Orbital and Magnetic Physics in Vanadium Spinels

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KITP Program
Moments and Multiplets in Mott Materials
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Outline

- Introduction to spinels and t$_{2g}$ orbital physics
- Controversy on orbital ordering in ZnV$_2$O$_4$
  - Different models for spin/orbital order in ZnV$_2$O$_4$: relative importance of Kugel-Khomskii superexchange, Jahn-Teller and relativistic spin-orbit couplings
  - Symmetry analysis: lesson from experiments in MnV$_2$O$_4$

- Self-organized 7-site cluster (heptamer) in AlV$_2$O$_4$
  - Heptamer scenario: 'molecule' of bonding states with anisotropic t$_{2g}$ orbitals
  - Implication to heavy-fermion compound LiV$_2$O$_4$
Lattice Structure of Spinels $AB_2O_4$

- $AO_4$ tetrahedra
- $BO_6$ octahedra (edge sharing)
Lattice Structure of Spinels $AB_2O_4$

- B spinels: A-site cations are nonmagnetic

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Lattice Structure of Spinels \( \text{AB}_2\text{O}_4 \)

- **B** spinels: A-site cations are nonmagnetic
- 3D network of edge-sharing \( \text{BO}_6 \) octahedra
Lattice Structure of Spinels $AB_2O_4$

- 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

<table>
<thead>
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<th>$d^1$</th>
<th>$d^2$</th>
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- 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 |

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| - 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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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 lattice degrees of freedom become relevant?
2. are there any cases where orbital fluctuations, either quantum or classical are relevant?
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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15. What happens to orbital order when going to metallic states --orbital melting
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Two Transitions and Controversy on Orbital Ordering in ZnV$_2$O$_4$

in collaboration with Hirokazu Tsunetsugu
Two Transitions in ZnV$_2$O$_4$

- cubic to tetragonal transition at $T_{c1} \sim 50$K (1st order)
- antiferromagnetic transition at $T_{c2} \sim 40$K (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
  - $\uparrow - \downarrow - \uparrow - \downarrow - \ldots$ in the $xy$ chains
  - $\uparrow - \uparrow - \downarrow - \downarrow - \ldots$ in the $yz/zx$ chains
- **moment at $T=0 \sim 0.6 \mu_B$**

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


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

\[ t_{\sigma}^{\text{nn}} = \sim -0.32\text{eV} \]
\[ t_{\sigma}^{\text{3rd}} = \sim -0.045\text{eV} \]

(Matsuno et al., 1999: for LiV$_2$O$_4$)
Model


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

\[ H_{SO}^{3rd} = -J_3 \sum_{\langle\langle ij \rangle\rangle} [h_{o-AF}^{(ij)} + h_{o-F}^{(ij)}] \quad : \text{3rd neighbor term} \]

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

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

\[ \begin{align*}
J &= \frac{(t_{\sigma}^{nn})^2}{U} \\
J_3 &= \frac{(t_{\sigma}^{3rd})^2}{U} \\
\bar{n}_{i\alpha} &= 1 - n_{i\alpha} \\
\eta &= J_H/U \\
A &= (1 - \eta)/(1 - 3\eta) \\
B &= \eta/(1 - 3\eta) \\
C &= (1 + \eta)/(1 + 2\eta)
\end{align*} \]
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spin F / orbital AF

\[ h_{o-\text{F}}^{(ij)} = C (1 - \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j) n_{i\alpha(ij)} n_{j\alpha(ij)} \]
Model


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

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\[ h_{o-\text{AF}}^{(ij)} = (A + B \vec{S}_i \cdot \vec{S}_j)(n_{i\alpha(ij)} \bar{n}_{j\alpha(ij)} + \bar{n}_{i\alpha(ij)} n_{j\alpha(ij)}) \quad \text{spin F / orbital AF} \]

\[ h_{o-\text{F}}^{(ij)} = C(1 - \vec{S}_i \cdot \vec{S}_j)n_{i\alpha(ij)} n_{j\alpha(ij)} \quad \text{spin AF / orbital F} \]

\[ J = \frac{(t_{\sigma}^{\text{nn}})^2}{U} \]

\[ J_3 = \frac{(t_{\sigma}^{\text{3rd}})^2}{U} \]

\[ \bar{n}_{i\alpha} = 1 - n_{i\alpha} \]

\[ \eta = \frac{J_H}{U} \]

\[ A = \frac{(1 - \eta)}{(1 - 3\eta)} \]

\[ B = \frac{\eta}{(1 - 3\eta)} \]

\[ C = \frac{(1 + \eta)}{(1 + 2\eta)} \]
Model


\[
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H_{\text{SO}}^{3\text{rd}} = -J_3 \sum_{\langle\langle ij \rangle\rangle} [h_{o-\text{AF}}^{(ij)} + h_{o-\text{F}}^{(ij)}] \quad \text{: 3rd neighbor term}
\]

\[
h_{o-\text{AF}}^{(ij)} = (A + B \vec{S}_i \cdot \vec{S}_j) (n_{i\alpha(ij)} \bar{n}_{j\alpha(ij)} + \bar{n}_{i\alpha(ij)} n_{j\alpha(ij)}) \quad \text{spin F / orbital AF}
\]

\[
h_{o-\text{F}}^{(ij)} = C (1 - \vec{S}_i \cdot \vec{S}_j) n_{i\alpha(ij)} n_{j\alpha(ij)} \quad \text{spin AF / orbital F}
\]

\[
\eta = J_H / U \\
A = (1 - \eta) / (1 - 3\eta) \\
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spin part: Heisenberg / orbital part: 3-state Potts
Model


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

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\[ h_{o-AF}^{(ij)} = (A + B \vec{S}_i \cdot \vec{S}_j) (n_{i\alpha(ij)} \tilde{n}_{j\alpha(ij)} + \tilde{n}_{i\alpha(ij)} n_{j\alpha(ij)}) \] spin F / orbital AF

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

+ tetragonal Jahn-Teller coupling

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

\[ J = (t_{nn}^n)^2 / U \]
\[ J_3 = (t_{3rd}^n)^2 / U \]
\[ \tilde{n}_{i\alpha} = 1 - n_{i\alpha} \]
\[ \eta = J_H / U \]
\[ A = (1 - \eta) / (1 - 3\eta) \]
\[ B = \eta / (1 - 3\eta) \]
\[ C = (1 + \eta) / (1 + 2\eta) \]
Monte Carlo Results

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

specific heat per site

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

magnetic susceptibility

- consistent estimates of entropy changes
Orbital and Spin Structure

- **orbital:** alternative stacking of $(d_{xy}, d_{zx})$ and $(d_{xy}, d_{yz})$ states
- **spin:** $\uparrow$-$\downarrow$-$\uparrow$-$\downarrow$-$\uparrow$-$\downarrow$ in the $xy$ chains and $\uparrow$-$\uparrow$-$\downarrow$-$\downarrow$-$\downarrow$-$\downarrow$ in the $yz/zx$ chains
Why the orbital ordering takes place first?
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- instability in the high-T (para) phase
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assuming orbital para: \( n_{i\alpha} \rightarrow \langle n_{i\alpha} \rangle = 2/3 \)
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\[
H_{SO} \rightarrow H_{\text{spin}}^{\text{eff}} = \tilde{J}_S \sum_{ij} \vec{S}_i \cdot \vec{S}_j + \tilde{J}_S^{(3)} \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j
\]

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

no long-range order at \( T=0 \) (Reimers et al., 1991)
Why the orbital ordering takes place first?

- Instability in the high-T (para) phase

Assuming orbital para:

\[ n_{i\alpha} \rightarrow \langle n_{i\alpha} \rangle = \frac{2}{3} \]

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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)

Spin correlations hardly develop by themselves alone
Why the orbital ordering takes place first?

- instability in the high-T (para) phase

assuming spin para:
Why the orbital ordering takes place first?

- Instability in the high-T (para) phase

Assuming spin para: \[ \vec{S}_i \cdot \vec{S}_j \rightarrow \langle \vec{S}_i \cdot \vec{S}_j \rangle = 0 \]
Why the orbital ordering takes place first?

- Instability in the high-T (para) phase

assuming spin para:  \( \vec{S}_i \cdot \vec{S}_j \rightarrow \langle \vec{S}_i \cdot \vec{S}_j \rangle = 0 \)

\[
H_{SO} \rightarrow H_{\text{eff}}^{\text{orbital}} = \tilde{J}_O \sum_{\langle ij \rangle} n_{i\alpha(ij)} n_{j\alpha(ij)} + \tilde{J}_O^{(3)} \sum_{\langle\langle ij \rangle\rangle} n_{i\alpha(ij)} n_{j\alpha(ij)}
\]

3-state Potts model with AF interactions which depend on both the bond direction and the orbital states
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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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\( \rightarrow \) (partial) lifting of degeneracy

tetragonal Jahn-Teller distortion assists to stabilize this orbital configuration

\( yz, zx \quad \Delta_{JT} \)

\( xy \)
Effective Spin Exchanges under the Orbital Order
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- $d_{xy}$ is singly occupied at all the sites $\rightarrow$ strong AF exchange in the xy chains $J$
Effective Spin Exchanges under the Orbital Order

- $d_{xy}$ 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 $J$

$J' \approx -0.1J$
Effective Spin Exchanges under the Orbital Order

- $d_{xy}$ 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 $\sim 0.02J$ → AF order at $T_N$
Effective Spin Exchanges under the Orbital Order

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- 3rd-neighbor exchange $J_3$ is $\sim 0.02J$ $\rightarrow$ 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 $\Delta S$ diverges logarithmically at $J_3=0$ due to the zero modes
- $\Delta S$ 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
Short Summary...

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

Tsunetsugu-Motome, 2003

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

Tchernyshyov, 2004

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

Khomskii-Mizokawa, 2005

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

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

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- orbitally-driven Peierls order
- $P\bar{4}_12\bar{1}2$
- approach from itinerant picture (band Jahn-Teller)

mean-field (Di Matteo et al.)
LSDA+U+SO (T. Maitra and R. Valenti)
Issue...
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?
role of relativistic spin-orbit interaction

• orbital ordering at T=0: mean-field analysis and first-principle calculation suggest the relevant role

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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
\( \text{MnV}_2\text{O}_4 \)

- \( \text{Mn}^{2+} = (3d)^5, \text{V}^{3+} = (3d)^2 \)
- single transition at 57K
  - cubic → tetragonal
  - non-collinear ferri
- low-T phase: \( I4_1/a \) (large single crystal)
  - diamond-glide symmetry is broken, but face-center symmetry is hold
    - peak intensity is \( \sim 10^{-4} \) times smaller compared to the fundamental peaks, difficult to observe in powder samples

Plumier and Sougi, 1987

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 Mn$\text{V}_2\text{O}_4$
- single crystal of Zn$\text{V}_2\text{O}_4$!
Self-organized 7-site Cluster (heptamer) in AlV$_2$O$_4$

in collaboration with Keisuke Matsuda and Nobuo Furukawa
(Atomic) Electronic Structure in AlV$_2$O$_4$

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?
Heptamer Scenario

Y. Horibe et al., 2006
new experimental finding: trimer formation in Kagome layers below $T_c$
Heptamer Scenario

- new experimental finding: trimer formation in Kagome layers below $T_c$
- spin-singlet formation in trimers? $\rightarrow$ sharp drop of the magnetic susceptibility?

Y. Horibe et al., 2006
Heptamer Scenario

- new experimental finding: trimer formation in Kagome layers below $T_c$
- spin-singlet formation in trimers? $\rightarrow$ 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
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  - $\rightarrow$ 18 electrons per heptamer

- $t_{2g}$ multi-orbital Hubbard model for each heptamer
  - $\sigma$ and $\pi$ transfer integrals
  - trigonal lattice distortion at the central site
  - Coulomb interactions
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bonding state: 2 electrons per bond
Multi-orbital Heptamer Model

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  \[\rightarrow 18 \text{ electrons per heptamer}\]

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  - \(\sigma\) and \(\pi\) transfer integrals
  - trigonal lattice distortion at the central site
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- **assumption**: \(\sigma\)-type bonding states for shortest V-V bonds
  \[\rightarrow 6 \text{ electrons remaining}\]
Ground-state Degeneracy

- exact diagonalization of the effective heptamer model
- two different singlet regimes: $\sigma$-type and $\pi$-type

![Graph showing trigonal distortion and $t_{\pi} / t_{\sigma}$ with $U=0$]
Ground-state Degeneracy

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- two different singlet regimes: $\sigma$-type and $\pi$-type

![Diagram showing trigonal distortion and $t_\pi / t_\sigma$ ratio]

- $\sigma$-type
- $\pi$-type $a_{1g}$
Ground-state Degeneracy

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Ground-state Degeneracy

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\[ \frac{U}{t_{\sigma}} = \frac{U}{t_{\pi}} \]

$U = 0$

$U = 4$
Ground-state Degeneracy

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Ground-state Degeneracy

- exact diagonalization of the effective heptamer model
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Singlet State in Heptamer

- singlet ground state for realistic parameters = $\sigma$-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
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$_2$O$_4$: Heavy-Fermion Behavior

- 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

Urano et al., 2000
Implication of $\text{AlV}_2\text{O}_4$?

- 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).
- Possibility: some cluster formation similar to $\text{AlV}_2\text{O}_4$.

Urano, PhD Thesis
Summary

- Introduction to spinels and t$_{2g}$ orbital physics

- Controversy on orbital ordering in ZnV$_2$O$_4$
  - Different models for spin/orbital order in ZnV$_2$O$_4$: relative importance of Kugel-Khomskii superexchange, Jahn-Teller and relativistic spin-orbit couplings
  - Symmetry analysis: lesson from experiments in MnV$_2$O$_4$

- Self-organized 7-site cluster (heptamer) in AlV$_2$O$_4$
  - Heptamer scenario: ‘molecule’ of bonding states with anisotropic t$_{2g}$ orbitals
  - Implication to heavy-fermion compound LiV$_2$O$_4$