Spin-Driven Spontaneous Currents and Charge Redistribution in Mott Insulators

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•Mott insulators

$$H = -\sum_{ij\sigma} t_{ij} (c^{+}_{i\sigma} c_{j\sigma} + c^{+}_{j\sigma} c_{i\sigma}) + \frac{U}{2} \sum_{i} (n_i - 1)^2,$$

•Standard paradigm: for U>>t and one electron per site electrons are localized on sites. All charge degrees of freedom are frozen out; only spin degrees of freedom remain in the ground and lowest excited states

$$H_S = \frac{4t^2}{U} (\vec{S}_1 \cdot \vec{S}_2 - 1/4).$$

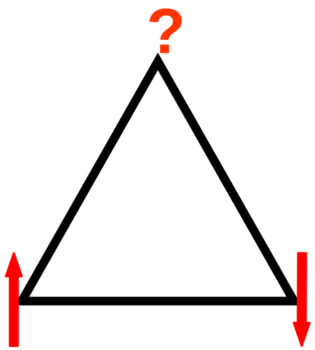
•Not the full truth!

•For certain spin configurations there exist in the ground state of strong Mott insulators **spontaneous electric currents** (and corresponding orbital moments)!

•For some other spin textures there may exist a **spontaneous charge redistribution**, so that $\langle n_i \rangle$ is not 1! This, in particular, can lead to the appearance of a spontaneous **electric polarization** (a purely ***electronic mechanism of multiferroic behaviour***)

•These phenomena, in particular, appear in frustrated systems, with **scalar chirality** playing important role

- Spin systems: often complicated spin structures, especially in frustrated systems – e.g. those containing triangles as building blocks



- Isolated triangles (trinuclear clusters) - e.g. in some magnetic molecules (V15, …)
- Solids with isolated triangles ($La_4Cu_3MoO_{12}$)
- Triangular lattices
- Kagome
- Pyrochlore

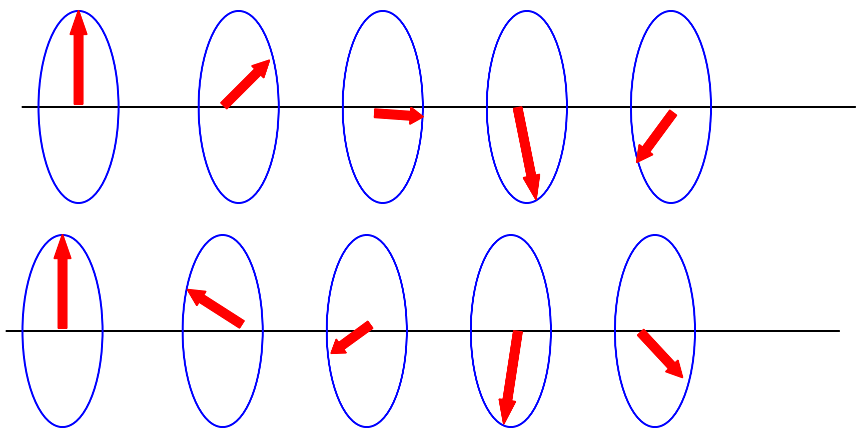
Often complicated ground states; sometimes $\langle \vec{\mathbf{S}}_i \rangle = 0$

spin liquids

Some structures, besides $\langle \vec{\mathbf{S}}_i \rangle$, are characterized by:

Vector chirality

$$\left[\vec{\mathbf{S}}_i \times \vec{\mathbf{S}}_j\right]$$

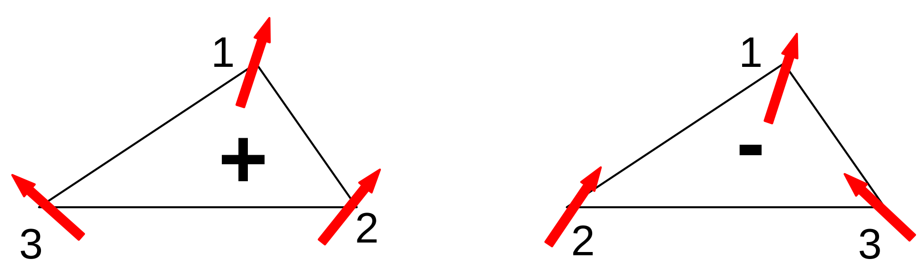


Scalar chirality

$$\chi_{123} = \vec{\mathbf{S}}_1 \left[\vec{\mathbf{S}}_2 \times \vec{\mathbf{S}}_3\right]$$

- solid angle

χ may be + or - :

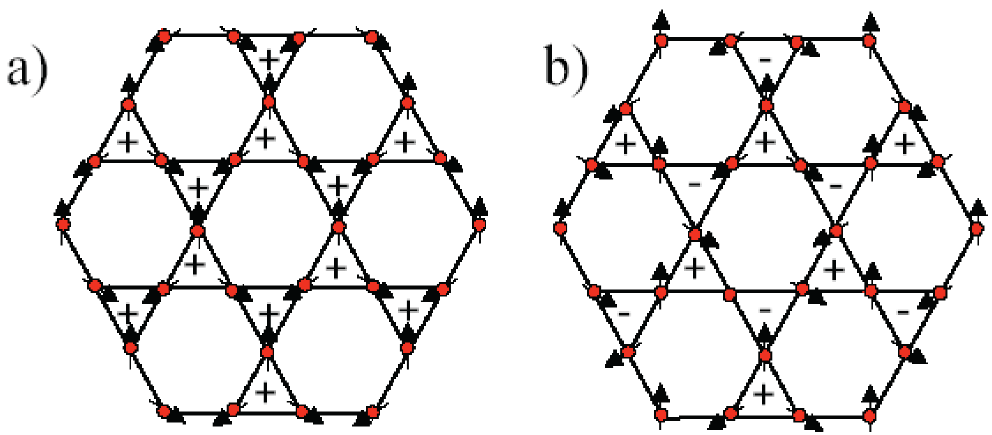


Scalar chirality χ is often invoked in different situations:

- Anyon superconductivity
- Berry-phase mechanism of anomalous Hall effect
- New universality classes of spin-liquids
- Chiral spin glasses

Chirality in frustrated systems: Kagome

a) Uniform chirality (q=0) b) Staggered chirality (√3x√3)



But what is the scalar chirality physically?

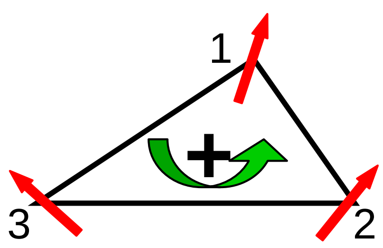
What does it couple to?

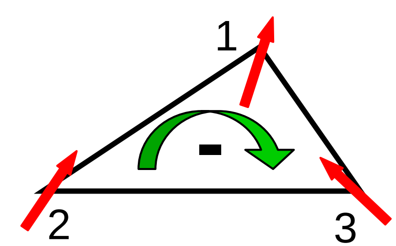
How to measure it?

Breaks time-reversal-invariance T and inversion P - like currents!

$\chi_{123} \neq 0$ means spontaneous circular electric current $j_{123} \neq 0$ and orbital moment $L_{123} \neq 0$

$$\boldsymbol{L_{123} \propto j_{123} \propto \chi_{123}}$$





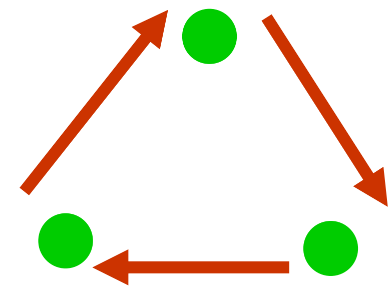
Couples to magnetic field:

$$-\vec{L}\vec{H} \sim -\chi H$$

Difference between Mott and band insulators

$$H = -\sum_{ij\sigma} t_{ij}(c^{+}_{i\sigma}c_{j\sigma} + c^{+}_{j\sigma}c_{i\sigma}) + \frac{U}{2}\sum_{i}(n_i - 1)^2, \qquad \langle n_i \rangle = 1.$$

- Only in the limit $U \to \infty$ electrons are localized on sites.
- At $t/U \neq 0$ electrons can hop between sites.



Orbital current

$$H_S = \frac{4t^2}{U}(\vec{S}_1 \cdot \vec{S}_2 - 1/4).$$

$$H = -t \sum c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum n_{i\uparrow} n_{i\downarrow} =$$

$$= H' + H_0$$

$t = 0$: localized electrons $\uparrow \; \downarrow \; \downarrow \; \uparrow \; \downarrow \; \downarrow$

Superexchange: virtual creation of polar states with $\langle n_i \rangle \neq 1$

$\uparrow \;\; \uparrow$ $\qquad$ $\Delta E = 0$ | $\uparrow \;\; \downarrow$ $\qquad$ $\Delta E = -\frac{t^2}{U}$

Calculate in perturbation theory in $t/U \ll 1$;
project to the (2^N-degenerate) states with $\langle n \rangle = 1$;
express through spin operators

$$c^{\dagger}_{i\uparrow} c_{i\uparrow} \leftrightarrow \tfrac{1}{2} + S^z_i \qquad c^{\dagger}_{i\uparrow} c_{i\downarrow} \leftrightarrow S^+_i$$

$$c^{\dagger}_{i\downarrow} c_{i\downarrow} \leftrightarrow \tfrac{1}{2} - S^z_i \qquad c^{\dagger}_{i\downarrow} c_{i\uparrow} \leftrightarrow S^-_i$$

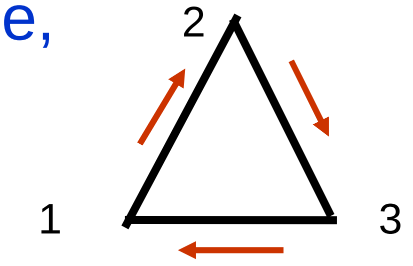
$$H_{eff} \sim \left\langle H' \frac{1}{H_0 - E_0} H' \right\rangle \sim \frac{t^2}{U} \langle c^{\dagger}_{i\sigma} c_{j\sigma} c^{\dagger}_{j\sigma'} c_{i\sigma'} \rangle \Rightarrow \frac{2t^2}{U} \vec{S}_i \vec{S}_j$$

Spin current operator and scalar spin chirality

- Current operator for Hubbard Hamiltonian on bond ij:

$$\vec{I}_{ij} = \frac{iet_{ij}\vec{r}_{ij}}{\hbar r_{ij}} \sum_{\sigma} (c^{+}_{i\sigma} c_{j\sigma} - c^{+}_{j\sigma} c_{i\sigma}).$$

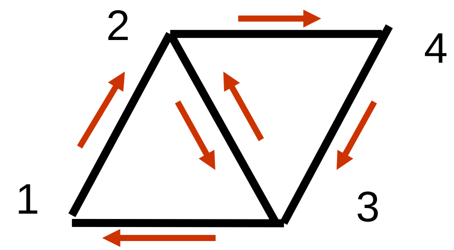
- Projected current operator: odd # of spin operators, scalar in spin space. For smallest loop, triangle,



$$\boxed{\vec{I}_{S,12}(3) = \frac{\vec{r}_{ij}}{r_{ij}} \frac{24et_{12}t_{23}t_{31}}{\hbar U^2} [\vec{S}_1 \times \vec{S}_2] \cdot \vec{S}_3.}$$

- Current via bond 23

$$I_{S,23} = I_{S,23}(1) + I_{S,23}(4).$$



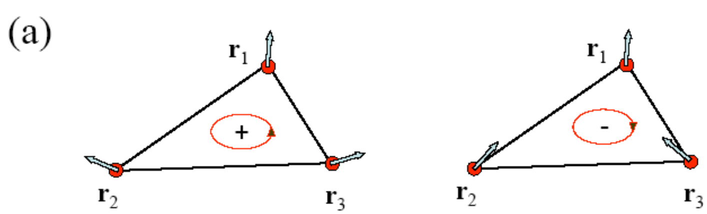
- On bipartite nn lattice I_S is absent.

Orbital currents in the spin ordered ground state $\langle \vec{S}_i \rangle \neq 0$

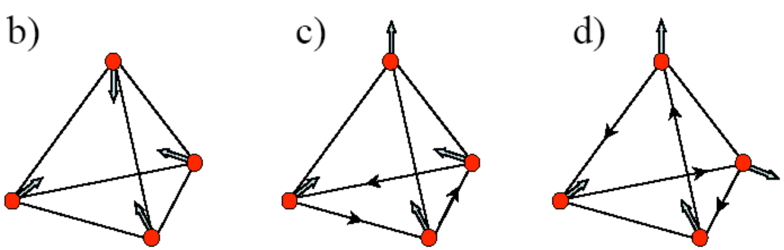
- Necessary condition for orbital currents is nonzero average chirality

$$\chi_{12,3} = [\vec{S}_1 \times \vec{S}_2] \cdot \vec{S}_3, \qquad \langle \chi_{ij,k} \rangle \neq 0.$$

- It may be inherent to spin ordering or induced by magnetic field



Triangles with $\pm$ chirality



On tetrahedron chirality may be nonzero but orbital currents absent.

Chirality in the ground state without magnetic ordering

- $$\left\langle \chi_{12,3} \right\rangle = \left\langle [\vec{S}_1 \times \vec{S}_2] \cdot \vec{S}_3 \right\rangle \neq 0, \qquad \left\langle \vec{S}_i \right\rangle = 0.$$

- Geometrically frustrated 2d system ⟶ Mermin-Wigner theorem ⟶ $\left\langle \vec{S}_i \right\rangle = 0.$

- State with maximum entropy may be with broken discrete symmetry $\left\langle \chi_{12,3} \right\rangle \neq 0.$

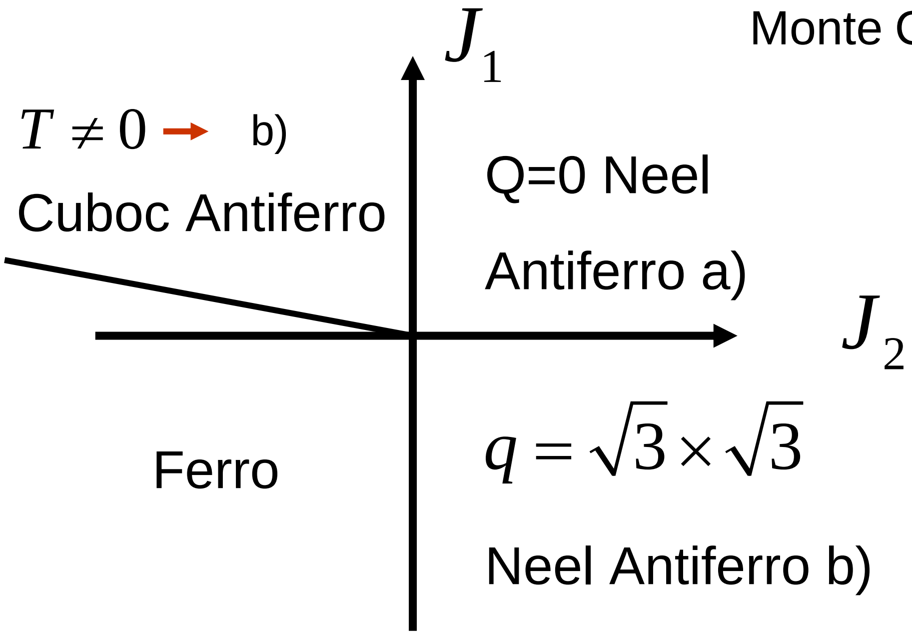
- Example: $J_1 - J_2$ model on kagome lattice:

$$H_S = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \vec{S}_i \cdot \vec{S}_\mathrm{k}.$$

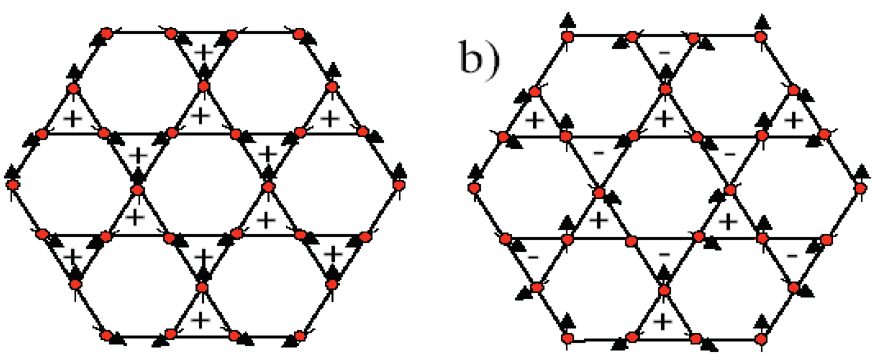
•(group of C.Lhuillier)

Ordering in $J_1 - J_2$ model on kagome lattice at T=0

Monte Carlo results by Domenge et al., 2007.



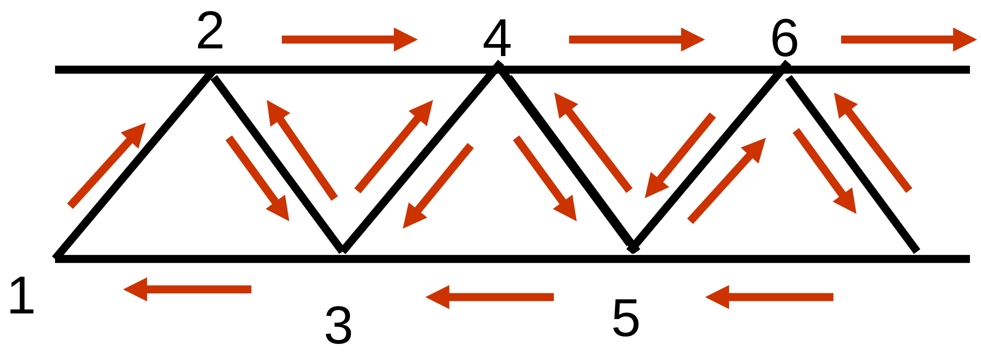
Phase diagram for classical order parameter

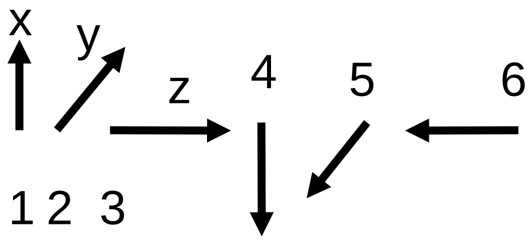


a) b)

For S=1/2 for low T cub'oc is chiral with orbital currents and without spin ordering.

Boundary and persistent current

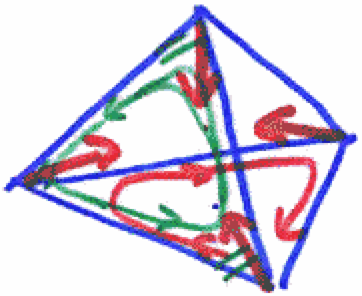




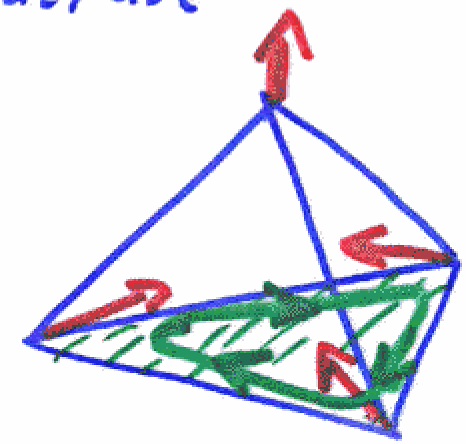
$$\chi = const$$

Boundary current in
gaped 2d insulator

- **Pyrochlores** with [111] anisotropy (a la spin ice, but with antiferro. exchange):

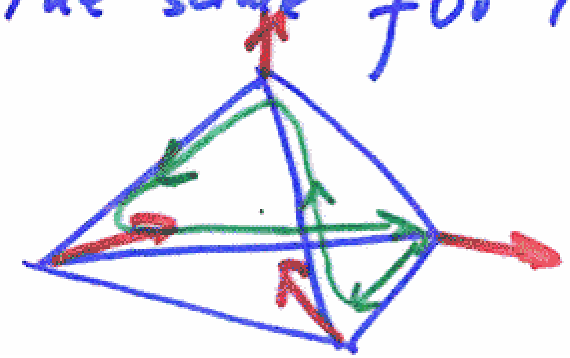


– currents compensate at each bond for 4-in structure



But in the field $H \parallel [111]$ (3 in – 1 out)
net current around basal triangle, and $\Sigma \parallel [111]$

The same for the field giving 2 in – 2 out



•Tetrahedra in exact solution:

Ground state - S=0, doubly-degenerate. In the ground state one can chose the state with chirality + or - .

Nonzero chirality → magnetic state. But currents at each edge = 0 **!** → magnetic octupole states?

Very similar to the situation with doubly-degenerate e_g orbitals:

$|z^2\rangle$ ------- $T^z=1/2$

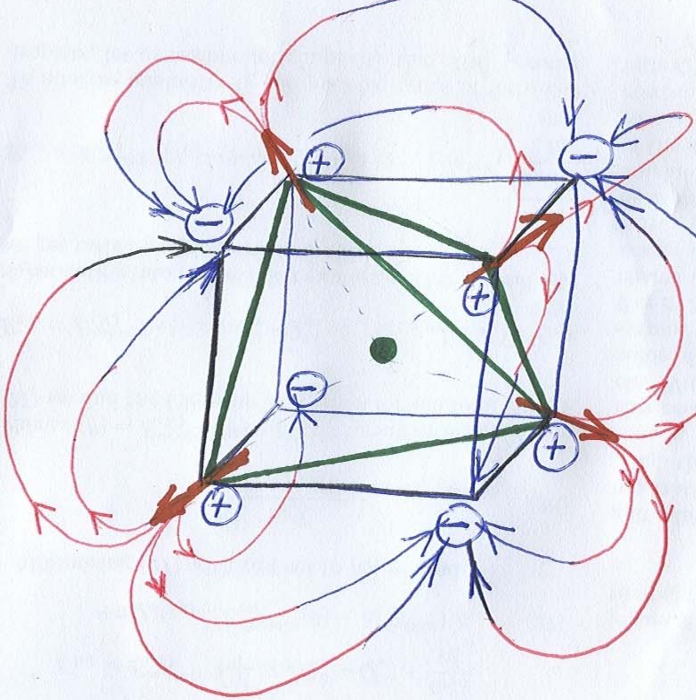
$|x^2-y^2\rangle$ --- $T^z=-1/2$

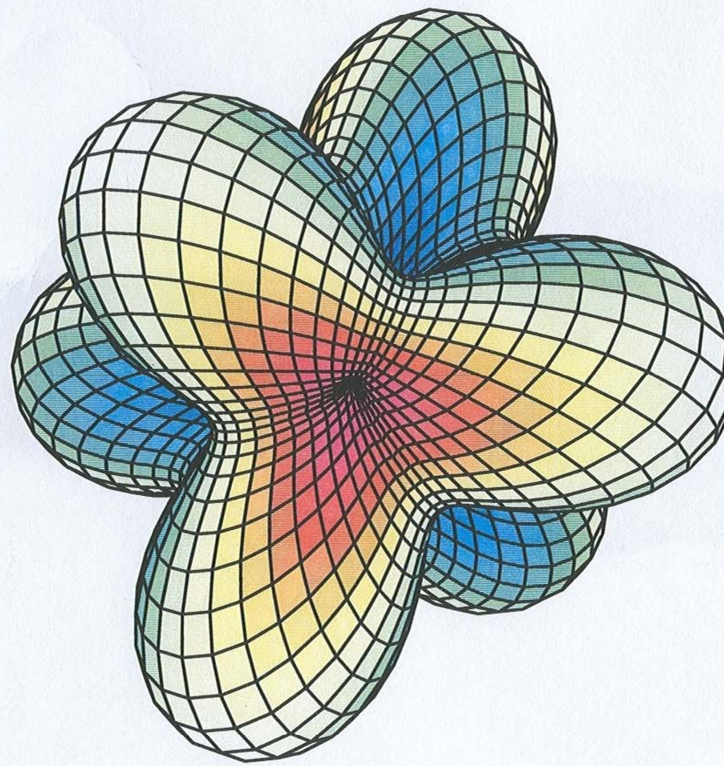
$(|z^2\rangle+i\,|x^2-y^2\rangle)$ ---- $T^y=1/2$, $(|z^2\rangle-i\,|x^2-y^2\rangle)$ ---- $T^y=-1/2$,

Eigenstates of T^y – states with magnetic octupoles!

Real combinations $a|z^2\rangle+b\,|x^2-y^2\rangle$ – states with electric quadrupoles.

The same for spin tetrahedra ?

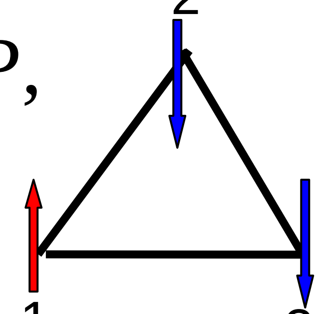




Spin-dependent electronic polarization

- Charge operator on site i: $$Q_i = e\sum_{\sigma} c_{i\sigma}^{+} c_{i\sigma}.$$
- Projected charge operator $$n_{S,i} = Pe^{S} n_i e^{-S} P,$$

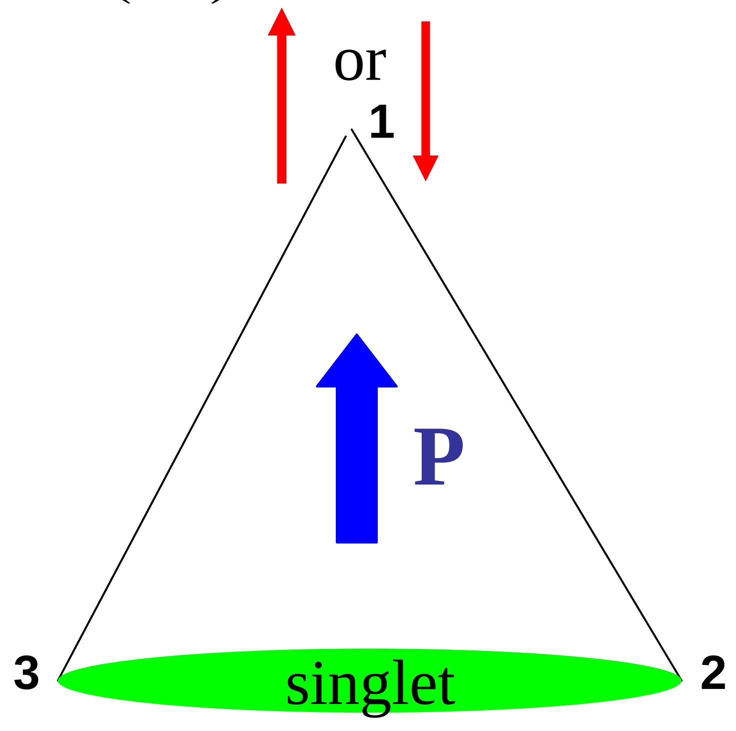
$$n_{S,1}(2,3) = 1 - \frac{8t_{12}t_{23}t_{31}}{U^2}[\vec{S}_1 \cdot (\vec{S}_2 + \vec{S}_3) - 2\vec{S}_2 \cdot \vec{S}_3].$$



- Polarization on triangle $$\vec{P}_{123} = e\sum_{i=1,2,3} n_{S,i}\vec{r}_i, \qquad \sum_i n_{S,i} = 3.$$
- Charge on site *i* is sum over triangles at site *i*.

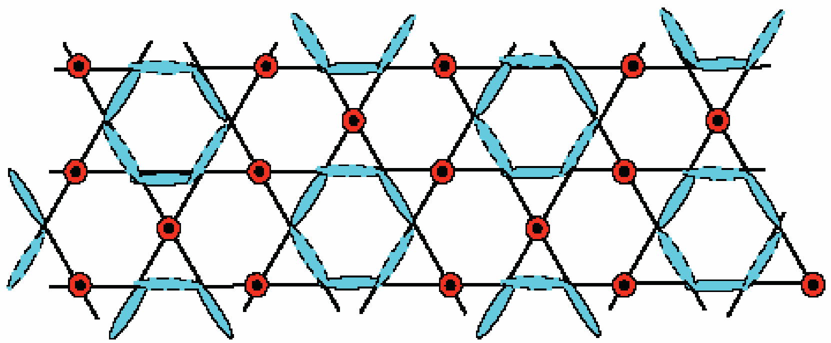
Electronic polarization on triangle

$$\langle n_1 \rangle = 1 + \delta n_1 = 1 - 8\left(\frac{t}{U}\right)^3 \left[\mathbf{S}_1(\mathbf{S}_2 + \mathbf{S}_3) - 2\mathbf{S}_2\mathbf{S}_3\right]$$



Purely electronic mechanism of multiferroic behavior!

Charges on kagome lattice



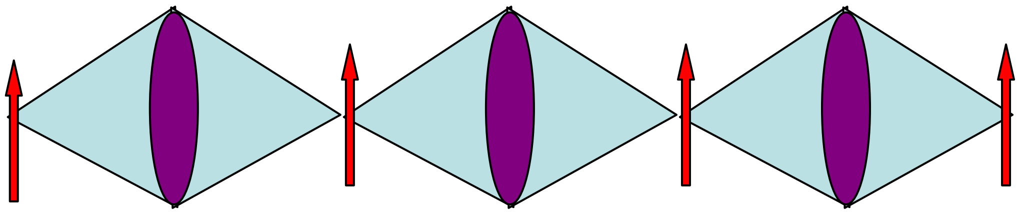
1/3 magnetization plateau:

Charge ordering for spins 1/3 in magnetic field: spin-driven CDW

- Typical situation at the magnetization plateaux!

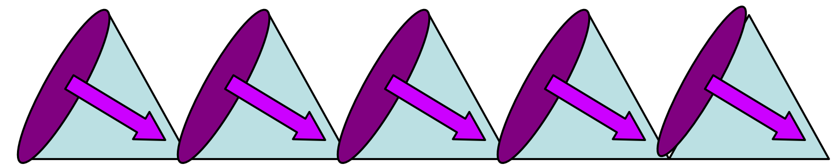
- Diamond chain (azurite $Cu_3(CO_3)_2(OH)_2$)

spin singlet

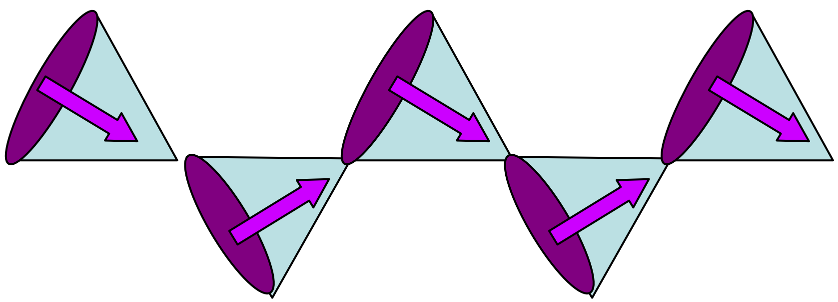


-will develop S-CDW

- Saw-tooth (or delta-) chain

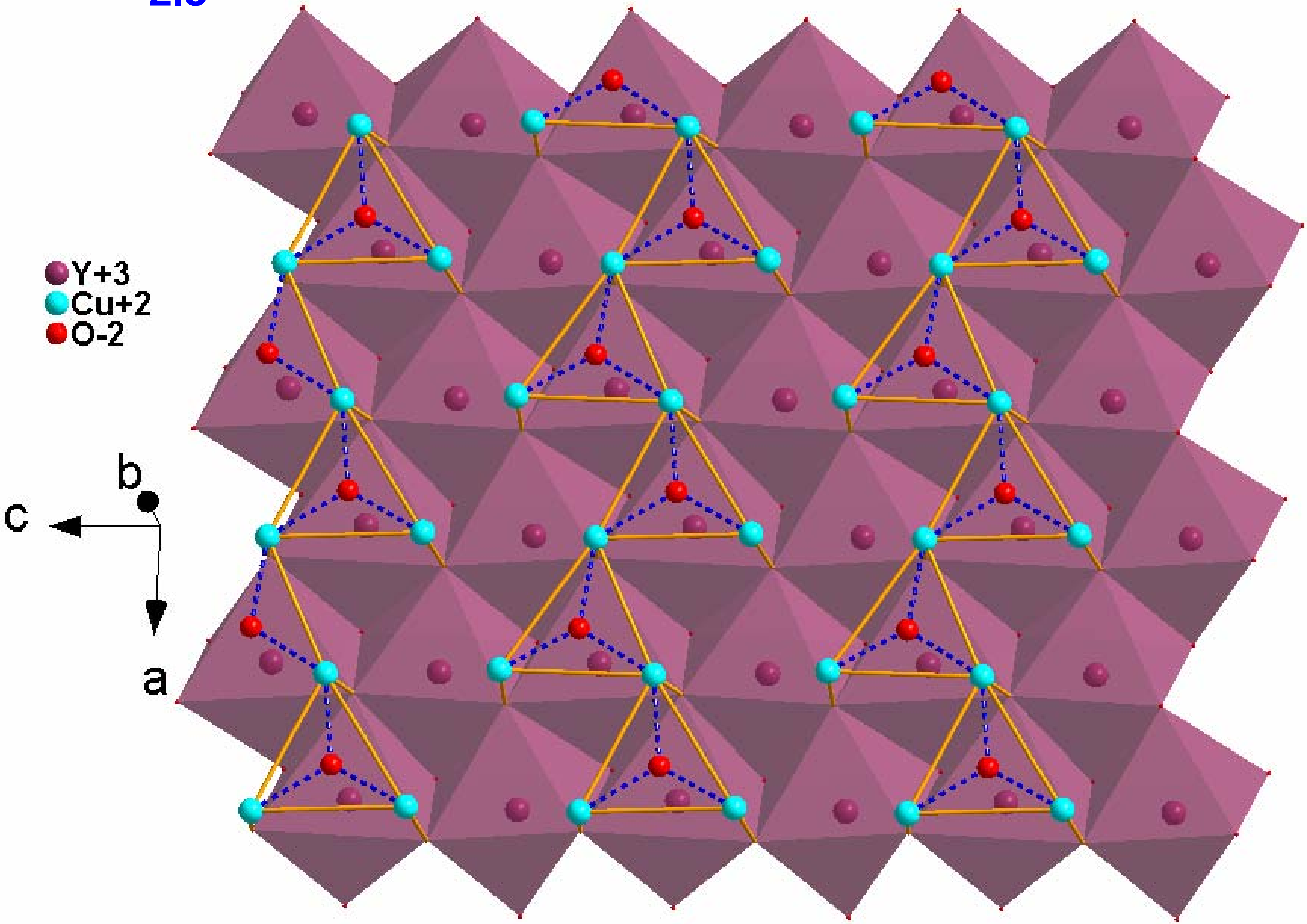


Net polarization

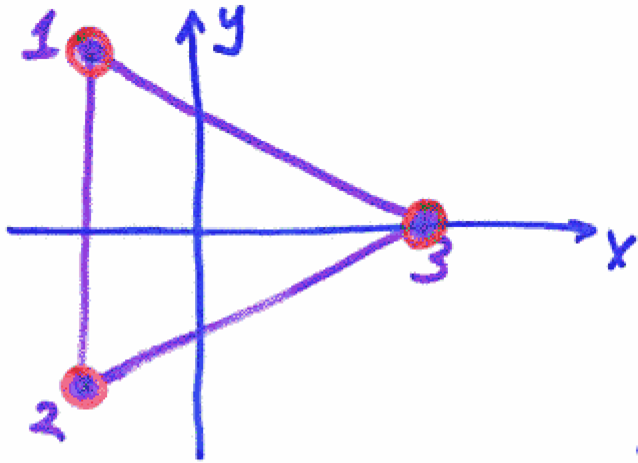


Net polarization

$CuYO_{2.5}$



Polarization of a triangle:



$$P_x = 4\sqrt{3}\,ea\left(\frac{t}{U}\right)^3\left[\vec S_1\cdot(\vec S_2+\vec S_3)-2\vec S_2\cdot\vec S_3\right]$$

$$P_y = 12\,ea\left(\frac{t}{U}\right)^3\vec S_1\cdot(\vec S_2-\vec S_3)$$

Dipole moments, or polarization, and current on a triangle, can be combined in one „isospin"-$\frac{1}{2}$:

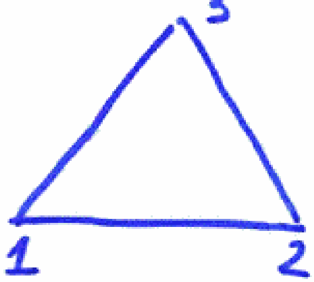
$$\left\{\begin{array}{l} \left.\begin{array}{l} P_x \longrightarrow -c\,T_x \\ P_y \longrightarrow c\,T_y \end{array}\right\} \text{real } (T\text{-even}) \\ \frac{ta}{U} I \longrightarrow c\,T_z \ \} \text{ imaginary } (T\text{-odd}) \end{array}\right.$$

– somewhat similar to pseudospin $\vec\tau$ for e_g-orbitals

$$\Big(\underbrace{\tau_z \rightarrow |z^2\rangle,\ \tau_x \rightarrow |x^2-y^2\rangle}_{\text{real } (T\text{-even})},\ \underbrace{\tau_y \rightarrow \frac{1}{\sqrt{2}}\left(|z^2\rangle \pm i\,|x^2-y^2\rangle\right)}_{\text{Im. } (T\text{-odd})}\Big)$$

Consequences for <u>dynamic properties</u>:

Equilateral triangle of $S=\frac{1}{2}$ with antiferro. exchang



$2^3 = 8$ states

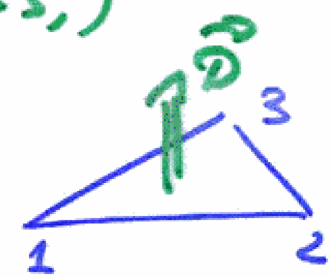
$S_{tot} = 3/2$

$S_{tot} = \frac{1}{2}$, $\chi = \pm$

Dzyaloshinskii-Moriya interaction:

$$-\vec{D}_{12}\cdot(\vec{S}_1\times\vec{S}_2) - \vec{D}_{23}(\vec{S}_2\times\vec{S}_3) - \vec{D}_{31}(\vec{S}_3\times\vec{S}_1)$$

E.g. $\vec{D}_{12} = \vec{D}_{23} = \vec{D}_3 \perp (123)$ plane



Splits ground state quartet

D

$(S^z = \frac{1}{2}, \chi = -)$
$(S^z = \frac{1}{2}, \chi = +)$

$(S^z = \frac{1}{2}, \chi = +)$
$(S^z = -\frac{1}{2}, \chi = -)$

(DM interaction plays a role of spin-orbit interaction for ground state quartet)

Isolated triangle: accounting for DM interaction

- DM coupling: $H_{DM} = \sum_{ij} D_{ij} \vec{S}_i \times \vec{S}_j .$
- For V15 $H_{DM} \approx D_z L_z S_z .$
- Splits lowest quartet into 2 doublets $\left|+\uparrow\right\rangle, \left|-\downarrow\right\rangle$ and $\left|+\downarrow\right\rangle, \left|-\uparrow\right\rangle$ separated by energy $\Delta = D_z .$
- Ac electric field induces transitions between $\chi = \pm 1.$
- Ac magnetic field induces transitions between $S_z = \pm 1/2.$

- ESR : magnetic field (**-HM**) causes transitions

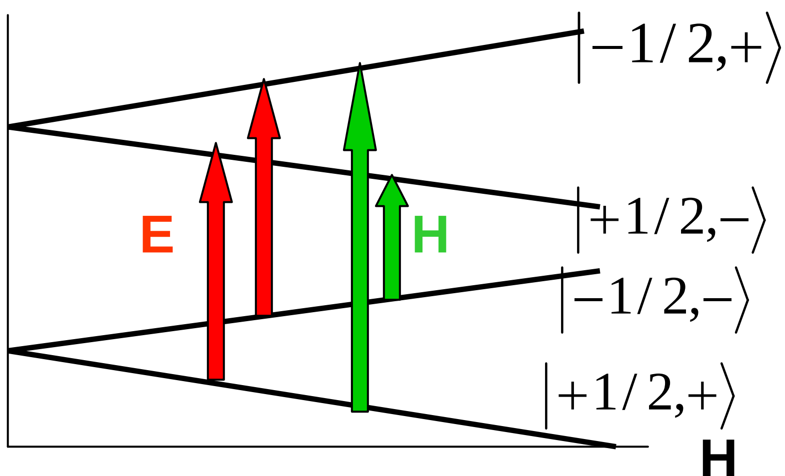
$$\left|1/2,\chi\right\rangle \rightarrow \left|-1/2,\chi\right\rangle,\ or\ \left|-1/2,\chi\right\rangle \rightarrow \left|1/2,\chi\right\rangle$$

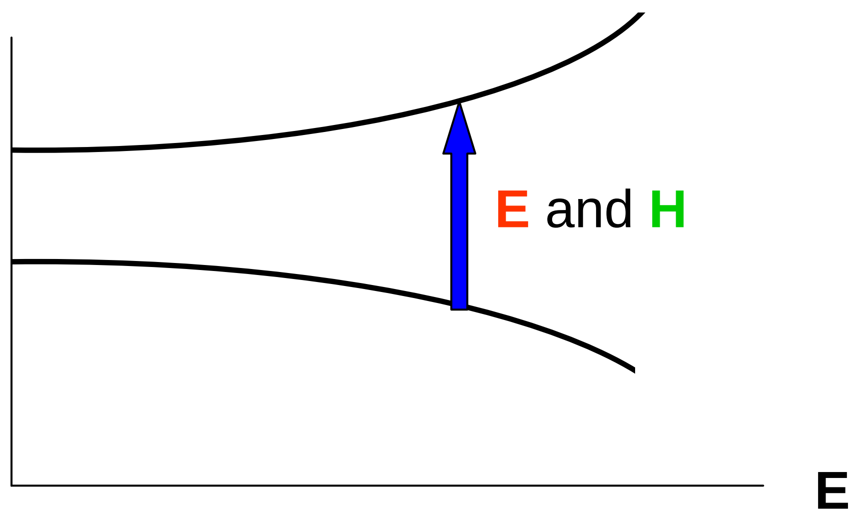
Here: electric field (**-Ed**) has nondiagonal matrix elements in χ:

$$\left\langle \chi=+\middle|\mathbf{d}\middle|\chi=-\right\rangle \neq 0$$ ⟹ electric field will cause

dipole-active transitions $\left|S^z,+\right\rangle \Leftrightarrow \left|S^z,-\right\rangle$

-- ESR caused by electric field E !

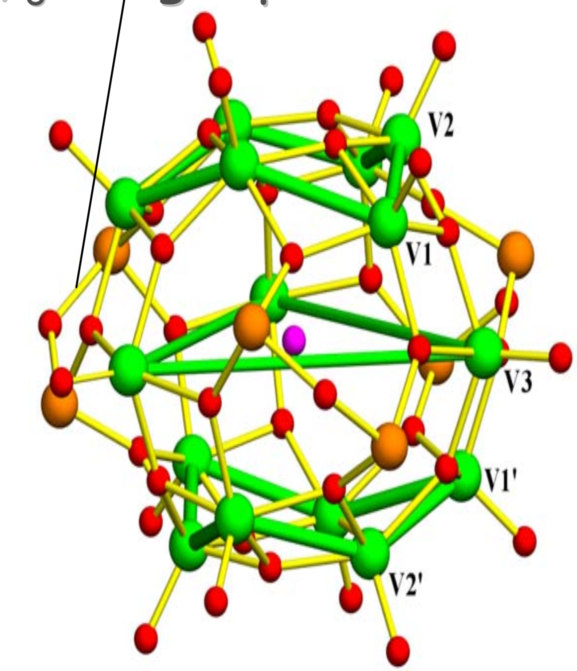




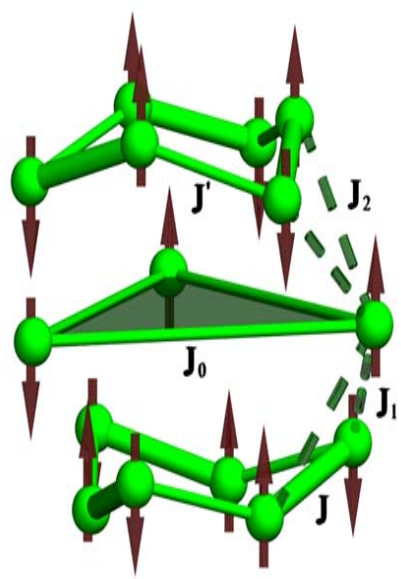
Qusispherical layered molecular structure of $K_6[V^{IV}_{15}As^{III}_6O_{42}(H_2O)]\cdot 8H_2O$ (V_{15} –cluster)

First observation of coherent states in which the fifteen cluster spins and the photons are entangled:

μ_3-oxo groups

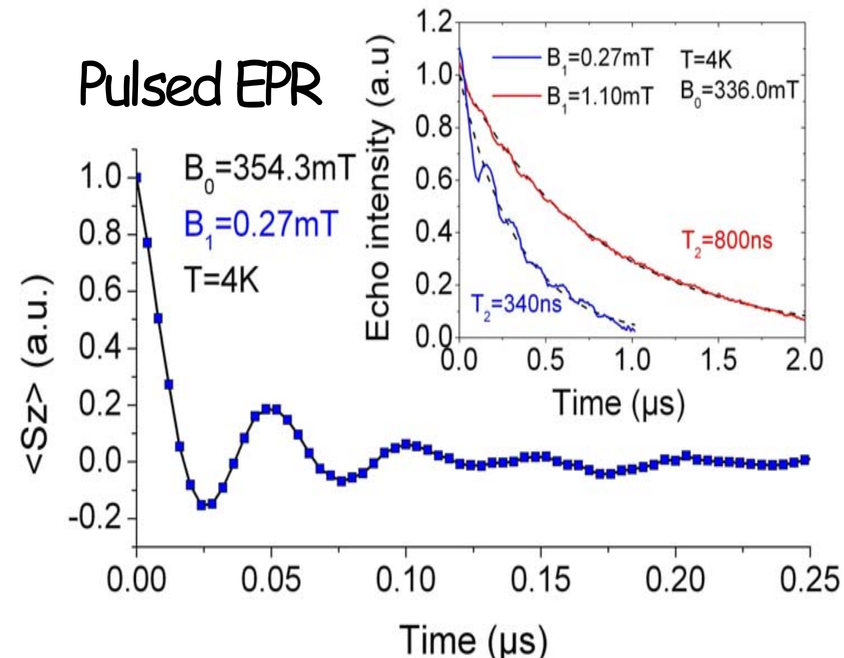


Metal network of $\{V_{15}As_6\}$



Spin-echo

Pulsed EPR

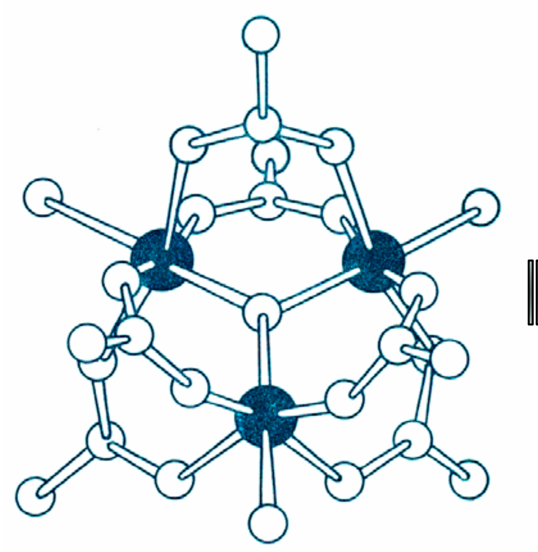


"Quantum oscillations in a molecular magnet"

S. Bertaina, S. Gambarelli, T.Mitra, B. Tsukerblat, A. Müller, B. Barbara, *Nature*, 2008.

From a triangle to extended frustrated systems

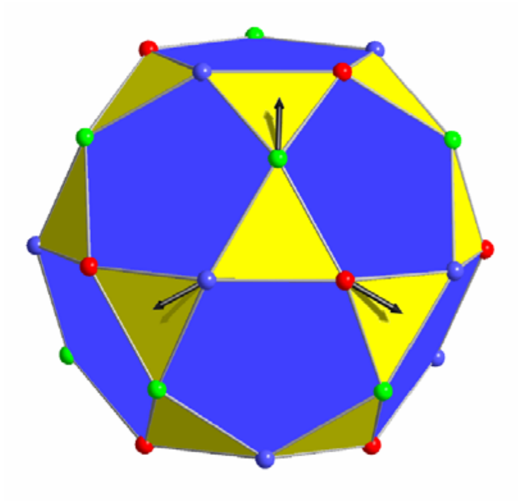
Frustrated trimeric carboxilates



Triads of the metal ions

$(Cr_3), (Fe_3),$
$(FeCr_2), (Fe_2Cr)$

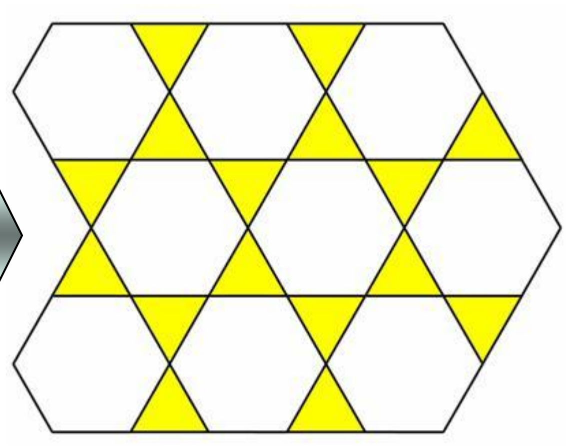
Frustrated nanoscopic systems



The M centers (colored spheres) of the $\{(Mo)Mo_5\}M_{30}$ type Keplerates ($M = V^{IV}, Fe^{III}$)

Achim Müller & coworkers

Crystal lattice



Kagomé lattice in which equilateral triangles are arranged around regular hexagons in a two dimensional plane.

Low frequency dynamic properties: negative refraction index

- Responses to ac electric and ac magnetic field are comparable for $J \approx 100$ K:

$$\varepsilon_{ik}(\omega) = \varepsilon_0 \delta_{ik} + \frac{8\pi}{V} \sum_n \frac{\omega_{n0} \langle 0 | P_{S,i} | n \rangle \langle n | P_{S,k} | 0 \rangle}{\omega_{n0}^2 - \omega^2 + i\delta},$$

- Spin-orbital coupling may lead to common poles in $\varepsilon_{ik}(\omega)$ and $\mu_{ik}(\omega)$ ➡

- Negative refraction index if dissipation is weak.

Chirality as a qubit?

Triangle: S=1/2, chirality (or pseudosin T) = ½

Can one use chirality instead of spin for quantum computation etc, as a qubit instead of spin?

We can control it by magnetic field (chirality = current = orbital moment) and by electric field

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Georgeot, Mila, arXiv 26 February 2009

CONCLUSIONS

- Contrary to the common belief, there are real charge effects in strong Mott insulators (with frustrated lattices): spin-driven spontaneous electric currents and orbital moments, and charge redistribution in the ground state

- Spontaneous currents are ~ scalar spin chirality $\chi_{123} = \vec{\mathbf{S}}_1 \left[\vec{\mathbf{S}}_2 \times \vec{\mathbf{S}}_3 \right]$

- Charge redistribution ($\langle n_i \rangle$ is not 1!) may lead to electric polarization (purely electronic mechanism of multiferroicity)

- Many consequences:

  - In the ground state: lifting of degeneracy; formation of spin-driven CDW, …….

  - In dynamics: electric field-induced "ESR"; rotation of electric polarization by spins; contribution of spins to low-frequency dielectric function; possibility of negative refraction index; etc