Structural, orbital, and magnetic order in vanadium spinels

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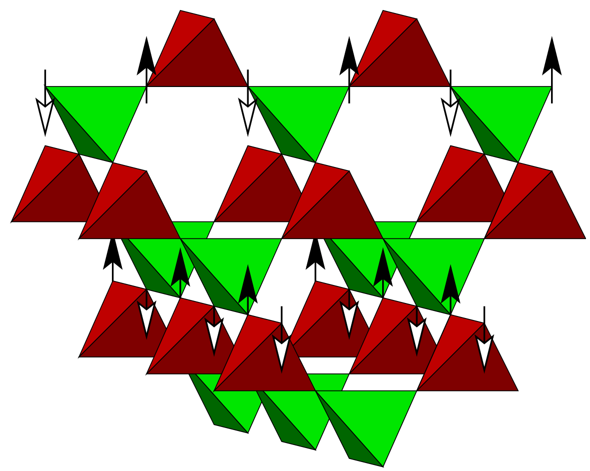


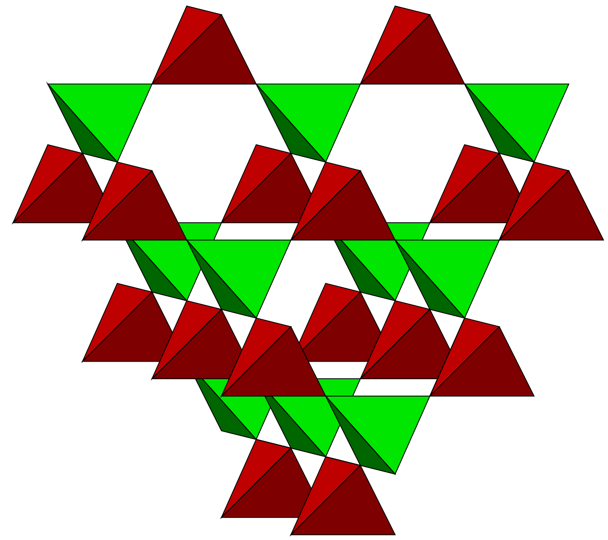
- Funding: NSF

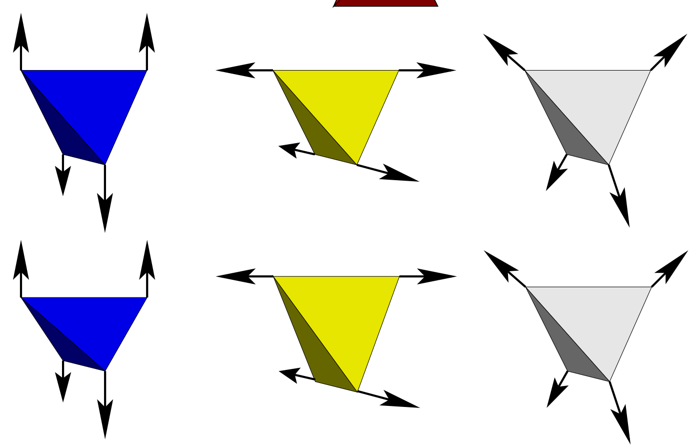
Frustrated Magnets. Montauk, NY. 17 September 2004

Frustrated spins couple to other degrees of freedom

- Degeneracy of the ground state.
- Sensitivity to small perturbations.
  - Heisenberg AF in pyrochlore.
  - Realized in spinel $ZnCr_2O_4$.
  - Spins couple to distortions:
  - $J(\mathbf{r}_{ij})\,\mathbf{S}_i \cdot \mathbf{S}_j$.
  - Spin-Peierls transition at 12 K.

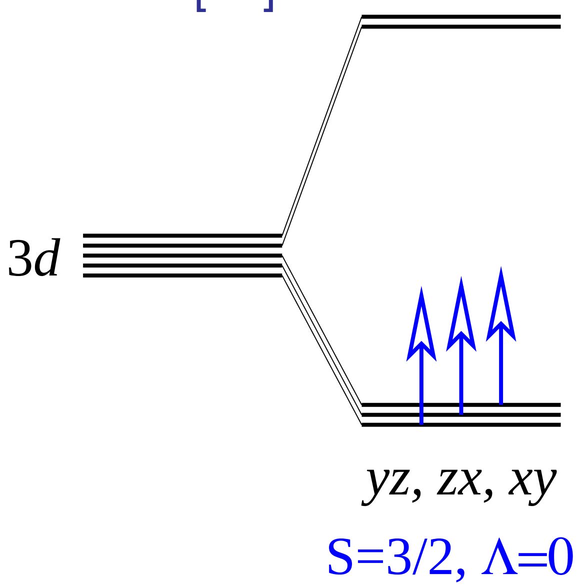
S.-H. Lee *et al.*, PRL **84**, 3718 (2000).
Yamashita and Ueda, PRL **85**, 4960 (2000).
O.T. *et al.*, PRL **88**, 067203 (2002).



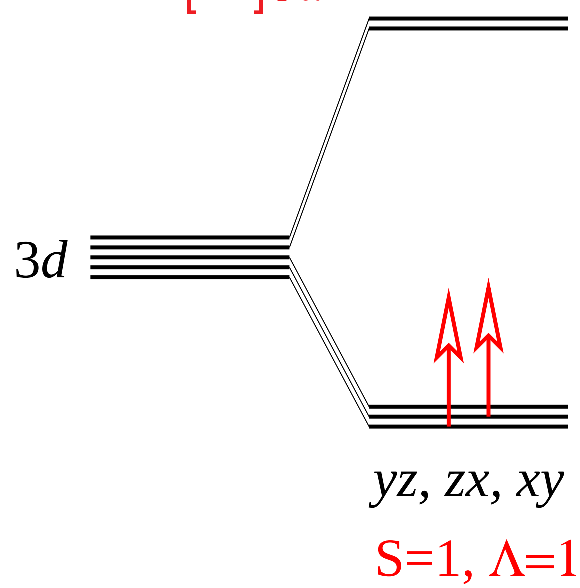


$Cr^{3+} \rightarrow V^{3+}$: frustrated spins + phonons + orbitals

$Cr^{3+} = [Ar]3d^3$



$V^{3+} = [Ar]3d^2$

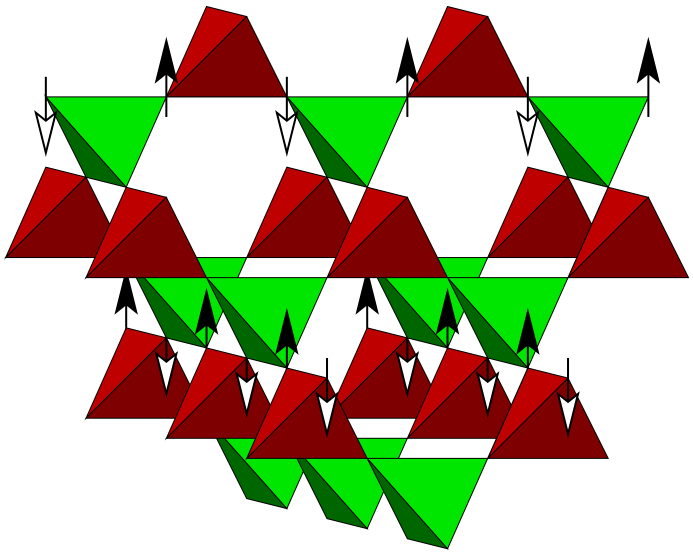


- Orbital motion is quenched.
- Isotropic (Heisenberg) spins.

- Orbital fluctuations.
- Spins couple to orbitals.

Spinels with V^{3+}: experiment

- A family of similar compounds:
  - MgV_2O_4, ZnV_2O_4, CdV_2O_4.
- Structural ordering at a high T:
  - Cubic $\longrightarrow$ flattened tetragonal.
  - $Fd\bar{3}m \longrightarrow I4_1/amd$ (or $I4_1/a$).
- Magnetic ordering at a lower T:
  - $\langle \boldsymbol{\mu} \rangle = 0.6\mu_B$, point along $[001]$,
  - alternate along $[110]$ and $[1\bar{1}0]$.
- Magnetic hystheresis above T_N:
  - $\chi_{\rm FC} \neq \chi_{\rm ZFC}$.



H. Nagamiya and M. Onoda, J. Appl. Phys. **81**, 5289 (1997).

Y. Ueda *et al.*, J. Phys. Soc. Japan **66**, 778 (1997).

M. Reehuis *et al.*, Eur. Phys. J. B **35**, 311 (2003).

S.-H. Lee *et al.*, cond-mat/0312558.

Spinels with V^{3+}: theory

- Competing interactions:
  - ◦ Single-ion Jahn-Teller effect.
  - ◦ Single-ion $\lambda \mathbf{L} \cdot \mathbf{S}$ coupling.
  - ◦ Inter-ion spin and orbital interactions.
- Energy scales are comparable:
  - ◦ $\Delta E_{\mathrm{JT}} \sim$ 20-40 meV in YVO_3.
  - ◦ $\lambda \approx 25$ meV in a free V^{3+}.
  - ◦ Inter-ion $K \approx 17$ meV.
- Suggested approaches:
  - ◦ Phenomenology—to identify possible phases.
  - ◦ Numerics—to explore phase diagram in detail.

K.I. Kugel and D.I. Khomskii, Sov. Phys. JETP **37**, 725 (1973).

T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).

H. Tsunetsugu and Y. Motome, Phys. Rev. B **68**, 060405 (2003).

Spinels with V^{3+}: phenomenology

Identify possible phases

- Use a perturbative approach:
  - Model I: Jahn-Teller coupling dominates.
  - Model II: $\lambda\,\mathbf{L}\cdot\mathbf{S}$ dominates.
  - Model III: Kugel-Khomskii interaction dominates.
- Compare against available data:
  - Structural distortion.
  - Magnetic order, spin excitations.
- Caveat: perturbative approach might overlook some phases.

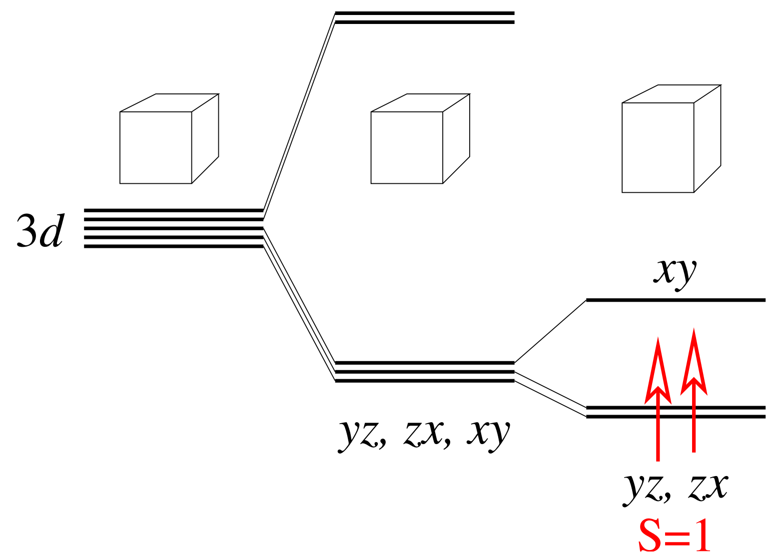
H. Tsunetsugu and Y. Motome, Phys. Rev. B **68**, 060405 (2003).

O.T., cond-mat/0401203.

D.I. Khomskii, unpublished.

Model I: Jahn-Teller coupling dominates

- Model I properties:
  - VO_6 octahedra are elongated.
  - Orbitals are fully ordered.
  - Spin anisotropy is weak.
- Experiment:
  - Powder X-ray scattering.
  - VO_6 octahedra are flattened.
- Model I is ruled out.



M. Onoda and J. Hasegawa, J. Phys. Condens. Matter **15**, L95 (2003).

M. Reehuis *et al.*, Eur. Phys. J. B **35**, 311 (2003).

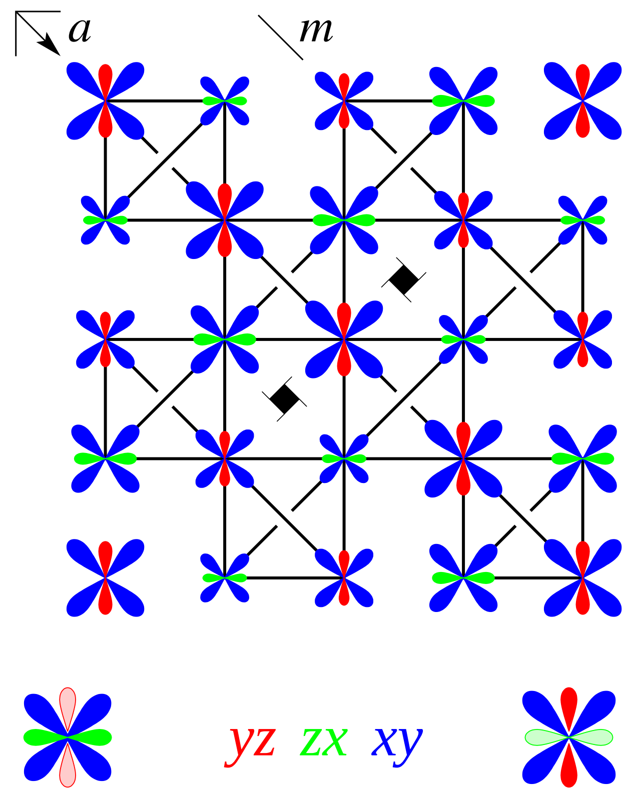
Model III: Kugel-Khomskii interaction dominates

- Model III properties:
  - Antiferro-orbital order.
  - yz, zx orbitals are staggered.
  - Symmetry $Fd\bar{3}m \rightarrow I4_1/a$.
- Powder X-ray scattering:
  - Consistent with $Fd\bar{3}m \rightarrow I4_1/amd$?
  - Partial orbital order?
- Model III is not ruled out.

H. Tsunetsugu and Y. Motome (2003).

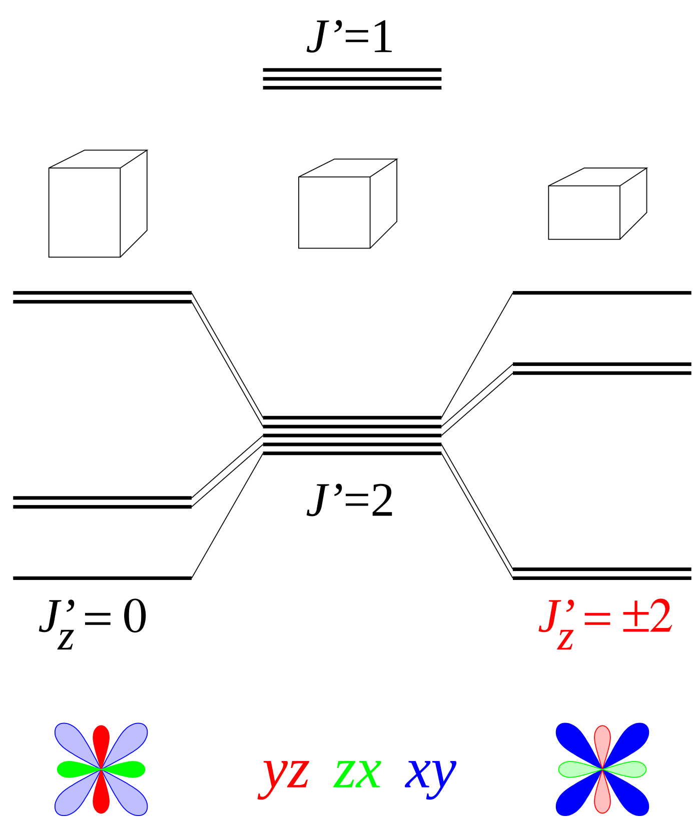
M. Reehuis *et al.* (2003).

S.-H. Lee *et al.* (2003).



Model II: $\lambda \mathbf{L} \cdot \mathbf{S}$ dominates

- $^3T_{1g}$ states of the group O_h:
  - $S = 1$ with $g_S = 2$.
  - $L' = 1$ with $g_L \approx -1$.
  - $\mathbf{J}' = \mathbf{L}' + \mathbf{S}$.
- Spin-orbit interaction:
  - $H_{LS} = \lambda \mathbf{L} \cdot \mathbf{S} = -\lambda \mathbf{L}' \cdot \mathbf{S}$.
  - $J' = 2$ with $g_J \approx 1/2$.
- Jahn-Teller distortion:
  - Flattened VO_6: $J'_z = \pm 2$.
  - $\boldsymbol{\mu} = \pm \mu_B$ along [001].
  - Single-ion Ising anisotropy.
  - $n_{yz} = n_{zx} = \frac{1}{2}$, $n_{xy} = 1$.

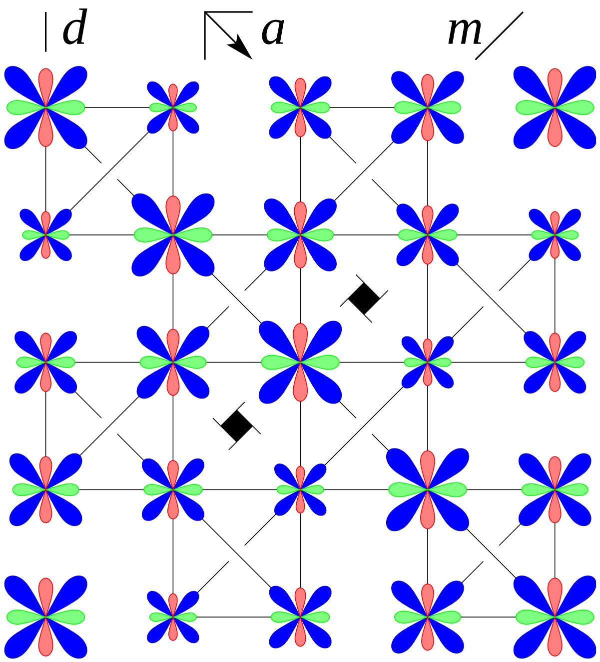


O.T., cond-mat/0401203.

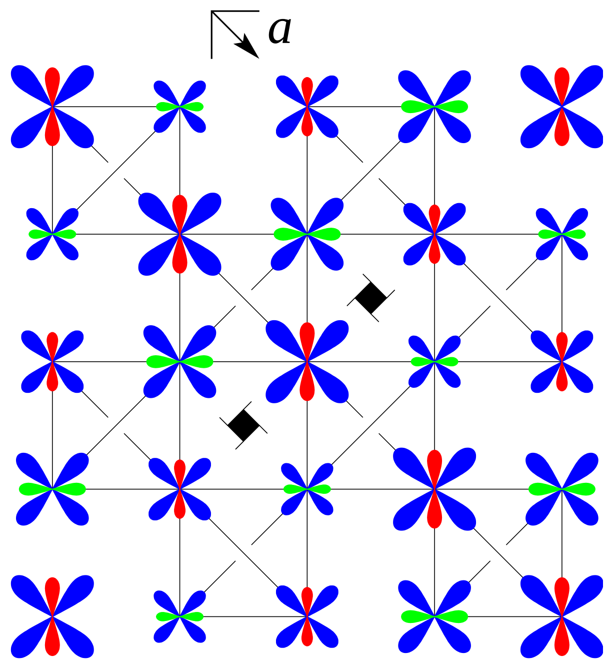
D.I. Khomskii, unpublished.

Model II vs Model III: structure and orbital order

- II: $\lambda\,\mathbf{L}\cdot\mathbf{S}$ dominates.
  - $Fd\bar{3}m \rightarrow I4_1/amd$.
  - Ferro-orbital order.

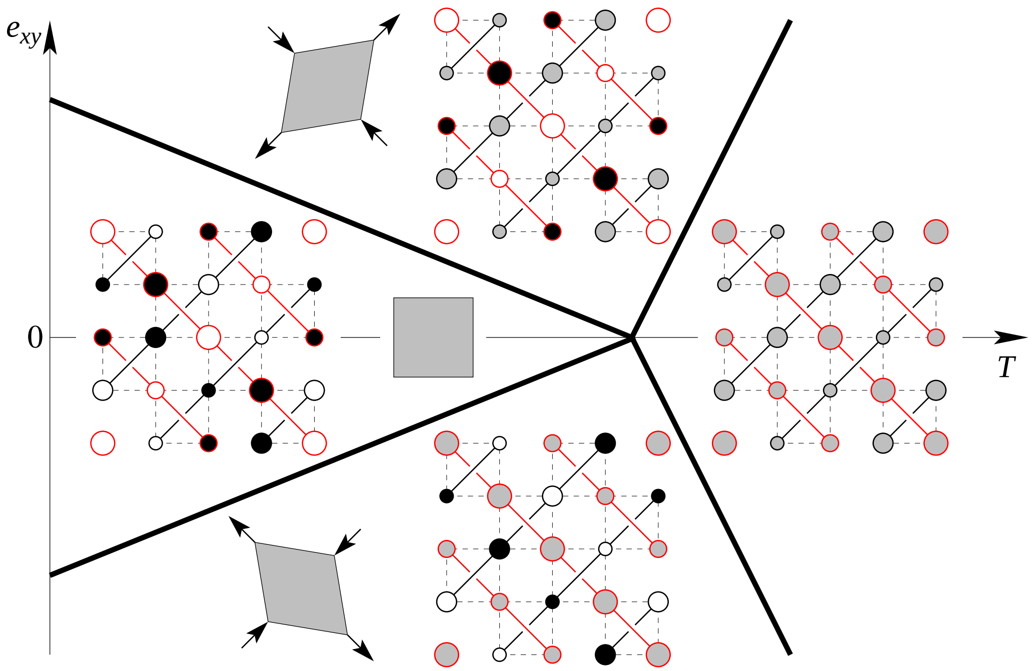


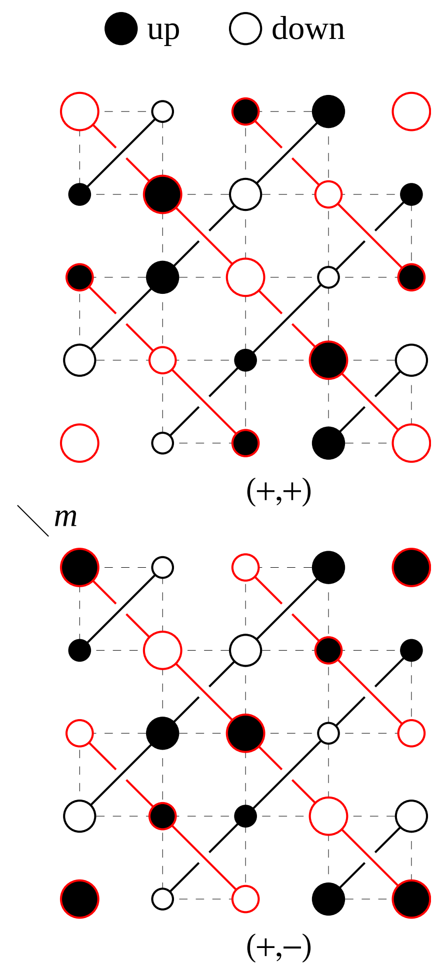
- III: Kugel-Khomskii dominates.
  - $Fd\bar{3}m \rightarrow I4_1/a$.
  - Antiferro-orbital order.



Model II: magnetic properties

- 2 sets of AF Ising chains: $[110]$ and $[1\bar{1}0]$.
- Coupling of $\times$ chains is frustrated.
- 2 staggered magnetizations: $\sigma_{[110]}$ and $\sigma_{[1\bar{1}0]}$.
- Tetracritical point in (e_{xy}, T) plane.





Distorted paramagnet: order and symmetry breaking

- Structural order parameter $\mathbf{f} = (f_1, f_2)$:
  - $f_1 = (a + b - 2c)/\sqrt{6}$, $f_2 = (a - b)/\sqrt{2}$,
  - or $f_1 = (n_{yz} + n_{zx} - 2n_{xy})/\sqrt{6}$, $f_2 = (n_{yz} - n_{zx})/\sqrt{2}$,
  - or $f_1 = (\chi_{xx} + \chi_{yy} - 2\chi_{zz})/\sqrt{6}$, $f_2 = (\chi_{xx} - \chi_{yy})/\sqrt{2}$.
- Symmetry-breaking fields $\mathbf{h} = (h_1, h_2)$:
  - stress $h_1 = (e_{xx} + e_{yy} - 2e_{zz})/\sqrt{6}$, $f_2 = (e_{xx} - e_{yy})/\sqrt{2}$,
  - or $h_1 = (H_x^2 + H_y^2 - 2H_z^2)/\sqrt{6}$, $f_2 = (H_x^2 - H_y^2)/\sqrt{2}$,
  - $-\mathbf{h} \cdot \mathbf{f} = -\chi_{xx} H_x^2 - \chi_{yy} H_y^2 - \chi_{zz} H_z^2$.
- History dependence:
  - cooling under stress determines the distortion axis,
  - and so should cooling in $\mathbf{H} \neq 0$,
  - hence $\chi_{\mathrm{FC}} \neq \chi_{\mathrm{ZFC}}$?
- Reality check:
  - need experiments on single crystals.

- Model II: Single-ion $\mathbf{L} \cdot \mathbf{S}$.
  - O.T., cond-mat/0401203.
- Structural and orbital properties:
  - $Fd\bar{3}m \to I4_1/amd$.
  - Ferro-orbital order.
  - $n_{yz} = n_{zx} < n_{xy}$.
- Magnetic properties:
  - Magn. moments $S+L$, 0.5–$1\mu_B$.
  - Single-ion Ising anisotropy.
  - Two sets of AF chains.
  - Two Ising order parameters.
  - Tetracritical point.
- Further experimental input is needed.
- Go beyond perturbation theory.

- Model III: Kugel-Khomskii terms.
  - Tsunetsugu, PRB **68**, 060405 (2003).
  - $Fd\bar{3}m \to I4_1/a$.
  - Antiferro-orbital order.
  - $n_{yz} \neq n_{zx} \neq n_{xy}$.
  - Magn. moments S-only, $2\mu_B$.
  - Weak anisotropy.
  - Two sets of AF chains.
  - Two Ising order parameters.
  - Tetracritical point.