# Orbital order in the spinel $ZnV_2O_4$

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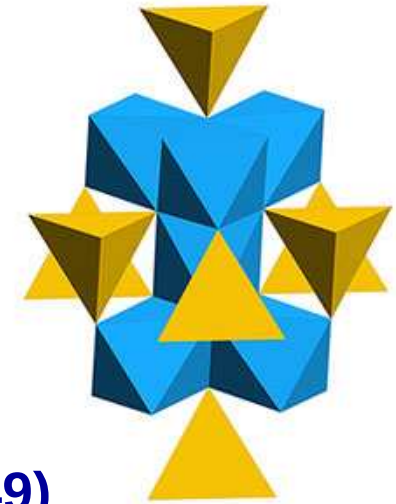


**Collaborator: Tulika Maitra (Univ. Twente)**

**Financial support: DFG (FOR 419, SFB/TRR 49)**

# Outline

- **Frustrated spinel structure**

- **$ZnV_2O_4$, spin=1** **Orbital ordering?**

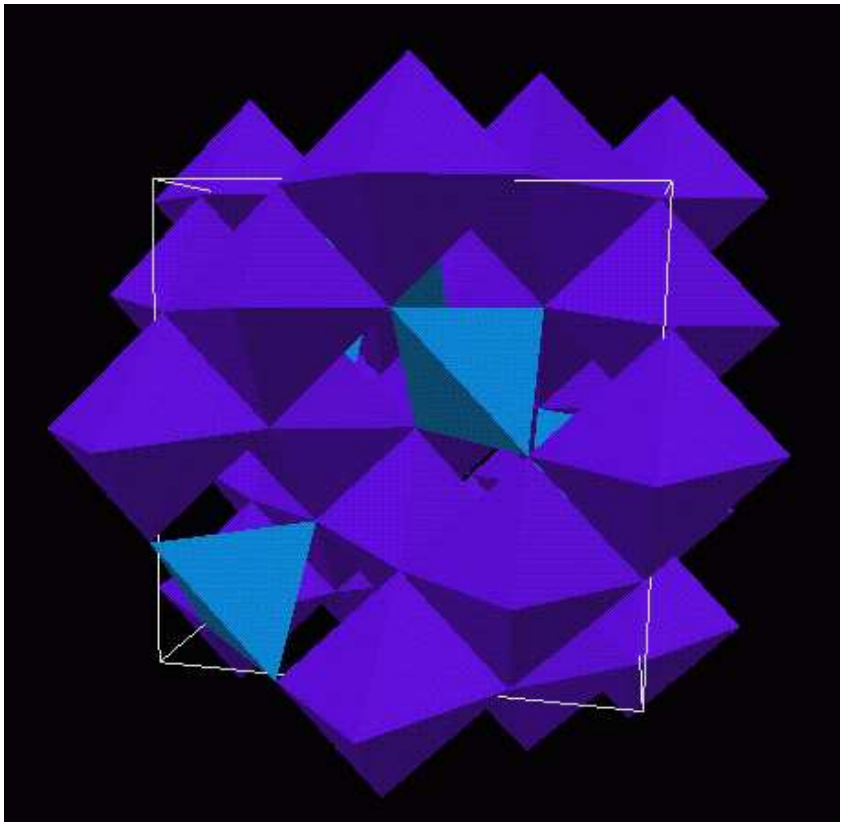
  **spin $\leftrightarrow$ orbital $\leftrightarrow$ lattice**

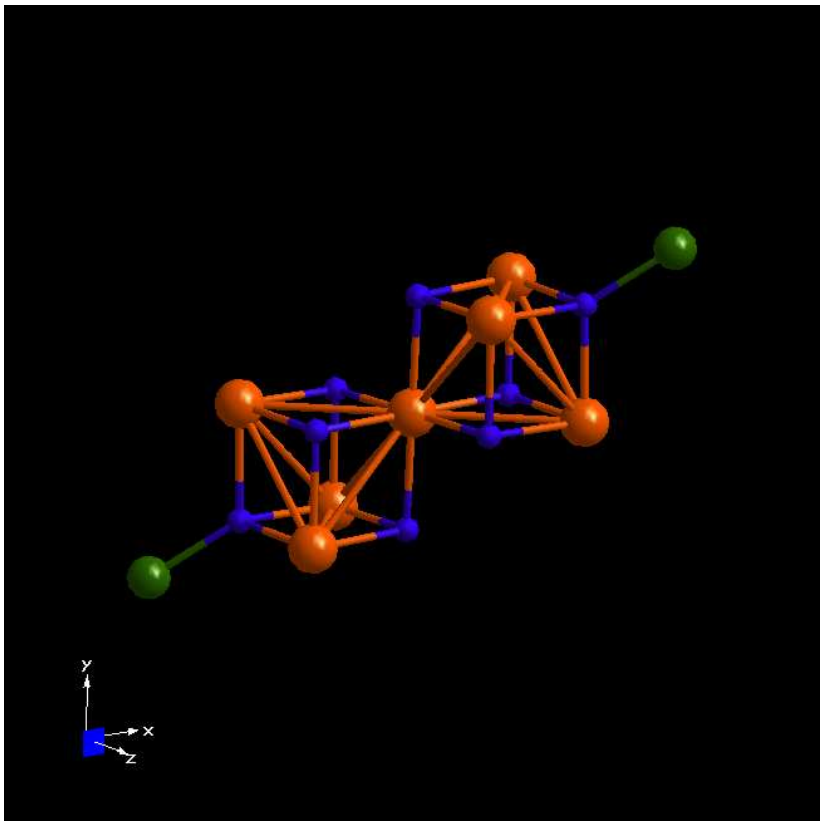
***ab initio* DFT + lattice models**

Maitra, Valentí PRL (2007) *in press*

# Spinel structure $AB_2O_4$

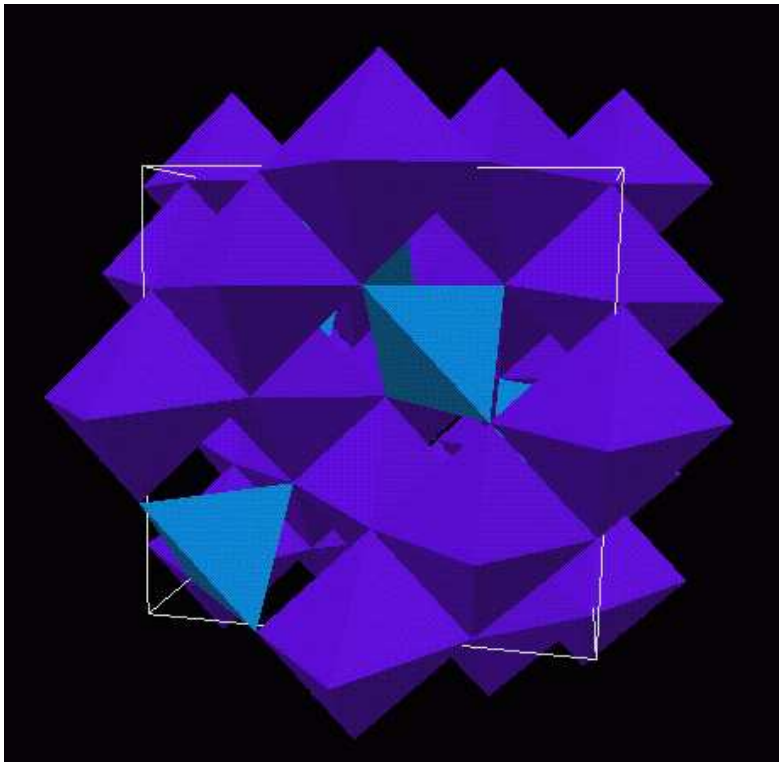
- **Cubic closed-packed array of O, cations A, B: $AB_2O_4$, A and B cations**
- **A atoms occupy tetrahedral sites**
- **$BO_6$ octahedra** **$B_4$ tetrahedra**






GEOMETRIC FRUSTRATION!

# Spinel structure $AB_2O_4$



- **Space Group** $Fd\overline{3}m$ **(227)** $O_h^7$

  $O_h$**:** $1, \overline{1}, 9(2), 9(\overline{2}), 4(\pm 3), 4(\pm\overline{3}), 3(\pm 4), 3(\pm\overline{4})$

- **A: (**$8a$**)** $(1/8, 1/8, 1/8)$

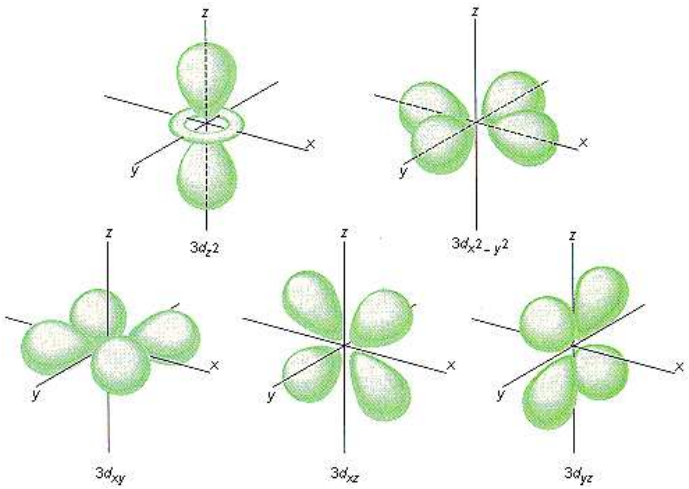
- **B: (**$16d$**)** $(1/2, 1/2, 1/2)$

- **O: (**$32e$**)** $(u, u, u)$

  **Perfect Spinel** $u = 1/4$

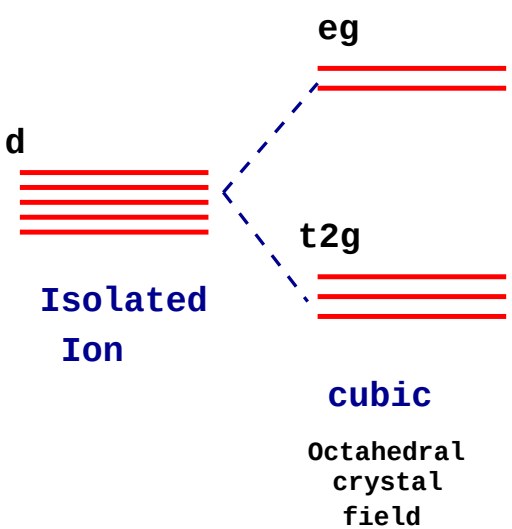
# Spinel structure $AB_2O_4$

## Crystal Field splitting




- **B 3d ion**

  **perfect spinel O:** $(u,u,u)$, $u = 1/4$

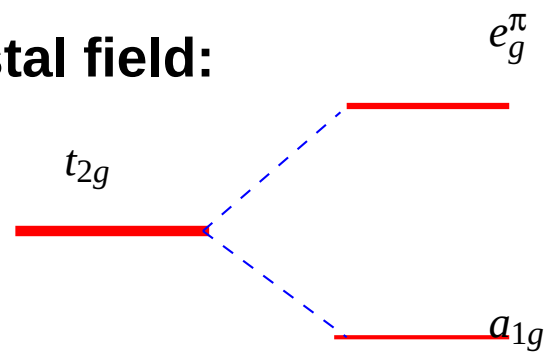



- **trigonally distorted octahedral crystal field:**

  $u = 1/4 + \delta$

  $\delta > 0$ trigonal expansion

  $\delta < 0$ trigonal compression

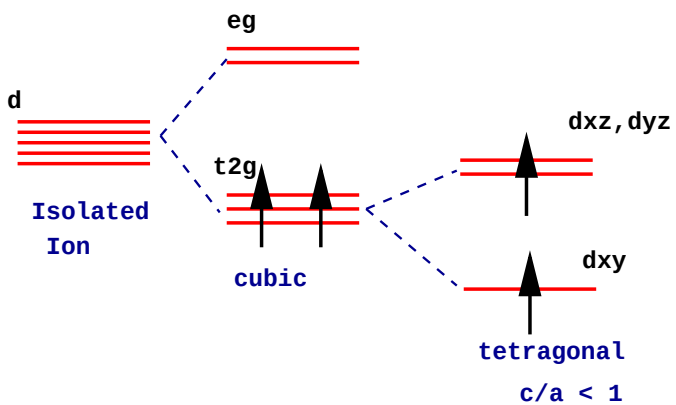


# Spinel $ZnV_2O_4$ — $V^{3+}$: $3d^2$

## Experiment

- **powder:** $T_c$=51K **cubic → tetragonal** (Ueda *et al.* JPSP (1997), Reehuis *et al.* EPJB (2003))

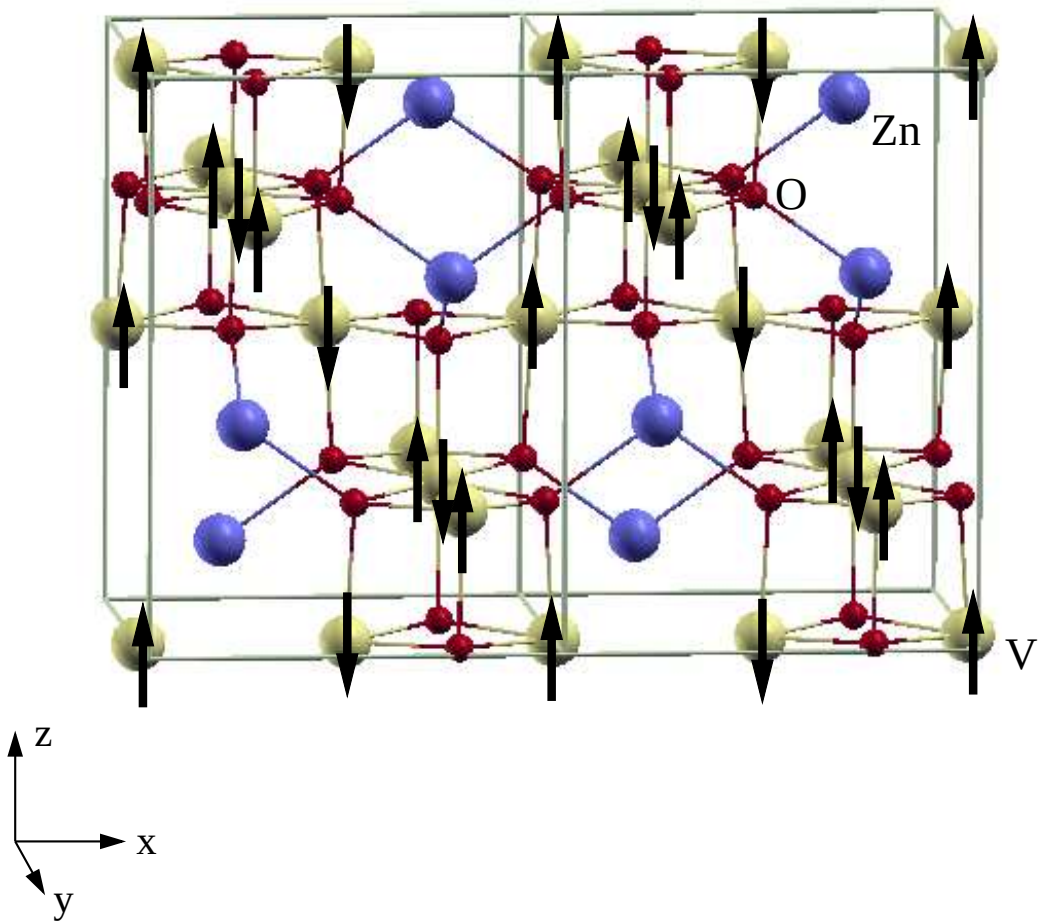
$Fd\bar{3}m \rightarrow I4_1/amd$ ($c/a$ = 0.995)




**orbital order?**

$T_N$=40K **Antiferromagnetic order**

# Antiferromagnetic order



# Spinel $ZnV_2O_4$ — $V^{3+}$: $3d^2$

**Experiment** $\rightarrow$ sensitive to sample preparation

- **single crystal: spin glass**, no phase transition

  (S.G. Ebbinghaus *et al.* Jour. All. a. Comp. ('04))

- **single crystal, powder:** $T_c$=50K **cubic** $\rightarrow$ **tetragonal**

  (S.H. Lee *et al.* PRL (2004)

$$F\bar{4}3m \rightarrow I\bar{4}m2 \text{ or } I\bar{4} \quad \text{(non-centrosymmetric)}$$

- **Which is the driving mechanism of the two phase transitions?**
- **How is the magnetic ordering stabilized?**

- **Geometrical frustration $\rightarrow$ huge degeneracy of the ground state.**
- **$3d^2$ system, strong correlation effects $\rightarrow$ spin and orbital degrees of freedom**
- **spin-orbit coupling (L=1, S=1)**

# Spinel $ZnV_2O_4$ — $V^{3+}$: $3d^2$

**Theory** → interplay of lattice, orbital and spin degrees of freedom?

## Effective-model approach:

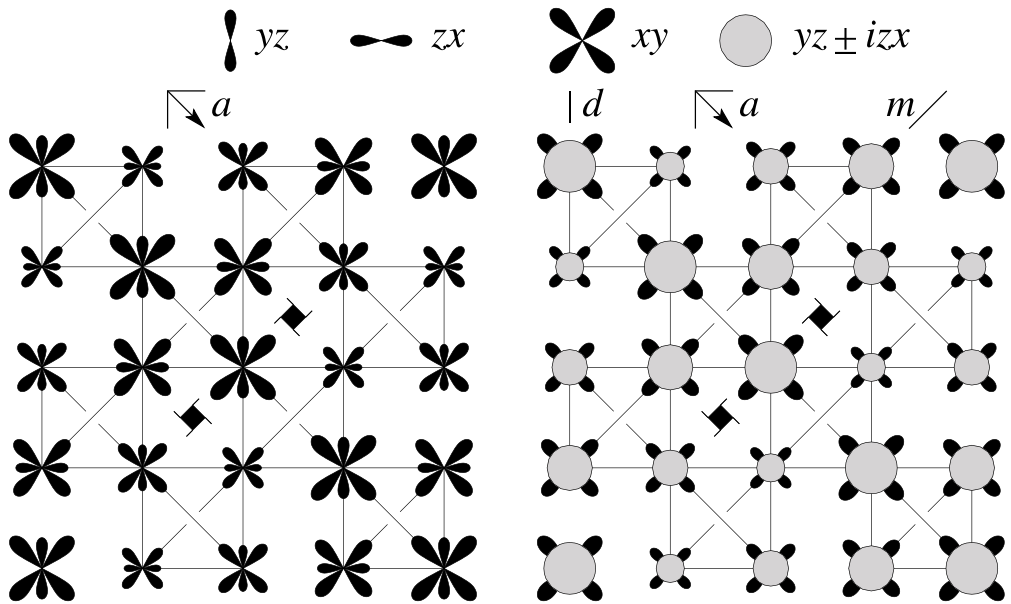
(Y. Yamashita *et al.* PRL '00, H. Tsunetsugu *et al.* PRB '03, O. Tchernyshyov PRL '04, Di Matteo *et al.* PRB '05)

**1) Jahn-Teller coupling**

**2) spin-orbital Kugel-Khomskii interaction (superexchange V-V interaction)**

**3) spin-orbit coupling (L=1, S=1) $-\lambda \mathbf{L}\cdot\mathbf{S}$**

**orbital order?**




(a) $I4_1/a$ (b) $I4_1/amd$

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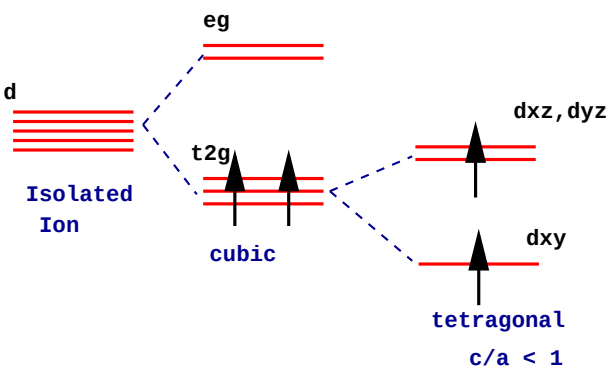


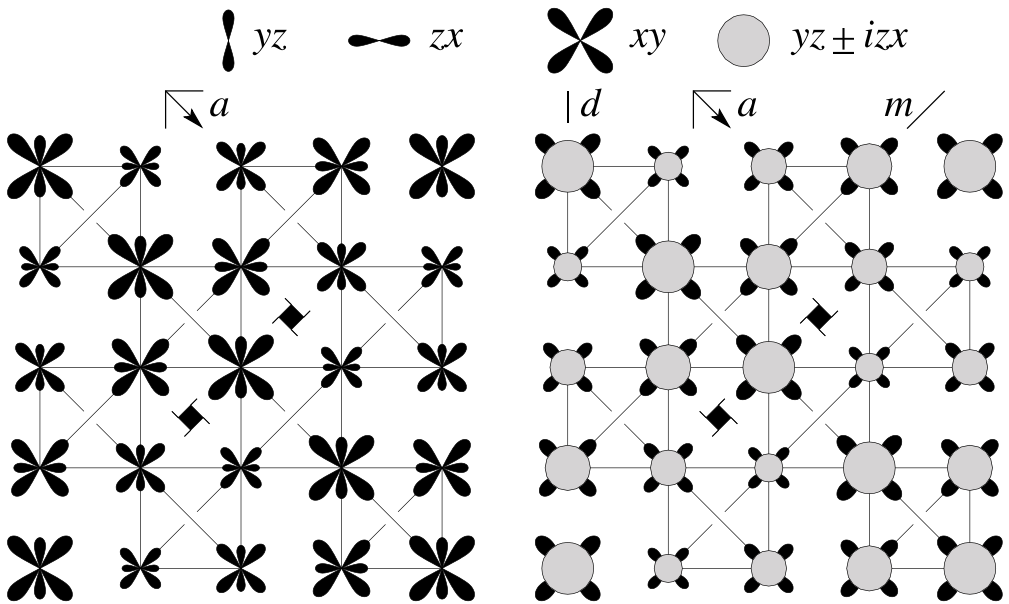


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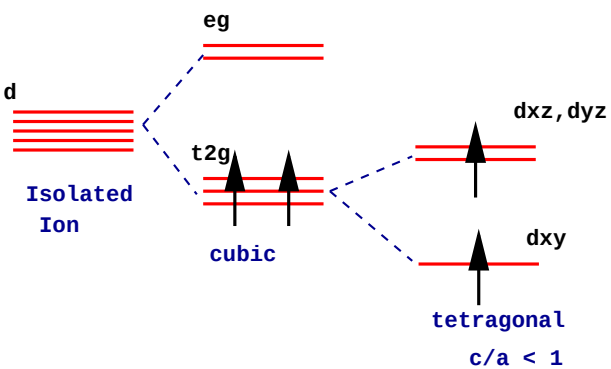


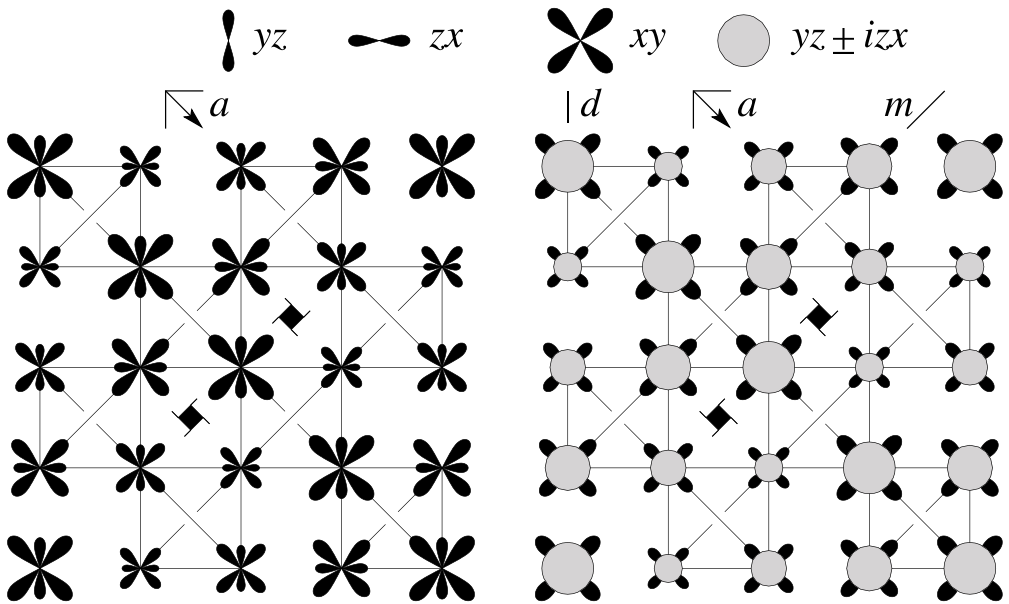


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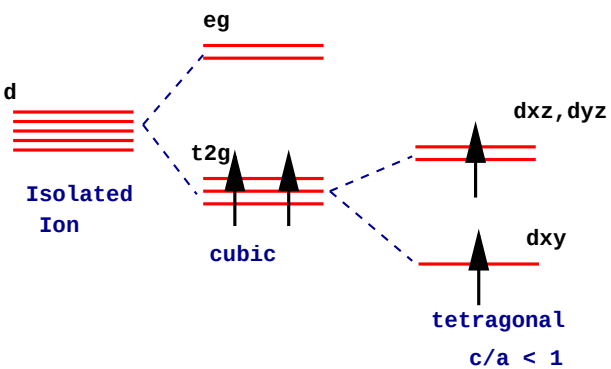


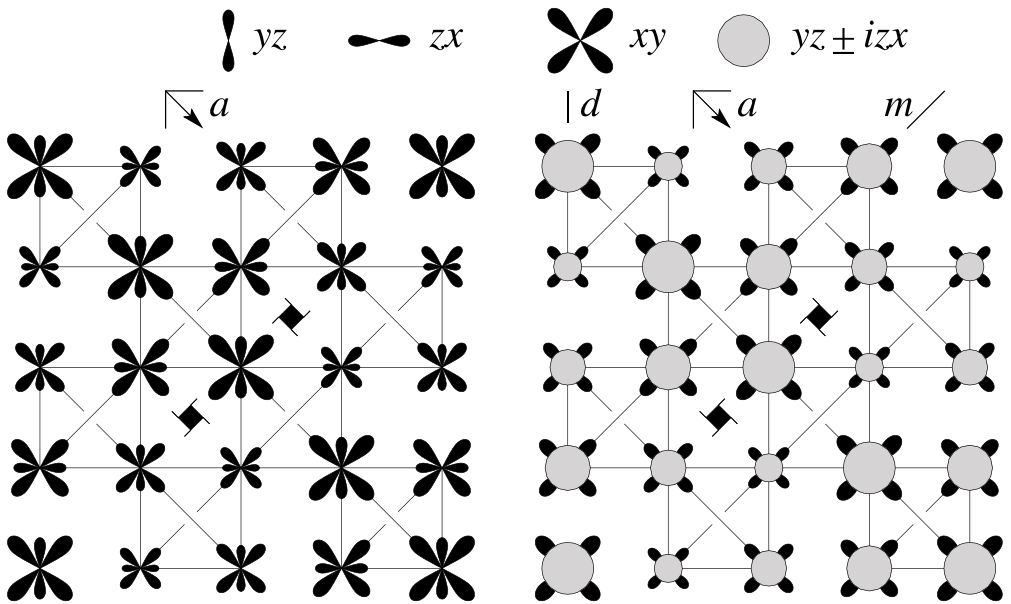


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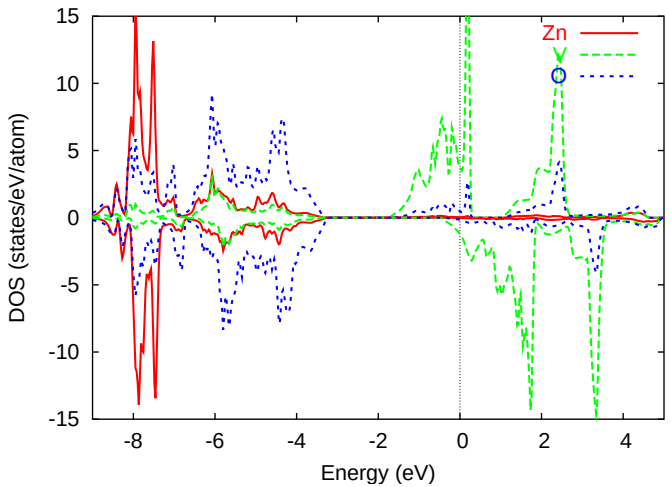
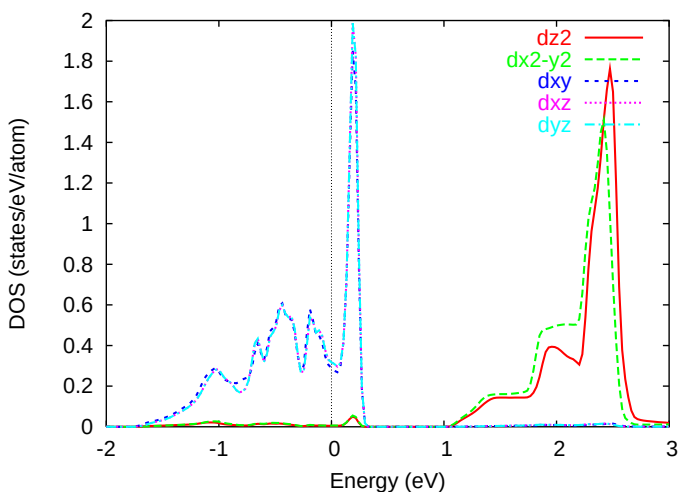
# Spinel $ZnV_2O_4$ — $V^{4+}$: $3d^2$

***ab initio* DFT calculations** (T. Maitra, R. Valentí PRL '07) **FPLAPW (WIEN2k)**

**$ZnV_2O_4$ in $I4_1/amd$: tetragonal+trigonal distorsion**

**LSDA-DOS**



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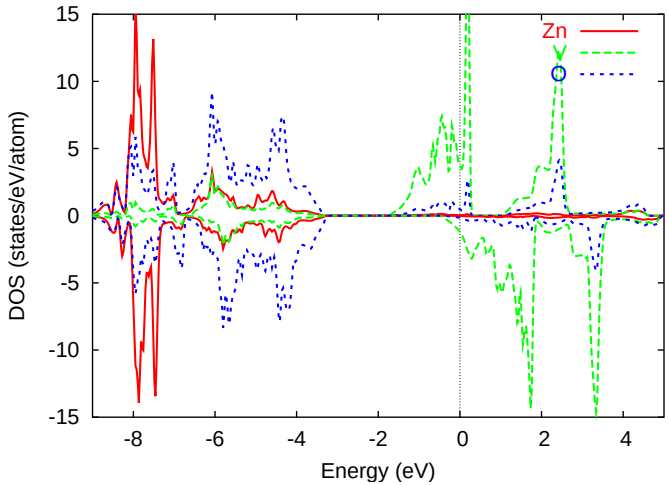
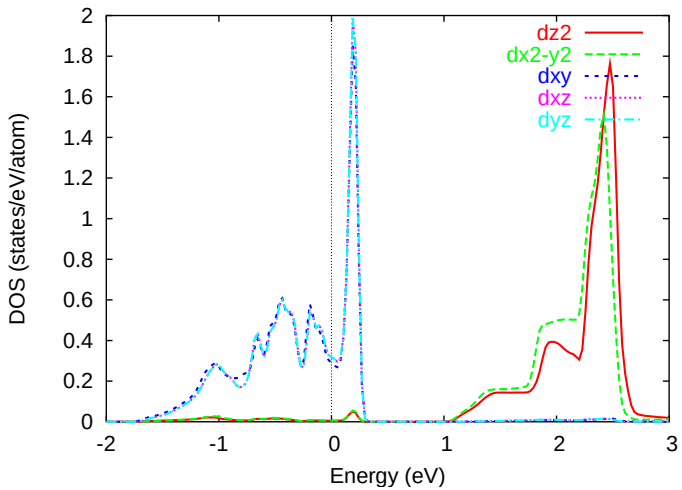
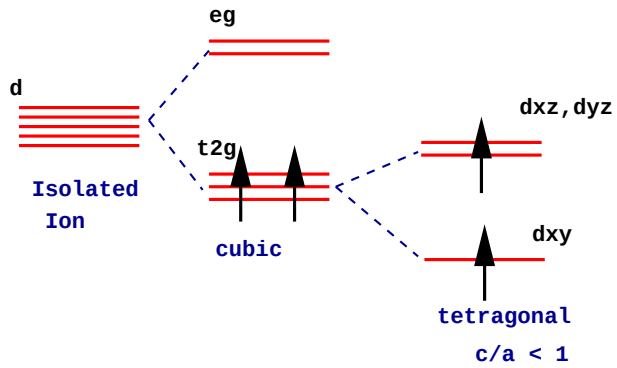
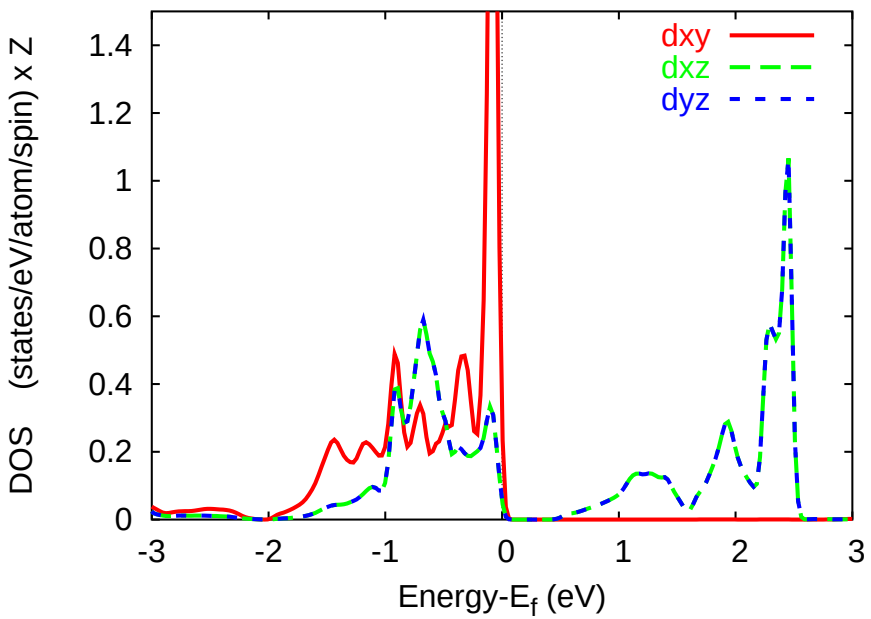


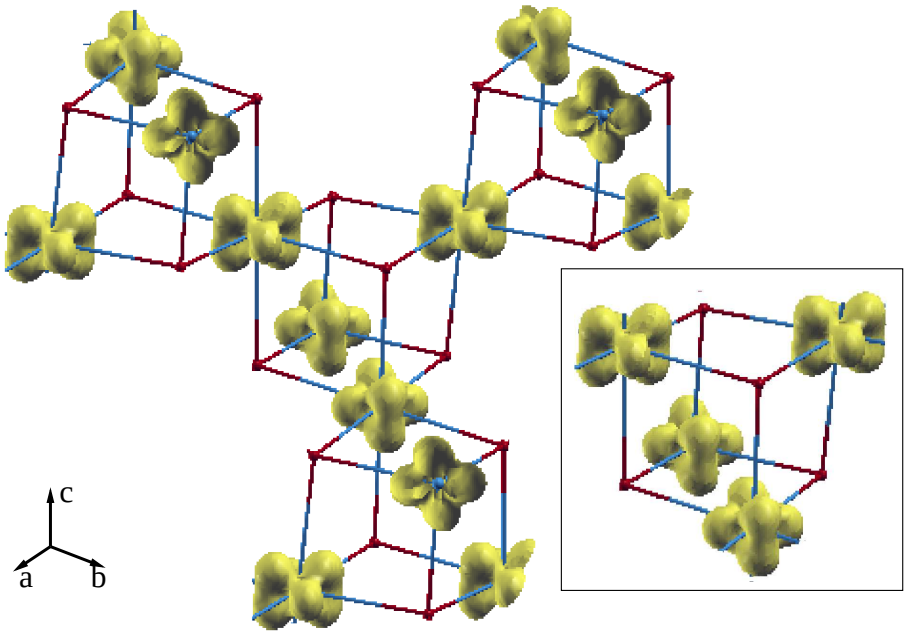

**LSDA+U-DOS U = 4-6 eV**

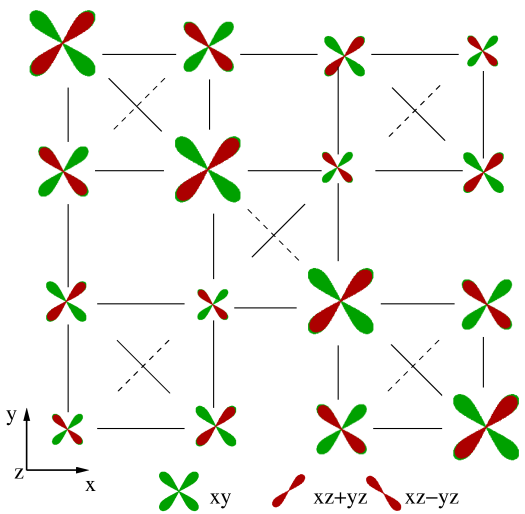


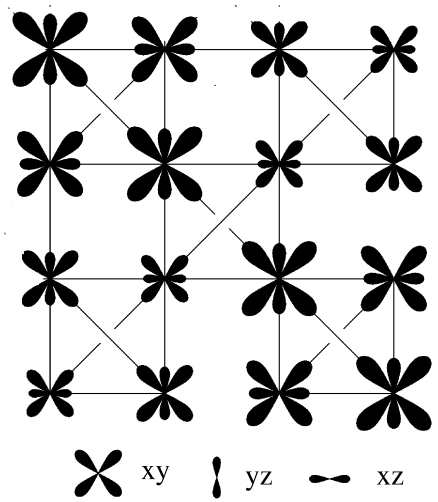



# Spinel $ZnV_2O_4$ — electron density

**LSDA+U** isovalue 0.6 e/Å$^3$




**DFT:** $d_{xz} \pm d_{yz}$

Tsunetsugu, Motome

PRB'03: $d_{xz}$, $d_{yz}$

**Jahn-Teller +**

**Kugel-Khomskii**

**orbital order: A-type**

**Antiferro-orbital along** $c$ **and ferro-orbital in** $ab$

**alternating** $d_{xz} + d_{yz}$, $d_{xz} - d_{yz}$

# Spinel $ZnV_2O_4$ — inclusion spin-orbit coupling

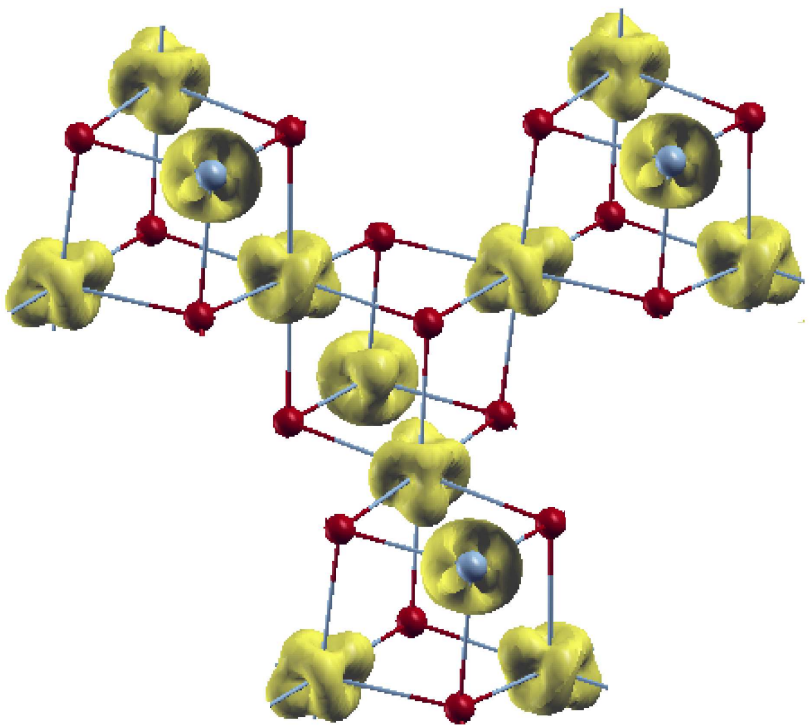
**relativistic *ab initio* DFT calculation: LSDA+U+SO** **second variational method**

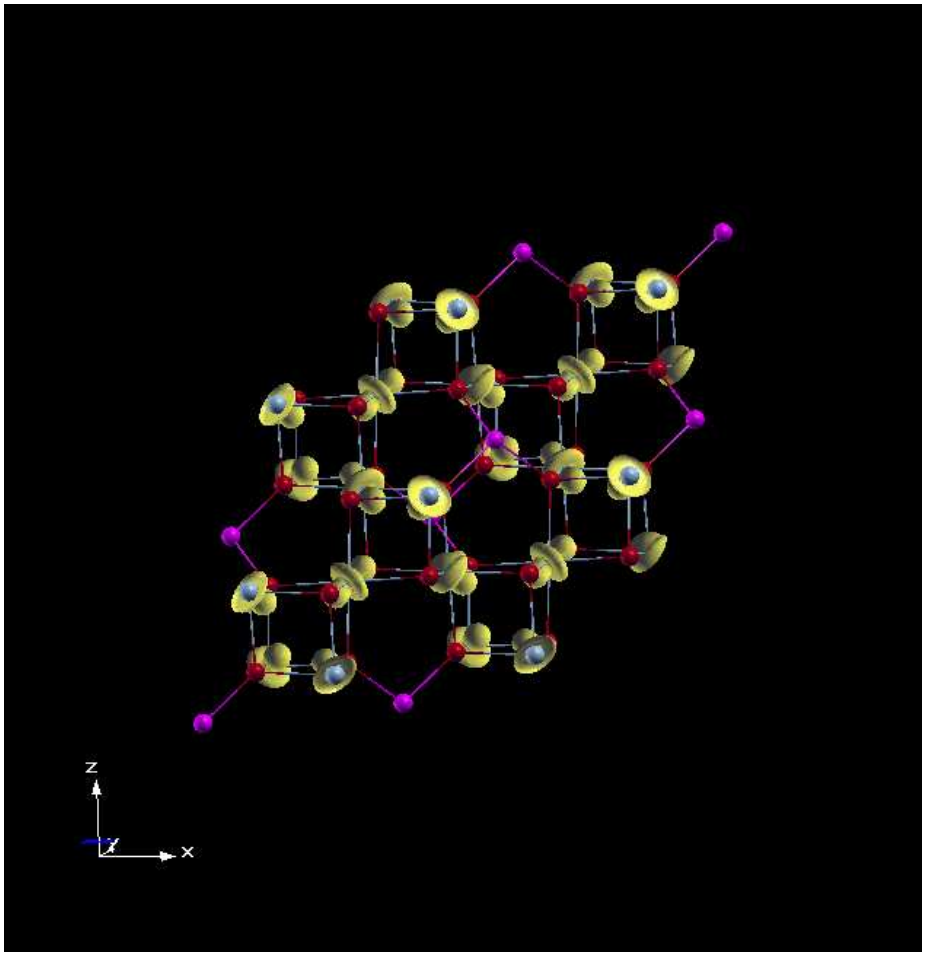
**electron density: tetragonal** **cubic**

no A-type orbital order

trigonal distortion $d_{xz} \pm i d_{yz}$

(compare di Matteo *et al.*, Tchernyshyov)



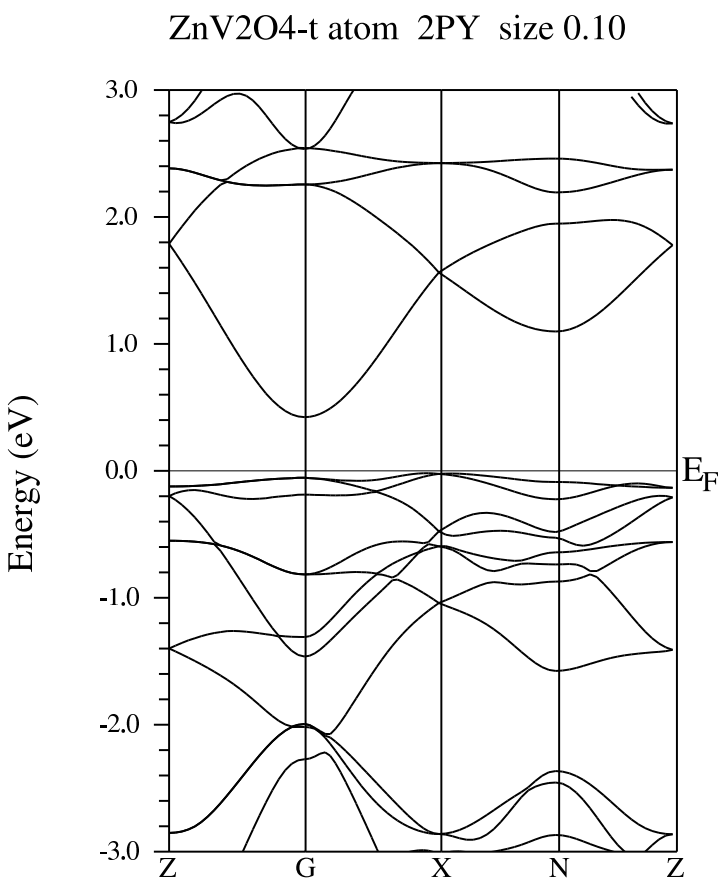



$l_z$**=0.75** $\mu_B$**,** $s$**=1.69** $\mu_B$

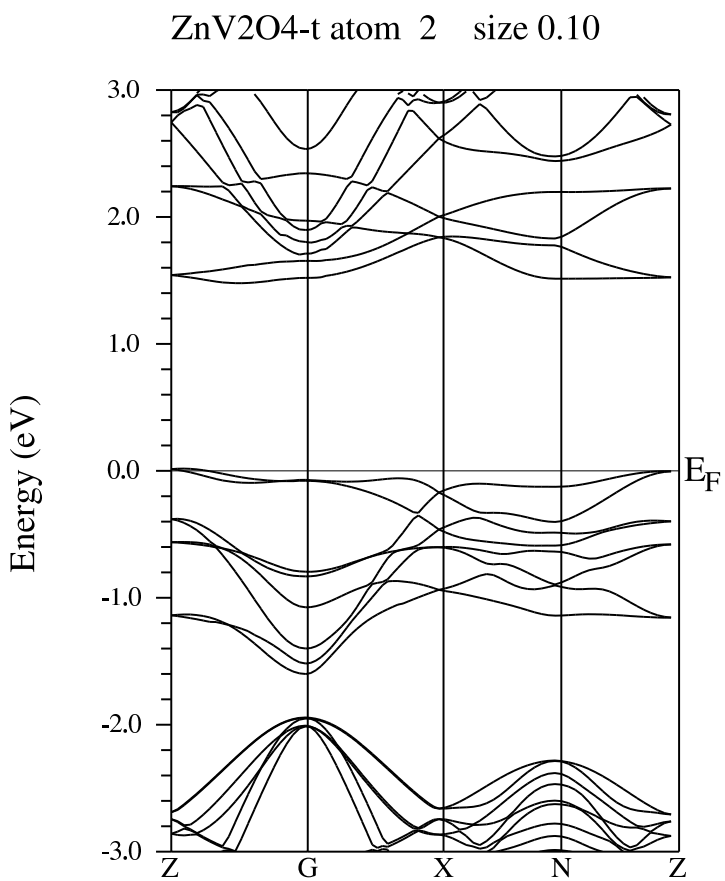
$j$ **= 0.94** $\mu_B$ **compares to experimental** $j$**=0.63** $\mu_B$**.**

# Spinel $ZnV_2O_4$ — Bandstructure

## LSDA+U



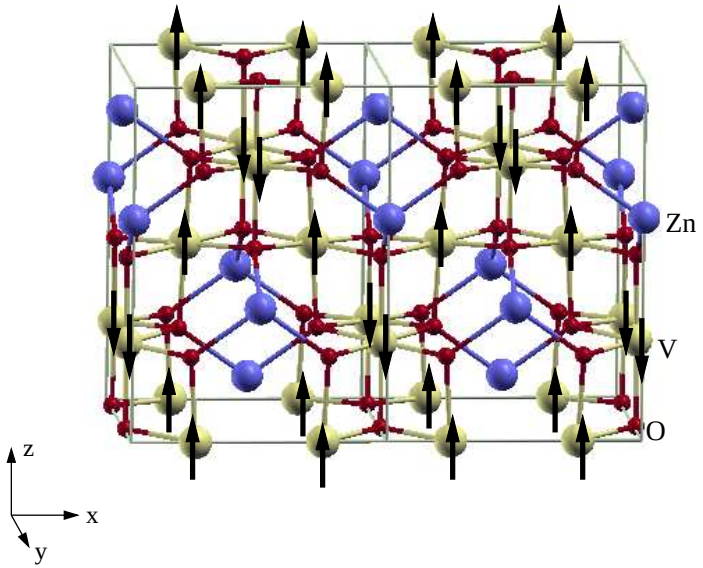

## LSDA+U+SO

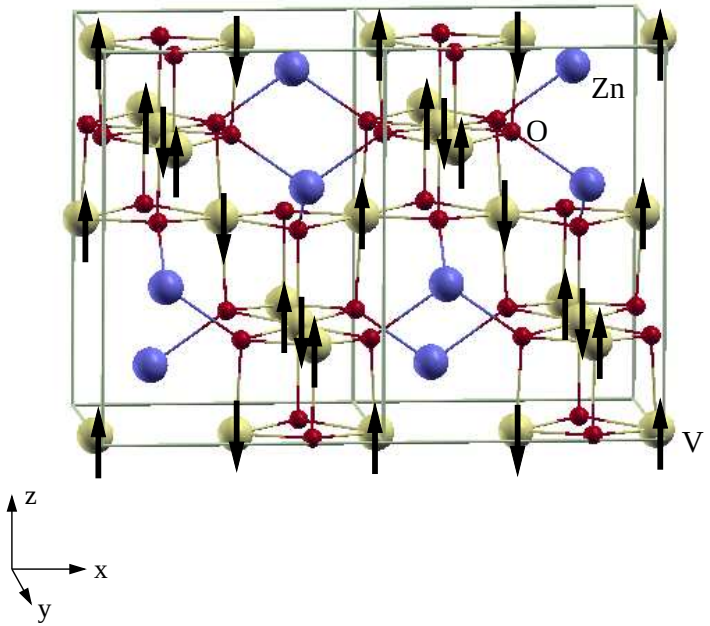



- **SO pushes unoccupied V d bands up in energy → increase band gap**
- **decrease of bandwidth**

# Spinel $ZnV_2O_4$

## Possible AFM configurations:



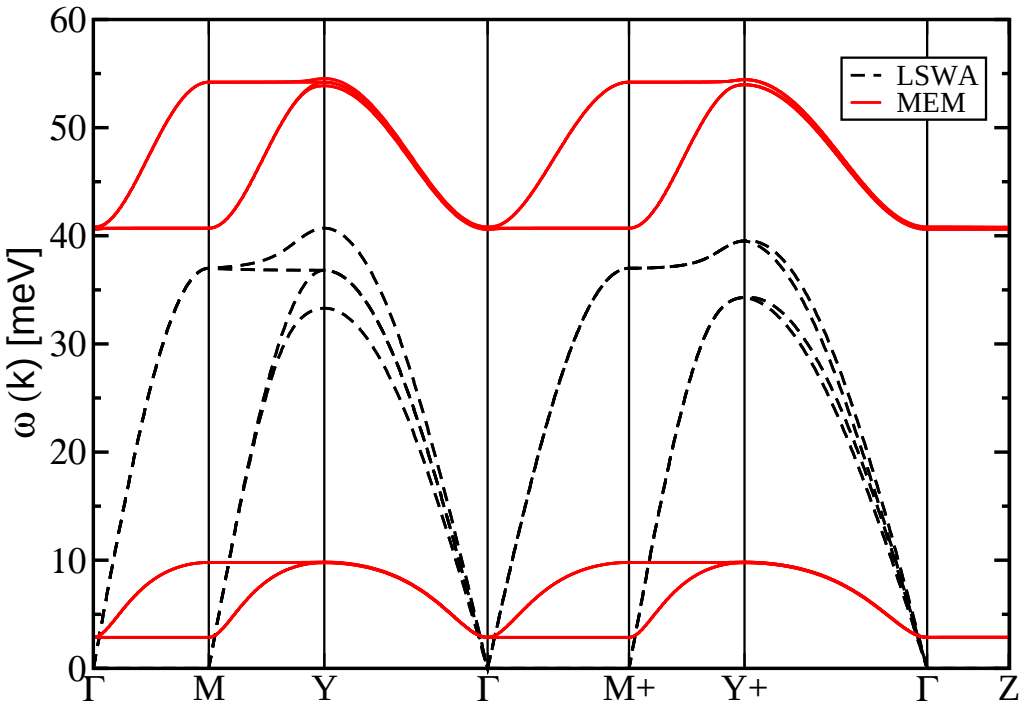

**the experimental configuration (Rehuuis *et al.* EPJB '03, Lee *et al.* PRL '04)**

**is energetically favorable (*ab initio* DFT) LSDA+U+SO**

# Magnetic excitations

Perkins, Sikora *to be published* '07

**spin-wave excitation spectrum above the magnetically ordered state**




**LSWA - Linear spin wave theory**
**MEM - Magnetic excitonic model**

- **orbital ordering with/without SO affects the spin-wave excitation spectrum**
- **decrease of bandwidth**

# Conclusions

- **$ZnV_2O_4$ orbital order is a subtle interplay:**

  **correlations effects $\leftrightarrow$ spin-orbit coupling $\leftrightarrow$ Jahn-Teller distortion**

- **relativistic *ab initio* DFT $\longrightarrow$ no A-type orbital order**

- **orbital distribution favors the observed AFM phase**

- **total magnetic moment agrees with experiment**

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---

**need for experiments!**