Magnetic structure and superexchange pathways in CsV_2O_5

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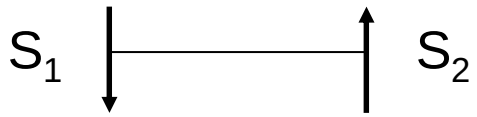
CsV_2O_5 : spin gap system

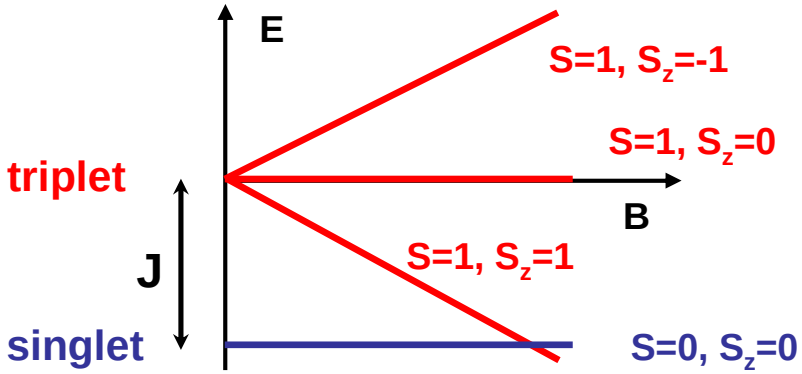
A material with a gap in the magnetic excitation spectra

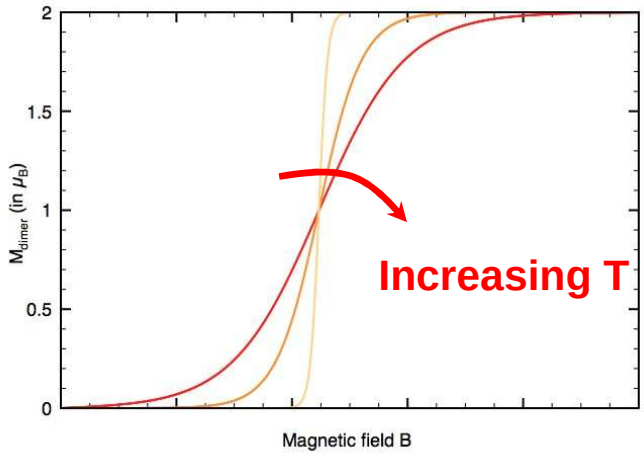
The simplest one : network of independent s=1/2 dimers

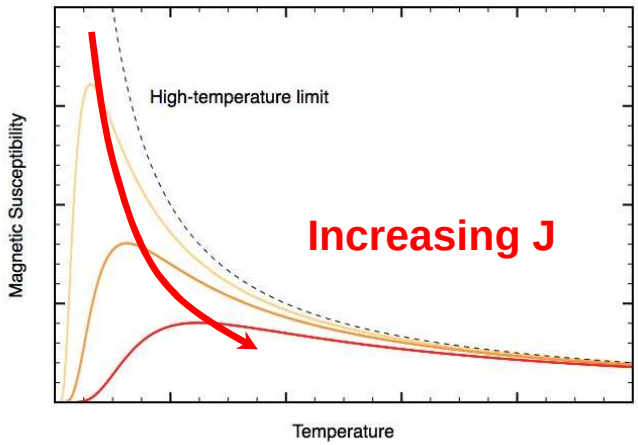


$$H = J\mathbf{S_1}\mathbf{S_2} - g\mu_B(S_{1z} + S_{2z})B_0$$

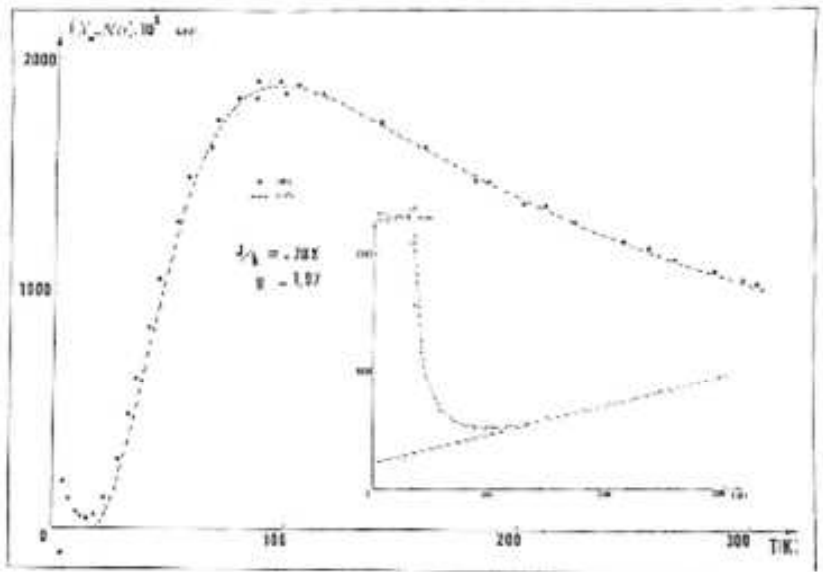
$$H = \frac{J}{2}(S^2 - S_1^2 - S_2^2) - g\mu_B(S_z)B_0$$



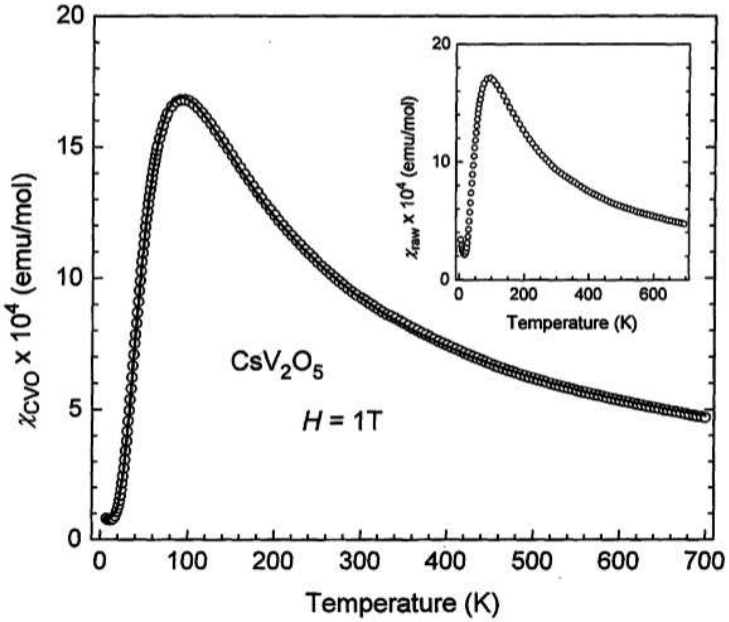




Confirmation : the magnetic susceptibility ...



J. Mur and J. Darriet
***C. R. Acad. Sc. Paris* 300 (1985) 599**



M. Isobe and Y. Ueda
***J. Phys. Soc. Jap.* 65 (1996) 3142**

Interpretation

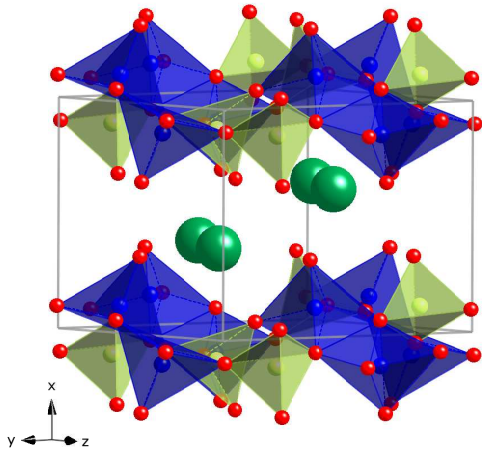
Isolated dimers :
J = 156 K

Isolated dimers :
J = 146 K

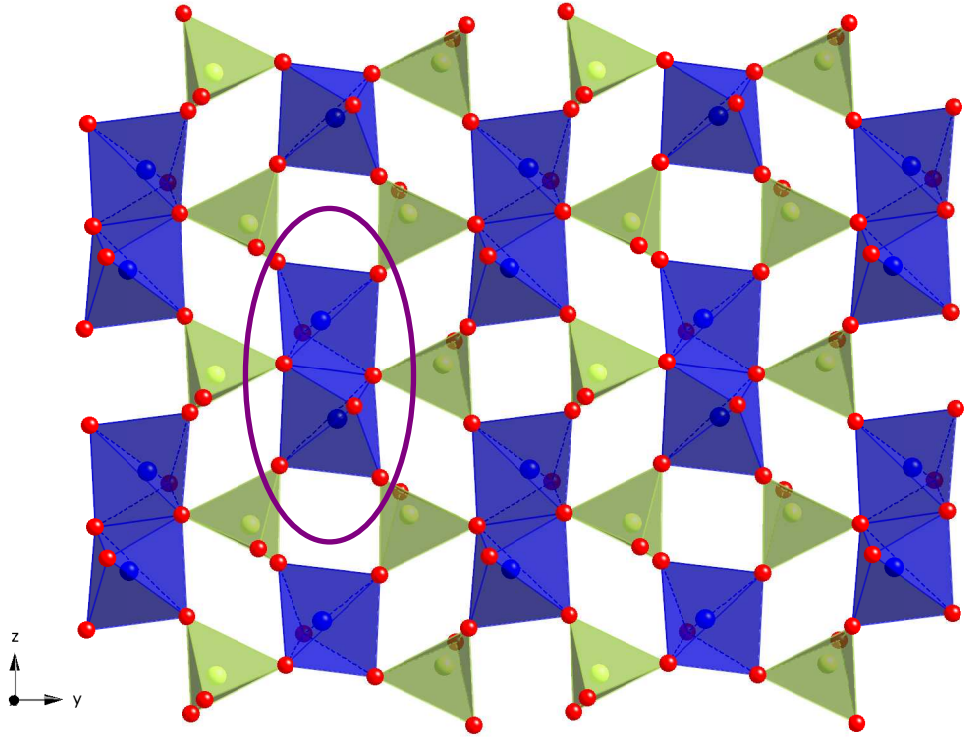
3) CsV_2O_5 Structural dimers formed by V^{4+} : [Ar] $3d^1$

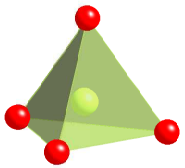
Space group $P2_1/c$

Layered vanadates



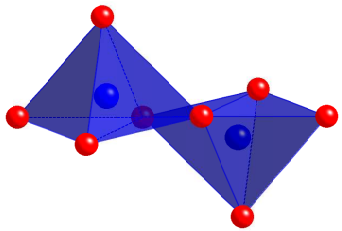
Structure of the layers





V^{5+} in tetrahedral coordination of oxygens

non-magnetic



V^{4+} in distorted square pyramids sharing edges

magnetic

A short history of CsV_2O_5 (part 2)

R. Valenti and T. Saha-Dasgupta
***Phys. Rev. B.* 65 (2002) 144445**

Tight-Binding fit (t_1 = 0.117, t_3=0.097eV) suggests an alternating Heisenberg chain

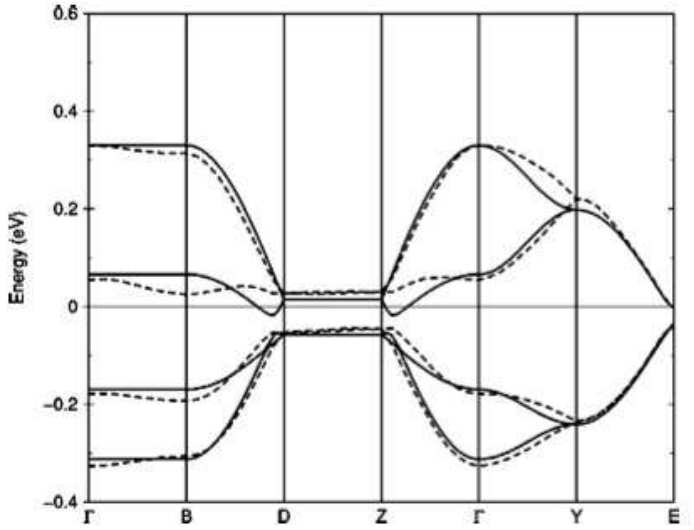
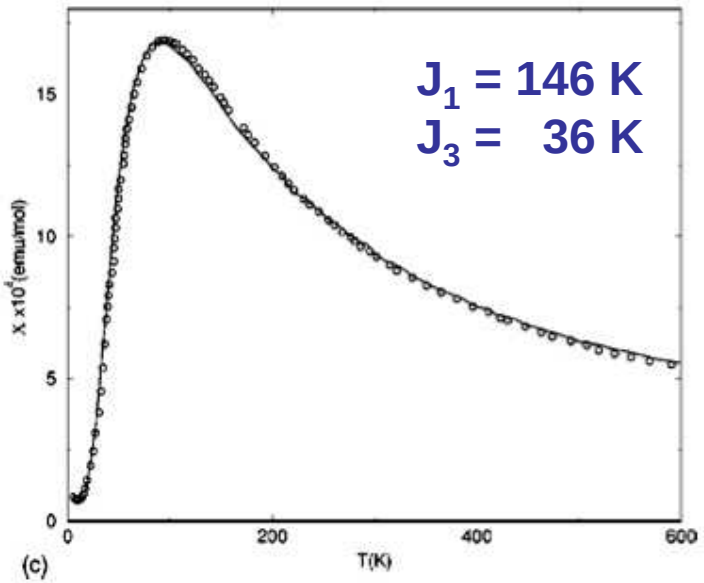


FIG. 5. Comparison of the tight-binding bands (solid lines) with the DFT bands (dashed lines). The tight-binding parameters (see Fig. 4) are (in eV) $\varepsilon_0 = -0.0215$, $t_1 = 0.117$, $t_2 = 0.015$, $t_3 = 0.097$, and $t_5 = 0.050$.



(i) First suggestion of the existence of other magnetic interactions
(ii) Mostly 1D chains : J_1 (intra-dimer) > J_3 (inter-dimer)
(iii) Also non negligible inter-chain interaction (2D structure)

This work

Estimation of J's by DFT total energy differences

- Mapping procedure with the Heisenberg Hamiltonian
- Hybrid functional for strongly correlated electrons

Analysis of the results

- New superexchange pathways
- Re-interpretation of the band structure

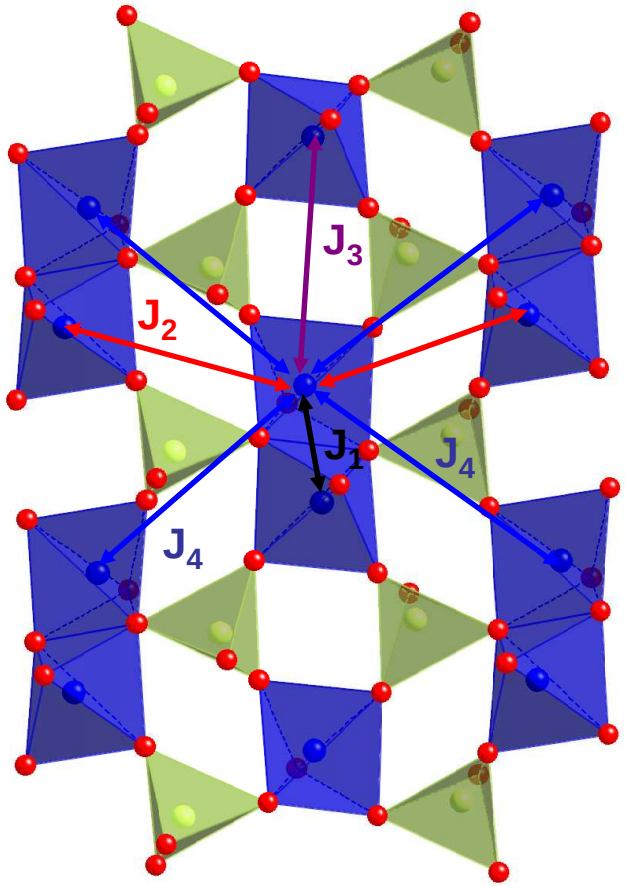
Conclusion

- Who are the dimers...

Magnetic interactions in CsV_2O_5

$$\hat{H} = \hat{H}_0 + \sum_{i>j} J_{ij}\hat{\mathbf{S}}_i\hat{\mathbf{S}}_j$$

Analysis of the magnetic couplings up to the fourth nearest neigbours



Interatomic distances :

J_1 : 3.073 Å
J_2 : 5.386 Å
J_3 : 5.503 Å
J'_4 : 5.950 Å
J''_4 : 6.653 Å

Simplified J_4 interaction:

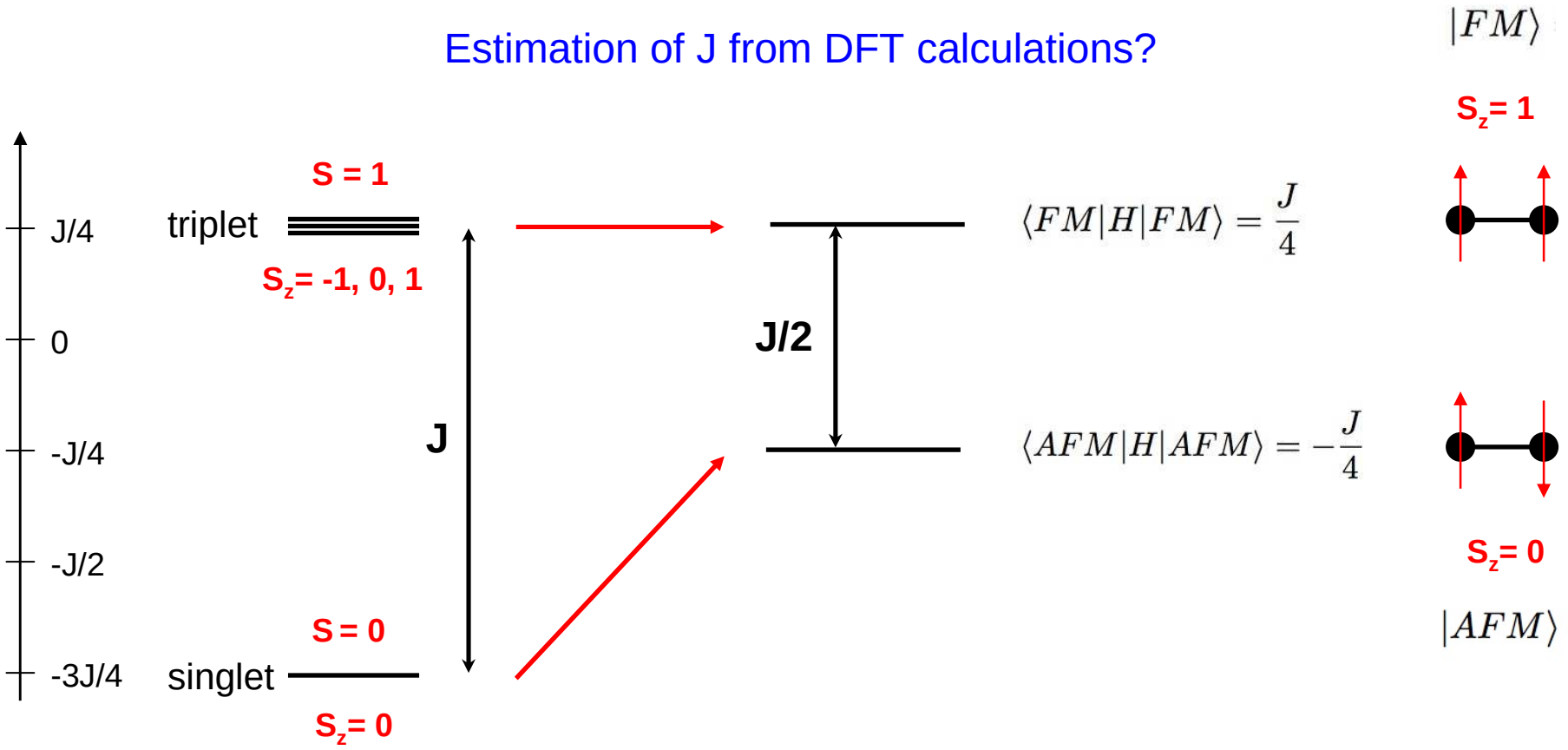
$J_4 = (J'_4+J''_4)/2$

Mapping of DFT energies : single dimer

A system formed by a single spin-1/2 dimer

Magnetic excitations written as a Heisenberg Hamiltonian $H = E_0 + J\mathbf{S}_i\mathbf{S}_j$

Estimation of J from DFT calculations?



Spin contaminated nature of the AFM solution (not an eigenstate of S^2)

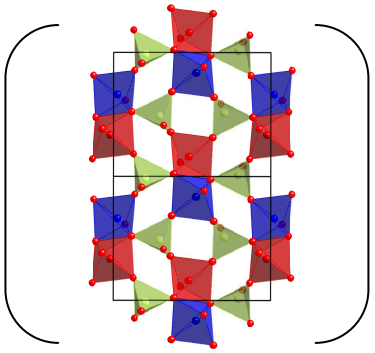
Mapping of DFT energies: generalization

Heisenberg Hamiltonian for a general system

$$\hat{H} = \hat{H}_0 + \sum_{i>j} J_{ij} \hat{\mathbf{S}}_i \hat{\mathbf{S}}_j$$

Defining a DFT (collinear spin arrangement) state

$$|\alpha\rangle =$$



A Kohn-Sham state (determinant) with a given projection of the spin in atom *i*

$$\hat{S}_{iz}|\alpha\rangle = \pm\tfrac{1}{2}|\alpha\rangle$$

The mean value of the Hamiltonian (the DFT total energy) :

$$\epsilon_\alpha = \langle\alpha|\hat{H}|\alpha\rangle = \epsilon_0 + \sum_{i>j} \frac{J_{ij}}{4}\sigma_i\sigma_j \qquad \sigma_i = \pm 1$$

can be written as an Ising Hamiltonian with the same J's

Mapping of DFT energies: calculation details

$$\epsilon_\alpha = \langle\alpha|\hat{H}|\alpha\rangle = \epsilon_0 + \sum_{i>j} \frac{J_{ij}}{4}\sigma_i\sigma_j = \epsilon_\alpha = \epsilon_0 + \sum_{i=1}^{4} a_{i\alpha}J_i$$

Total energies with wien2k : all electron, full potential, LAPW+lo implementation of Density Functional Theory

The subspace spanned by the strongly correlated (V-*3d*) electrons are treated with the PBE0 hybrid functional:

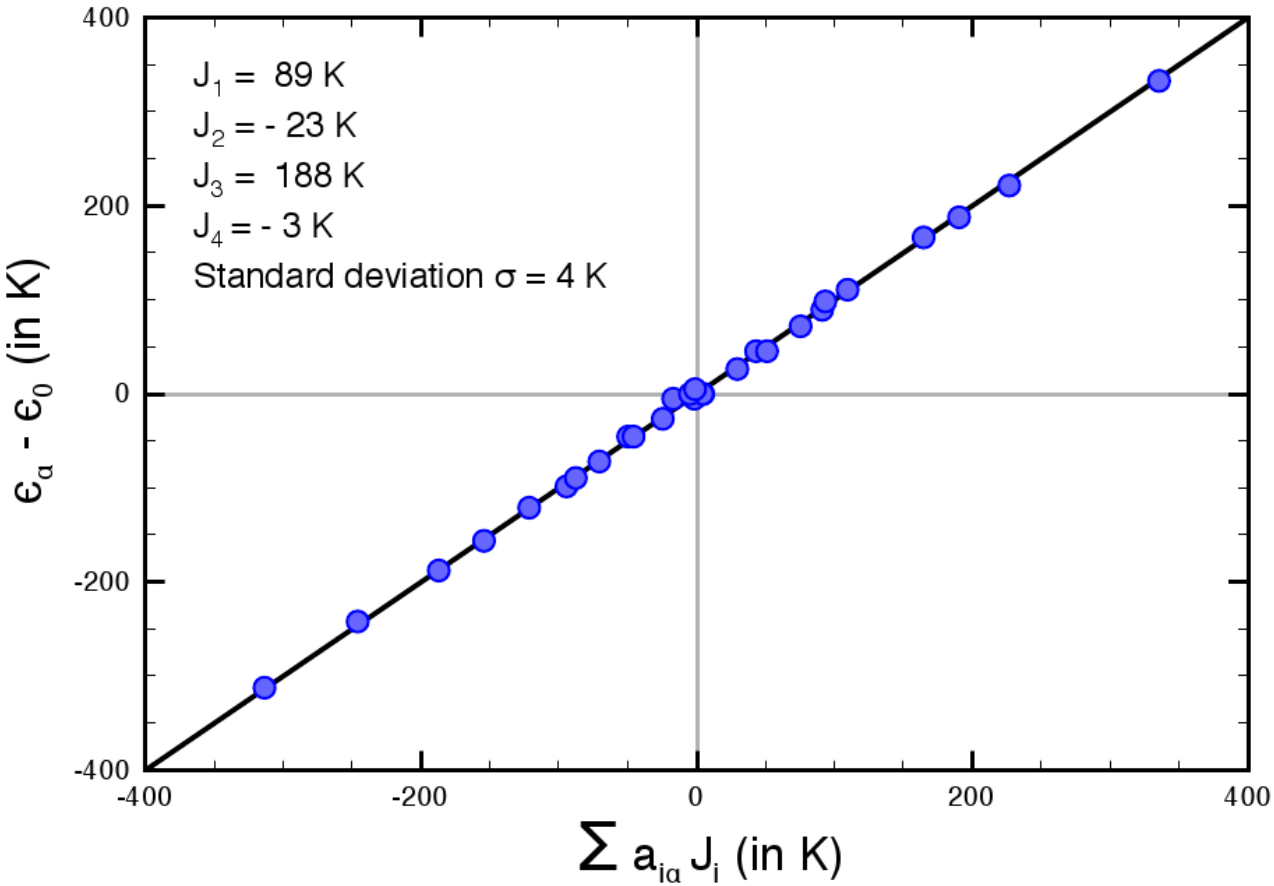
$$E_{xc}^{\mathrm{PBE0}}[\rho] = E_{xc}^{\mathrm{PBE}}[\rho] + \tfrac{1}{4}(E_x^{\mathrm{HF}}[\Psi_{\mathrm{sel}}] - E_x^{\mathrm{PBE}}[\rho_{\mathrm{sel}}])$$

64 atoms supercells
8 vanadium atoms (spins)

256 configurations in total
28 inequivalent by symmetry

Mapping of DFT energies: fitting procedure

$$F = \sum_{\alpha=1}^{28} g_\alpha \left(\epsilon_\alpha - \epsilon_0 - \sum_{i=1}^{4} a_{i\alpha} J_i \right)^2$$



Numerical results

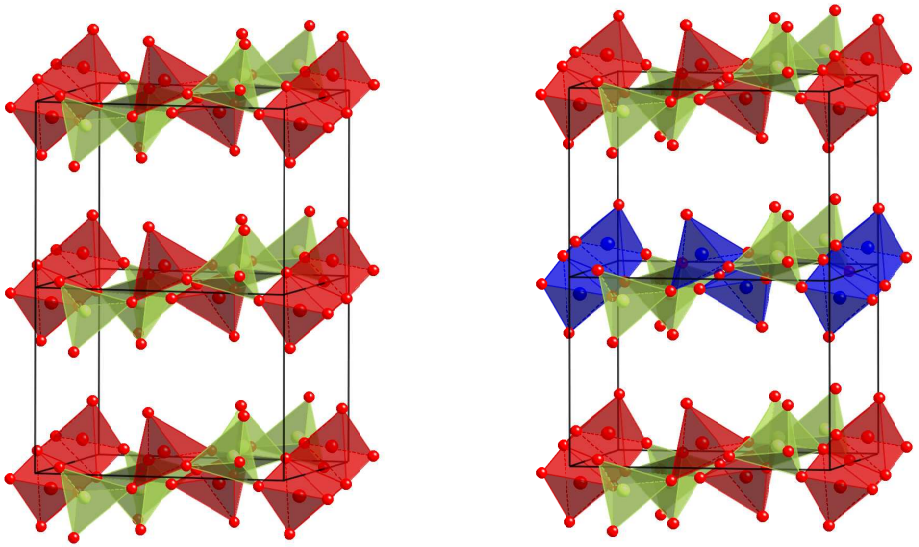
Ex. Int. (K)	J_1	J_2	J_3	J_4
PBE0	89	-23	188	-3
PBE	180	-54	378	-11

- **Dominant AF interactions along the chain**
- **Third nearest- neighbor $J_3 > J_1$**
- **Small and ferromagnetic inter-chain interaction**
- **A semi-local functional GGA increases the amplitudes by ~ 2 with respect to the exact exchange one**

Interplane coupling ?

64-atom supercells (doubled perpendicularly to the planes yz)

FM AFM



UP

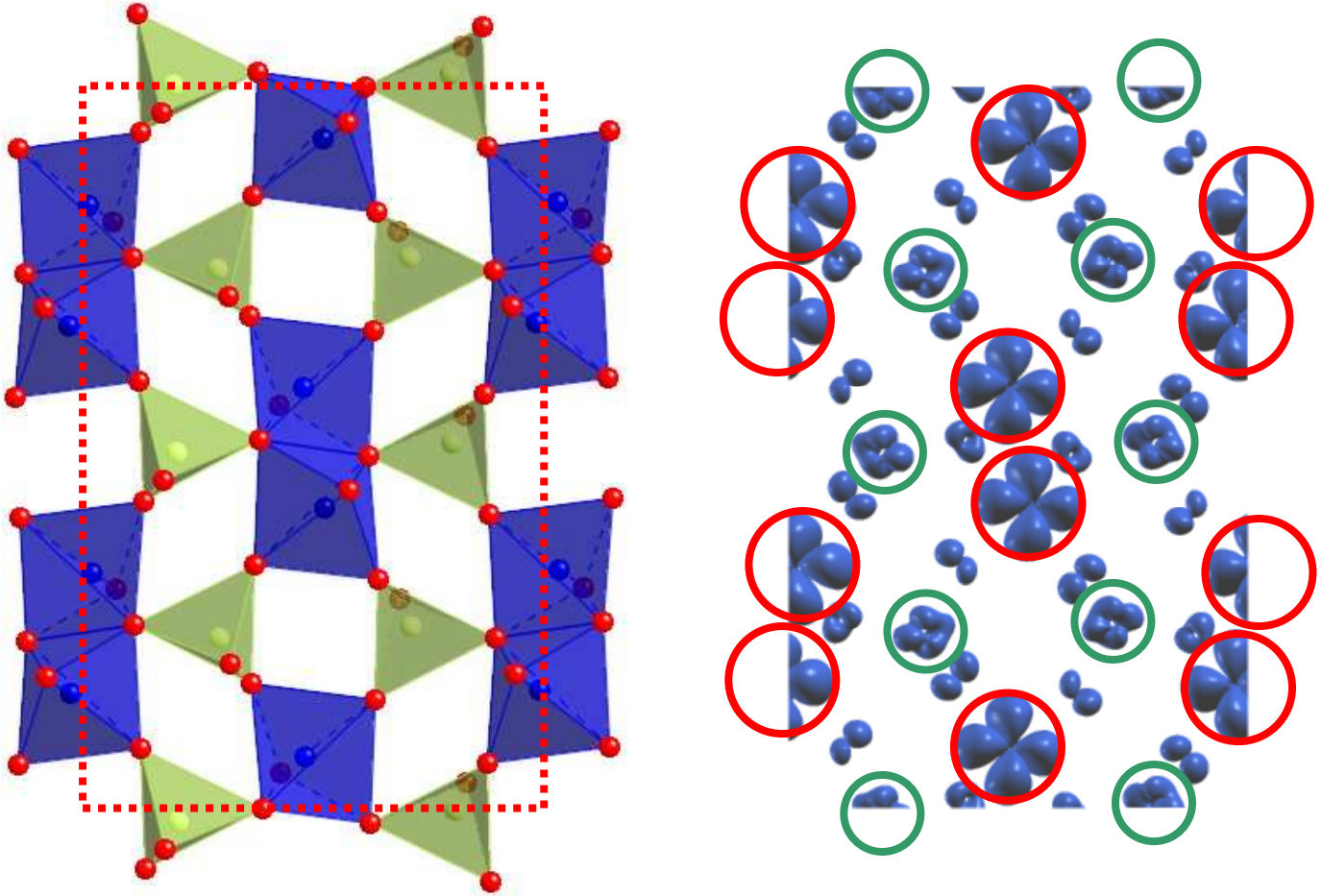
DN

$E_{FM} - E_{AFM} \approx 0$

- **No interaction between the planes**

Why is the inter-dimer interaction bigger than the intra-dimer one

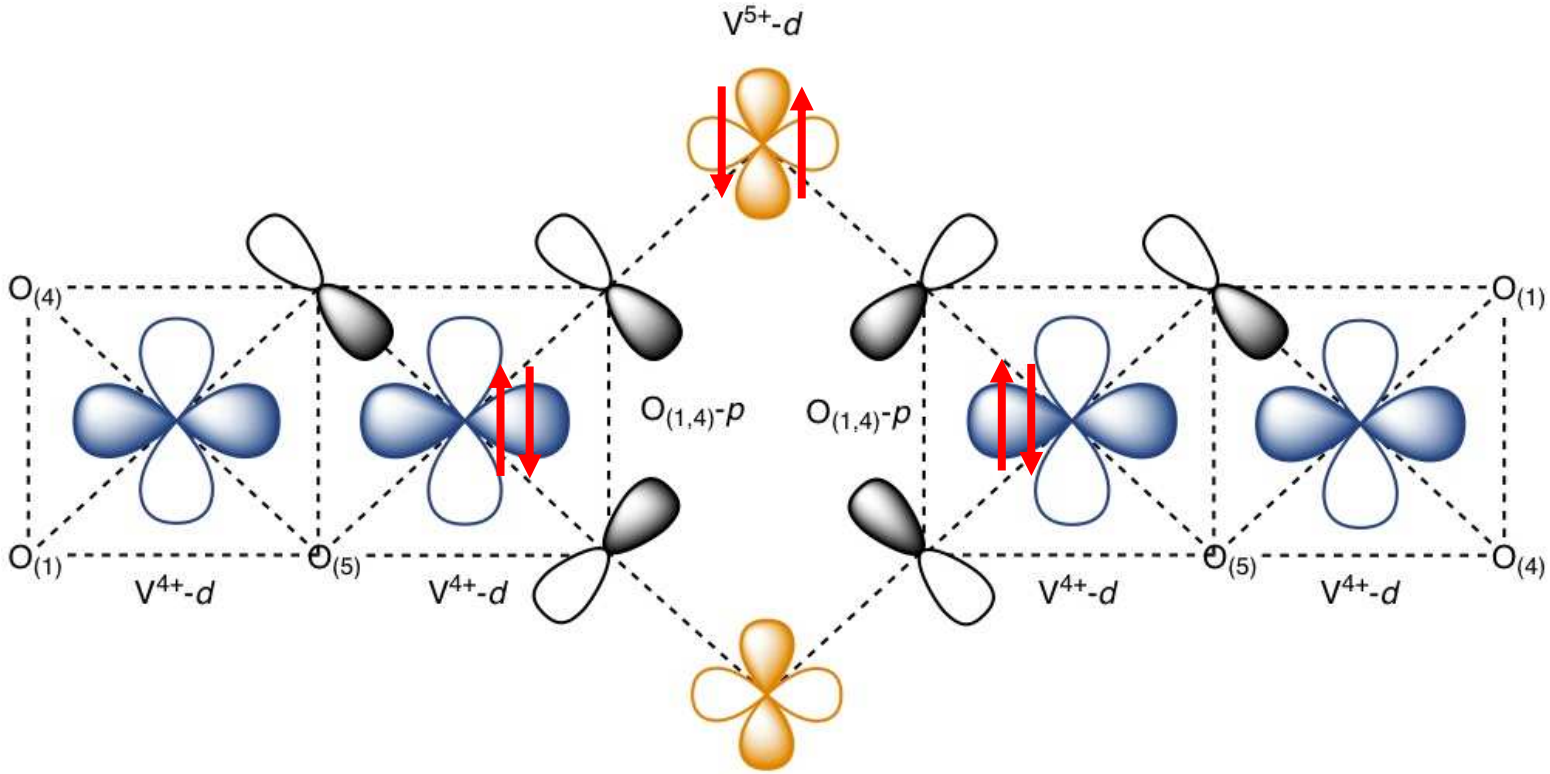
Electron density associated to the V^{4+}-$d_{y^2-z^2}$ majority bands



Proposed superexchange paths

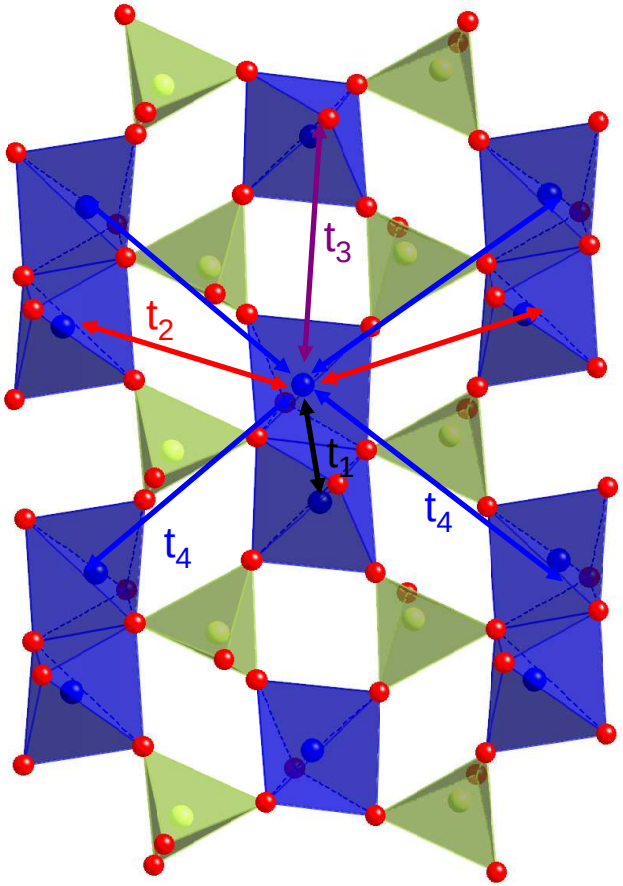
J_1 is weak due to close-to-orthogonal arrangement of the V^{4+}-*d* and O-*p* orbitals

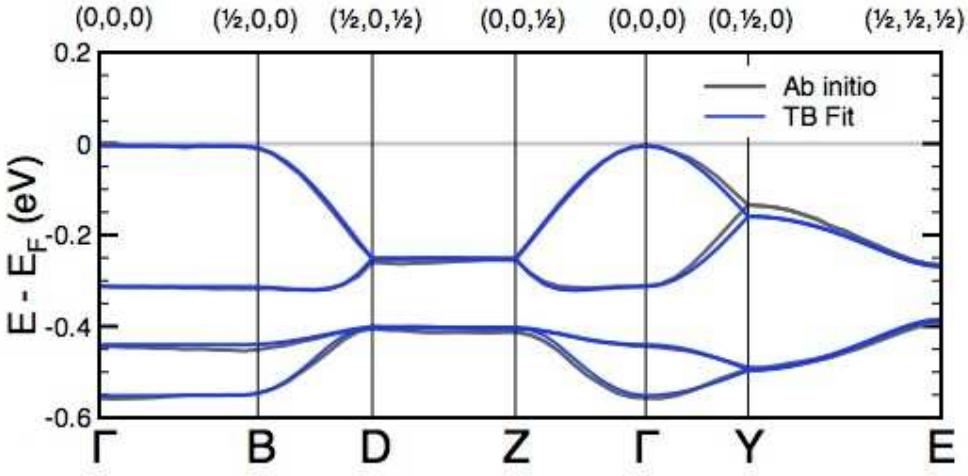
Large AFM J_3 is supported by a superexchange pathway involving V^{5+}-*d* orbitals



Revisiting the band structure : tight-binding fit

Effective hopping integrals between magnetic ions :





With t_1 ~ 55 meV
t_2 ~ 25 meV
t_3 ~ 117 meV
t_4 ~ 26 meV

With t_1 ~ 117 meV
t_2 ~ 25 meV
t_3 ~ 55 meV
t_4 ~ 26 meV

Ambiguity with the TB model
Unitary transformation U exists such that :

$$U^{-1}\, H(t_1,t_2,t_3,t_4)\, U = H(t_3,t_2,t_1,t_4)$$

Conclusions

The dimers are not the structural ones...

- A new picture of the magnetic interactions in CsV_2O_5

The sole consideration of topology is misleading to understand the magnetic interactions of low dimensional magnetic oxides :

- Non magnetic bridging units have to be considered in the design of new systems
- Another example $(VO)_2P_2O_7$: super-exchange path through PO_4 units

LDA (GGA) over-estimates the exchange interactions

- Certainly due to an over-delocalization of the correlated electrons
- Needs Hybrid functionals, LSDA+*U*, …