Spin correlations are critical: $\langle \mathbf{S}_0 \cdot \mathbf{S}_\mathbf{r} \rangle \sim C/r^2$.

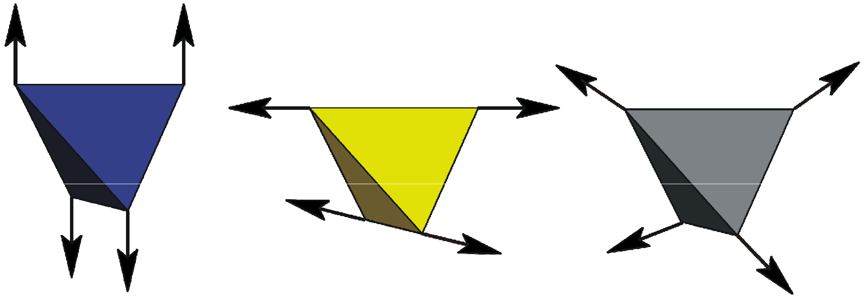
G. H. Wannier, R.M.F. Houtappel (1950)

Geometrical frustration

Pyrochlore antiferromagnet



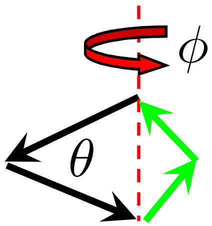
$$E = J_1 \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j = \frac{J_1}{2} \sum_{\boxtimes} \mathbf{S}_{\boxtimes}^2 + \text{const.}$$



Pyrochlore lattice:

- No spin order as $T \to 0$.
- A classical spin liquid below Θ_{CW}.
- Extensive ground-state degeneracy.
- Finite entropy at $T = 0$: $S_{\text{Pauling}} = \frac{1}{2} \log \frac{3}{2}$ (Ising spin).
- Artificial magnetic field: $\mathbf{S}_{\boxtimes} = 0 \Longrightarrow \nabla \cdot \mathbf{B} = 0.$
- Dipolar spin correlations: $\langle B_\alpha(0) B_\beta(\mathbf{r}) \rangle \propto \frac{3\cos^2\theta - 1}{r^3}$.

Single tetrahedron:



- Ground state: $\mathbf{S}_{\boxtimes} = 0$
- Quantum spins: $2S + 1$.
- Classical spins: rigid rotation $+(\theta, \phi)$.

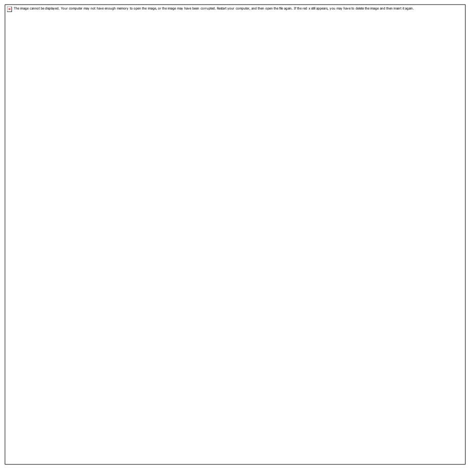
Huge degeneracy $\longrightarrow$ Hypersensitivity

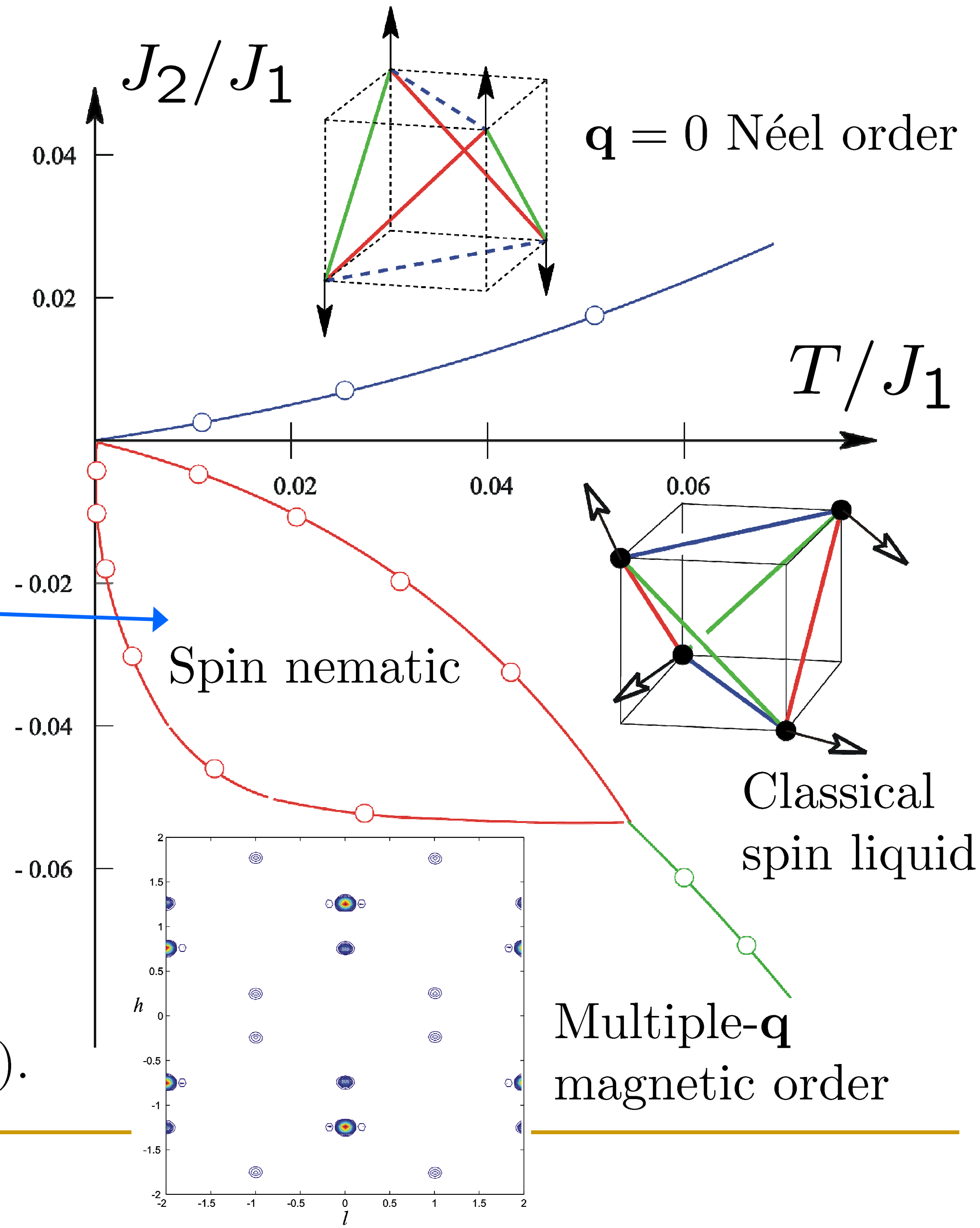
Relieving the frustration:

- Further neighbor interactions:
  Néel order, spin nematic.
- Dzyaloshinskii-Moriya $\mathbf{D} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$:
  Non-collinear magnetic order.
- Quantum fluctuations:
  Valence-Bond Crystal ($S = 1/2$).
- Coupling to orbital degrees of freedom:
  Néel order, ex: ZnV_2O_4, MnV_2O_4.
- Coupling to lattice:
  Néel order, ex: $ZnCr_2O_4$, $CdCr_2O_4$.

Phase diagram:

$J_1 - J_2$ Heisenberg spins
on pyrochlore lattice



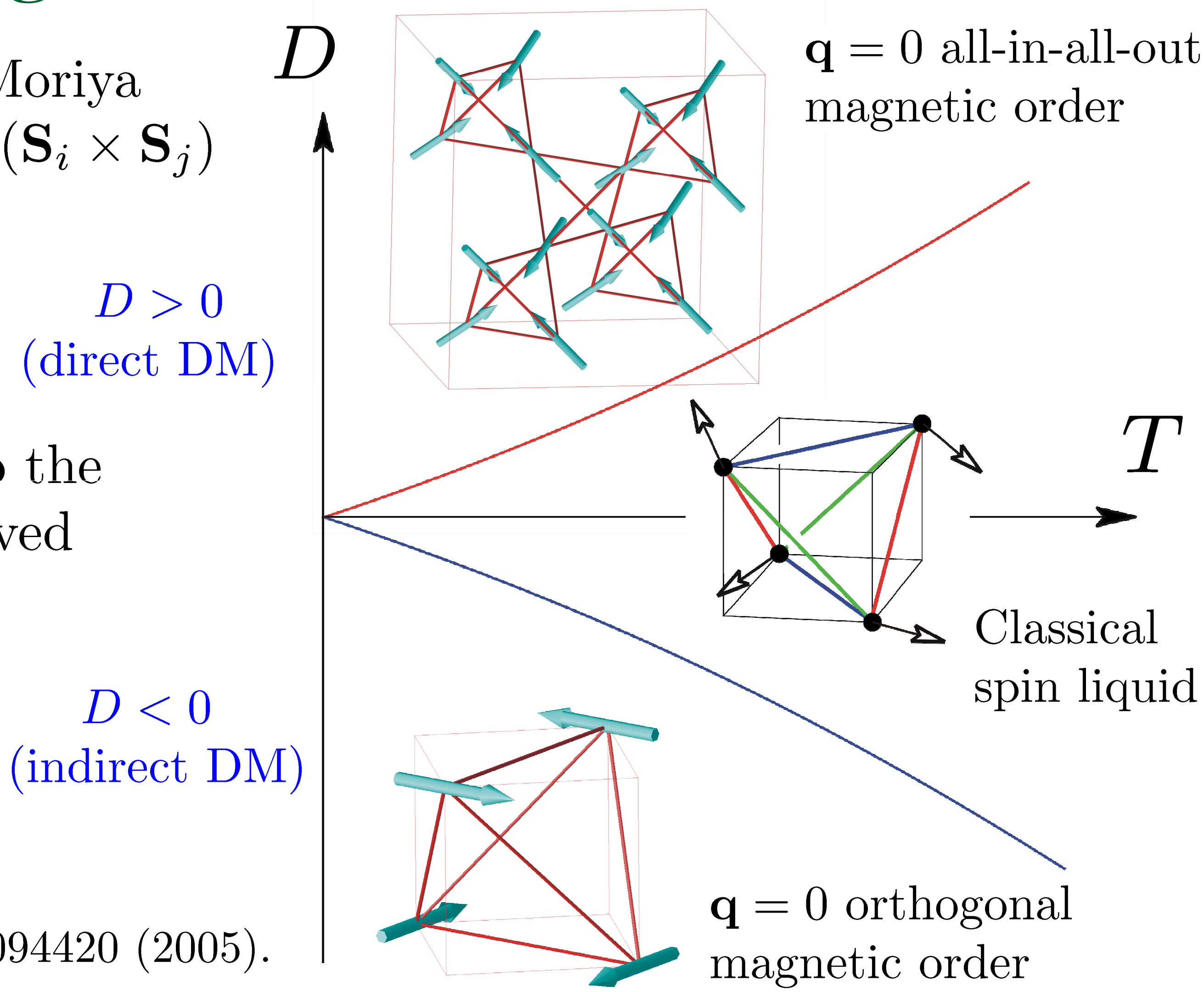


G.-W. Chern, R. Moessner, and
O. Tchernyshyov, (in preperation).

Phase diagram:

Dzyaloshinskii-Moriya interaction: $\mathbf{D} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$

- Important to the spirals observed in $CdCr_2O_4$.



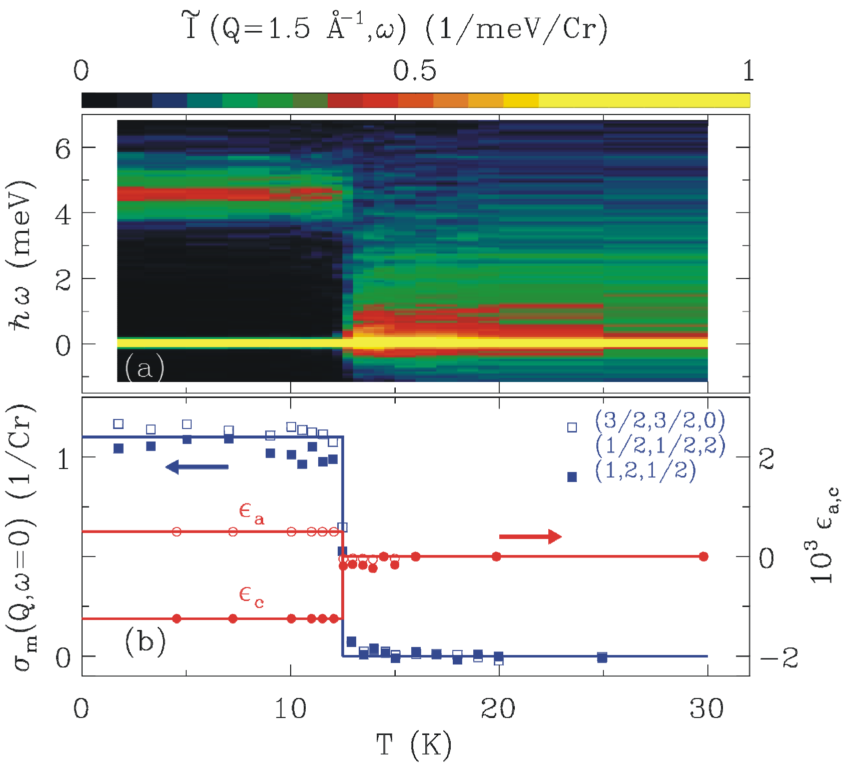
Elhajal *et al.*
Phys. Rev. B **71** 094420 (2005).

What do pyrochlore magnets actually do ?

S.-H. Lee *et al.* (2000)

Spinel $ZnCr_2O_4$

- Cr^{3+}: $3d^3$, $S = 3/2$, $L = 0$.
- Heisenberg antiferromagnet.
- $J = 4.5$ meV, $\Theta_{CW} =$ 390 K.
- No spin order down to 12 K.
- First-order transition at $T = 12$ K:
  Cubic $Fd\bar{3}m \rightarrow$ Tetragonal $I4_1/amd$.
  Paramagnetic $\rightarrow$ AF spin order.
- Spin-Peierls-like phase transition ?



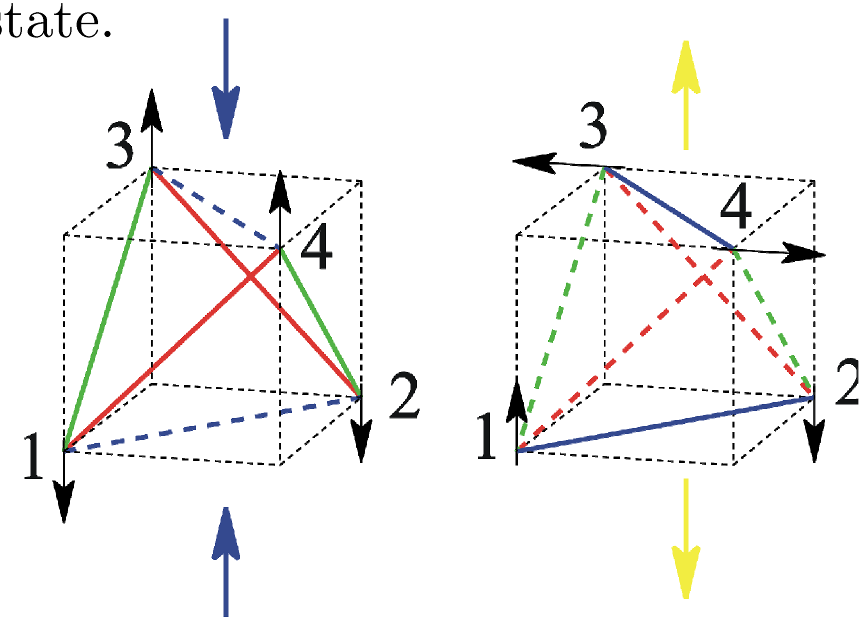
Spin-Teller effect: single tetrahedron

- High symmetry: T_d group.
  Continuously degenerate ground state.

- Spin-Lattice coupling:
  $E_{ij} = J(r_{ij})\,\mathbf{S}_i \cdot \mathbf{S}_j.$

- Unequal angles between spin:
  $F_{ij} = -(dJ/dr_{ij})\,(\mathbf{S}_i \cdot \mathbf{S}_j).$

- Spin-driven Jahn-Teller effect.

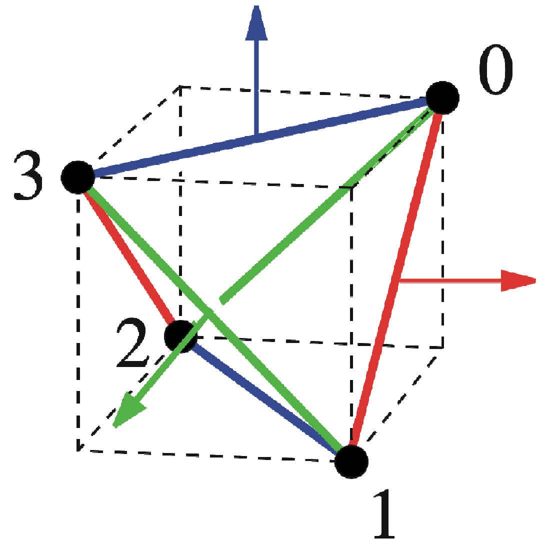


Y. Yamashita and K. Ueda (2000).
O. Tchernyshyov., R. Moessner, S.L. Sondhi (2002).

Spin-Teller instability: Group-theoretical analysis

O. Tchernyshyov *et al.*, (2002).

- Forces on red, green, and blue bonds:
  - $f_{xx} = \mathbf{S}_0 \cdot \mathbf{S}_1 + \mathbf{S}_2 \cdot \mathbf{S}_3$.
  - $f_{yy} = \mathbf{S}_0 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_1$.
  - $f_{zz} = \mathbf{S}_0 \cdot \mathbf{S}_3 + \mathbf{S}_1 \cdot \mathbf{S}_2$.
- $3f = A_1 + E$.
- Singlet A_1: Breathing phonon mode $F_{A_1} = f_{xx} + f_{yy} + f_{zz} = \text{const}$.



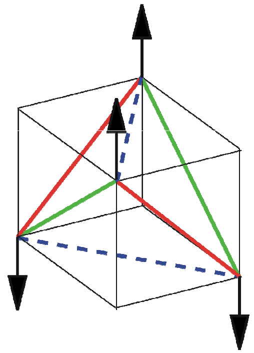
- Doublet E $\mathbf{f} = (f_1, f_2)$:
  - $f_1 = (f_{xx} + f_{yy} - 2f_{zz})/\sqrt{6}$.
  - $f_2 = (f_{xx} - f_{yy})/\sqrt{2}$.
- Effective coupling: $-J'\,(\mathbf{f} \cdot \mathbf{x})$
  - x_1: tetragonal distortion.
  - x_2: orthorhombic distortion.

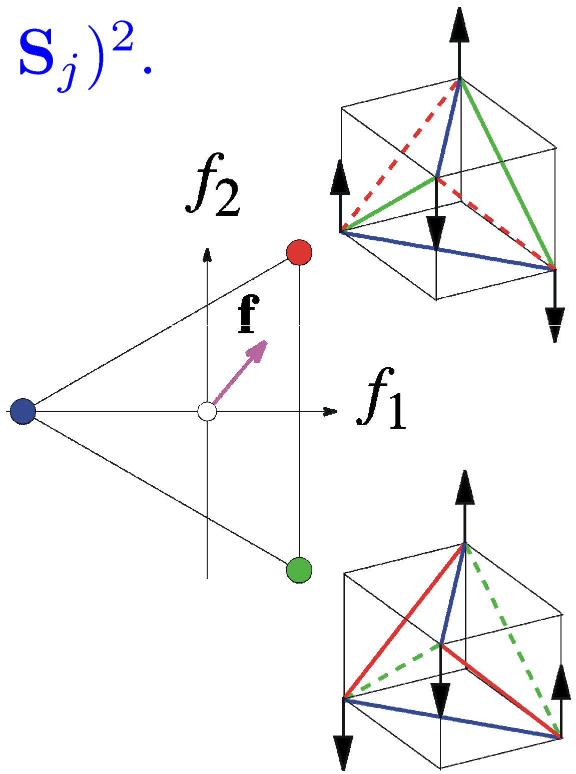
Ground states of magnetoelastic coupling

$$E(\mathbf{x}, \mathbf{f}) = \frac{kx^2}{2} - J' \, (\mathbf{x} \cdot \mathbf{f}).$$

$$\Rightarrow E_{\text{eff}}(\mathbf{f}) = -\frac{J'^2}{2k} \, |\mathbf{f}|^2 = -K \sum_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j)^2.$$

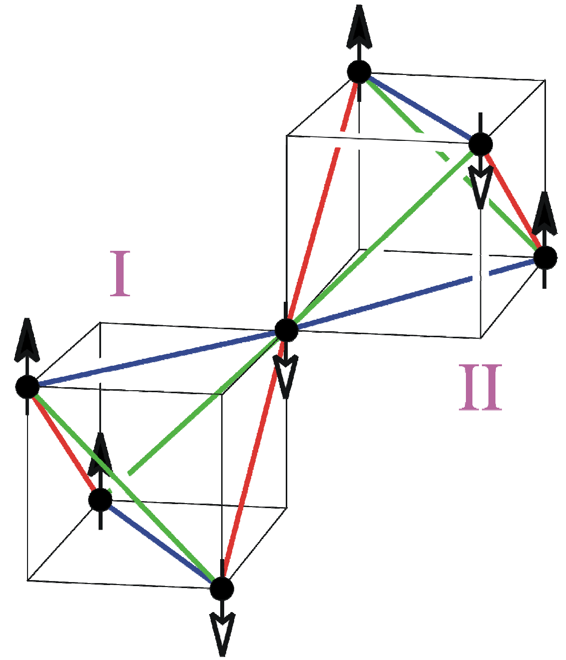
- Collinear gound states:
  - 3 primary colors. ($q = 3$ Potts).
  - Tetragonal distortion: along x, y, and z.
  - 2 frustrated and 4 happy bonds.
- White = undistorted.



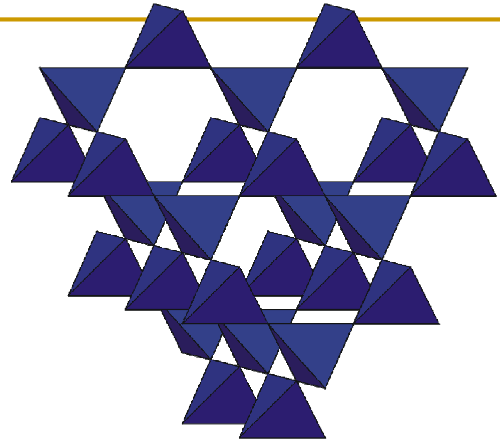


Generalization to pyrochlore lattice

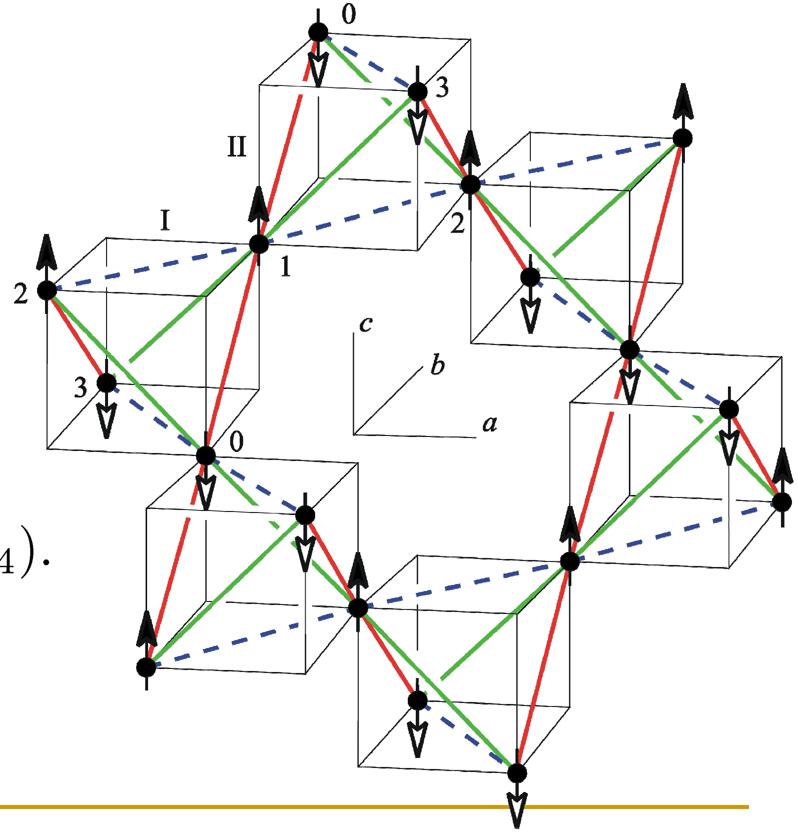
- Distortion with $\mathbf{q} = 0$:
  two inequivalent tetrahedra I and II.
- Inversion: $\mathbf{f}^{\mathrm{I}} \xrightarrow{I} \mathbf{f}^{\mathrm{II}}$.
- Symmetry group: $Fd\bar{3}m \to O_h = T_d \bigotimes I$.
- Bond variables: $\mathbf{g} = \mathbf{f}^{\mathrm{I}} + \mathbf{f}^{\mathrm{II}}, \quad \mathbf{u} = \mathbf{f}^{\mathrm{I}} - \mathbf{f}^{\mathrm{II}}$.
  Even (E_g) and odd (E_u) phonons.
- Integrating out phonons:
  $E_{\mathrm{eff}}(\mathbf{g}, \mathbf{u}) = -(J'^2/2k_g)|\mathbf{g}|^2 - (J'^2/2k_u)|\mathbf{u}|^2$.
- Coupling term $\propto (1/k_u - 1/k_g)\,(\mathbf{f}^{\mathrm{I}} \cdot \mathbf{f}^{\mathrm{II}})$
  - $k_g < k_u$ (softer E_g): Ferromagnetic $q = 3$ Potts model.
  - $k_u < k_g$ (softer E_u): Antiferromagnetic $q = 3$ Potts model.



Softer even phonon

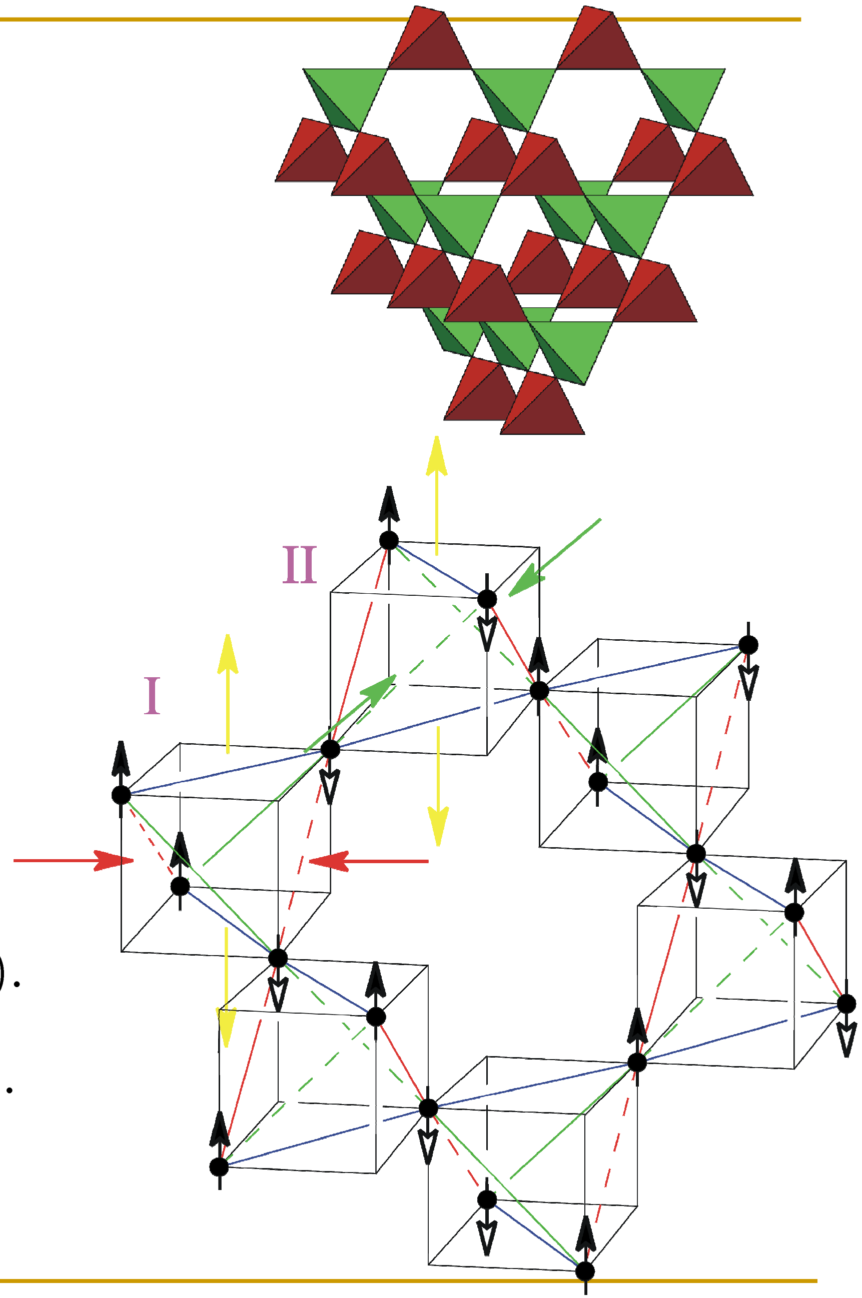


- Softer $\mathbf{q} = 0$ even phonon E_g.
- Bond order: Blue state.
- Macroscopic tetragonal distortion:
  $a = b > c$ (c.f. $\mathrm{ZnCr_2O_4}$).
- Spin-Peierls transition:
  - order parameter: $\mathbf{g} = \mathbf{f}^{\mathrm{I}} + \mathbf{f}^{\mathrm{II}}$.
  - Landau free energy:
    $\mathcal{F} = a g^2 + b\, g^3 \cos 3\theta_g + c g^4$.
  - 1st-order transition. (c.f. $\mathrm{ZnCr_2O_4}$).
- $\mathbf{q} = 0$ Néel order.



Softer odd phonon

- Softer $\mathbf{q} = 0$ odd phonon E_u.
- Bond order: red+green state.
- Tetragonal distortion $a = b < c$:
  - Tetrahedra A: flattened $\parallel x$.
  - Tetrahedra B: flattened $\parallel y$.
- Spin-peierls order parameter $\mathbf{u} \neq 0$, $\mathbf{g} \neq 0$.
- Collinear spin order with $\mathbf{q} = (0, 0, 1)$.
- The commensurate limit of $CdCr_2O_4$.

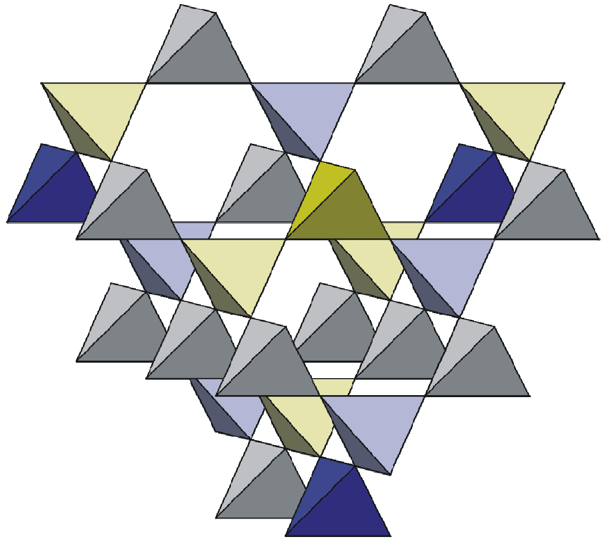


Lattice distortion: $ZnCr_2O_4$

- 1st-order phase transition at $T = 12.5$ K.
- Overall distortion: $a = b > c$.
- Non-uniform lattice distortion: soft even phonon with $\mathbf{q} = \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$.
- Quadrupled unit cell: $\sqrt{2} \times \sqrt{2} \times 2$.
- Spin-peierls order parameters: $\mathbf{g}_{(\frac{1}{2}\frac{1}{2}\frac{1}{2})}, \mathbf{g}_{(\frac{1}{2}\frac{\bar{1}}{2}\frac{\bar{1}}{2})}, \mathbf{g}_{(\frac{\bar{1}}{2}\frac{1}{2}\frac{\bar{1}}{2})}, \mathbf{g}_{(\frac{\bar{1}}{2}\frac{\bar{1}}{2}\frac{1}{2})}$.
- Magnetic order at $T = 12.5$ K.
  - Non-collinear spin order.
  - $\mathbf{q} = \{\frac{1}{2}, \frac{1}{2}, 0\}$ and $\mathbf{q} = \{1, 0, \frac{1}{2}\}$.

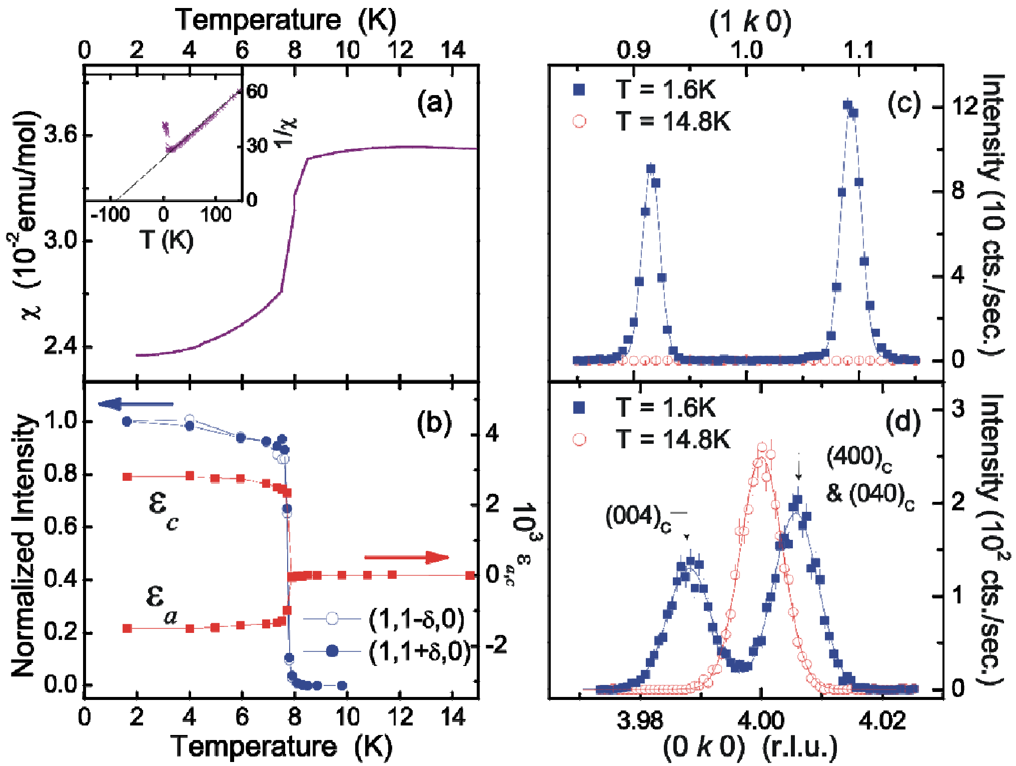
S.-H. Lee *et al.* (2007).

H. Ueda *et al.* (2003).



CdCr2O4: Experiments

- 1st-order transition at $T = 7.8$ K.
- Tetragonal distortion $a = b < c$. red+green state.
- Incommensurate magnetic order: $\mathbf{Q} = (0, \delta, 1)$ with $\delta \sim 0.09$.
- Coplanar spins: $\mathbf{S} \perp y$-axis. (the spiral axis).

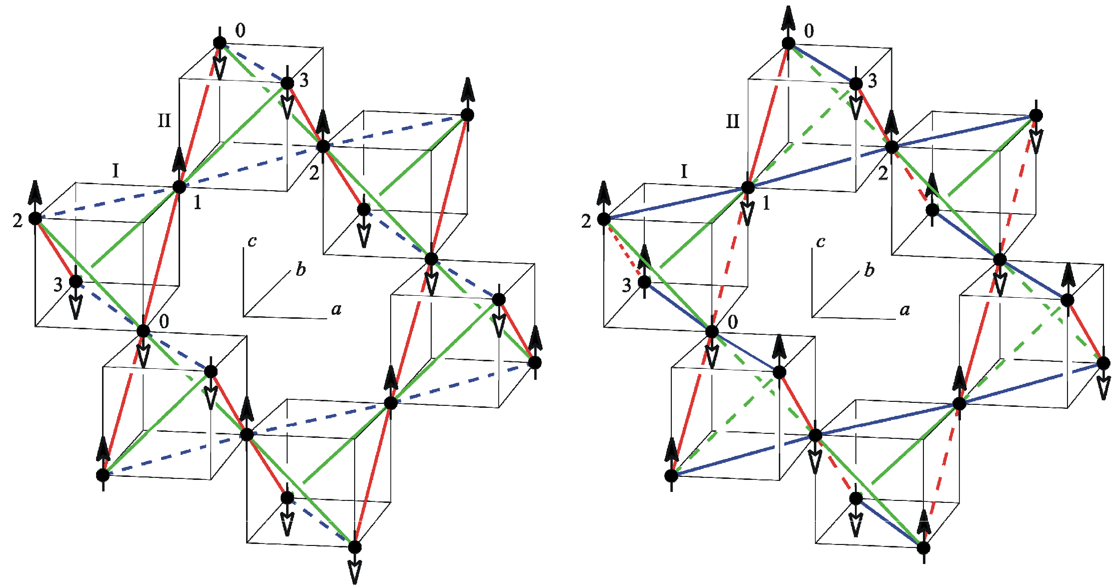


J.-H. Chung *et al.*, (2005)

CdCr2O4: *ab initio* Calculation

- LSDA+U method.
- $U = 3$ eV, $J_H = 0.9$ eV.
- $a = 8.54$ Å(ab initio)
  $a = 8.59$ Å(Exp)

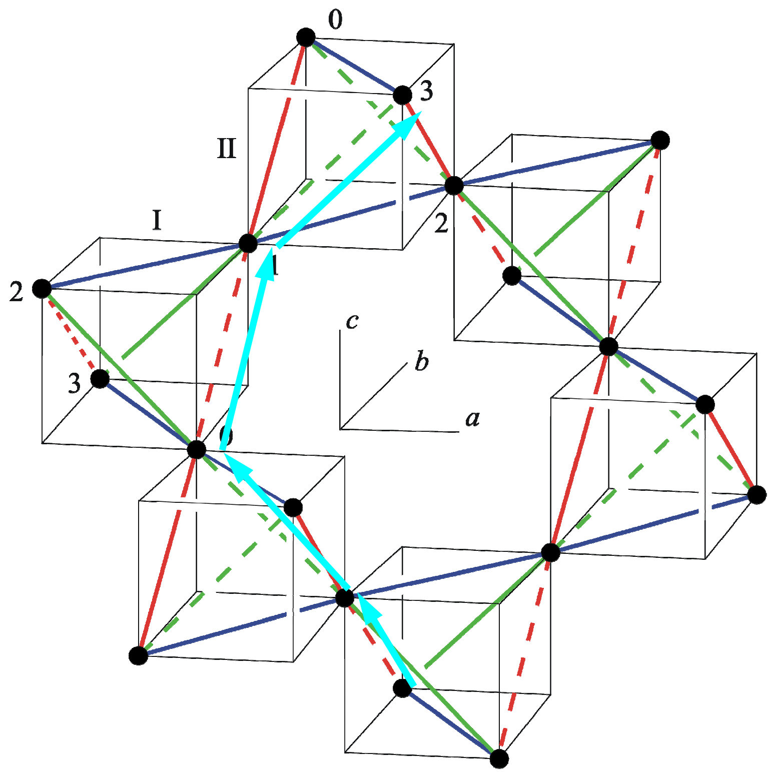
C. Fennie (unpublished).



	$I4_1/amd$ (E_g)	$I4_122$ (E_u)	Experiment
$\Delta\epsilon_a \times 10^3$	$+3.2$	-2.9	-1.7
$\Delta\epsilon_c \times 10^3$	-9.5	$+2.5$	$+2.5$
ΔE_S (meV/f.u.)	$+0.7$	-5.4	
	blue state	red+green state	

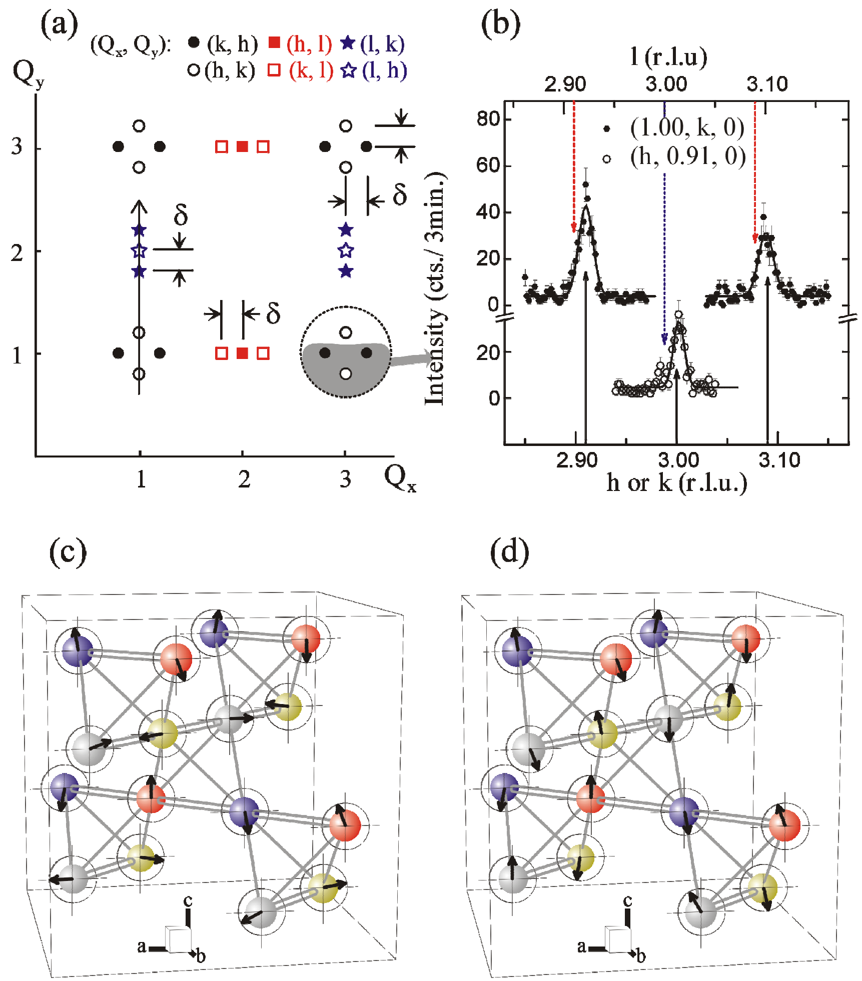
A Chiral pyrochlore lattice

- Broken parity: red+green distortion.
- Frustrated (parallel spins) bonds form a spiral.



A theory for the spiral magnetic order ?

- Magnetic spirals:
  - $\mathbf{q} = (0, \delta, 1)$.
  - $\mathbf{S} \perp y$-axis.
- The red+green state:
  - Chiral lattice.
  - Spin-orbital
    $\Rightarrow$ magnetic spirals ?
  - $\mathbf{q} = (0, 0, 1)$ collinear spins
    $\Rightarrow \mathbf{q} = (0, \delta, 1)$ spiral ?



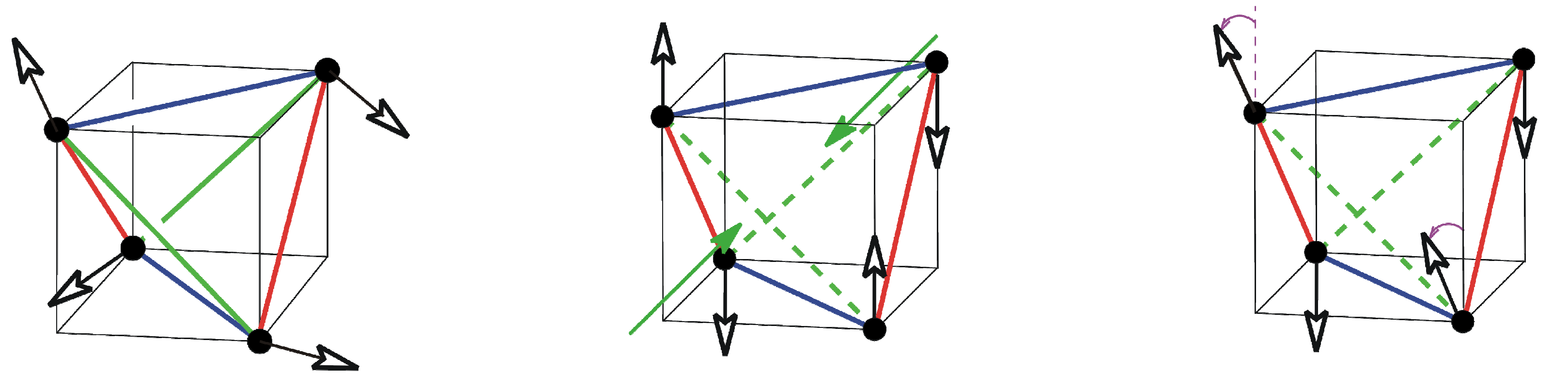
Theoretical model: Energy scales

$$J \gg K \gg D$$

- NN exchange: $J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$.
- Hard constraint: $\mathbf{S}_{\boxtimes} = 0$.
- Huge degeneracy.

- Spin-lattice coupling: $k(\delta r)^2/2 - J'\delta r\,(\mathbf{S}_i \cdot \mathbf{S}_j)$. $\Rightarrow -K(\mathbf{S}_i \cdot \mathbf{S}_j)^2$.
- Broken parity.
- Collinear spins.

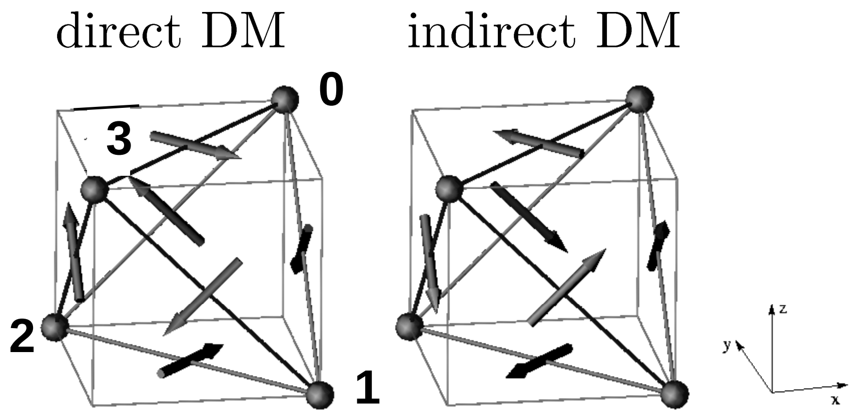
- Spin-orbital coupling $\longrightarrow$ DM interaction: $\mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$.
- Spiral magnetic order.
- Chiral ground state.

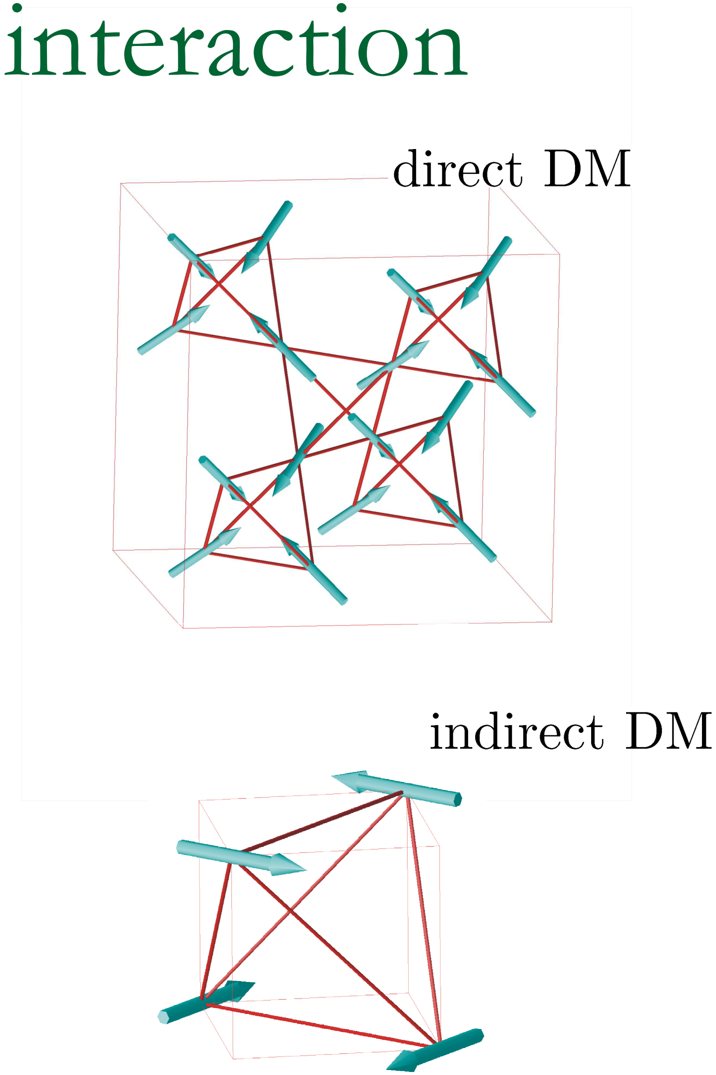


Dzyaloshinskii-Moriya interaction

- Spin-orbital coupling
  $\Rightarrow$ DM interaction:

$$E_{\mathrm{DM}} = \sum_{\langle ij \rangle} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j).$$





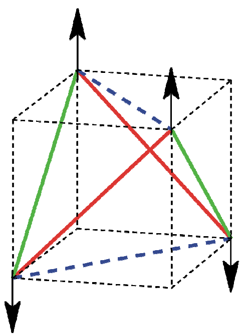
M. Elhajal *et al.*, (2005).

Staggered magnetizations

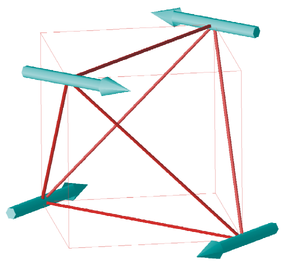
$$E_{\mathrm{DM}} = -D\big[\hat{\mathbf{x}}\cdot(\mathbf{L}_2\times\mathbf{L}_3) + \hat{\mathbf{y}}\cdot(\mathbf{L}_3\times\mathbf{L}_1) + \hat{\mathbf{z}}\cdot(\mathbf{L}_1\times\mathbf{L}_2)\big].$$

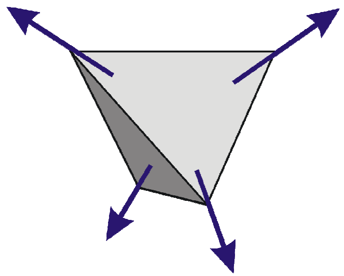
- $\mathbf{S}_{\boxtimes} = \mathbf{S}_0 + \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 = 0.$
- $\mathbf{L}_1 = \mathbf{S}_0 + \mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3.$
- $\mathbf{L}_2 = \mathbf{S}_0 - \mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3.$
- $\mathbf{L}_3 = \mathbf{S}_0 - \mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3.$

- Chirality of DM interaction:
  $D > 0$: direct.
  $D < 0$: indirect.



$\mathbf{L}_1 = \mathbf{L}_2 = 0,\ \mathbf{L}_3 = 4S\hat{\mathbf{z}}.$





$\mathbf{L}_1 = \frac{4S}{\sqrt{3}}\hat{\mathbf{x}},\ \mathbf{L}_2 = \frac{4S}{\sqrt{3}}\hat{\mathbf{y}},\ \mathbf{L}_3 = \frac{4S}{\sqrt{3}}\hat{\mathbf{z}}.$

$\mathbf{L}_1 = 2S(\hat{\mathbf{x}}+\hat{\mathbf{y}}),\ \mathbf{L}_2 = 2S(\hat{\mathbf{x}}-\hat{\mathbf{y}}),\ \mathbf{L}_3 = 0.$

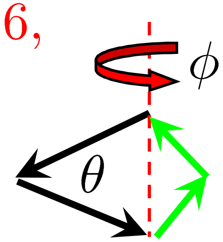
Independent degrees of freedom

Classical spins on a tetrahedron:

- Ground state constraint: $\mathbf{S}_{\boxtimes} = 0$.
- $D = 8 - 3 = 5$: (θ, ϕ) + rigid rotation .

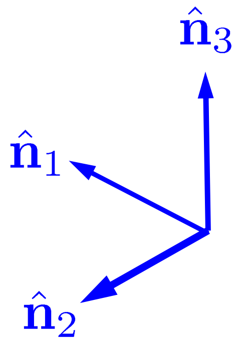
$D = 2$: bond doublet $\mathbf{f} = (f_1, f_2)$

$$f_1 = (\phi_1^2 + \phi_2^2 - 2\phi_3^2)/\sqrt{6},$$
$$f_2 = (\phi_1^2 - \phi_2^2)/\sqrt{2}.$$



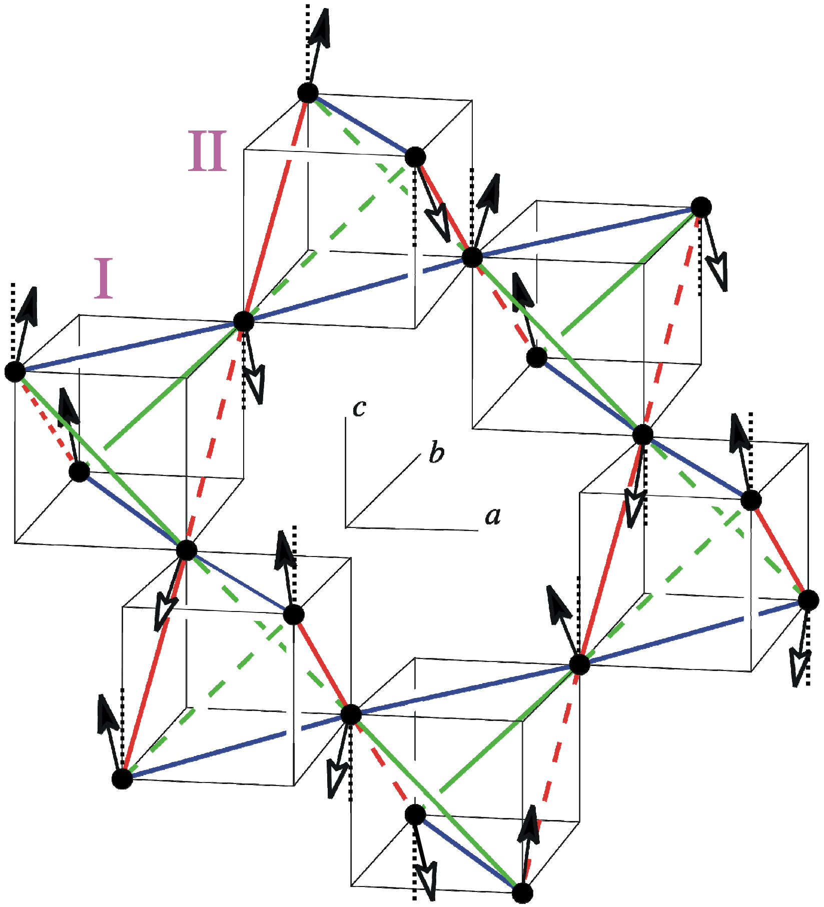
- Parametrization: $\mathbf{L}_i = 4S\,\phi_i\,\hat{\mathbf{n}}_i$.
  - $\phi_1^2 + \phi_2^2 + \phi_3^2 = 1$.
  - $\hat{\mathbf{n}}_i \perp \hat{\mathbf{n}}_j$.

$D = 3$:
Euler angles
for the triad $\hat{\mathbf{n}}_i$



Perturbing the collinear state

- Néel order of red+green state:
  - $\mathbf{q} = (0,0,1)$. $e^{i\mathbf{q}\cdot\mathbf{r}} = \pm 1$.
  - $\mathbf{L}_1^{\mathrm{I}} = 4S\,\hat{\mathbf{n}}\,e^{i\mathbf{q}\cdot\mathbf{r}}$, $\mathbf{L}_2^{\mathrm{I}} = \mathbf{L}_3^{\mathrm{I}} = 0$.
  - $\mathbf{L}_2^{\mathrm{II}} = 4S\,\hat{\mathbf{n}}\,e^{i\mathbf{q}\cdot\mathbf{r}}$, $\mathbf{L}_1^{\mathrm{II}} = \mathbf{L}_3^{\mathrm{II}} = 0$.
- Add a small perturbation on I:
  - $\mathbf{L}_i^{\mathrm{I}} = 4S\,\phi_i(\mathbf{r})\,\hat{\mathbf{n}}_i(\mathbf{r})\,e^{i\mathbf{q}\cdot\mathbf{r}}$.
  - $\phi_1 \approx 1 - (\phi_2^2 + \phi_3^2)/2$.
  - $\phi_2,\ \phi_3 \ll 1$.
- The magnetic state of type-II tetrahedra is encoded in $\mathbf{L}_i^{\mathrm{I}}$.



Magnetic state of sublattice II

- Constraint from J:

$$\mathbf{S}^{\mathrm{II}}_{\boxtimes} = \mathbf{S}^{\mathrm{I}}_0(\mathbf{r}) + \mathbf{S}^{\mathrm{I}}_1(\mathbf{r}+\mathbf{a}_1)$$
$$+\mathbf{S}^{\mathrm{I}}_2(\mathbf{r}+\mathbf{a}_2) + \mathbf{S}^{\mathrm{I}}_3(\mathbf{r}+\mathbf{a}_3) = 0$$

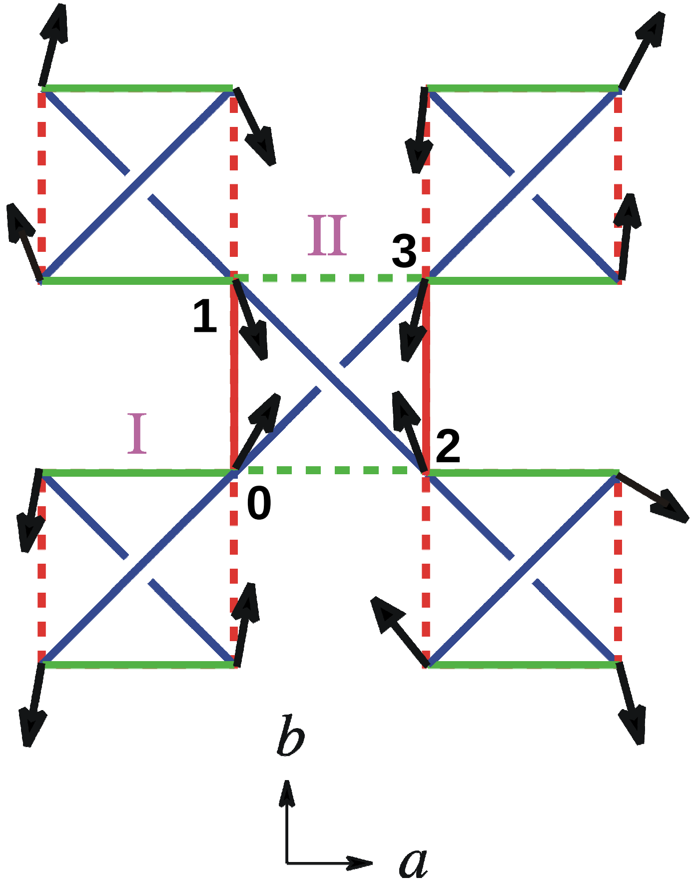
- Gradient expansion:

$$\mathbf{S}^{\mathrm{II}}_{\boxtimes} = \phi_3\,\hat{\mathbf{n}}_3 - \partial_y\,\hat{\mathbf{n}}_1 = 0.$$

$$\implies \quad \phi_3 = \hat{\mathbf{n}}_3 \cdot \partial_y\,\hat{\mathbf{n}}_1$$

- Néel vectors of type-II tetrahedron:

$$\mathbf{L}^{\mathrm{II}}_1 = \phi_2\,\hat{\mathbf{n}}_2 - \partial_z\,\hat{\mathbf{n}}_1,$$
$$\mathbf{L}^{\mathrm{II}}_2 = \hat{\mathbf{n}}_1, \quad \mathbf{L}^{\mathrm{II}}_3 = -\partial_x\,\hat{\mathbf{n}}_1.$$



Effective energy functional

- Magneto-elastic energy $E_{me} = -K_u|\mathbf{u}|^2 = -K_u\,(\mathbf{f}^{\mathrm{I}} - \mathbf{f}^{\mathrm{II}})^2$:

$$\Rightarrow E_{me} = K_u S^4 \left[(\partial_x \hat{\mathbf{n}}_1)^2 + (\partial_y \hat{\mathbf{n}}_1)^2 + 2\,(\partial_z \hat{\mathbf{n}}_z)^2 - (\hat{\mathbf{n}}_2 \cdot \partial_z \hat{\mathbf{n}}_1)^2\right].$$

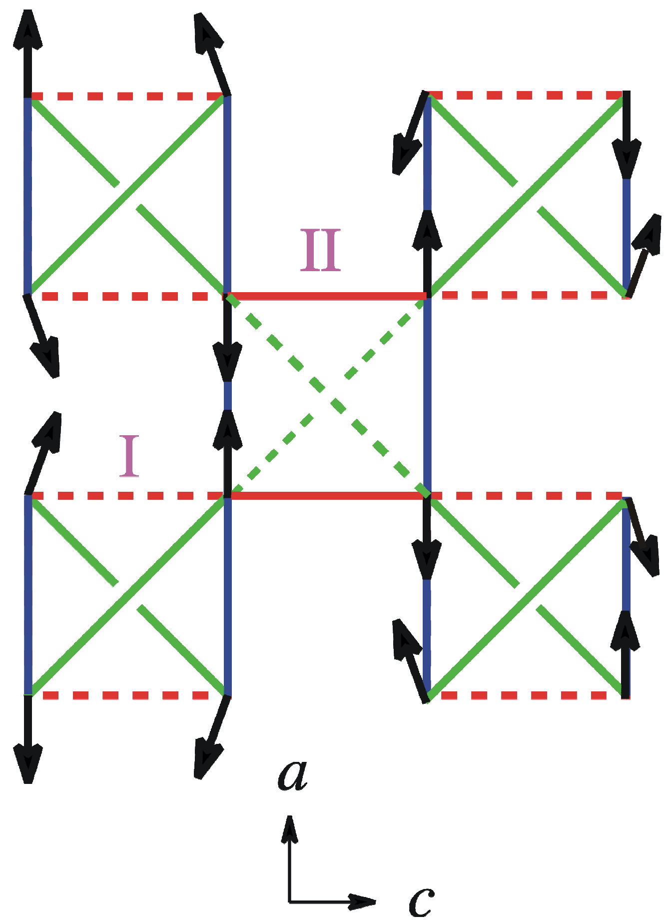
- DM interaction $E_{\mathrm{DM}} = \sum_{\langle ij\rangle} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$: Lifshitz invariants

$$\Rightarrow E_{\mathrm{DM}} = -DS^2\,\hat{\mathbf{n}}_1 \cdot \left(\hat{\mathbf{x}} \times \partial_x \hat{\mathbf{n}}_1 + \hat{\mathbf{y}} \times \partial_y \hat{\mathbf{n}}_1 - \hat{\mathbf{z}} \times \partial_z \hat{\mathbf{n}}_1\right).$$

- Minimization of $E_{me} + E_{\mathrm{DM}} \longrightarrow$ Magnetic spirals.

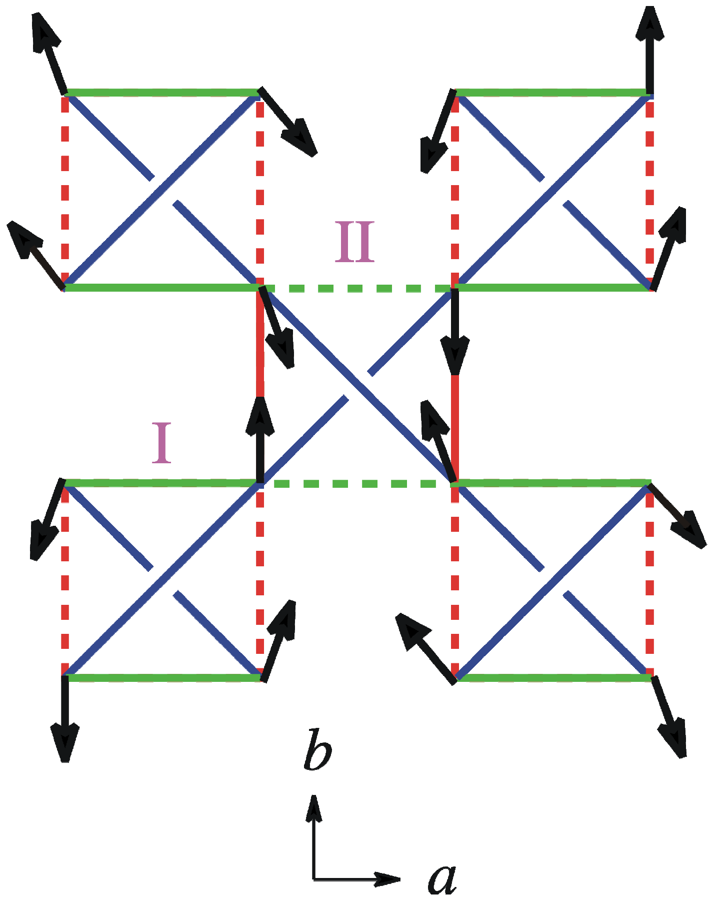
Spiral magnetic order I

- Coplanar spins rotating about the y-axis:
  - $\mathbf{L}_1^{\mathrm{I}} = 4S\, e^{i\mathbf{q}\cdot\mathbf{r}}(\cos\delta y,\, 0,\, \sin\delta y).$
  - $\mathbf{L}_2^{\mathrm{I}} = \delta\,\hat{\mathbf{y}} \times \mathbf{L}_1^{\mathrm{I}}, \;\; \mathbf{L}_3^{\mathrm{I}} = 0.$
  - $\delta = D/K_u S^2$ (~ 0.09 Exp.)
  - $\mathbf{q}_M = (0, \delta, 1).$
- Sublattice II remains collinear.
- Equivalent to spirals rotating about the x-axis: I $\longleftrightarrow$ II.
- Consistent with experiments.



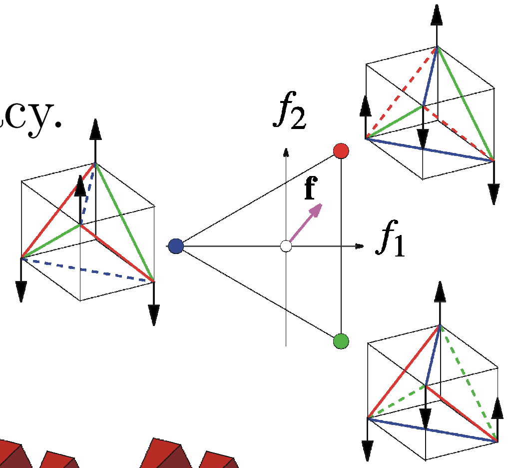
Spiral magnetic order II

- Coplanar spins rotating about the z axis:
  - $\mathbf{L}_1^{\mathrm{I}} = 4S\, e^{i\mathbf{q}\cdot\mathbf{r}}\,(\cos\delta z,\, \sin\delta z,\, 0)$.
  - $\delta = D/K_u\, S^2$.
  - $\mathbf{q}_M = (0, 0, 1+\delta)$.
- Preserve the symmetry between sublattices I and II.
- Not observed in experiment.
- Unfavorable due to large AF J_3: $E_{\mathrm{NNN}} = J_3 S^2 (\partial_z \hat{\mathbf{n}}_1)^2$. ($J_3 \approx 0.3\, J_1$ *ab initio* calculation).

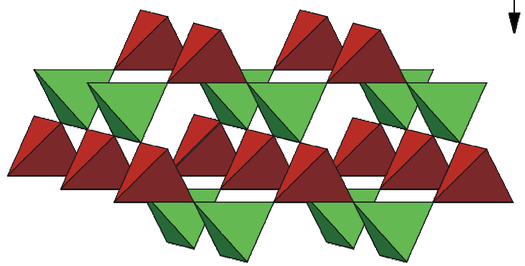


Summary

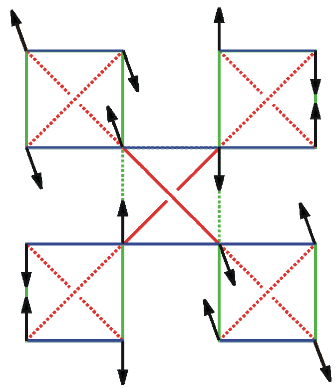
- Geometrical frustration leads to extensive degeneracy.



- Frustration relief through spin-lattice couplng: Collinear spins and falttened tetrahedron.
- Red+green state for $CdCr_2O_4$:
  - Tetragonal distortion $a = b < c$.
  - Collinear spin order with $\mathbf{q} = (0, 0, 1)$.
  - Broken parity and a chiral lattice.



- Spiral magnetic order in $CdCr_2O_4$:
  - Spin-orbital coupling transfers the lattice chirality to spins: $\mathbf{q} = (0, 0, 1) \to (0, \delta, 1)$.
  - Dzyaloshinskii-Moriya interaction.



- Effective field theory for the spirals.

Open questions

- $CdCr_2O_4$
  - $I4_1/amd$ v.s. $I4_122$. Broken parity ?
  - X-ray scattering. Second-harmonic generation.
  - Spin-Peirls order parameter $\mathbf{u} \to -\mathbf{u}$: 2nd-order transition v.s. strong 1st-order transition at $T = 7.8$ K ?
  - Spinwave spectrum. DM induced excitation gap ?
- $ZnCr_2O_4$
  - Nonuniform distortion dominated by $\mathbf{q} = \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ phonons.
  - 8-component spin-Peierls order parameter $\mathbf{g}_{\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}}$: no cubic term in Landau expansion v.s. strong 1st-order transition at $T = 12.5$ K.
  - Non-collinear magnetic order below T_c ? $\mathbf{q} = \{\frac{1}{2}, \frac{1}{2}, 0\}$ and $\{1, 0, \frac{1}{2}\}$.