Orbital and Magnetic Physics in Vanadium Spinels

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KITP Program
Moments and Multiplets in Mott Materials
Sep. 25, 2007

Outline

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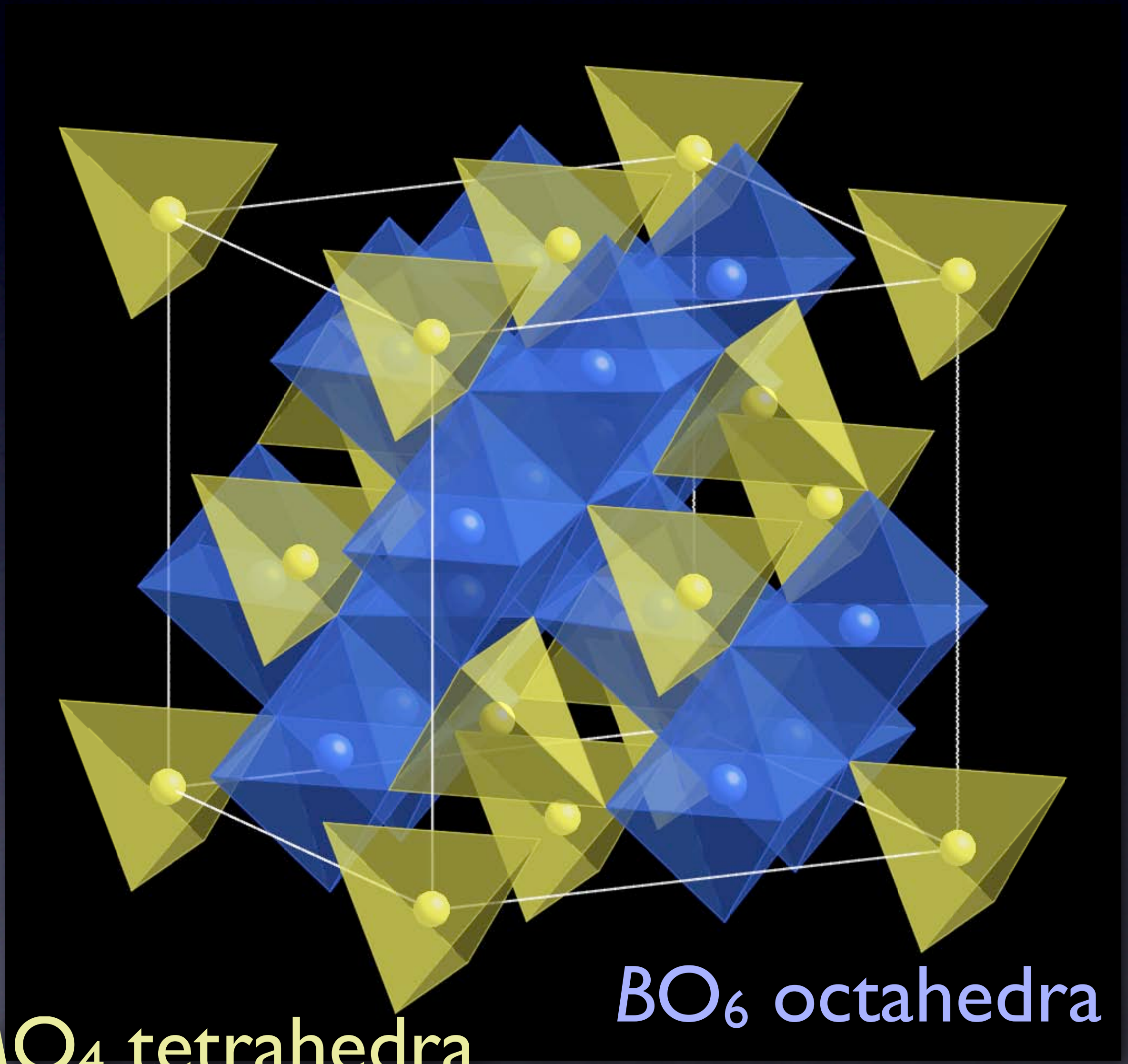
- introduction to spinels and t_{2g} orbital physics
- controversy on orbital ordering in ZnV_2O_4
  - different models for spin/orbital order in ZnV_2O_4: relative importance of Kugel-Khomskii superexchange, Jahn-Teller and relativistic spin-orbit couplings
  - symmetry analysis: lesson from experiments in MnV_2O_4
- self-organized 7-site cluster (heptamer) in AlV_2O_4
  - heptamer scenario: ‘molecule’ of bonding states with anisotropic t_{2g} orbitals
  - implication to heavy-fermion compound LiV_2O_4

Lattice Structure of Spinels AB_2O_4



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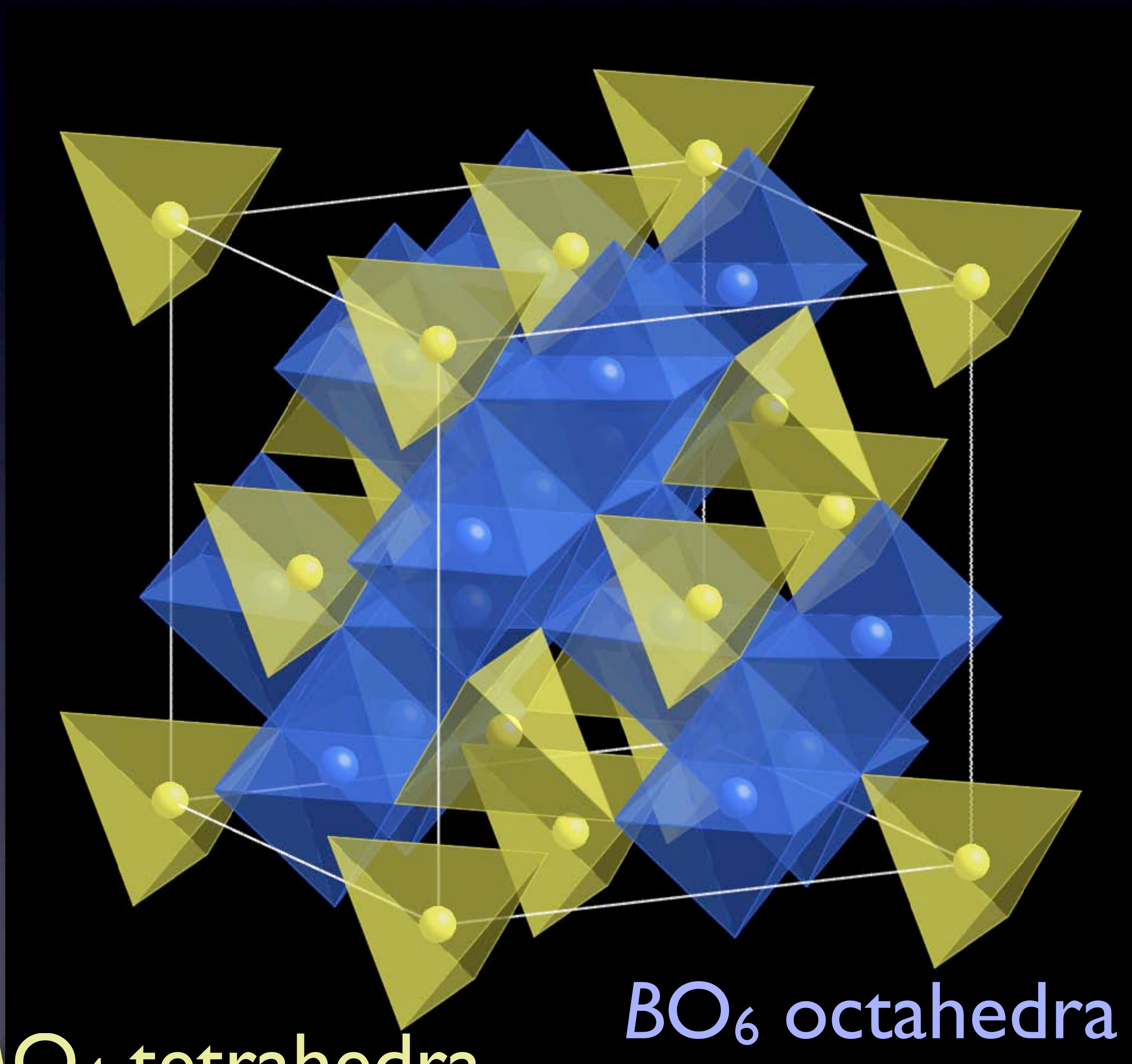

- *B* spinels: *A*-site cations are nonmagnetic

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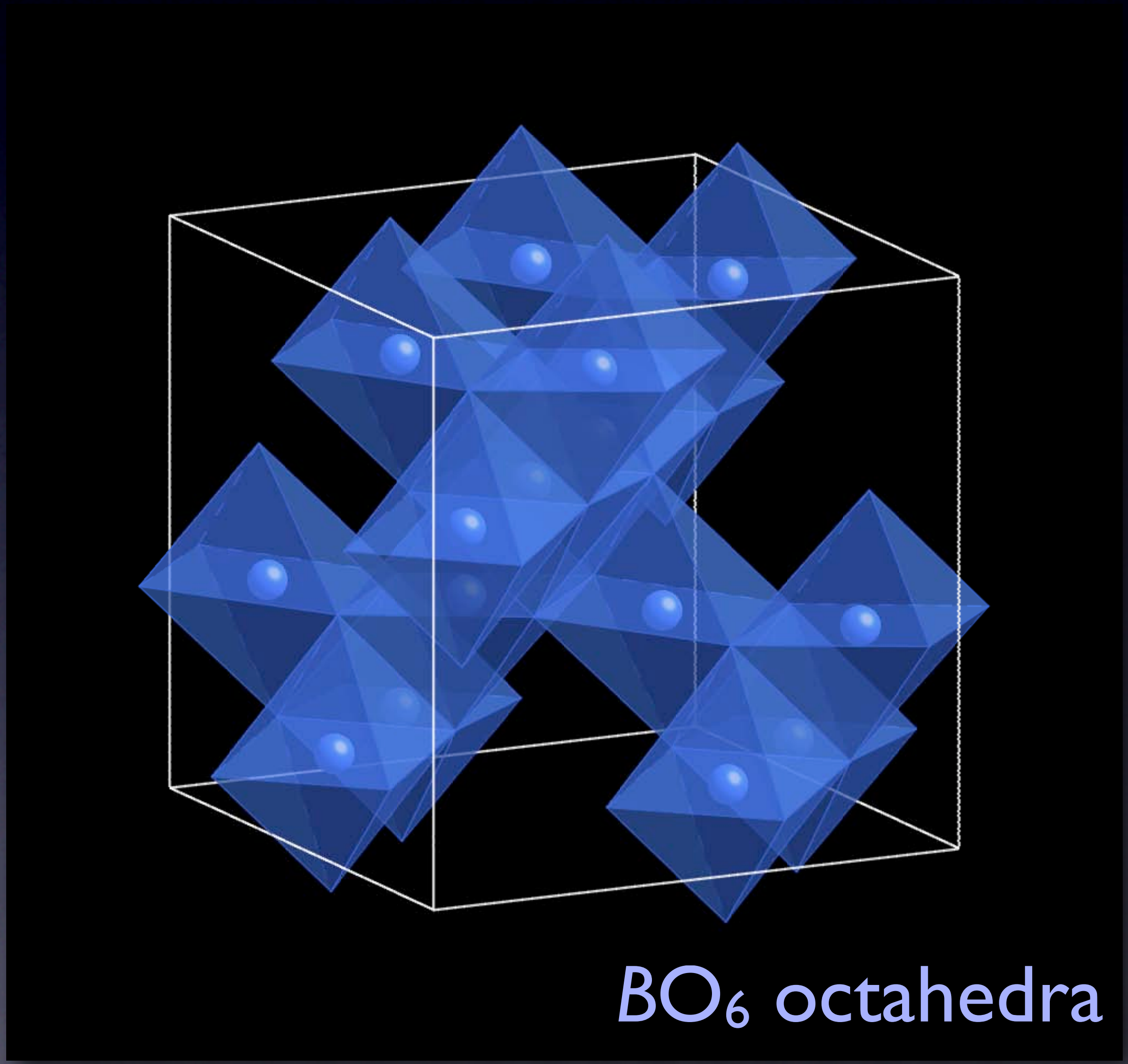

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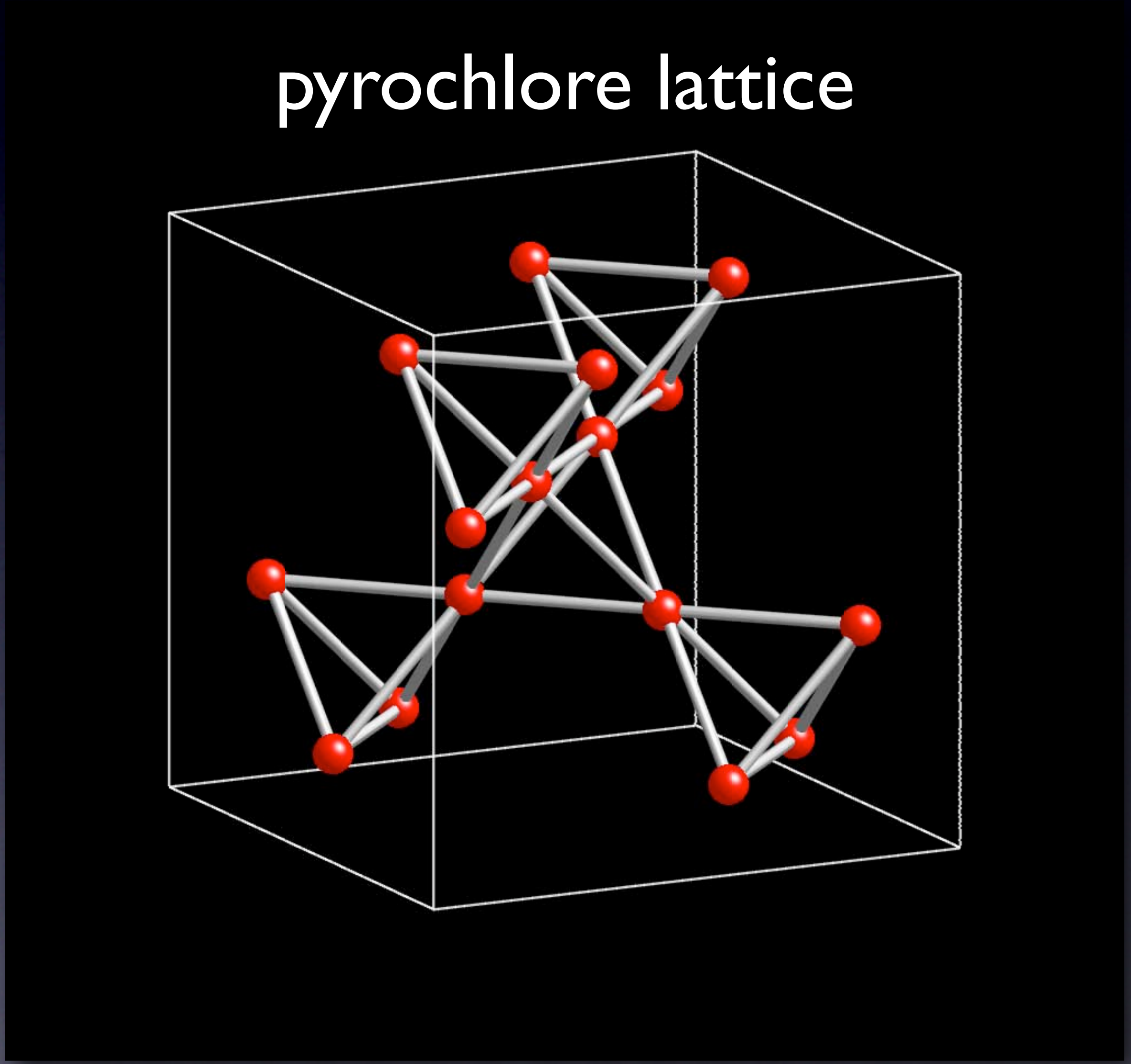

- *B* spinels: *A*-site cations are nonmagnetic
- 3D network of edge-sharing BO_6 octahedra
- 3D network of corner-sharing B_4 tetrahedra → pyrochlore lattice: strong geometrical frustration

B Spinels with t_{2g} Electrons

d^1 $MgTi_2O_4$	d^2 AV_2O_4 (*A*=Zn,Mg)	d^3 ACr_2O_4 (*A*=Cd,Hg,Zn)
• metal-insulator transition • spin-singlet ground state • helical dimerization • orbital-Peierls scenario	• two successive transitions • complicated AF ordering • dimensionality reduction • competition between spin and orbital degrees of freedom	• single transition • half-magnetization plateau • spin-lattice coupling (spin Jahn-Teller mechanism) • self-organized ‘hexamer’ in high-T para phase
$d^{0.5}$ $LiTi_2O_4$	$d^{1.5}$ LiV_2O_4	$d^{2.5}$ AlV_2O_4
• superconductivity below 12.4 K (BCS mechanism)	• metallic down to 300 mK • absence of any transition • heavy-fermion behavior • metal-insulator transition by applying pressure	• structural transition with spin-singlet formation • self-organized 7-site cluster ‘heptamer’ ?

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Experimenter of the week
Participants' Interests
Social activities

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Participant Directory
Participant's photos
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Transport info
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Three main questions related to the physics of orbital degrees of freedom came to the fore in the discussion of Wednesday (biased view --JvdB).

We know that orbitals can order and that they couple to the lattice, but the questions are:
1. is there any material in which the *quantum* character of orbital degrees of freedom become relevant?
2. are there any cases where orbital *fluctuations*, either quantum or classical are relevent?
3. does orbital ordering have interesting *textures*, *symmetries* and/or *excitations*?

Also 15 more or less detailed discussion topics came up:
1. What is the role of vibronic coupling in cooperative Jahn-Teller systems
2. The importance of relativistic spin orbit coupling in eg and t2g systems
3. Orbital and frustration: frustration due to orbital degrees of freedom --- orbitals in frustrated lattices
4. Relative importance of electron-lattice effects (Jahn Teller) versus electronic effects (superexchange).
5. Role of geometry: differences for the situation of 180 degree O-TM-O bonds, 90 degree O-TM-O bonds and edge sharing octahedra
6. Reduced dimensionality due to orbitals
7. Importance of direct d-d electronic hopping versus d-oxygen-d hopping, especially in t2g spinels
8. Orbitals in charge transfer insulators
9. Role of orbital degrees of freedom at metal-insulator transitions
10. Orbital liquids -- quantum effects
11. Orbital waves -- orbitons
12. Importance of long-range interactions in short-range orbital (cooperative Jahn Teller) models
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14. Orbital textures, orbital domains and their effect on electronic degrees of freedom
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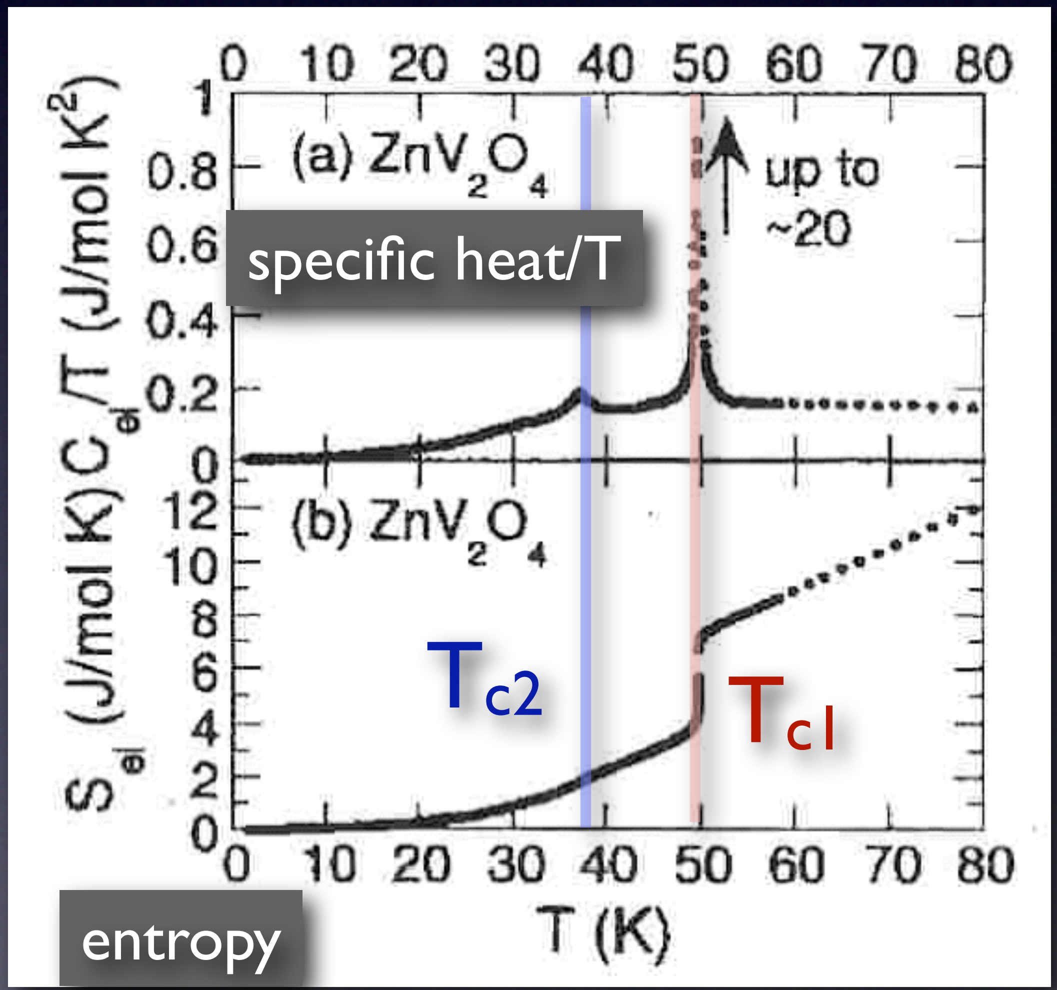
Two Transitions and Controversy on Orbital Ordering in ZnV_2O_4

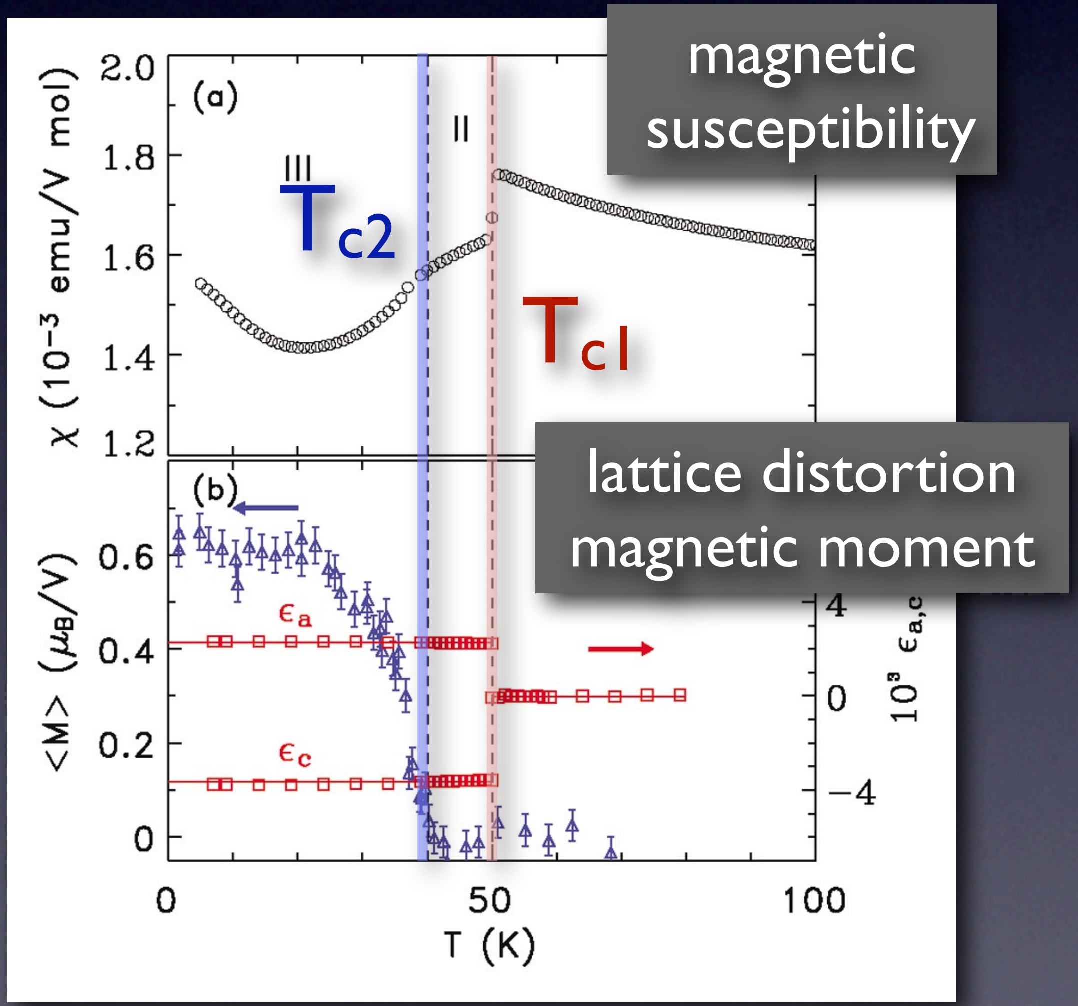
in collaboration with Hirokazu Tsunetsugu

Two Transitions in ZnV_2O_4

- cubic to tetragonal transition at T_{c1}~50K (1st order)
- antiferromagnetic transition at T_{c2}~40K (2nd order)



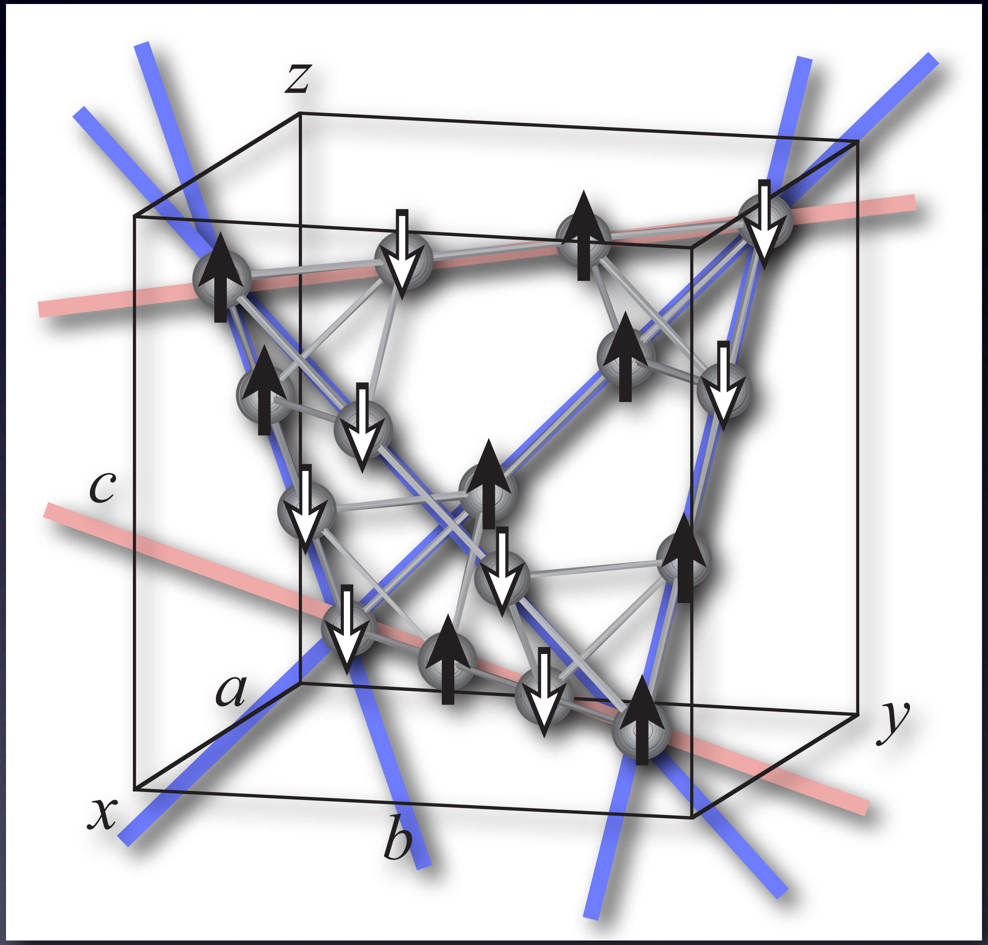
Kondo *et al.*, 2000



Ueda *et al.*, 1997
Lee *et al.*, 2004

Lattice symmetry and Magnetic Order

- lattice symmetry: $I4_1/amd$ (*powder sample*)
- orbital order: undetermined
- spin order: antiferromagnetic
  ↑-↓-↑-↓-... in the xy chains
  ↑-↑-↓-↓-... in the yz/zx chains
- moment at T=0 ~ $0.6\mu_B$



Niziol, 1973

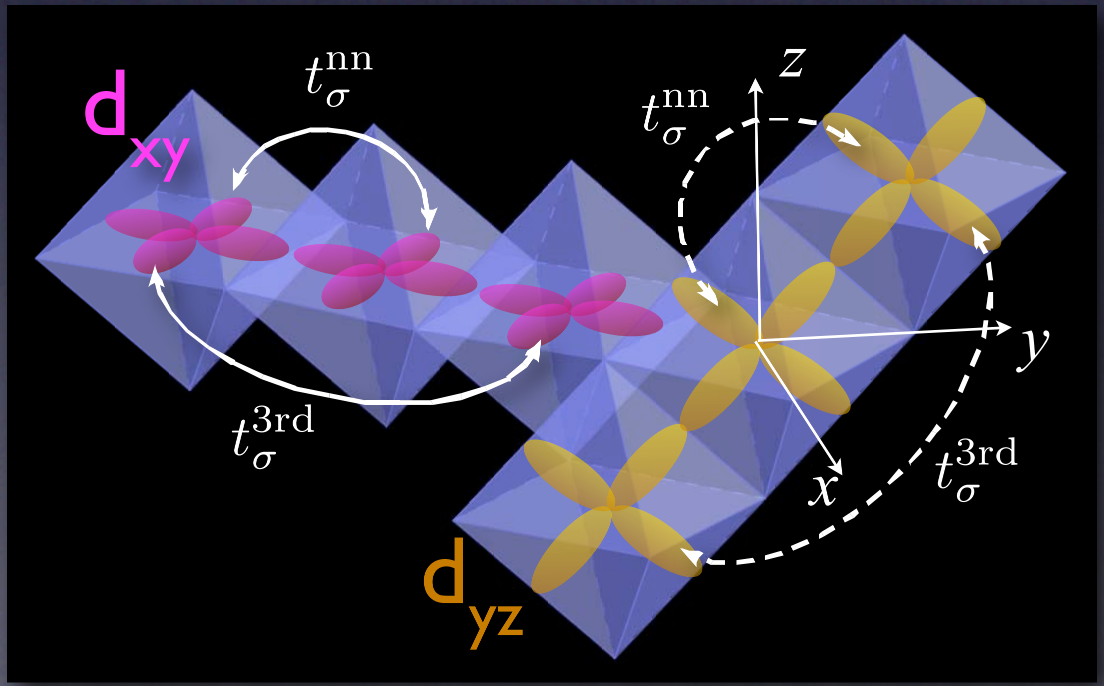
Questions

- What is the microscopic mechanism of two transitions? Who is the main player? Kugel-Khomskii superexchanges, Jahn-Teller or relativistic spin-orbit coupling?
- How is the complex AF ordering stabilized? Why is the moment at T=0 reduced so largely?
- What is the role of orbital degree of freedom? Is there orbital ordering ? If yes, what type of ordering sets in?

Model

Tsunetsugu and Motome (2003, 2004, 2005)

- Kugel-Khomskii type model derived from 3-fold multi-orbital Hubbard model + tetragonal Jahn-Teller coupling
  - assumptions: σ-type transfer integrals only, classical phonon, neglecting spin-orbit coupling and trigonal distortion



$t_\sigma^{\mathrm{nn}} = \sim -0.32\mathrm{eV}$

$t_\sigma^{\mathrm{3rd}} = \sim -0.045\mathrm{eV}$

(Matsuno *et al.*, 1999: for LiV_2O_4)

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$$H_{\rm SO}^{\rm nn} = -J \sum_{\langle ij \rangle} \left[h_{\rm o-AF}^{(ij)} + h_{\rm o-F}^{(ij)} \right]$$: nearest neighbor term

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$$J = (t_\sigma^{\rm nn})^2/U \qquad A = (1-\eta)/(1-3\eta)$$

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$$h_{\rm o-AF}^{(ij)} = (A + B\vec{S}_i \cdot \vec{S}_j)(n_{i\alpha(ij)}\bar{n}_{j\alpha(ij)} + \bar{n}_{i\alpha(ij)} n_{j\alpha(ij)})$$

$$h_{\rm o-F}^{(ij)} = C(1 - \vec{S}_i \cdot \vec{S}_j) n_{i\alpha(ij)} n_{j\alpha(ij)}$$

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spin part: Heisenberg / orbital part: 3-state Potts

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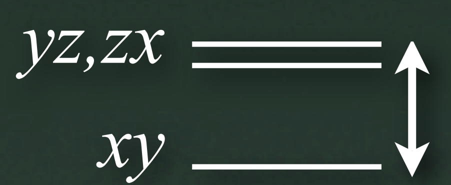
spin part: Heisenberg / orbital part: 3-state Potts

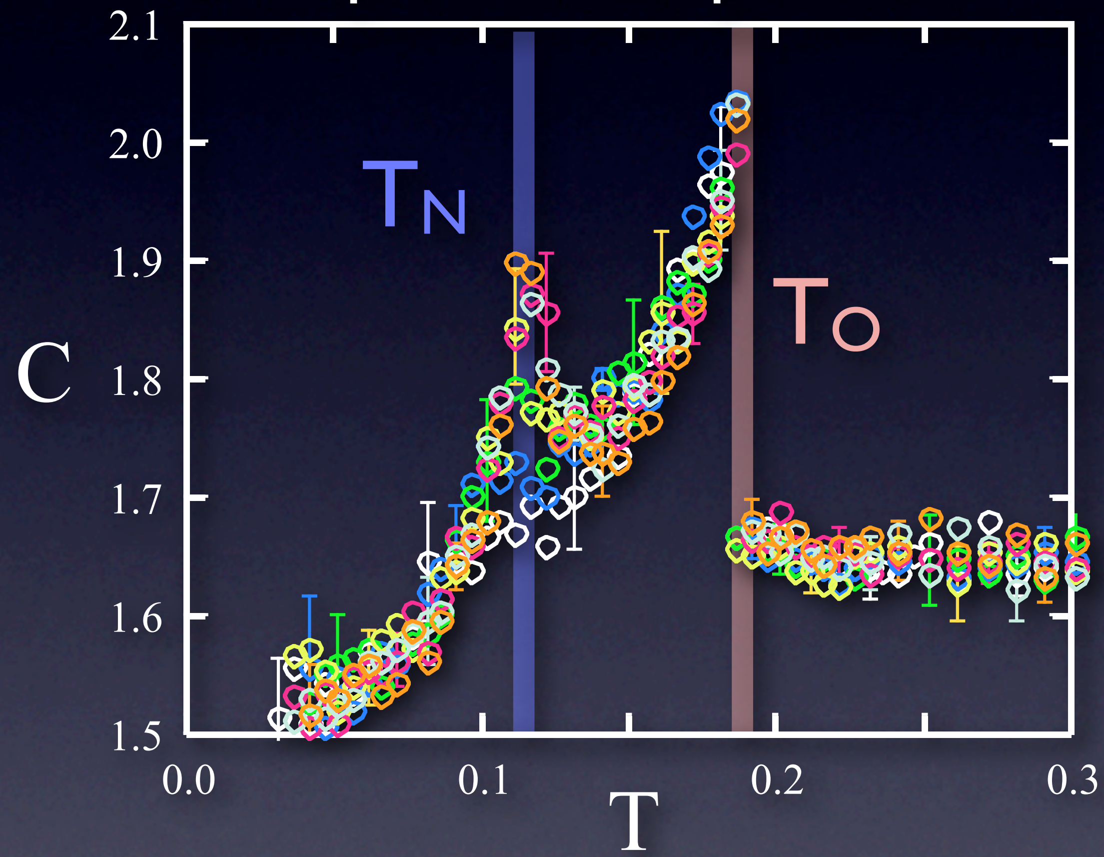
+ tetragonal Jahn-Teller coupling

$$H_{\rm JT} = g \sum_i Q_i (n_{i,yz} + n_{i,zx} - 2n_{i,xy}) + \sum_i Q_i^2/2 - \lambda \sum_{\langle ij \rangle} Q_i Q_j$$



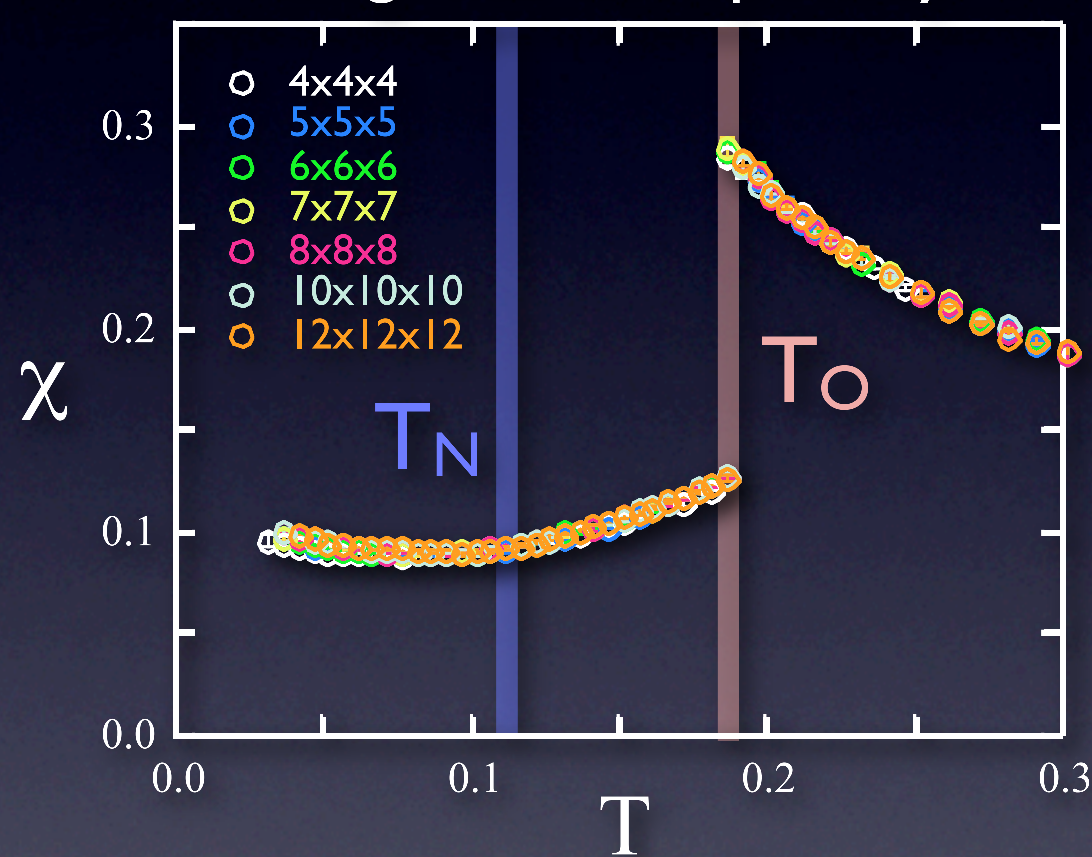
Monte Carlo Results

specific heat per site



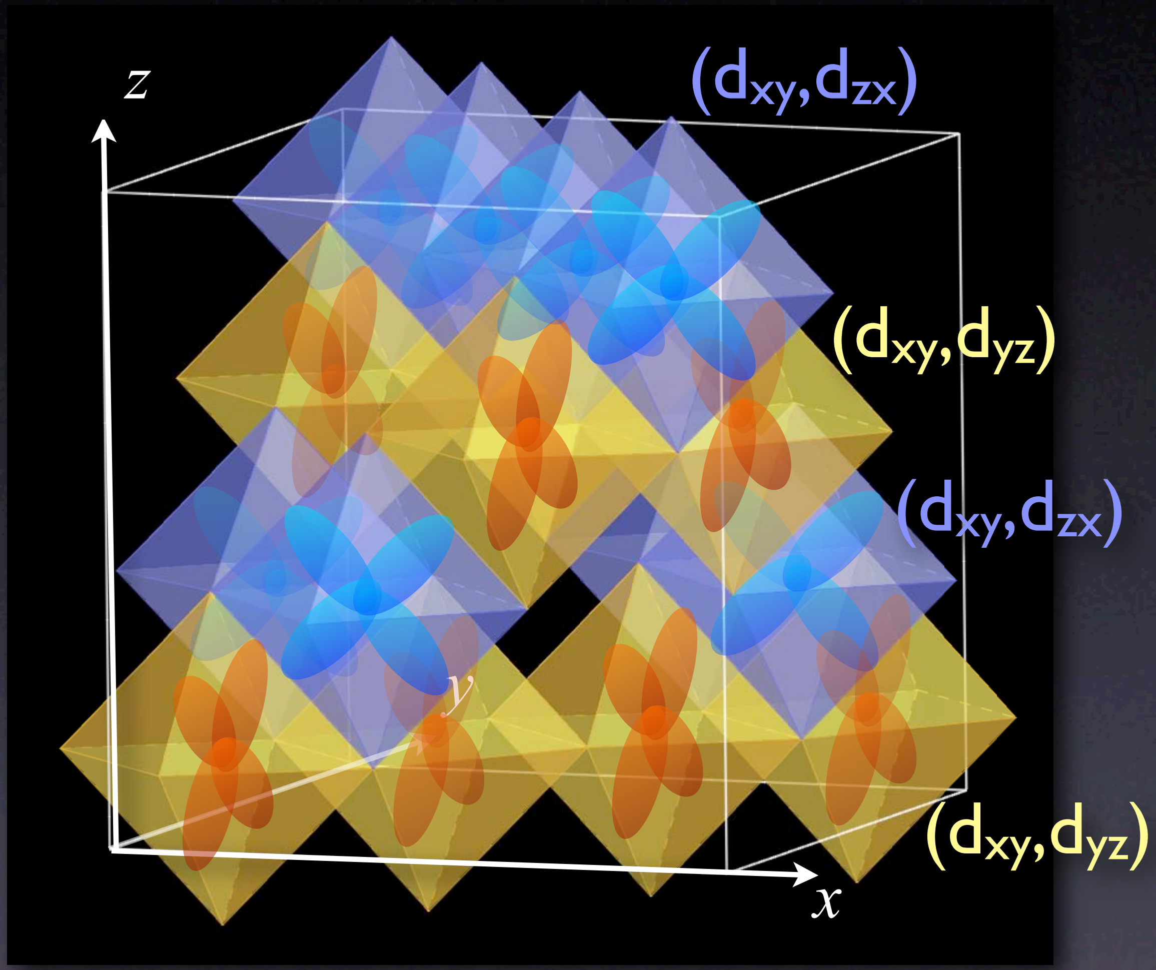
- 1st order at $T=T_O$, 2nd order at $T=T_N$
- consistent estimates of entropy changes

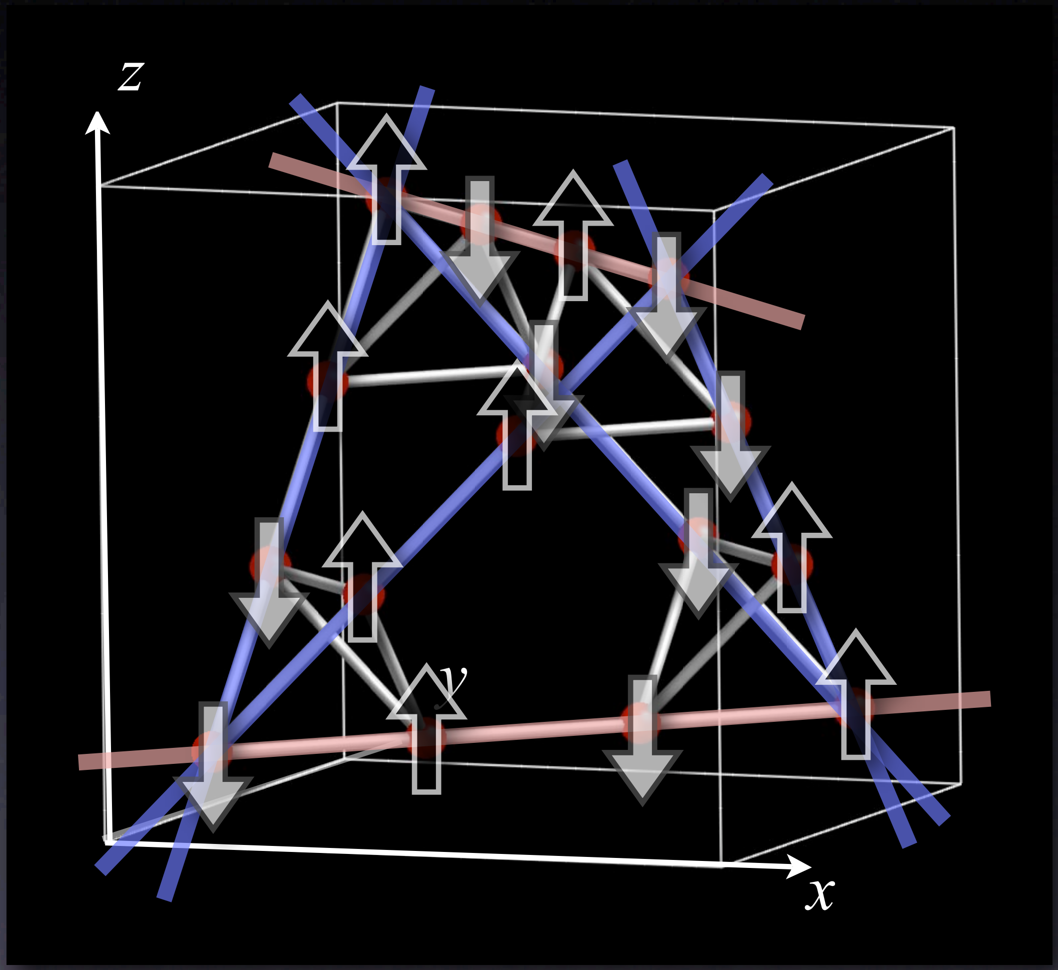
magnetic susceptibility



- sudden drop at $T=T_O$
- tiny change at $T=T_N$

Orbital and Spin Structure





- orbital: alternative stacking of (d_{xy}, d_{zx}) and (d_{xy}, d_{yz}) states
- spin: ↑-↓-↑-↓- in the xy chains and ↑-↑-↓-↓- in the yz/zx chains

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isotropic Heisenberg model with AF
nearest- and third-neighbor exchanges

no long-range order at T=0 (Reimers *et al.*, 1991)

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spin correlations hardly develop by themselves alone

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3-state Potts model with AF interactions which depend on both the bond direction and the orbital states

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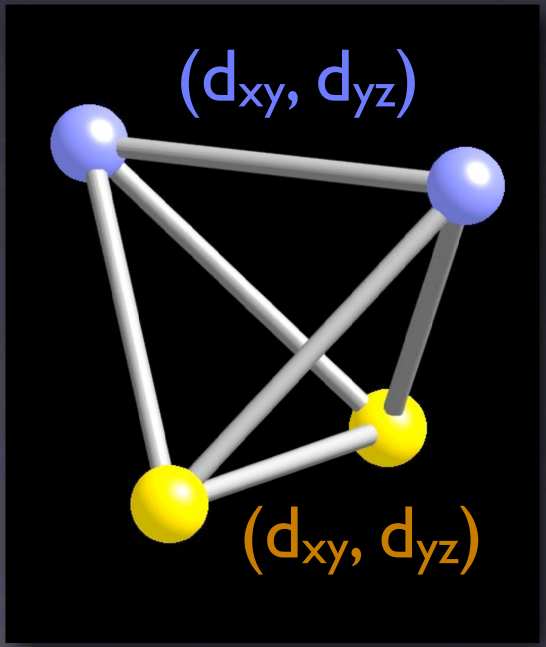

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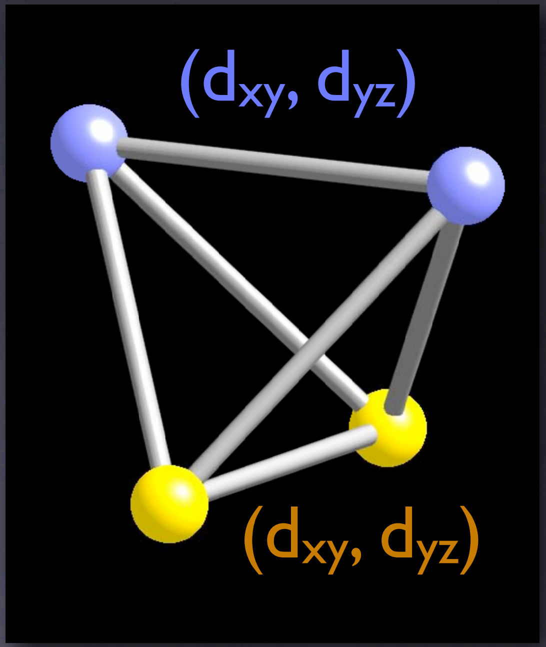

3-state Potts model with AF interactions which depend on both the bond direction and the orbital states

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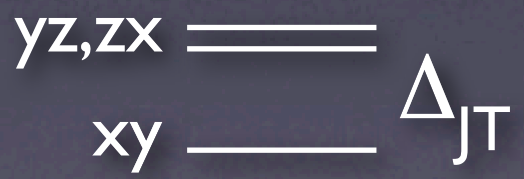
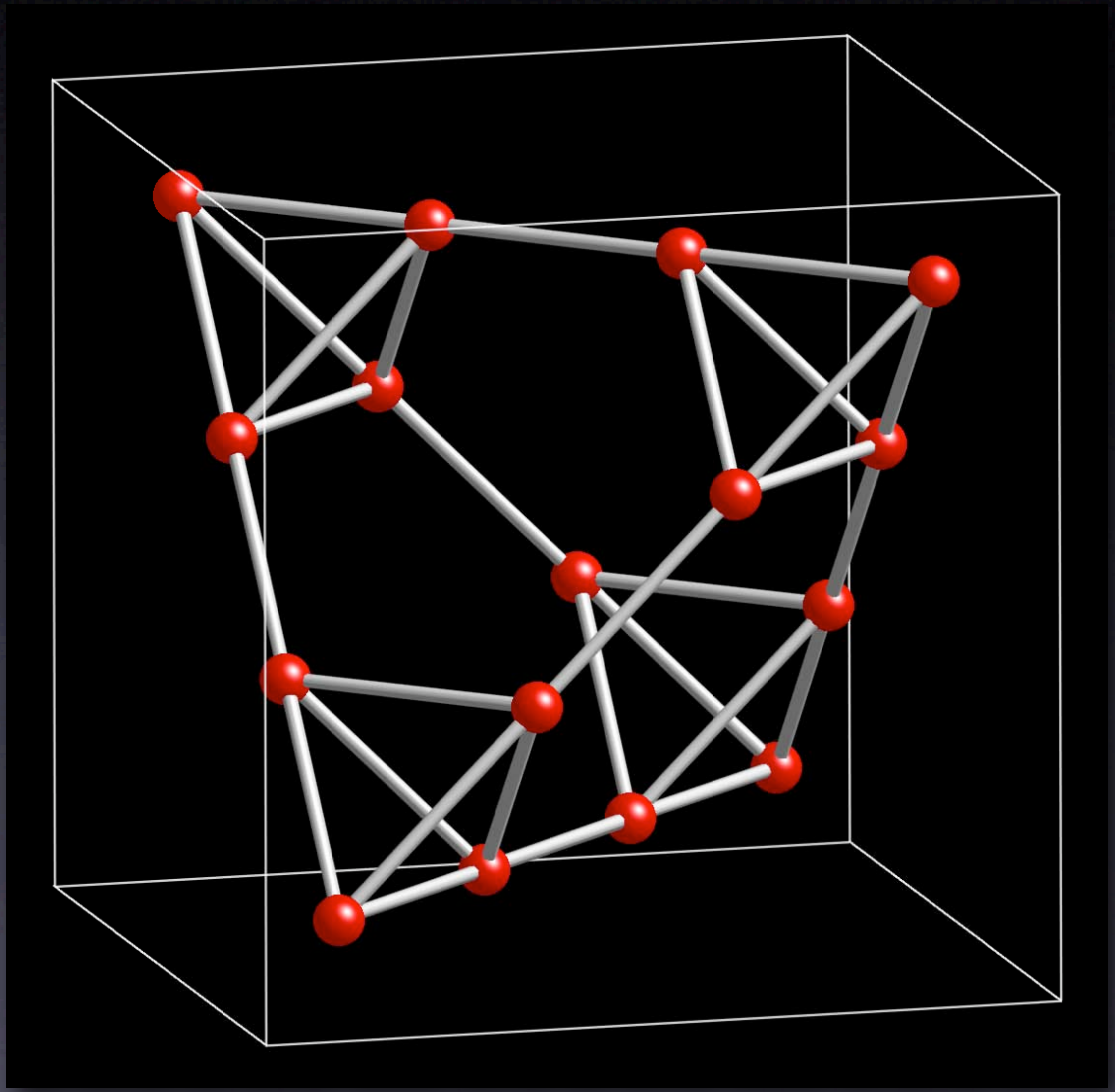
tetragonal Jahn-Teller distortion assists to stabilize this orbital configuration

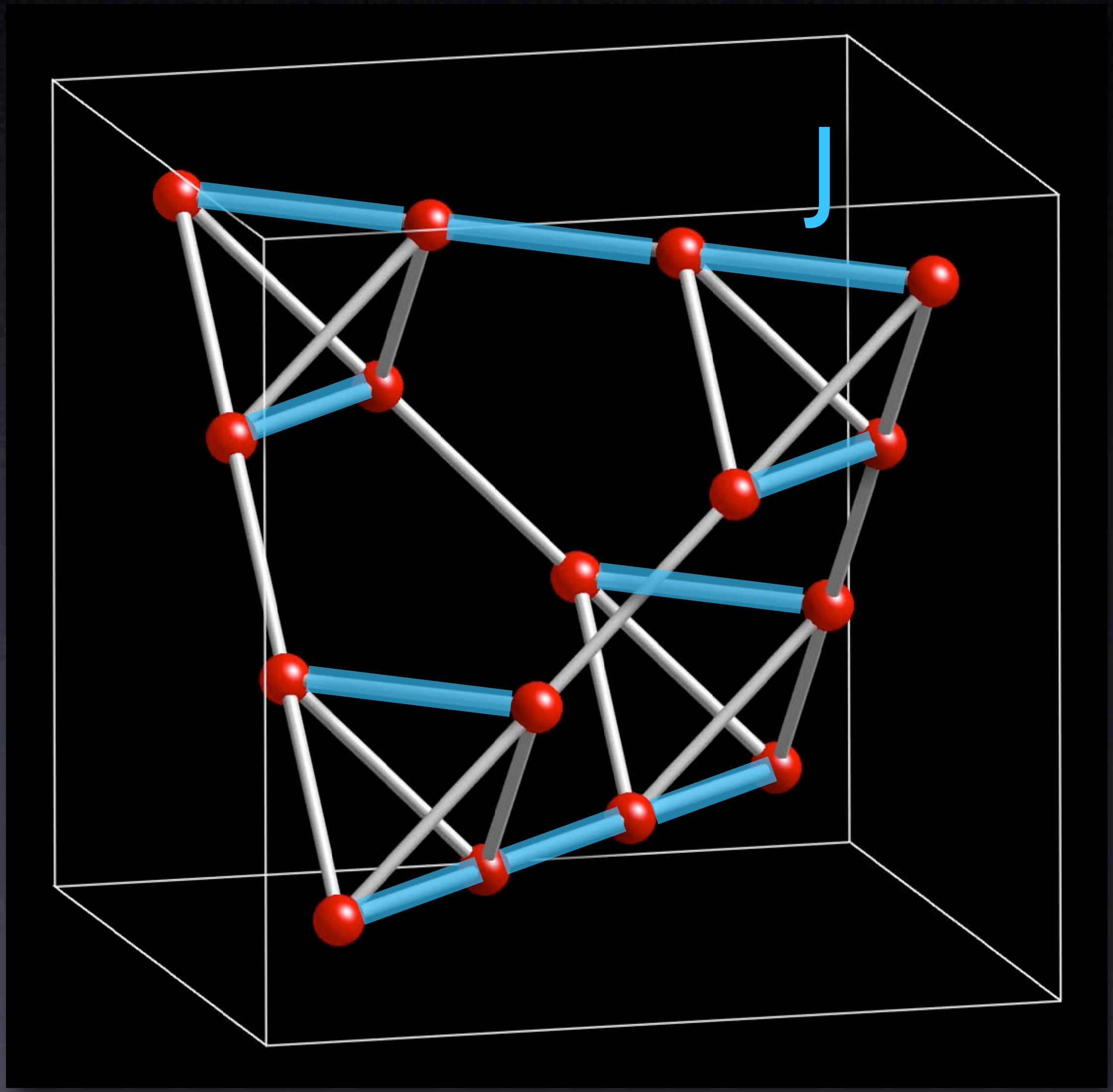


Effective Spin Exchanges under the Orbital Order



Effective Spin Exchanges under the Orbital Order

- d_{xy} is singly occupied at all the sites → strong AF exchange in the xy chains J



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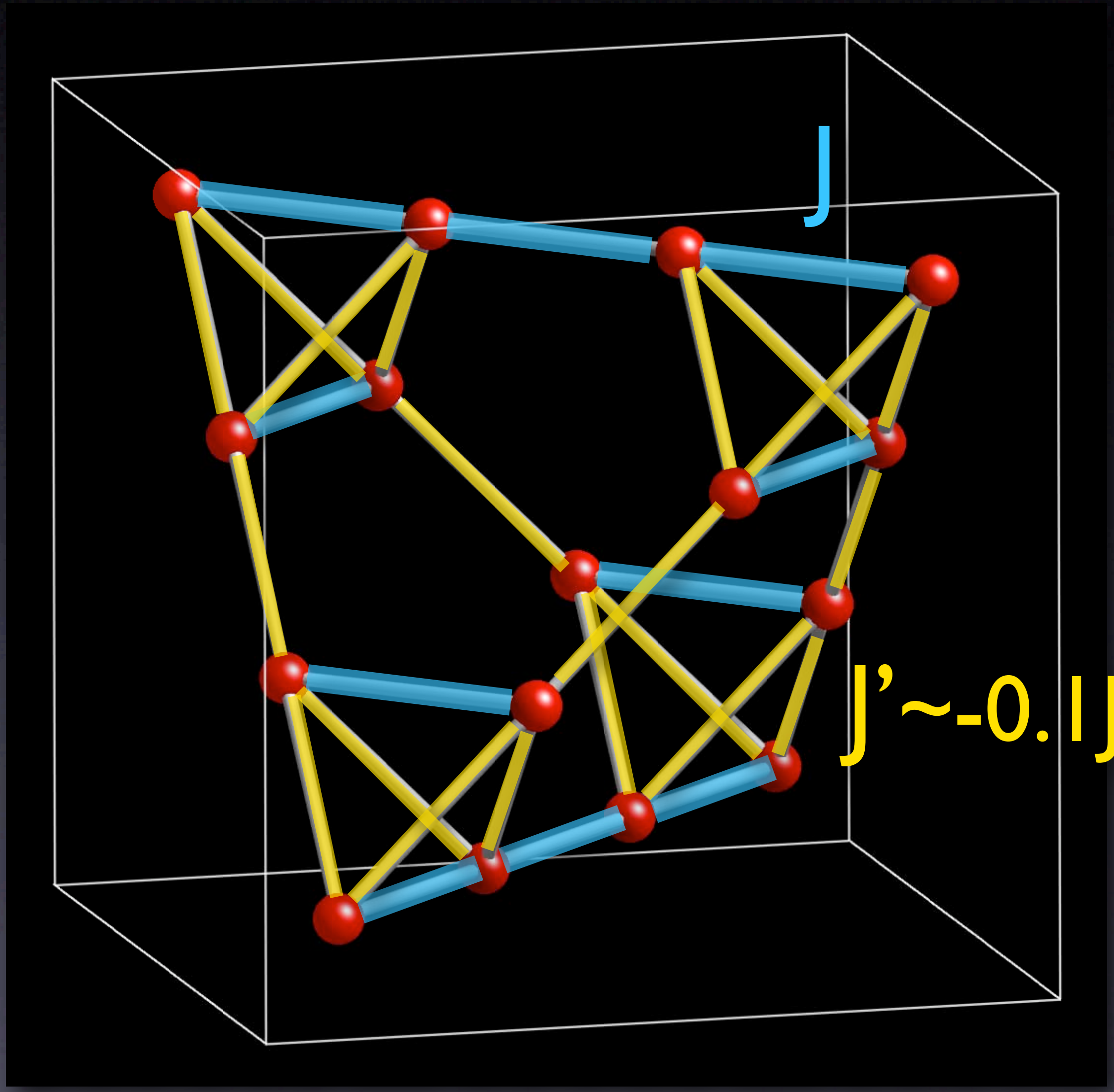
- n.n. exchange couplings in the yz/zx chains J' are ferromagnetic and about 10 times weaker than the AF exchange in the xy chains J



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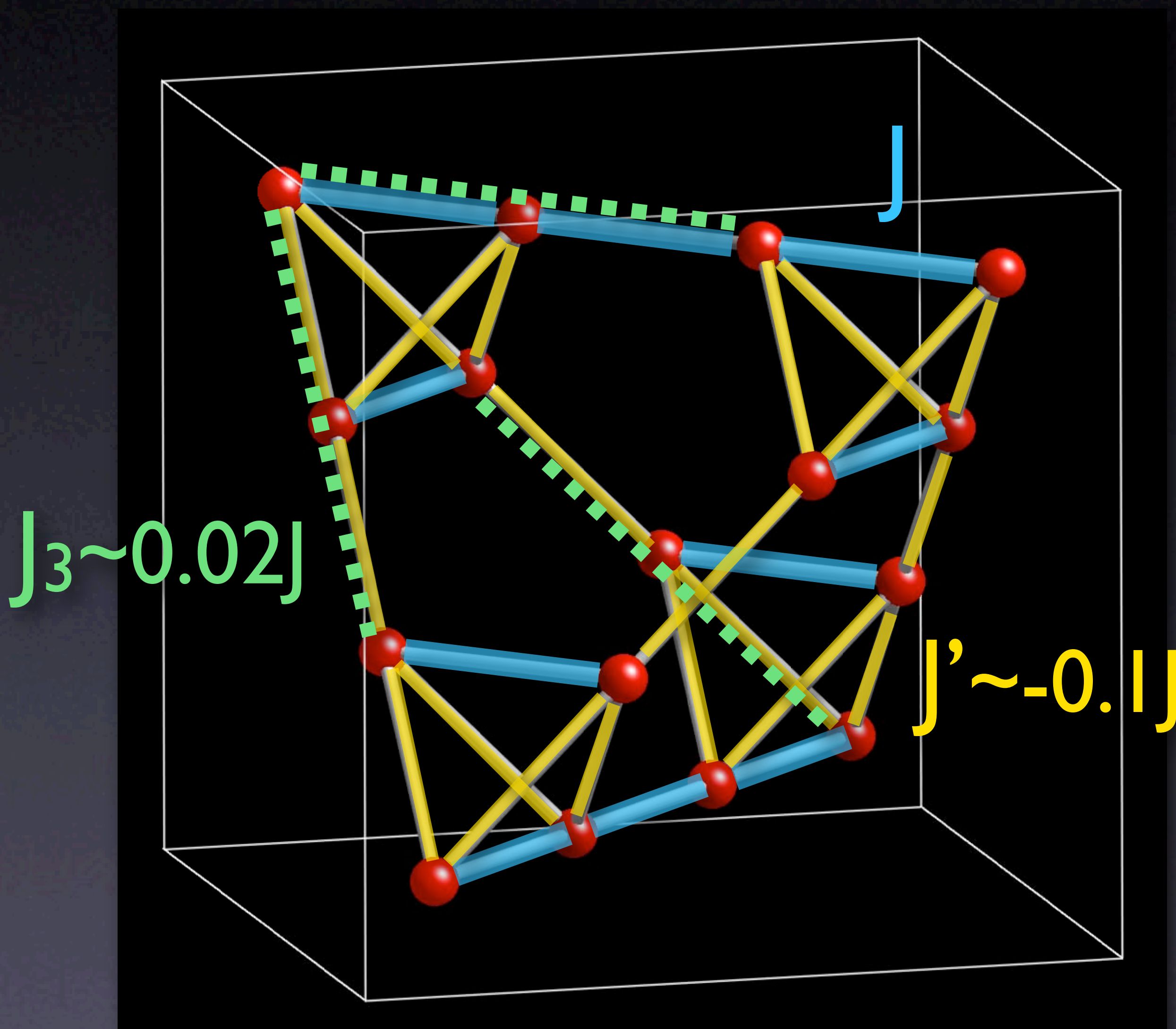
- 3rd-neighbor exchange J_3 is ~0.02J → AF order at T_N



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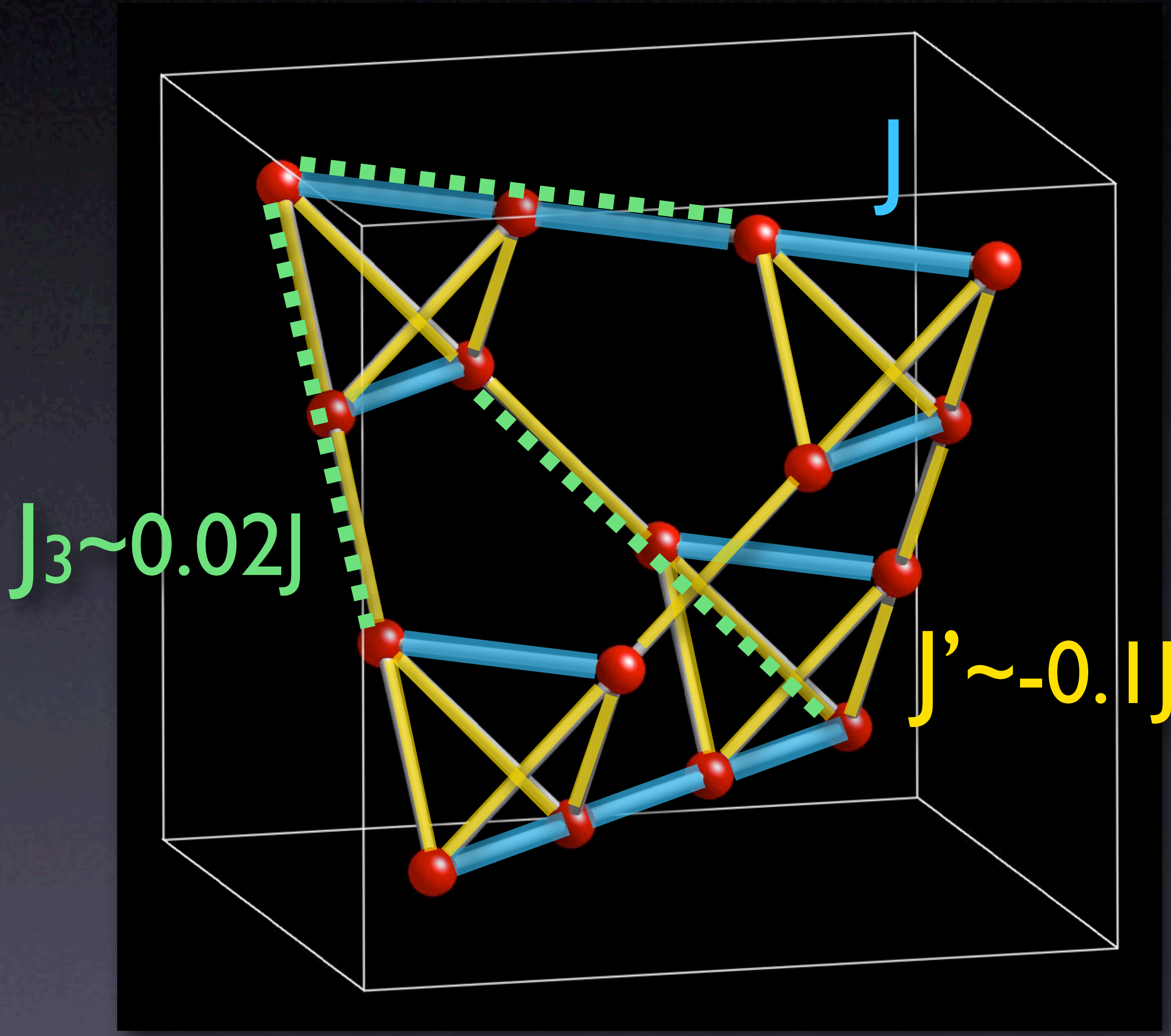
- d_{xy} is singly occupied at all the sites → strong AF exchange in the xy chains J
- n.n. exchange couplings in the yz/zx chains J' are ferromagnetic and about 10 times weaker than the AF exchange in the xy chains J
- 3rd-neighbor exchange J_3 is ~0.02J → AF order at T_N

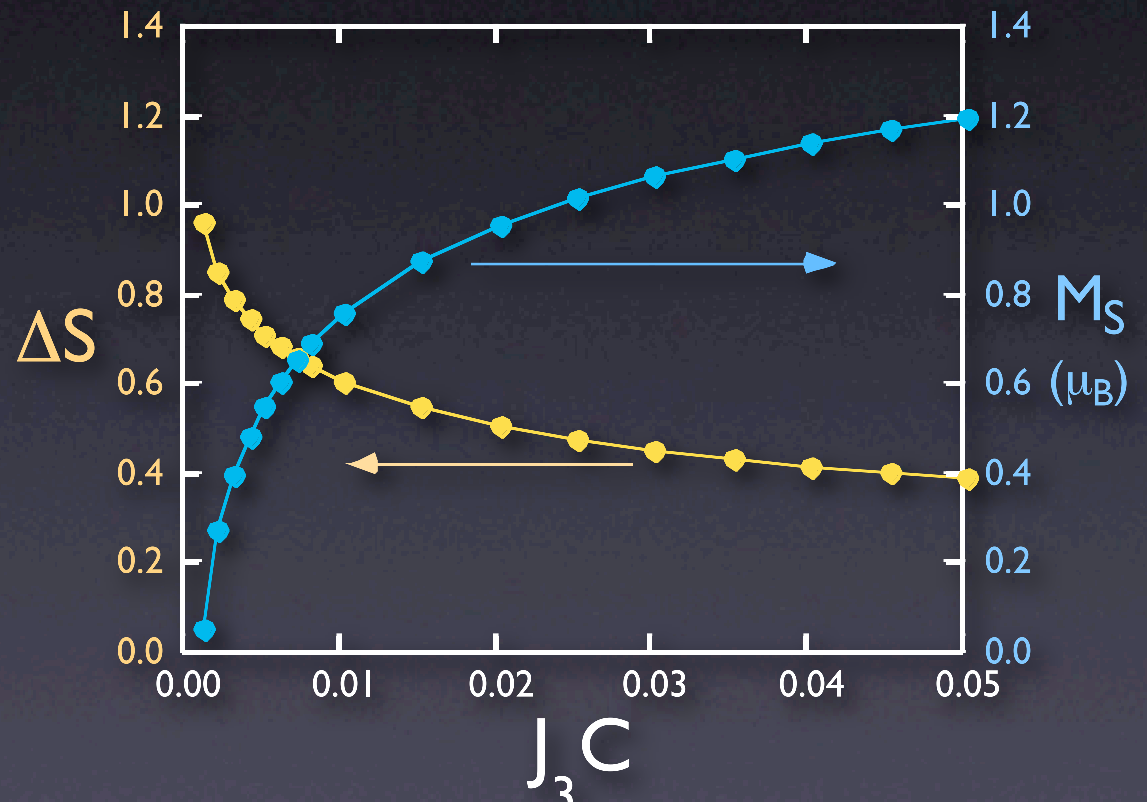


weakly-coupled 1D spin chains (dimensionality reduction)

Quasi-1D Quantum Fluctuation: Large Reduction of AF Moment

- linear spin-wave analysis for the spin and orbital ordered ground state
- moment reduction ΔS diverges logarithmically at $J_3=0$ due to the zero modes
- ΔS is large in the small J_3 region: $M_S \sim 1\,\mu_B$ at $J_3 \sim 0.02J$

  consistent with the experimental result $\sim 0.6\mu_B$ (Lee *et al.*, 2004)



Short Summary...

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- Kugel-Khomskii spin-orbital exchange + tetragonal Jahn-Teller
- classical Monte Carlo simulation and mean-field type analysis
- linear spin-wave analysis of effective spin model

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- Kugel-Khomskii spin-orbital exchange + tetragonal Jahn-Teller
- classical Monte Carlo simulation and mean-field type analysis
- linear spin-wave analysis of effective spin model

- ☑ two transitions with reasonable estimates of trasition temperatures as well as entropy changes
- ☑ T-dep of magnetic susceptibility consistent with experiment
- ☑ magnetic order consistent with the neutron scattering result
- ☑ reduced magnetic moment at T=0
- ☑ A-type antiferro orbital order with tetragonal distortion

Three Different Models

In all models, xy orbital is singly occupied at all the sites (not shown in the figures)

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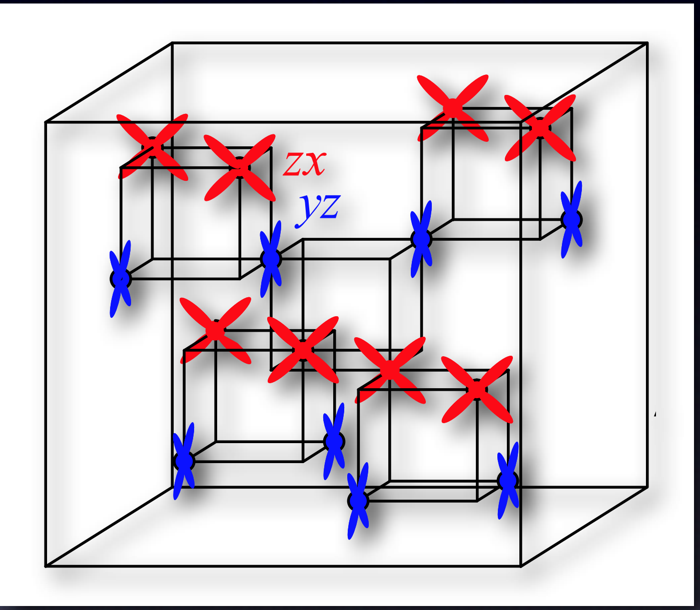
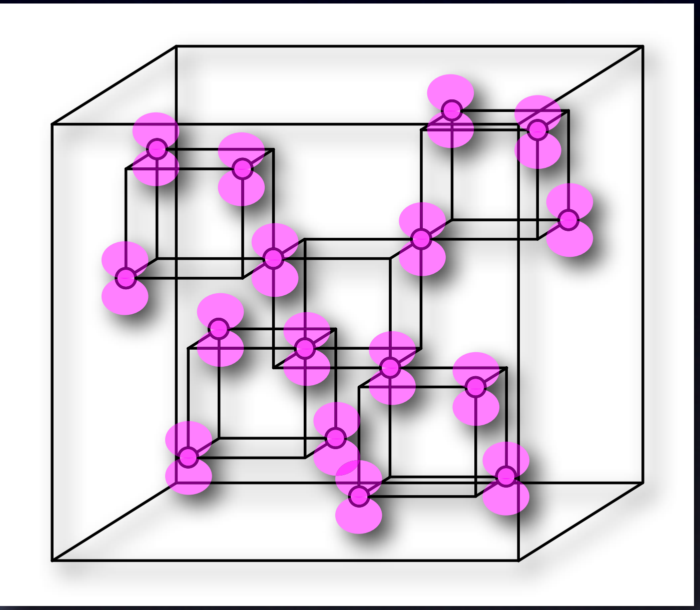
Tsunetsugu-Motome, 2003



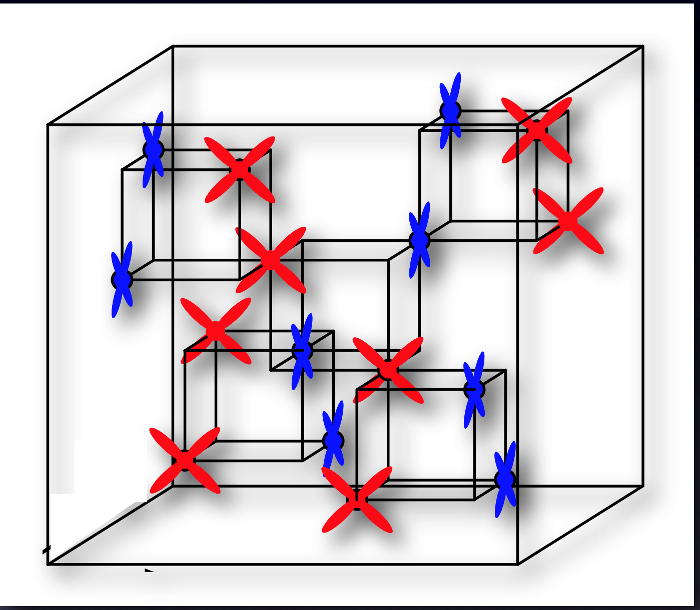
- A-type orbital order
- $I4_1/a$
- spin-orbital superexchanges

Tchernyshyov, 2004



- uniform orbital order
- $I4_1/amd$
- relativistic spin-orbit coupling

Khomskii-Mizokawa, 2005



- orbitally-driven Peierls order
- $P4_12_12$
- approach from itinerant picture (band Jahn-Teller)

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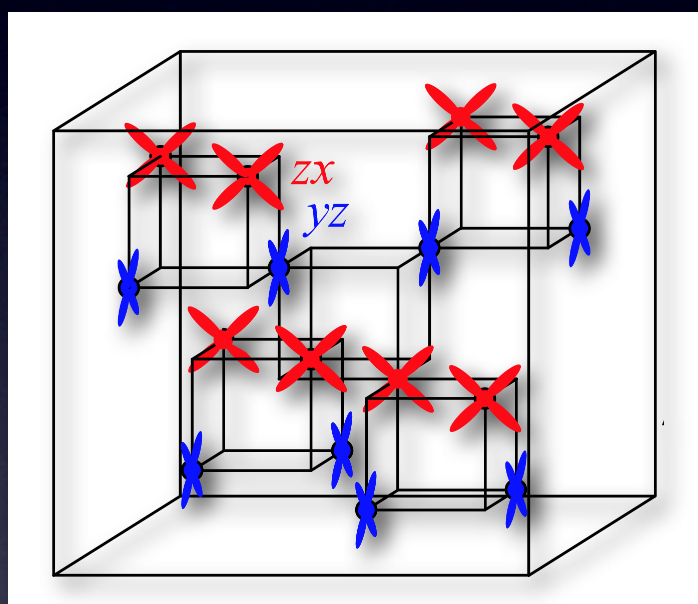

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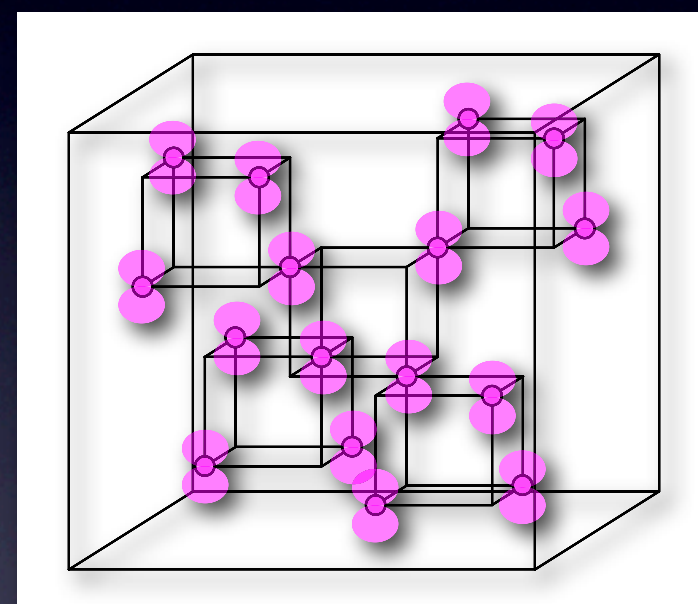

- uniform orbital order
- $I4_1/amd$
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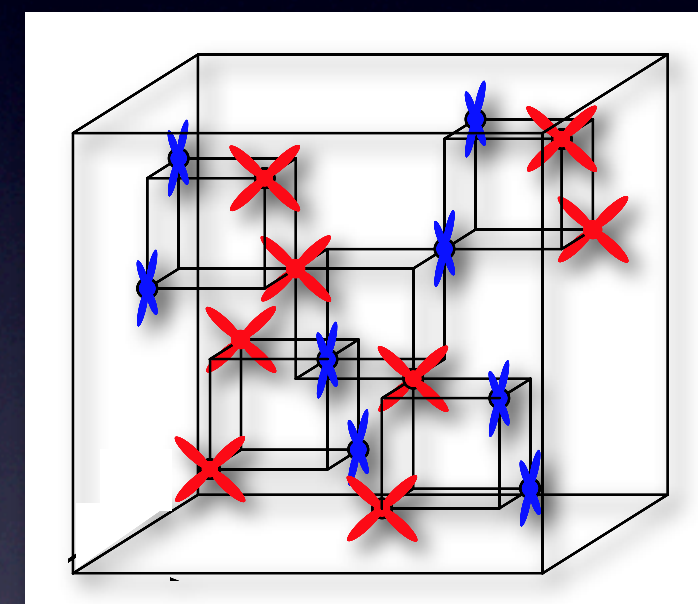
mean-field (Di Matteo *et al.*)
LSDA+U+SO (T. Maitra and R. Valenti)

Khomskii-Mizokawa, 2005



- orbitally-driven Peierls order
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Issue...

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- role of relativistic spin-orbit interaction
  - orbital ordering at T=0: mean-field analysis and first-principle calculation suggest the relevant role
  - thermodynamics: single or two transitions? In general, systems with dominant spin-orbit coupling shows a single transition with concomitant ordering of spin and orbital.
  - reduced AF moment: due to dimensionality reduction and/or L-S coupling?

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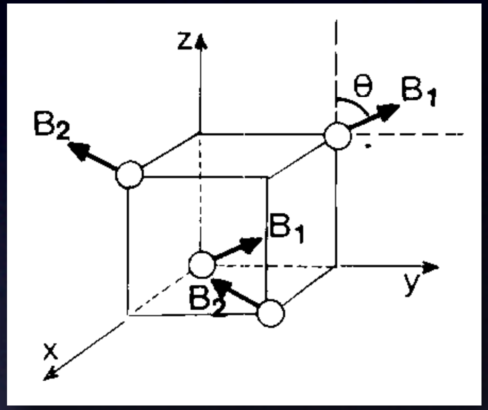
  - reduced AF moment: due to dimensionality reduction and/or L-S coupling?
- Remark: X-ray diffraction has been done only for powder samples...

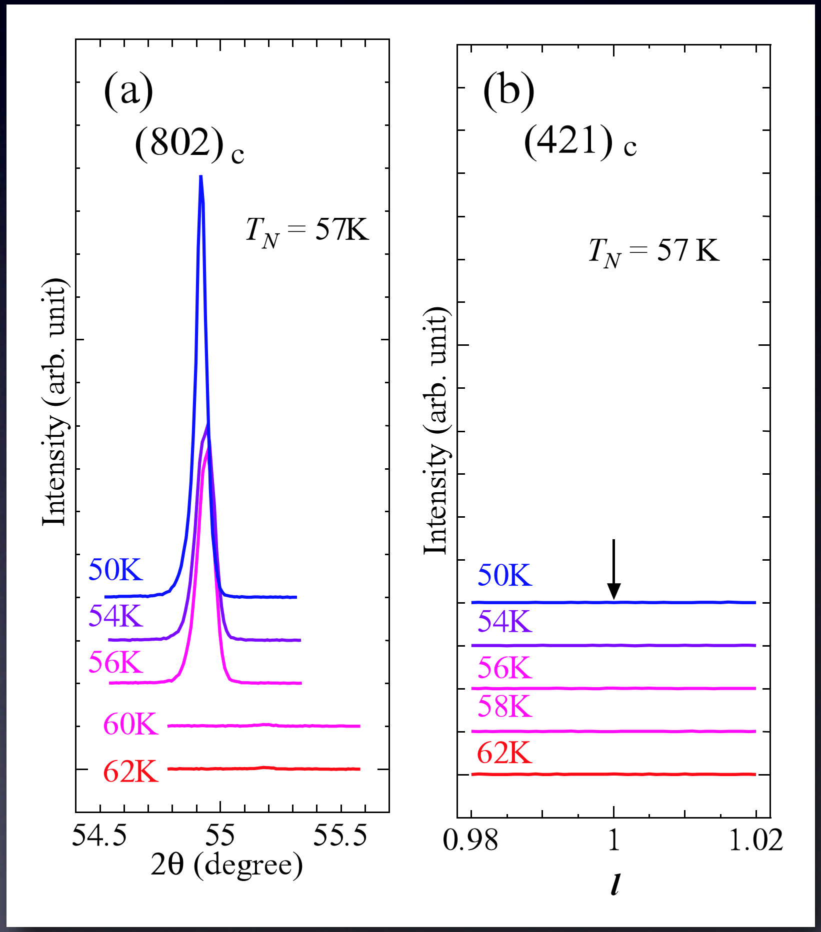
Lesson from Related Spinel MnV_2O_4

- $Mn^{2+} = (3d)^5, V^{3+} = (3d)^2$
- single transition at 57K
  - cubic → tetragonal
  - non-collinear ferri

Plumier and Sougi, 1987



- low-T phase: $I4_1/a$ (*large single crystal*)
  - diamond-glide symmetry is broken, but face-center symmetry is hold
  - peak intensity is ~10^{-4} times smaller compared to the fundamental peaks, <u>difficult to observe in powder samples</u>



Suzuki *et al.*, 2007

Other Issues...

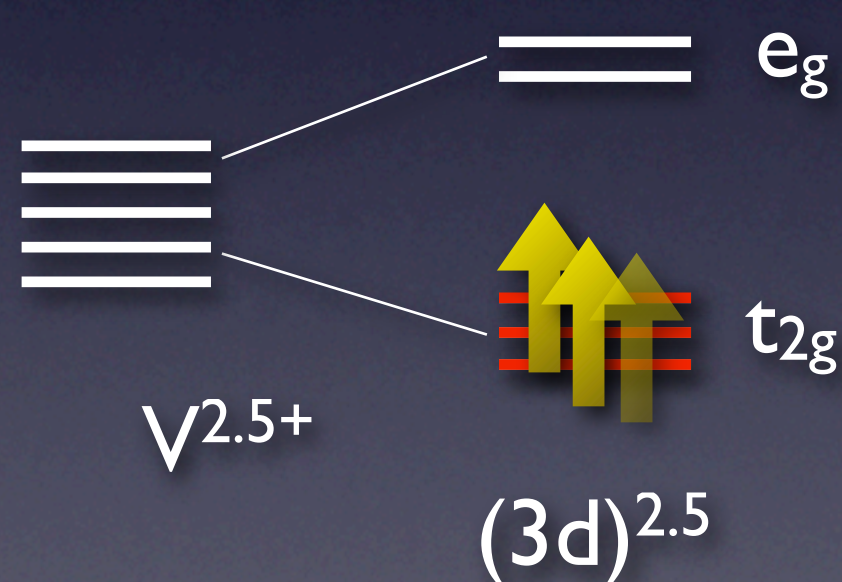
- role of trigonal distortion
  - quantitative difference in Cd compound
- d-d direct vs d-p-d (d-p-p-d) indirect transfers
- orbital and spin ordering in MnV_2O_4
- single crystal of ZnV_2O_4 !

Self-organized 7-site Cluster (heptamer) in AlV_2O_4

in collaboration with Keisuke Matsuda and Nobuo Furukawa

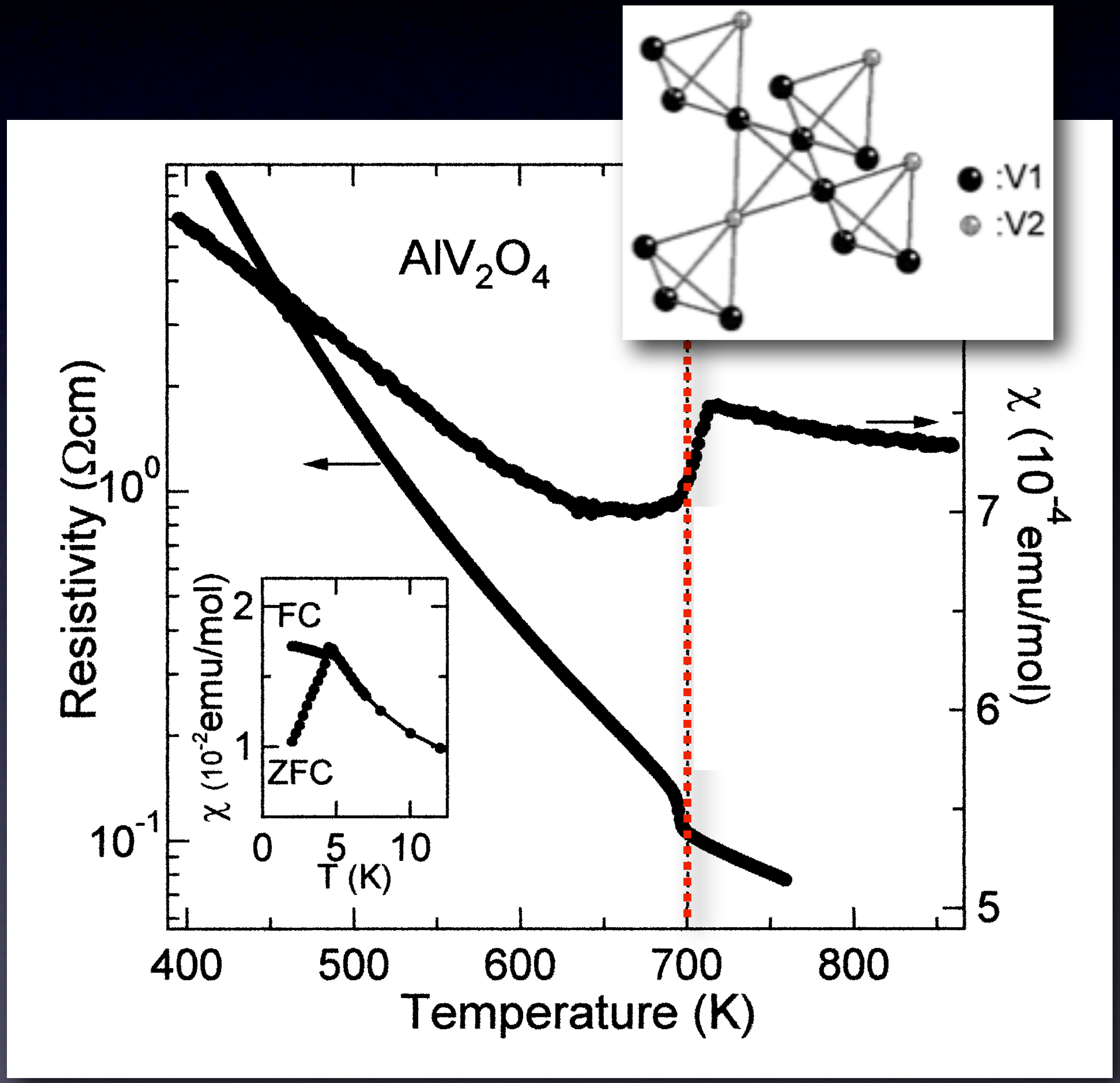
(Atomic) Electronic Structure in AlV_2O_4

- mixed valence: $V^{2.5+} = (3d)^{2.5}$
- charge, spin and orbital degrees of freedom are all active



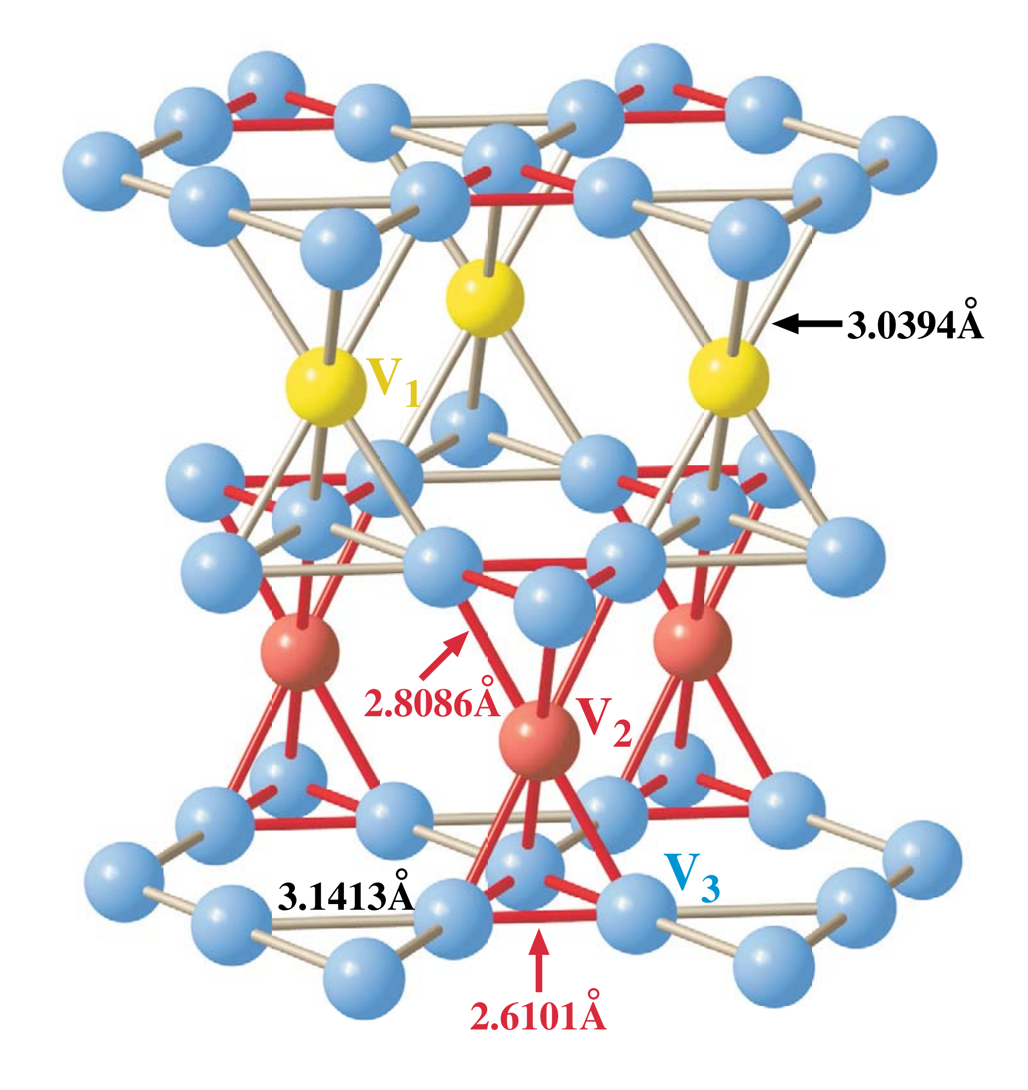
Phase Transition at T~700K

- structural change: doubling of the unit cell along the [111] direction
- shoulder in the resistivity
- sudden drop in the magnetic susceptibility followed by Curie behavior at lower temperatures
- valence-skipping-type charge ordering ?



K. Matsuno *et al.*, 2001

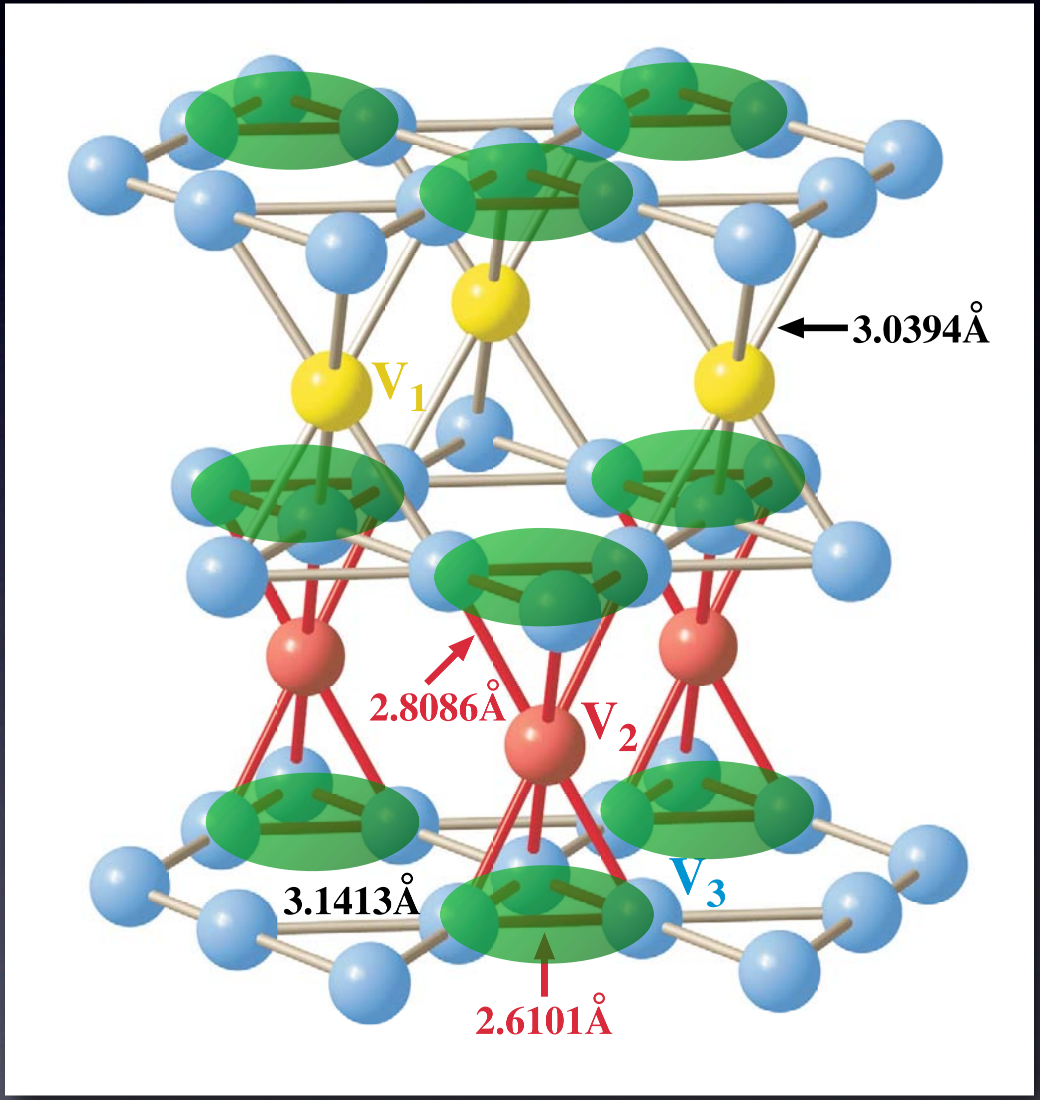
Heptamer Scenario



Y. Horibe *et al.*, 2006

Heptamer Scenario

- new experimental finding: trimer formation in Kagome layers below T_c



Y. Horibe *et al.*, 2006

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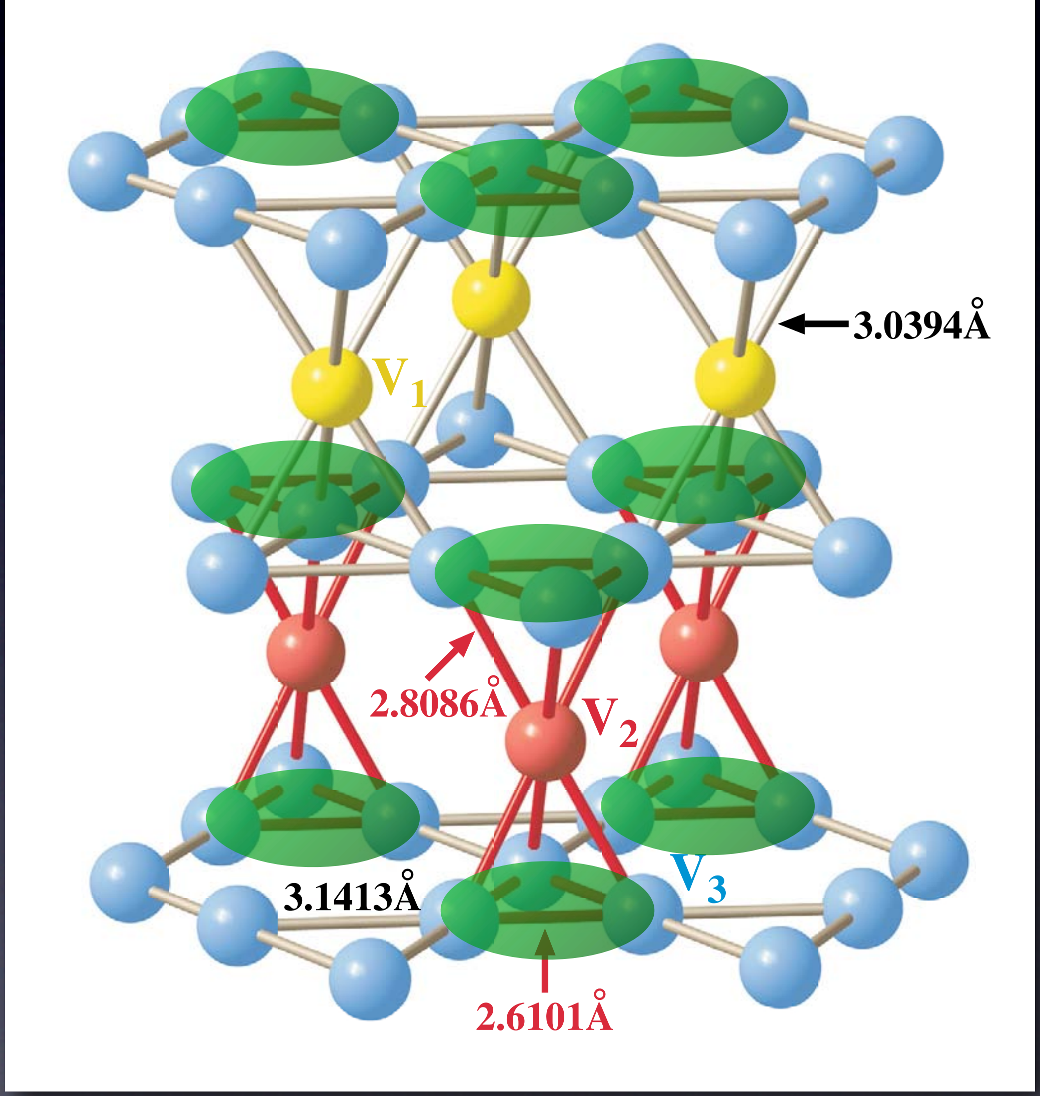
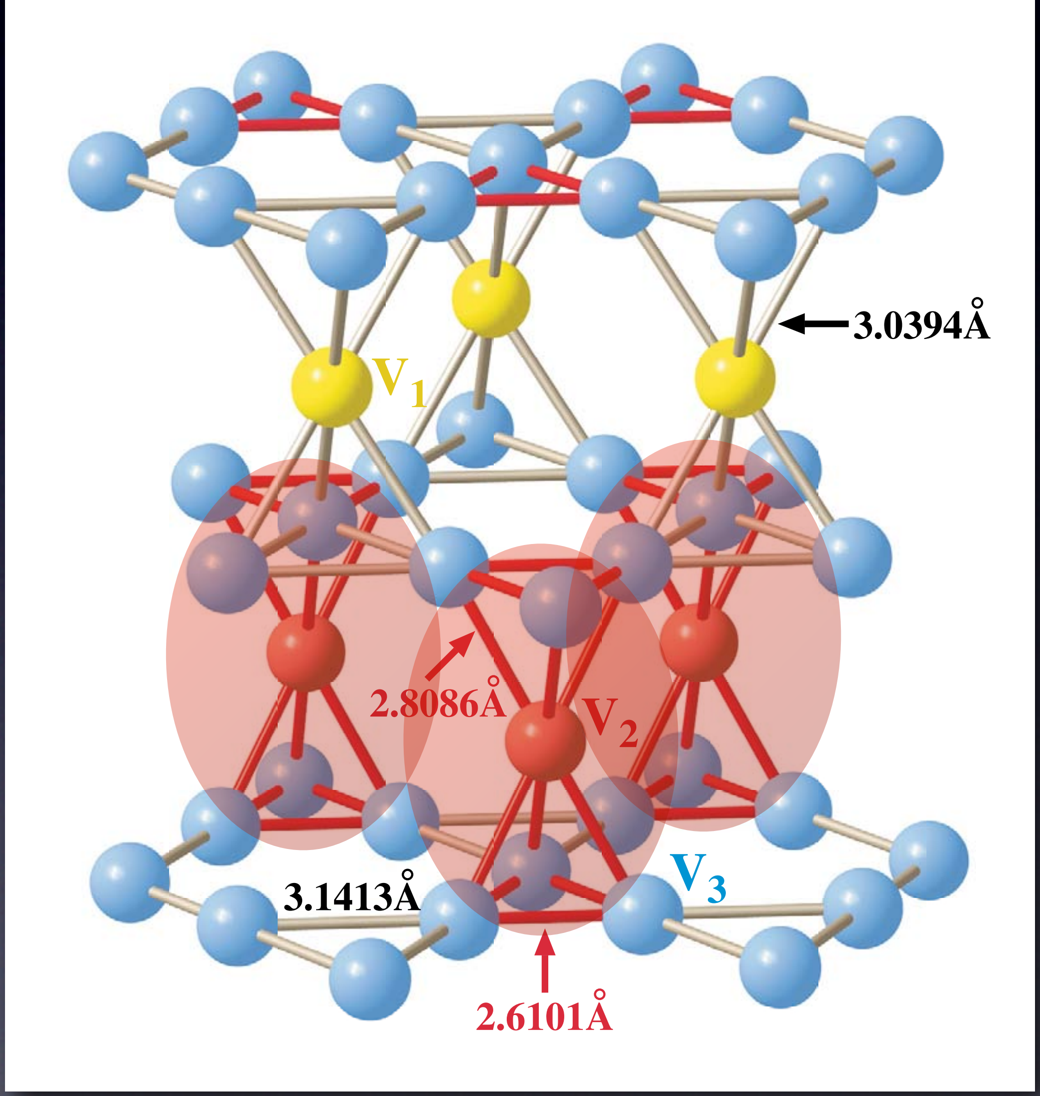


Y. Horibe *et al.*, 2006

Heptamer Scenario

- new experimental finding: trimer formation in Kagome layers below T_c
- spin-singlet formation in trimers? → sharp drop of the magnetic susceptibility?
- We propose a singlet state emerging from the 7-site clusters (heptamers)



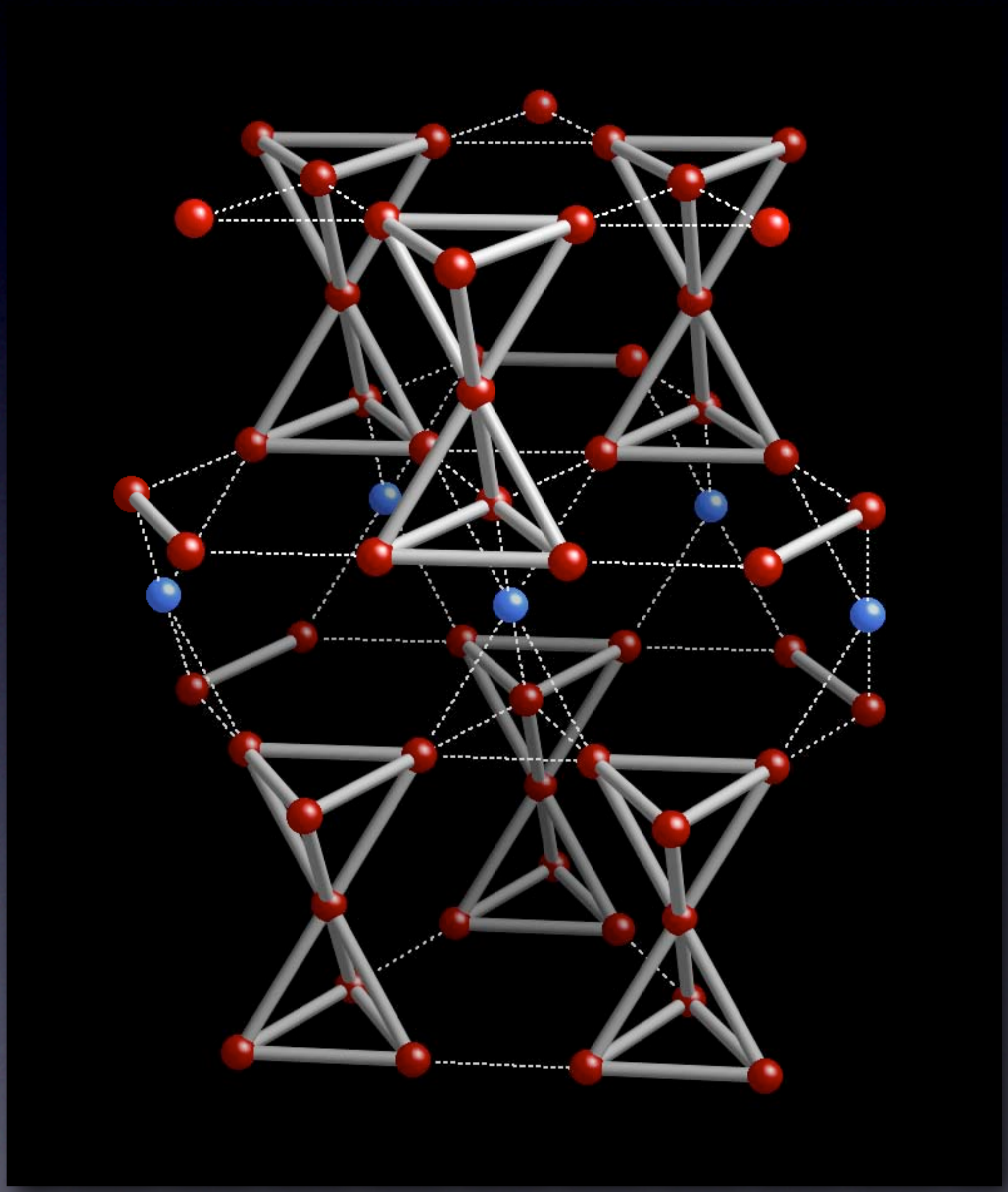
Y. Horibe *et al.*, 2006

Questions

- What is the mechanism of the heptamer formation? How is the degeneracy in the frustrated pyrochlore system lifted?

- Is the heptamer in a spin-singlet state? How does the singlet state emerge in each heptamer?

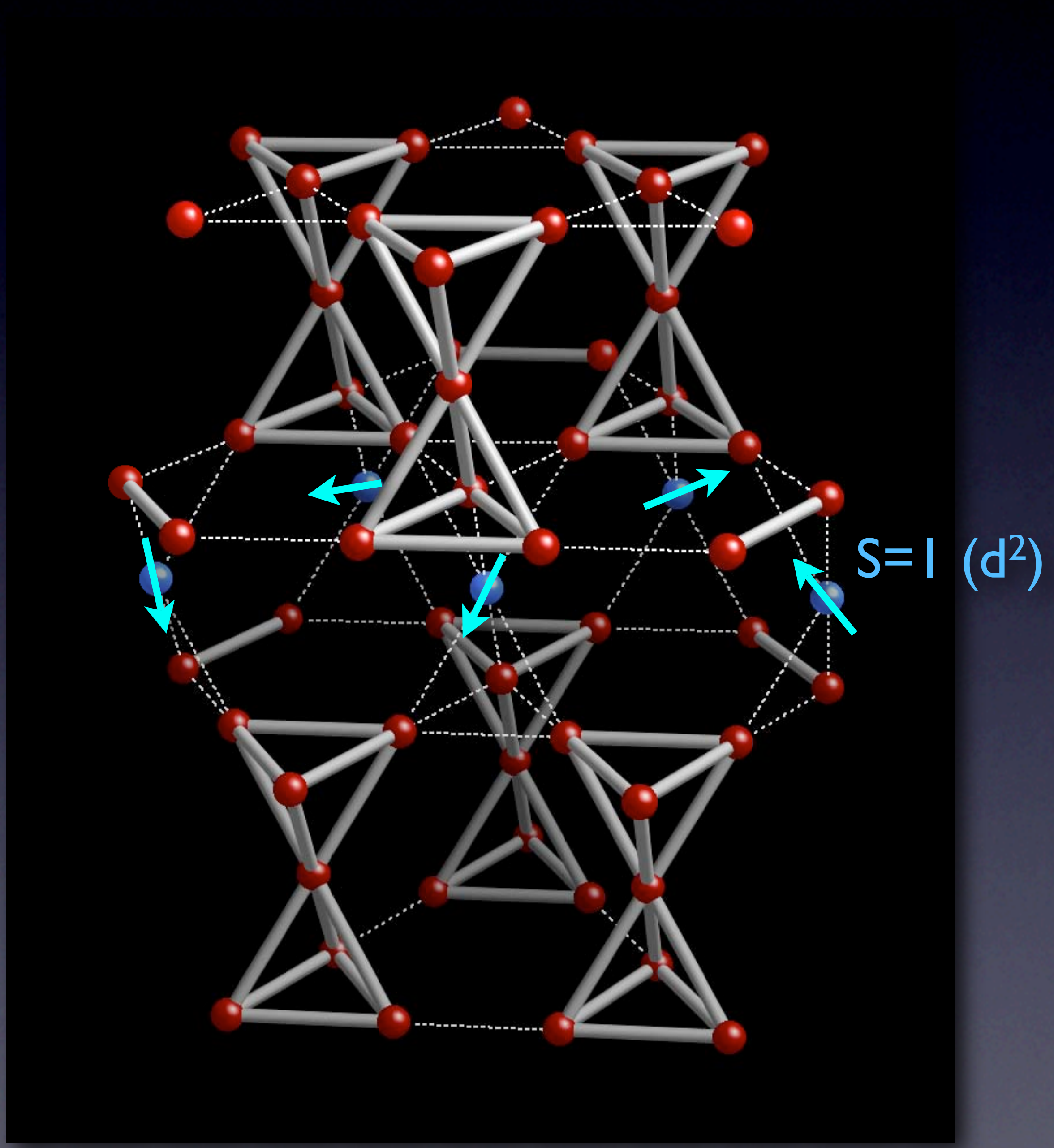
Multi-orbital Heptamer Model



Multi-orbital Heptamer Model

- *assumption:* S=1 localized moments at *isolated* V sites (leading Curie behavior at low T)

  → 18 electrons per heptamer



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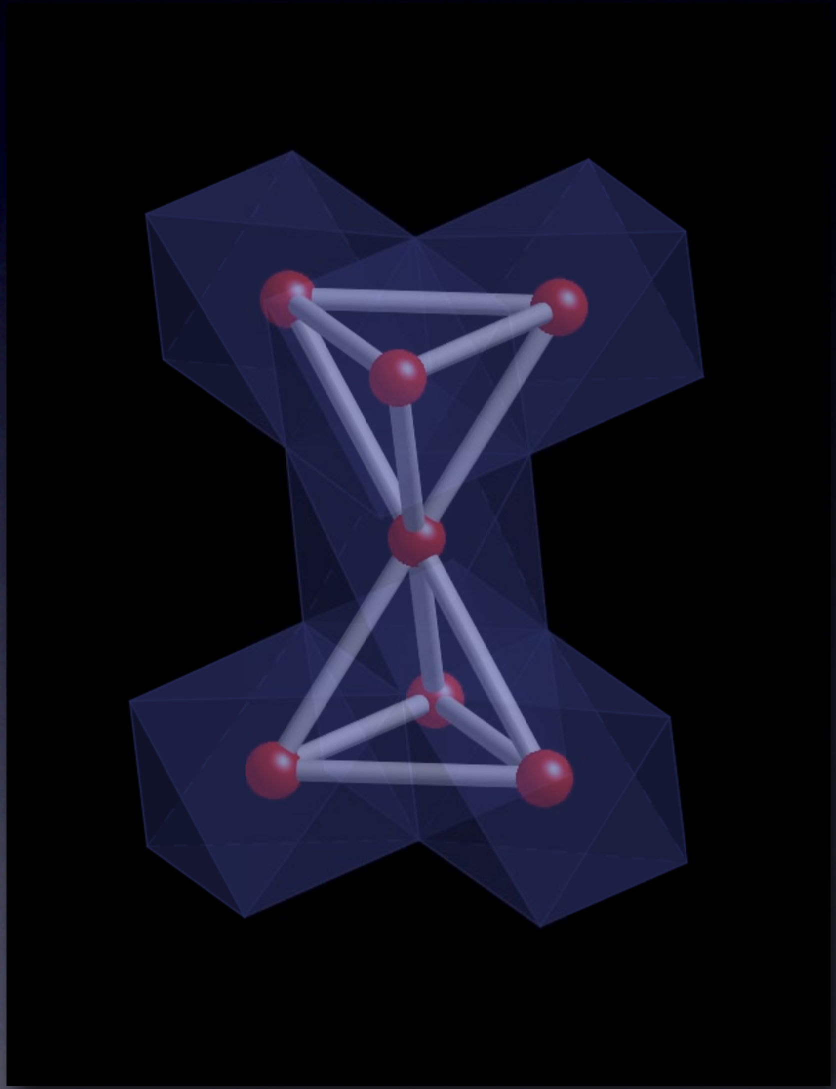
- t_{2g} multi-orbital Hubbard model for each heptamer
  - σ and π transfer integrals
  - trigonal lattice distortion at the central site
  - Coulomb interactions



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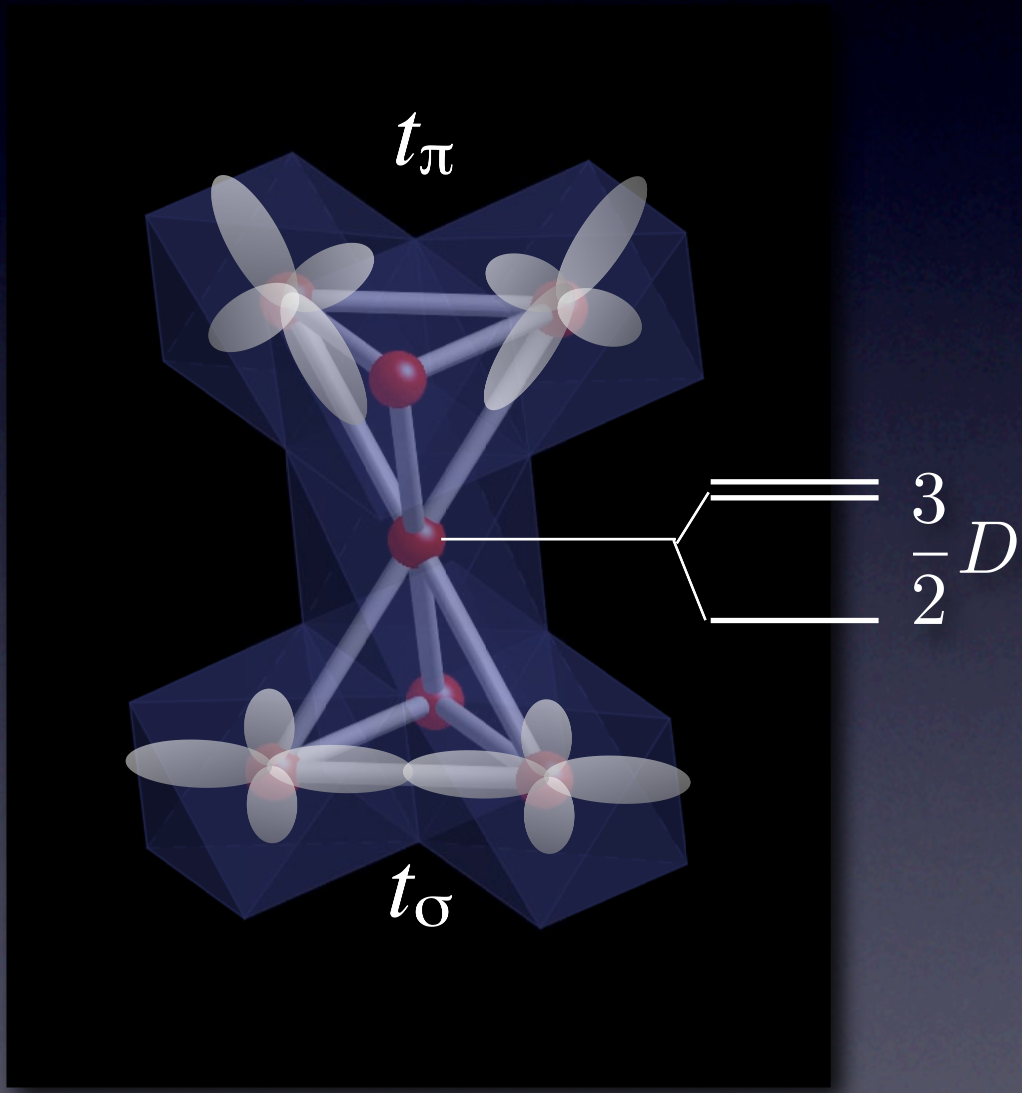

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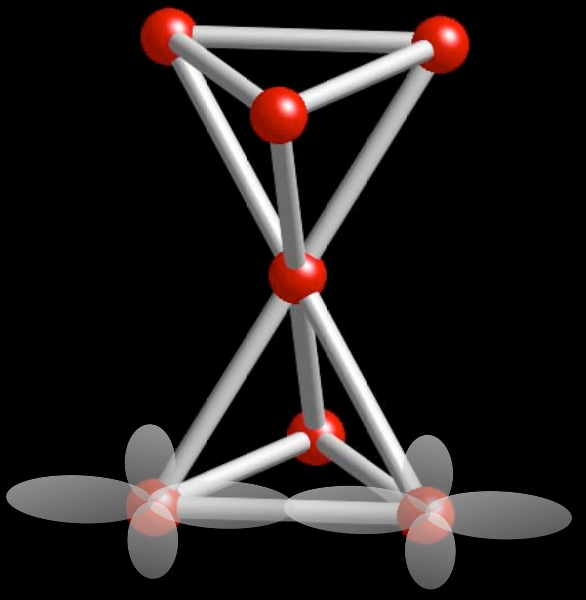

bonding state:
2 electrons per bond

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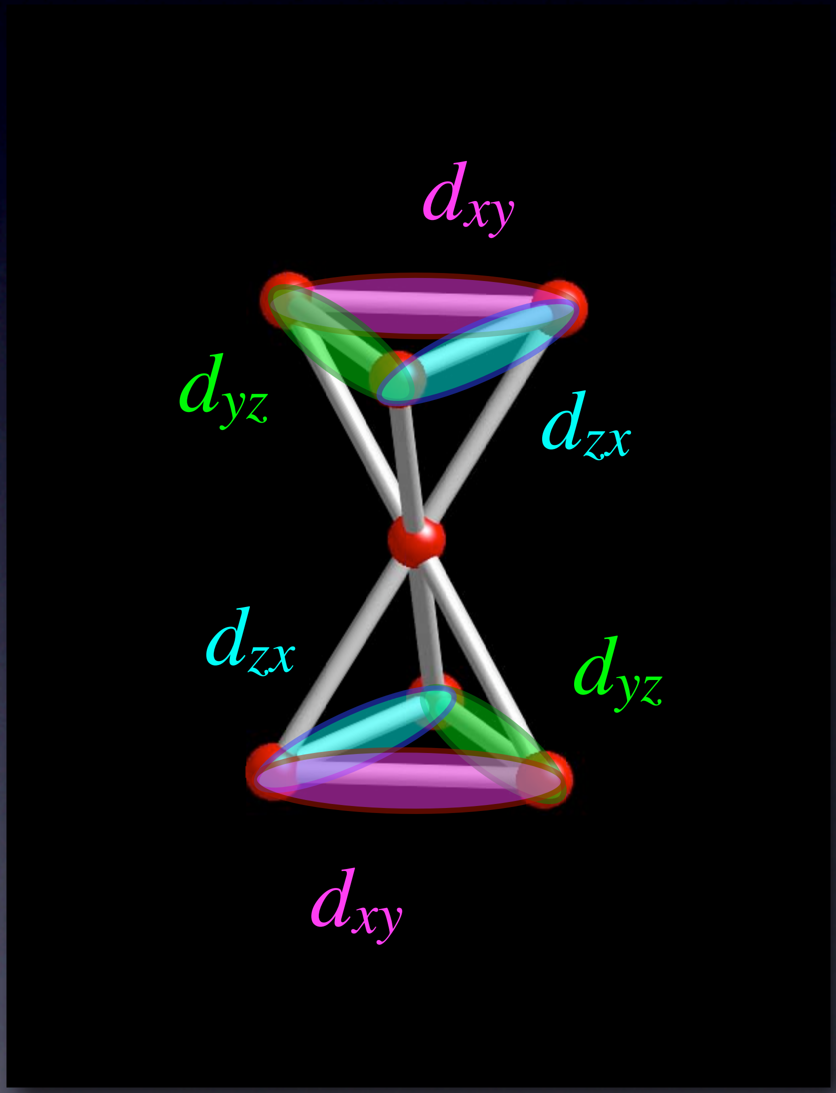
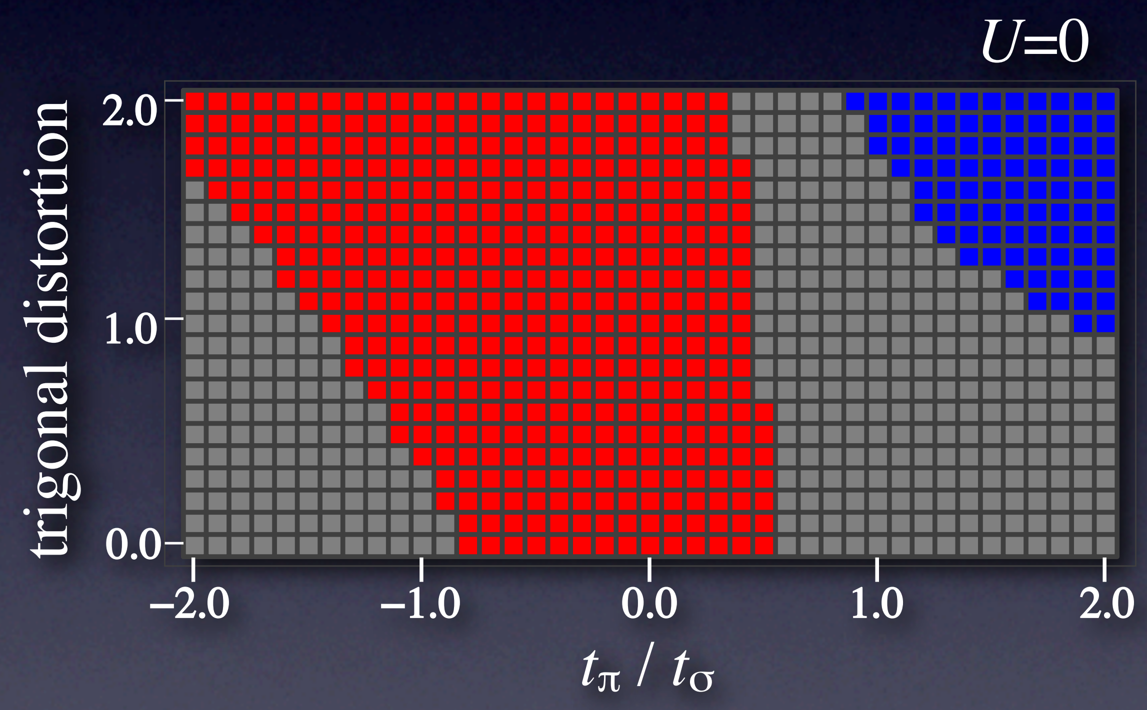


Ground-state Degeneracy

- exact diagonalization of the effective heptamer model
- two different singlet regimes: σ-type and π-type



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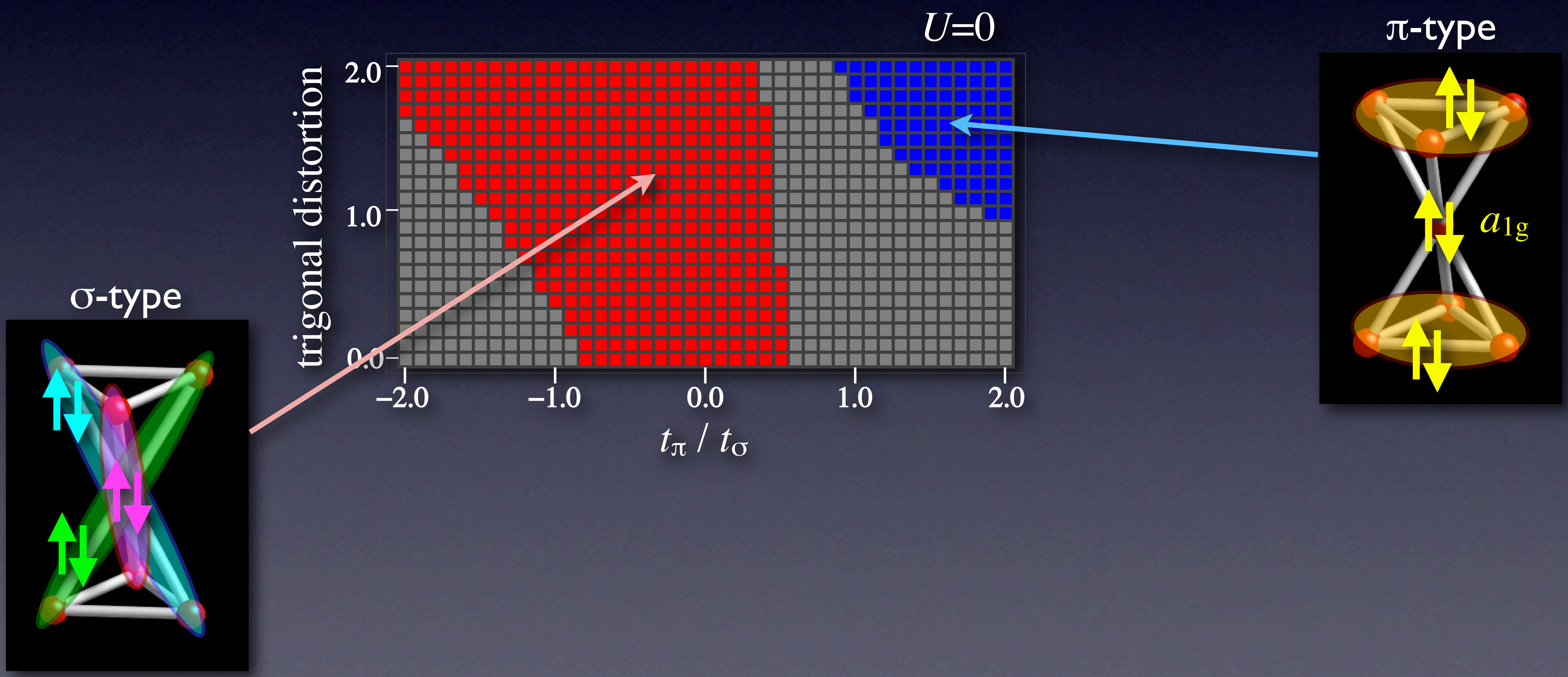

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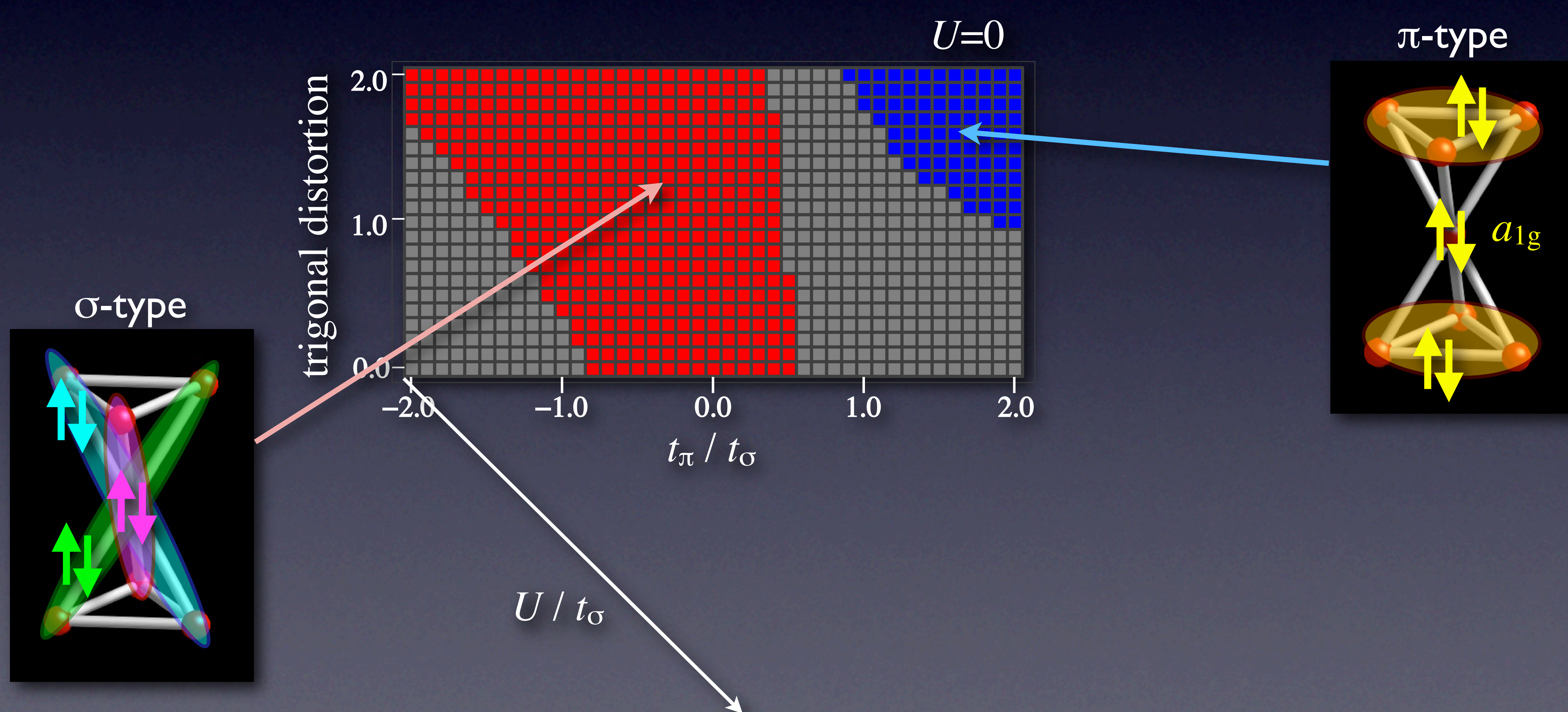

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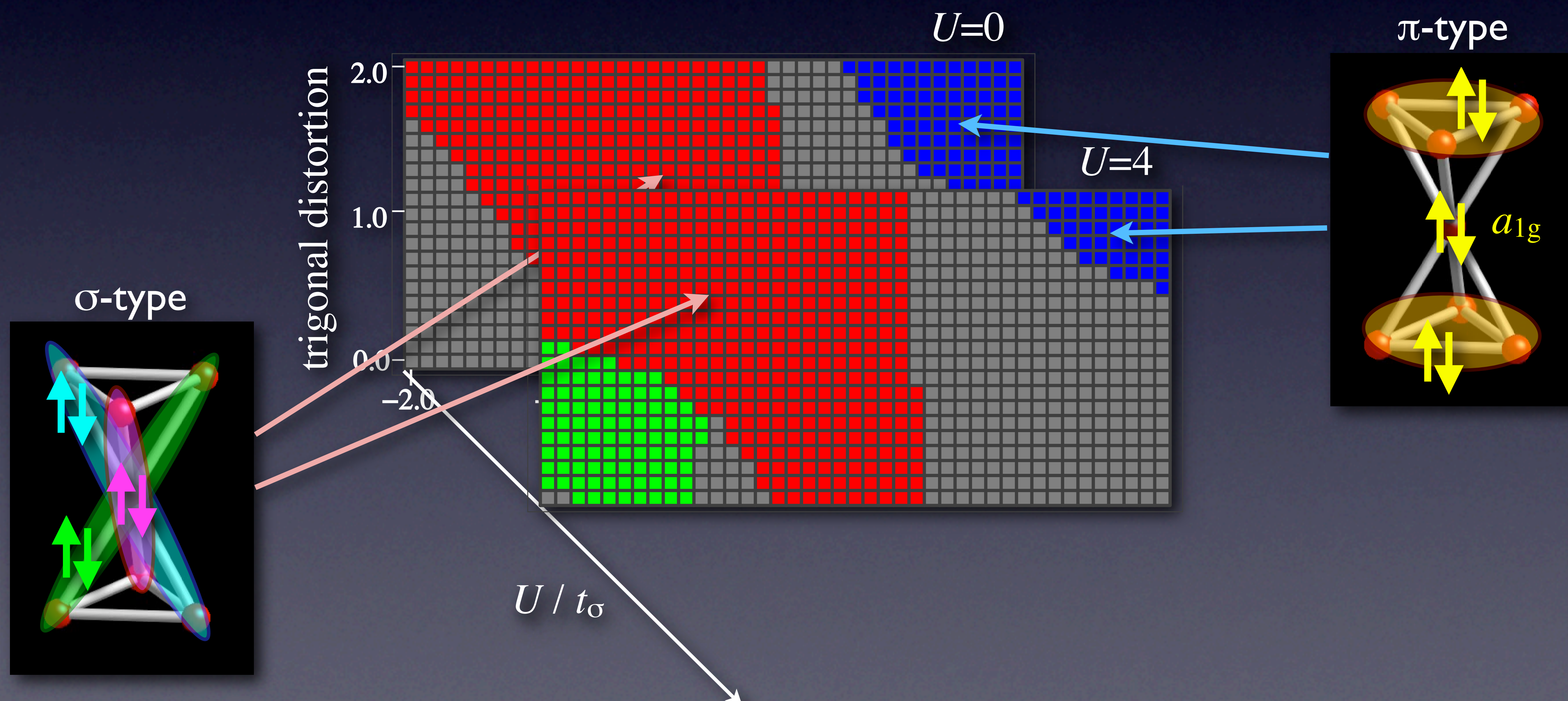

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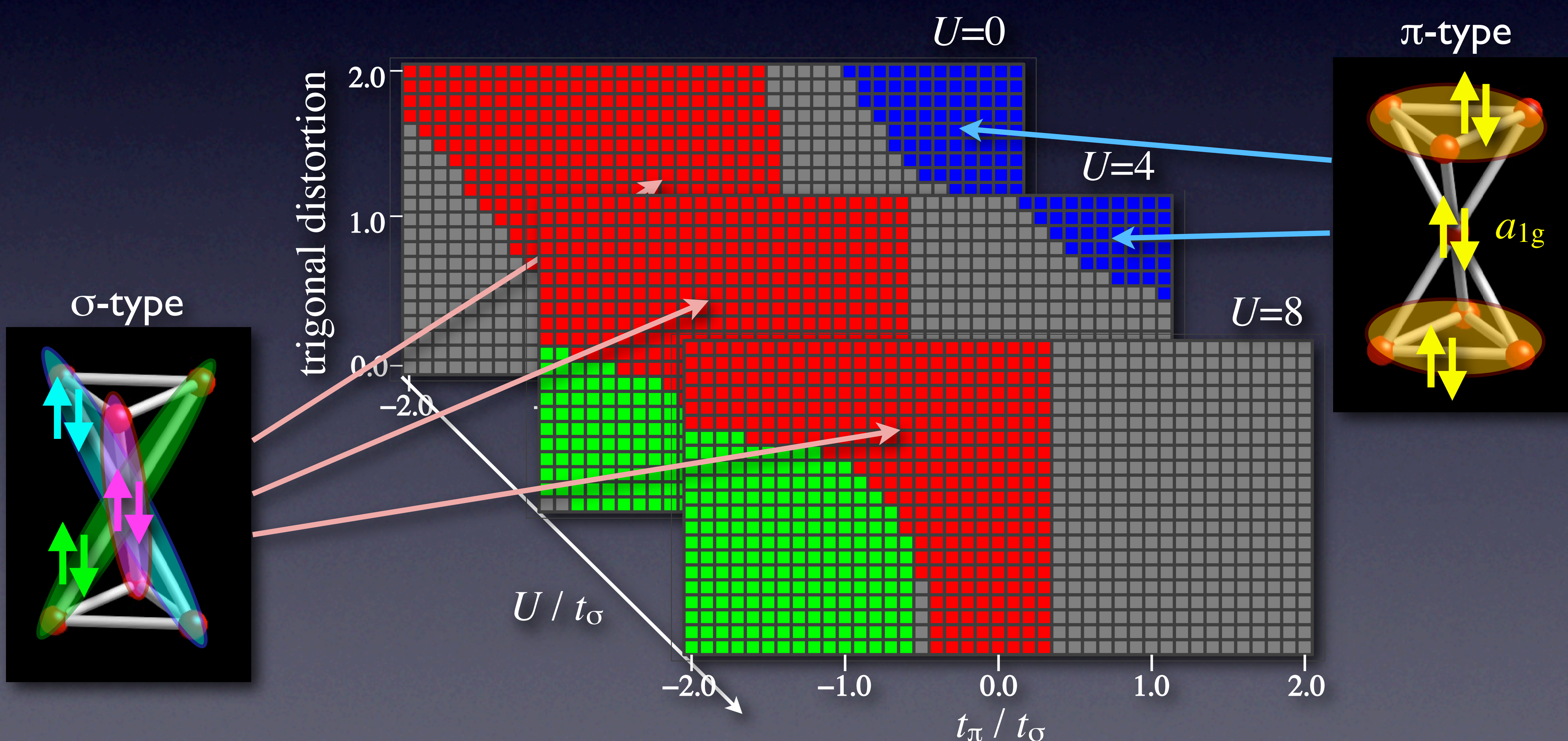

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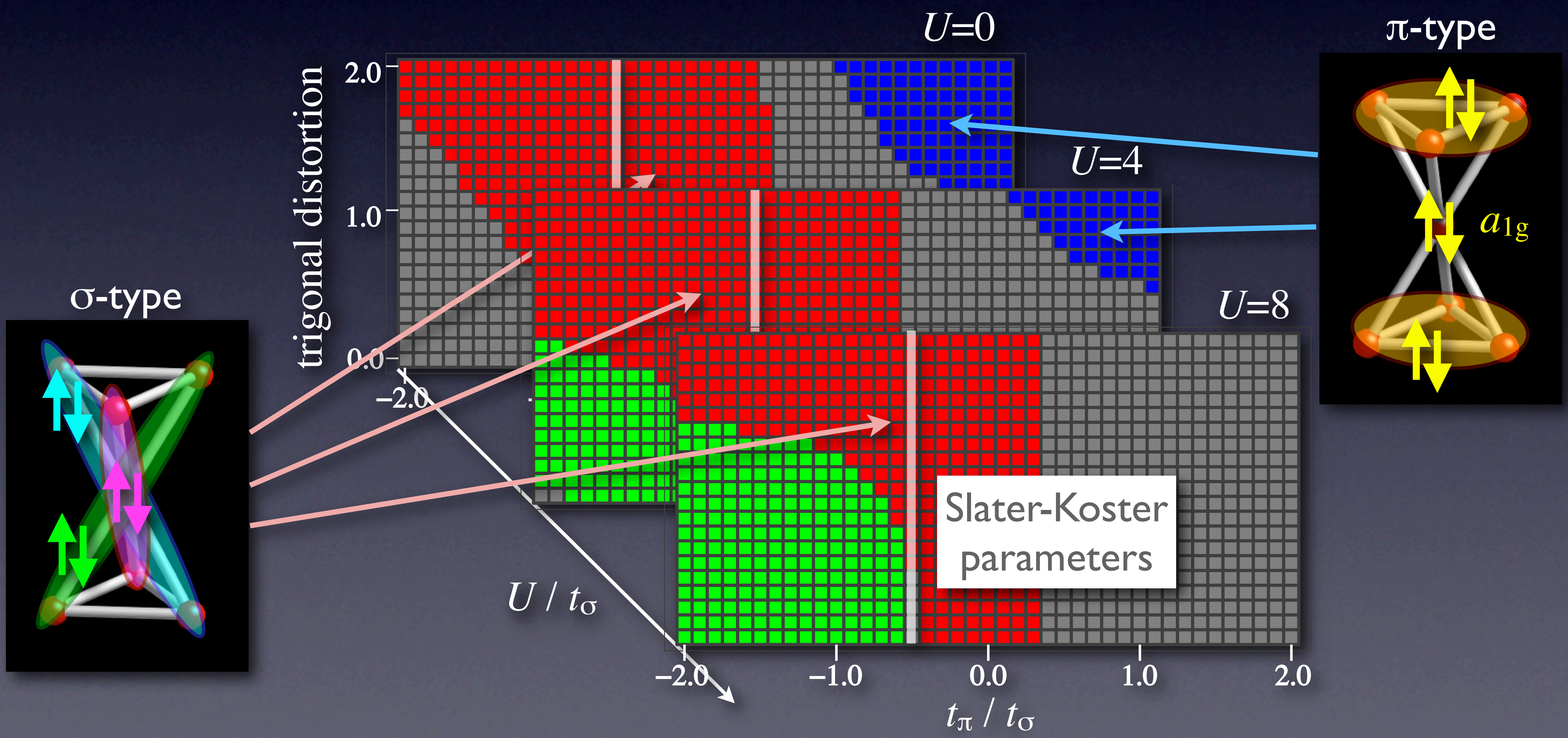


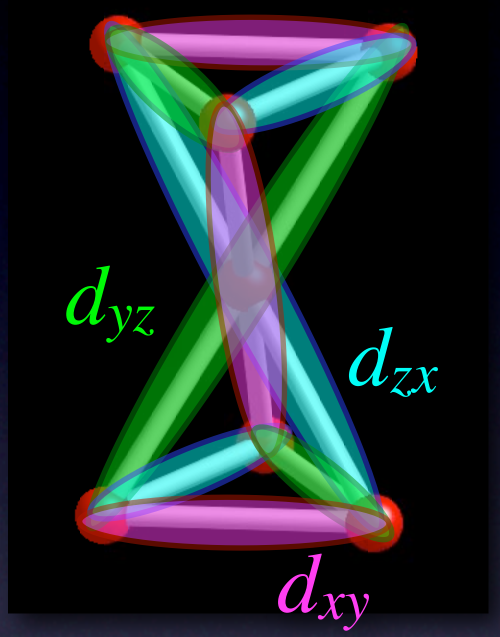
Singlet State in Heptamer

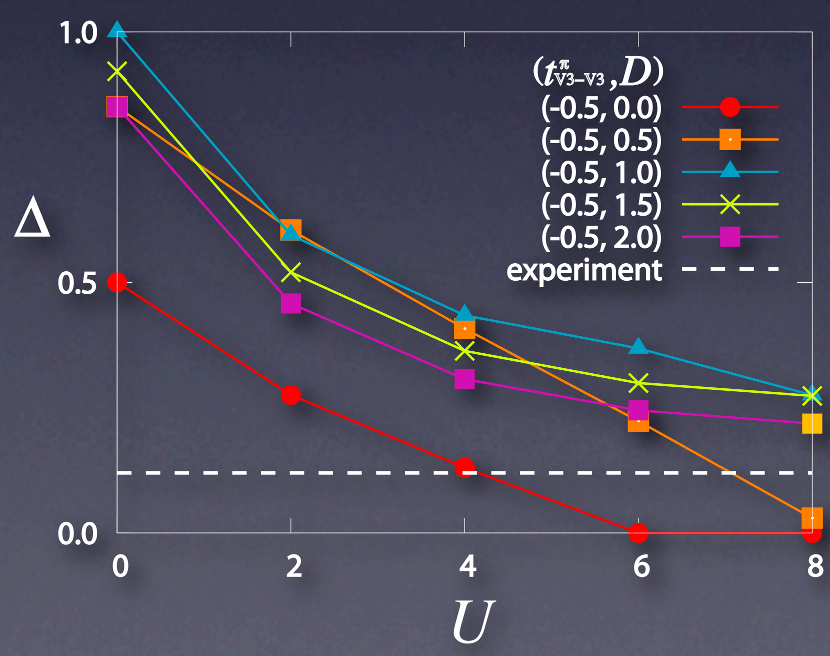
- singlet ground state for realistic parameters = σ-type

  ‘molecule’ of the bonding states with three t_{2g} orbitals

- estimate of the spin gap is larger than the experimental one: heptamer-heptamer coupling?

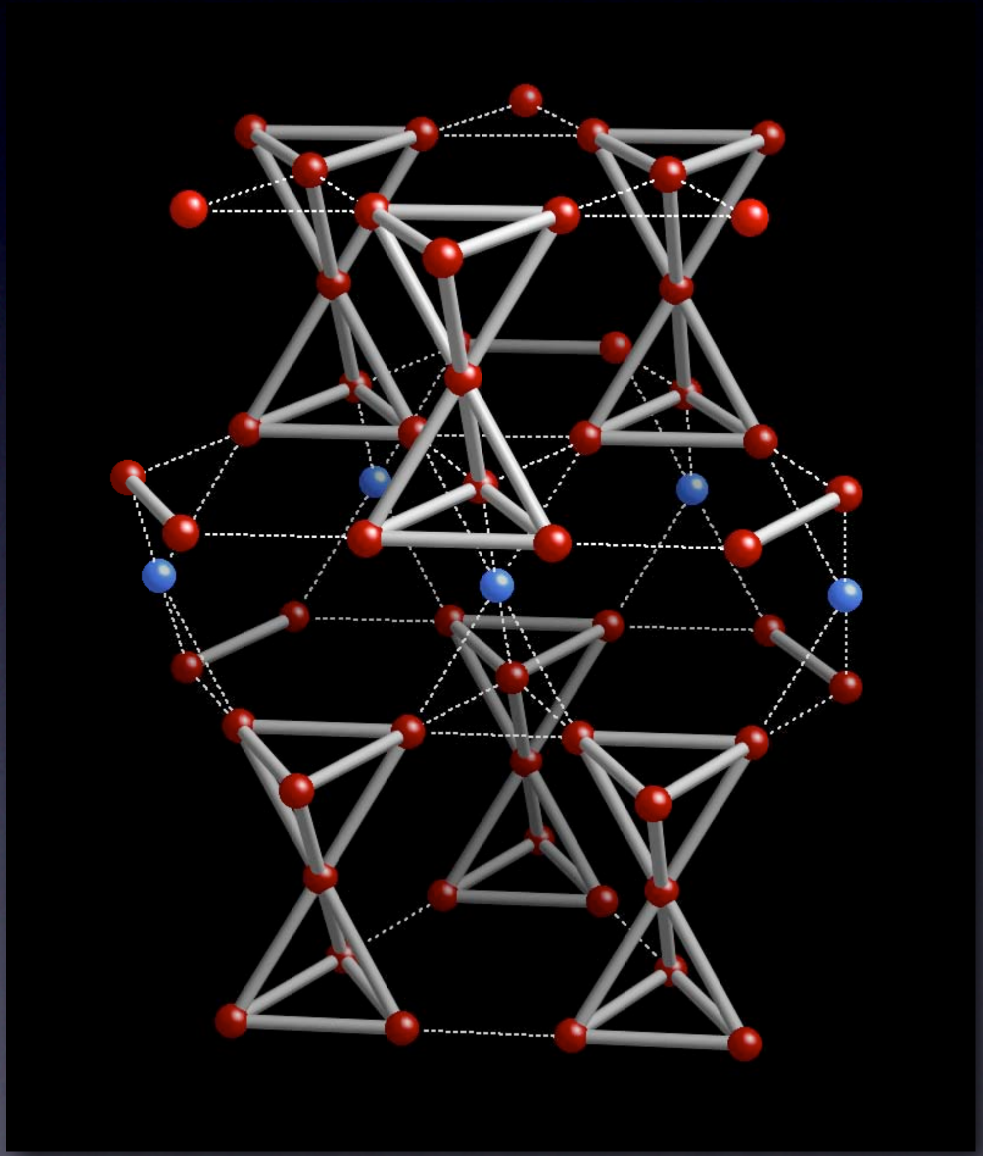
- comprehensive understanding of the T-dependence of magnetic susceptibility



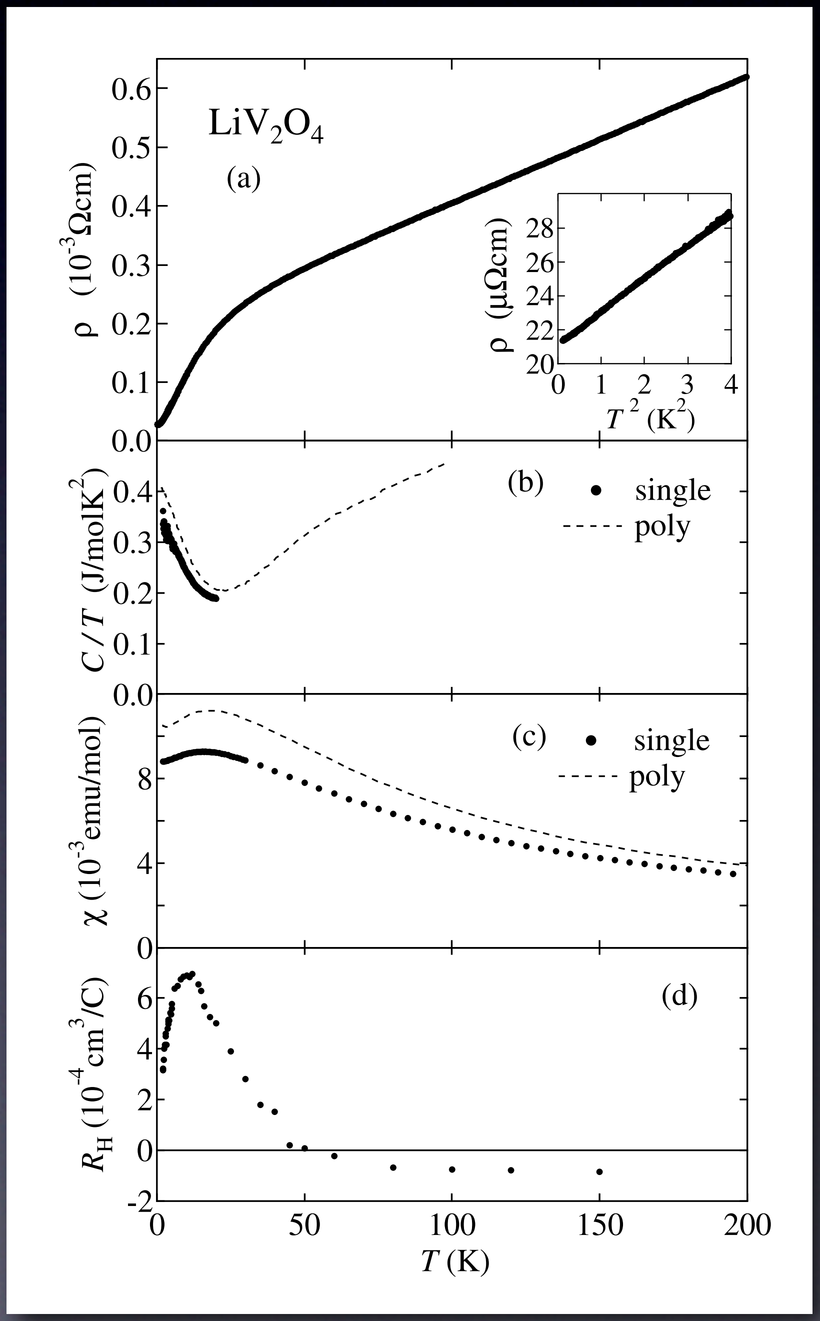


Open Issues...

- Once the heptamers are assumed to be stable, experimental results at low-T phase are explained comprehensively.
- What is the mechanism of the heptamer formation? How is the degeneracy in the frustrated pyrochlore system lifted?
- Is similar phenomenon seen in other mixed-valence compounds?



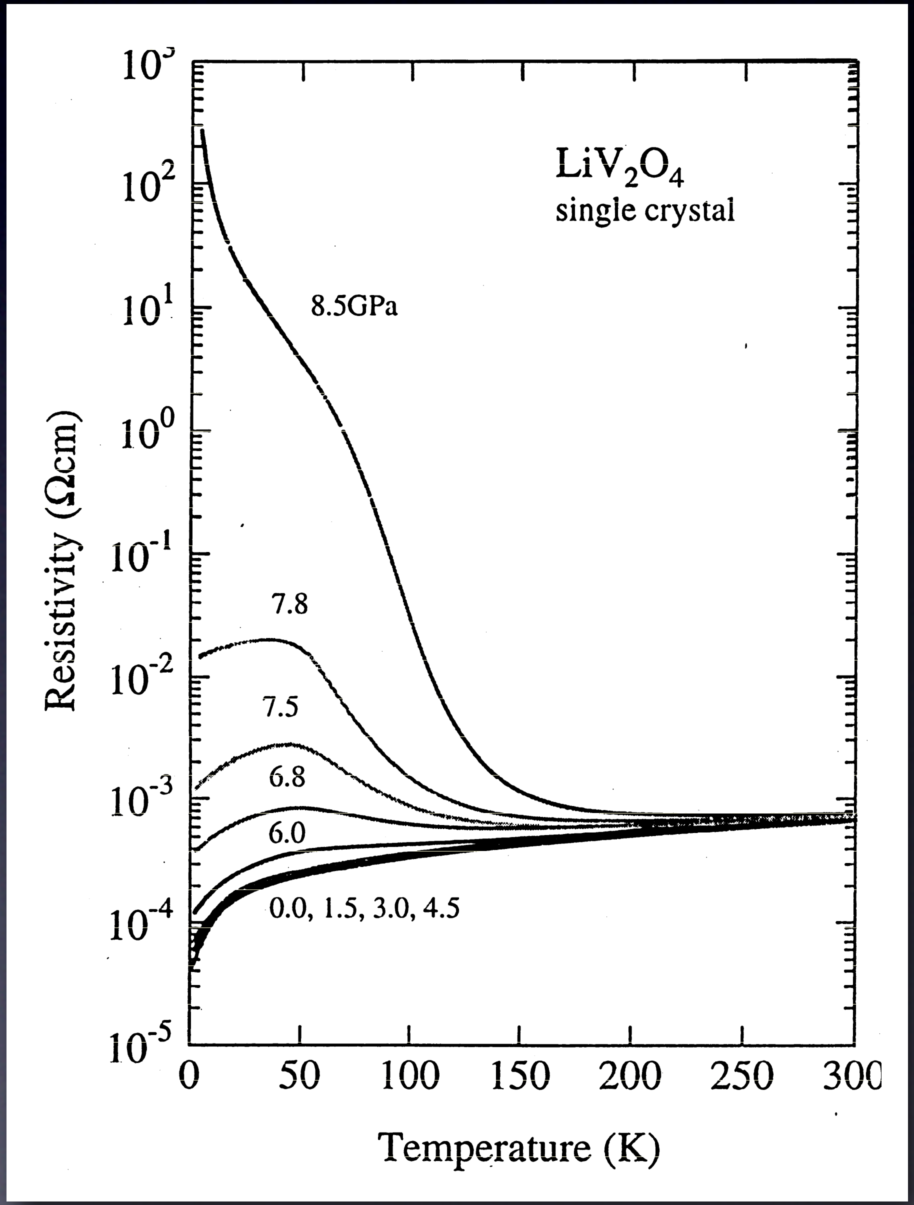
Another Mixed-Valence Compound LiV_2O_4 : Heavy-Fermion Behavior



Urano *et al.*, 2000

- mixed valence: $V^{3.5+} = (3d)^{1.5}$
- heavy mass (Kondo *et al.*, 1997)
- cubic, metallic, no magnetic ordering (Rogers *et al.*, 1967; Chmaissem *et al.*, 1997; Mahajan *et al.*, 1997; Merrin *et al.*, 1998)
- only t_{2g} electrons: new mechanism for heavy fermion behavior?
  - Kondo scenario
  - geometrical frustration + correlation

Implication of AlV_2O_4 ?



Urano, PhD Thesis

- metal-to-insulator transition by applying pressure: *opposite to usual pressure effect*
- short and long V-V bonds in the insulating state (EXAFS by Niitaka *et al.*, unpublished)
- <u>possibility</u>: some cluster formation similar to AlV_2O_4

Summary

- introduction to spinels and t_{2g} orbital physics
- controversy on orbital ordering in ZnV_2O_4
  - different models for spin/orbital order in ZnV_2O_4: relative importance of Kugel-Khomskii superexchange, Jahn-Teller and relativistic spin-orbit couplings
  - symmetry analysis: lesson from experiments in MnV_2O_4
- self-organized 7-site cluster (heptamer) in AlV_2O_4
  - heptamer scenario: 'molecule' of bonding states with anisotropic t_{2g} orbitals
  - implication to heavy-fermion compound LiV_2O_4