

Frustrated chain magnetism from interplay of  
water induced crystal field splitting and  
correlation in  $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$

*Deepa Kasinathan*

*Max Planck Institute for Chemical Physics of Solids - Dresden*

Collaborators:

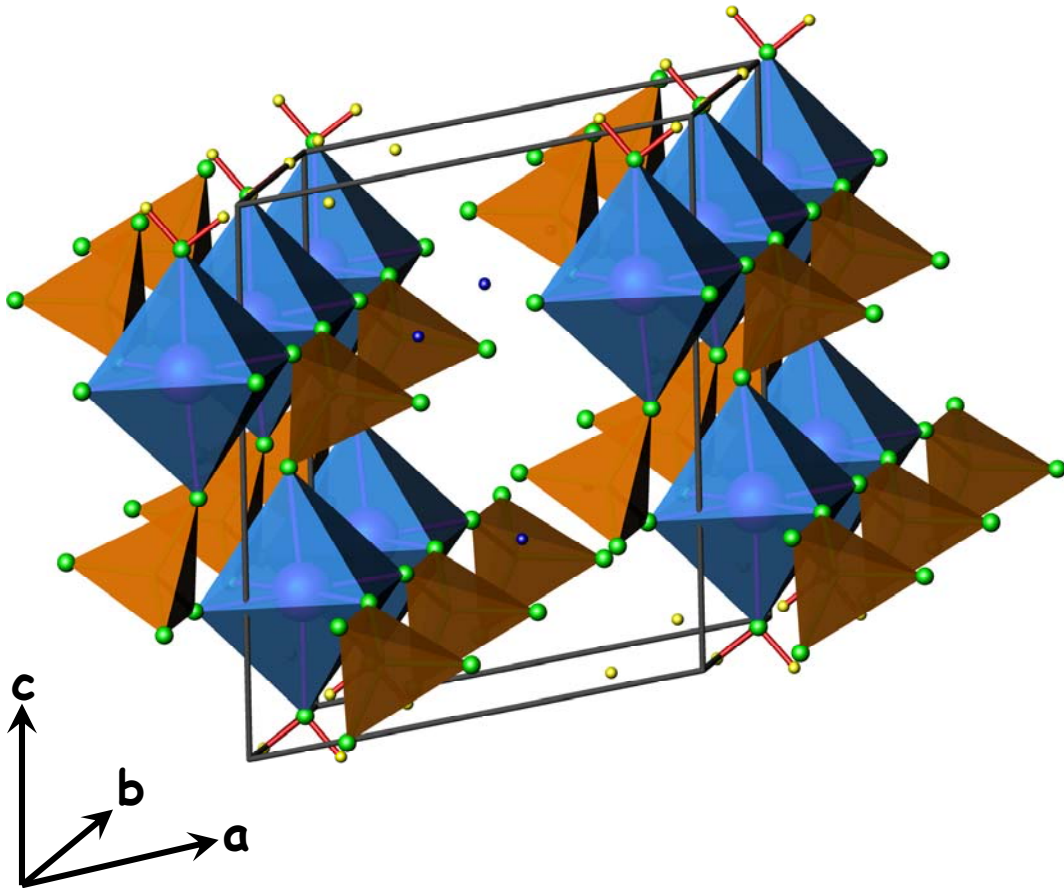
Klaus Koepernik (IFW, Dresden)

Oleg Janson (MPI CPfS, Dresden)

Helge Rosner (MPI CPfS, Dresden)

---

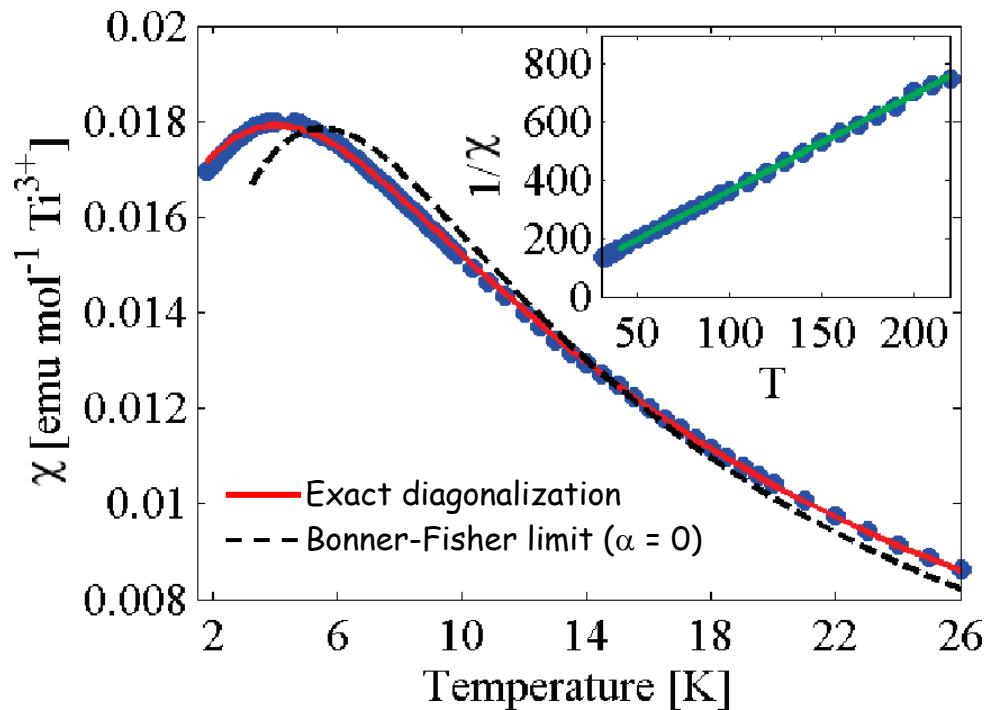
# Structure of $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$



- Recently synthesized material
- $\text{Ti}^{3+}$  ion ( $d^1$ )  $\equiv$   $\text{Cu}^{2+}$  ion ( $d^9$ )
- Monoclinic structure
- Bluish purple crystals
- Double chains of  $\text{TiO}_6$  octahedra connected by  $\text{SO}_4$  tetrahedra along the " $b$ " axis
- The double chains are separated along " $a$ " by  $\text{K}^+$  ions and along " $c$ " by interpenetrating  $\text{H}_2\text{O}$  molecules

• Nilsen *et. al.*, Chem. Mater. **20**, pg.8, (2008)

## Susceptibility measurement



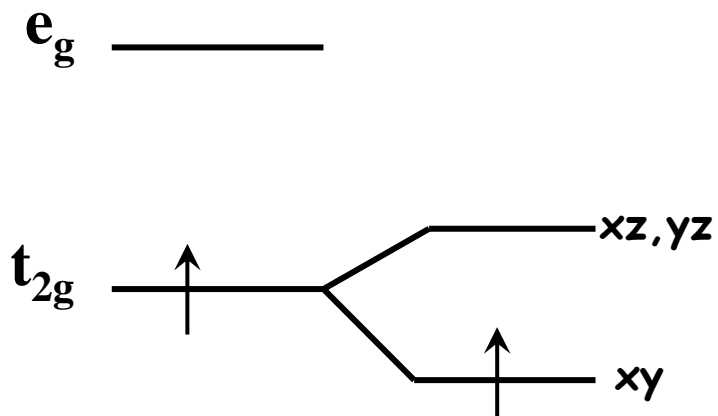
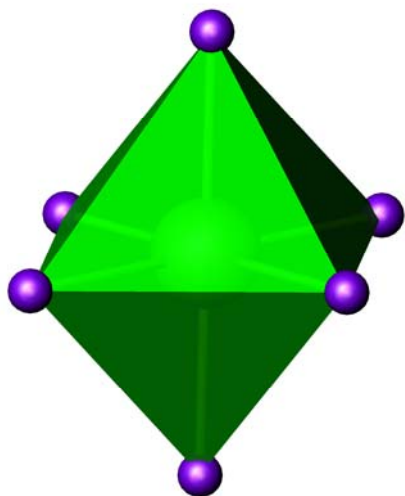
- Nilsen *et. al.*, Chem. Mater. 20, pg.8, (2008)

- Short range order at  $T = 4.5 \text{ K}$
- No signs of long range order
- Fit to  $H = J_1 \sum \mathbf{S}_n \mathbf{S}_{n+1} + J_2 \sum \mathbf{S}_n \mathbf{S}_{n+2} \rightarrow$  Frustrated chain model (FCM)
- Exotic quantum ground states  $\rightarrow \alpha = J_2/J_1$
- Both  $J_1$  &  $J_2$  - AFM is rare!

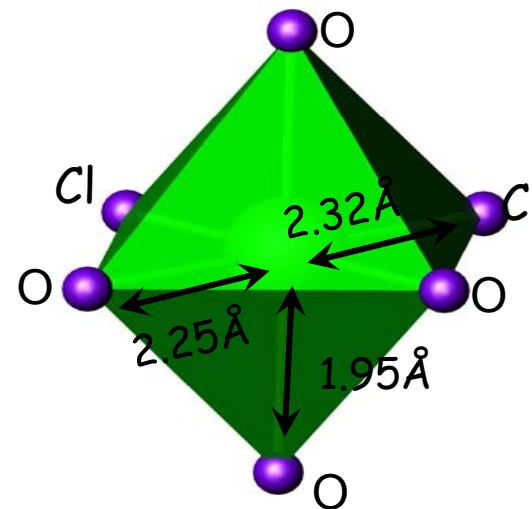
•  $J_1 \approx 9.5 \text{ K}, \alpha \approx 0.29, J_2 = 2.8 \text{ K} \rightarrow S = \frac{1}{2} \text{ FCM}$

# Local crystal field

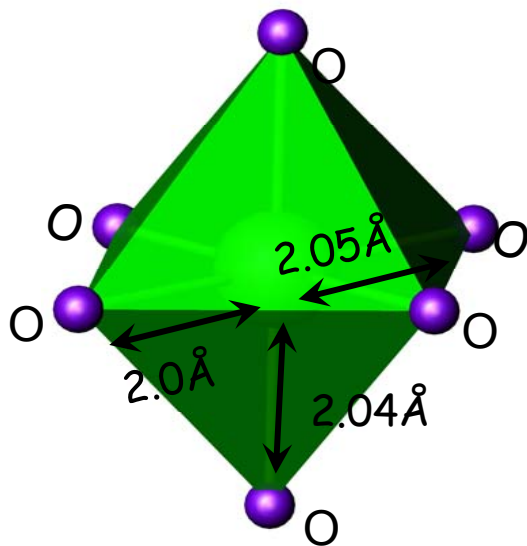
Octahedral crystal field



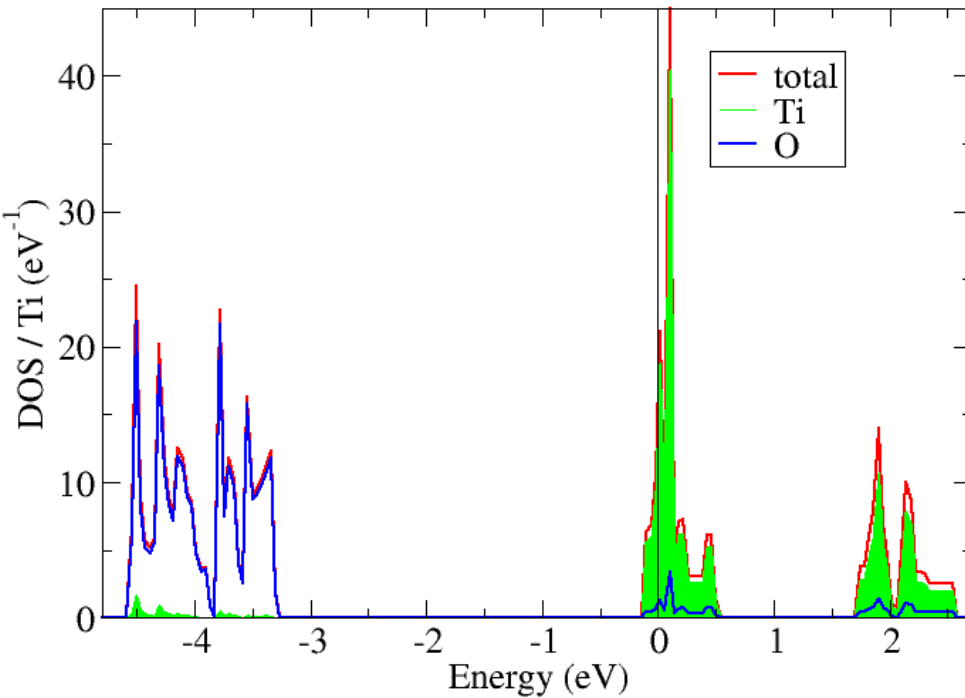
TiOCl



$\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$

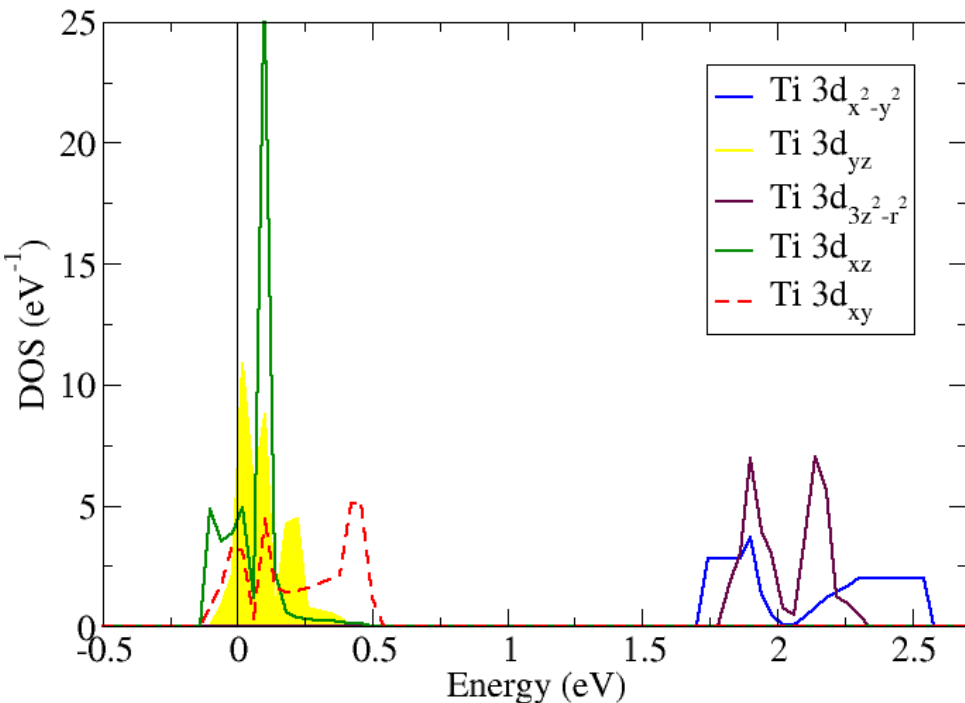


# LDA - Density of States



- Metallic solution within LDA, inadequate treatment of the Coulomb term
- LDA+U  $\rightarrow$  Gap opening
- Fermi level  $\rightarrow$  mostly Ti states  $\rightarrow$  Mott like in contrast to cuprates (charge transfer)
- Ti is in  $3d^1$  state

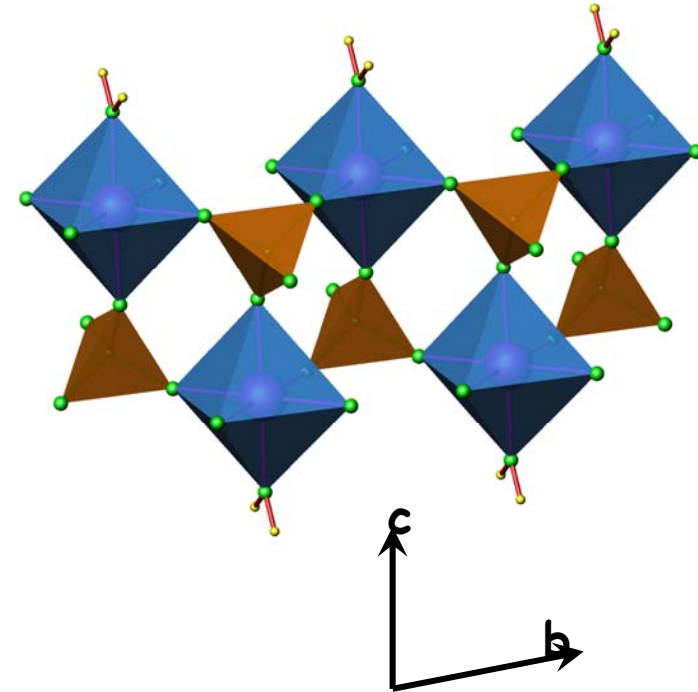
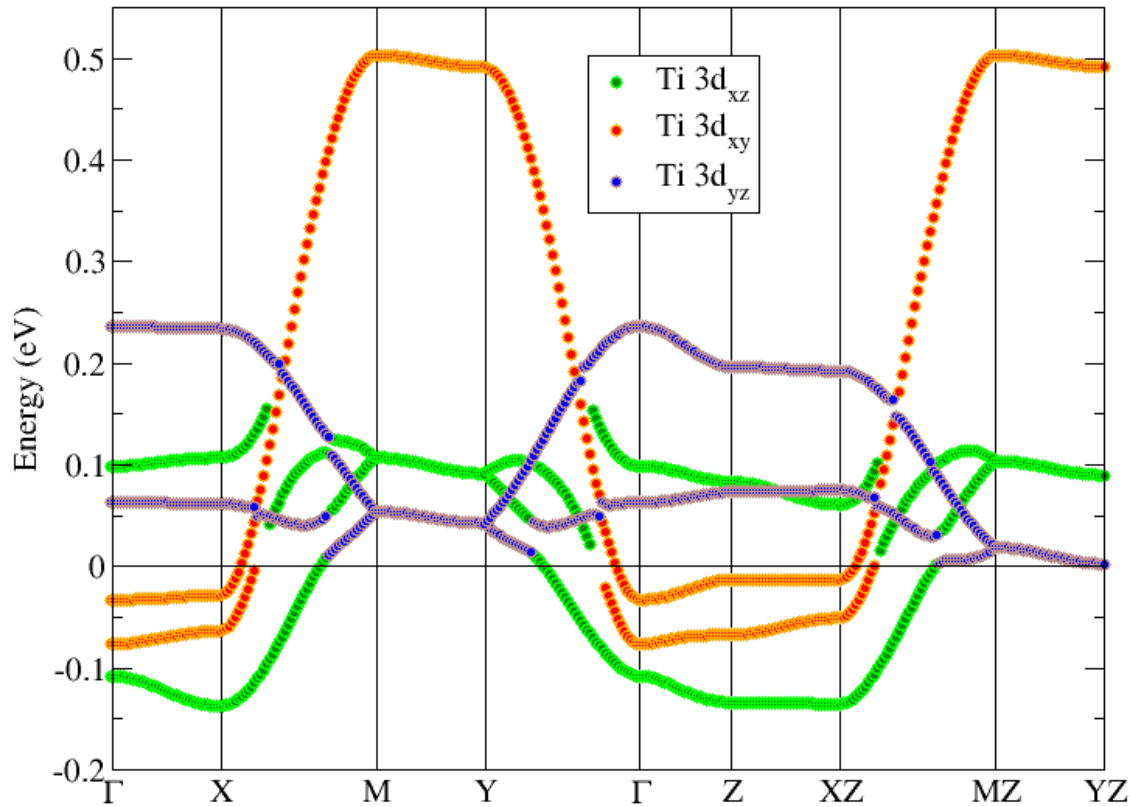
# LDA - Density of States



- Metallic solution within LDA, inadequate treatment of the Coulomb term
- LDA+U  $\rightarrow$  Gap opening
- Fermi level  $\rightarrow$  mostly Ti states  $\rightarrow$  Mott like in contrast to cuprates (charge transfer)
- Ti is in  $3d^1$  state

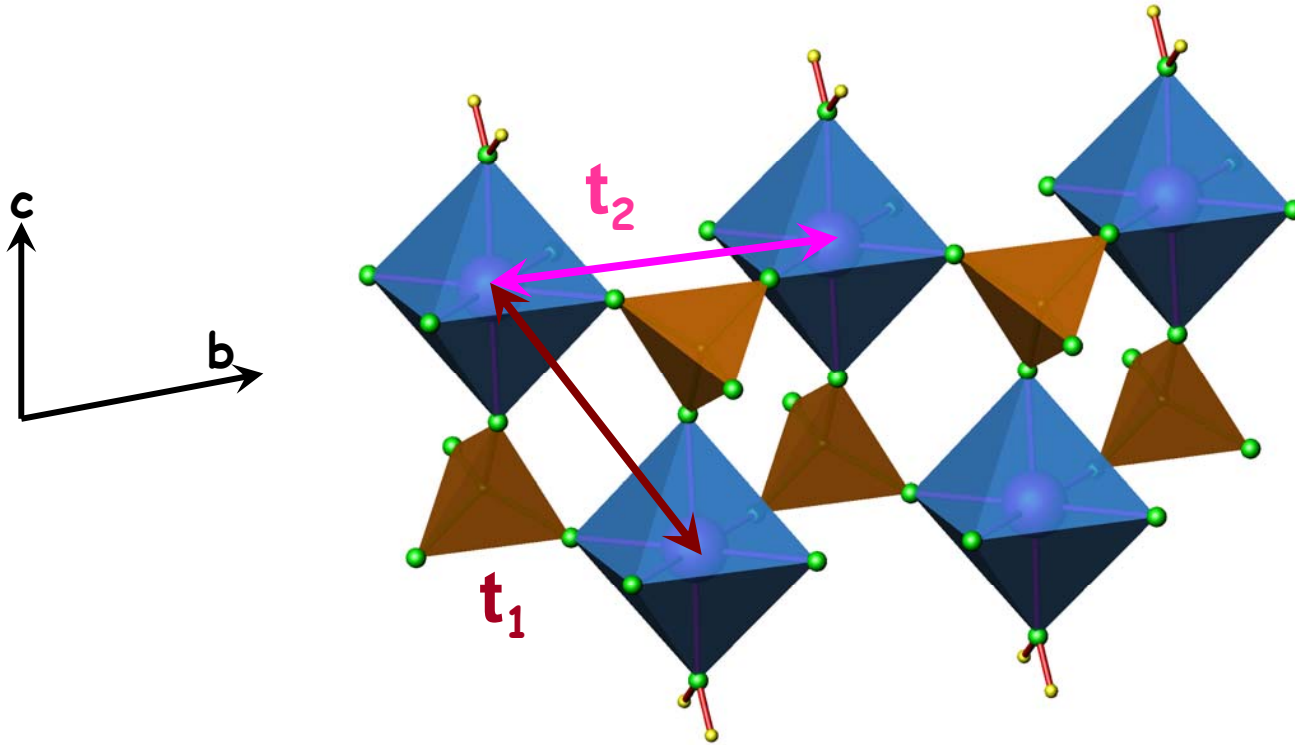
- Octahedral crystal field:  $t_{2g}$  and  $e_g$  states split, with  $t_{2g}$  states lower in energy
- Tetrahedral distortion splits the triplet  $t_{2g}$  levels into a singlet  $a_g$  ( $d_{xy}$ , lower in energy) and a doublet  $e_g'$  ( $d_{yz}$  &  $d_{xz}$ , higher in energy) Ex.  $\text{TiOCl}$
- Monoclinic symmetry of this compound lifts the degeneracy within the  $e_g'$  doublet
- In  $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ : Ti -  $3d_{xz}$  is lower in energy than  $3d_{xy}$

# LDA - Band structure



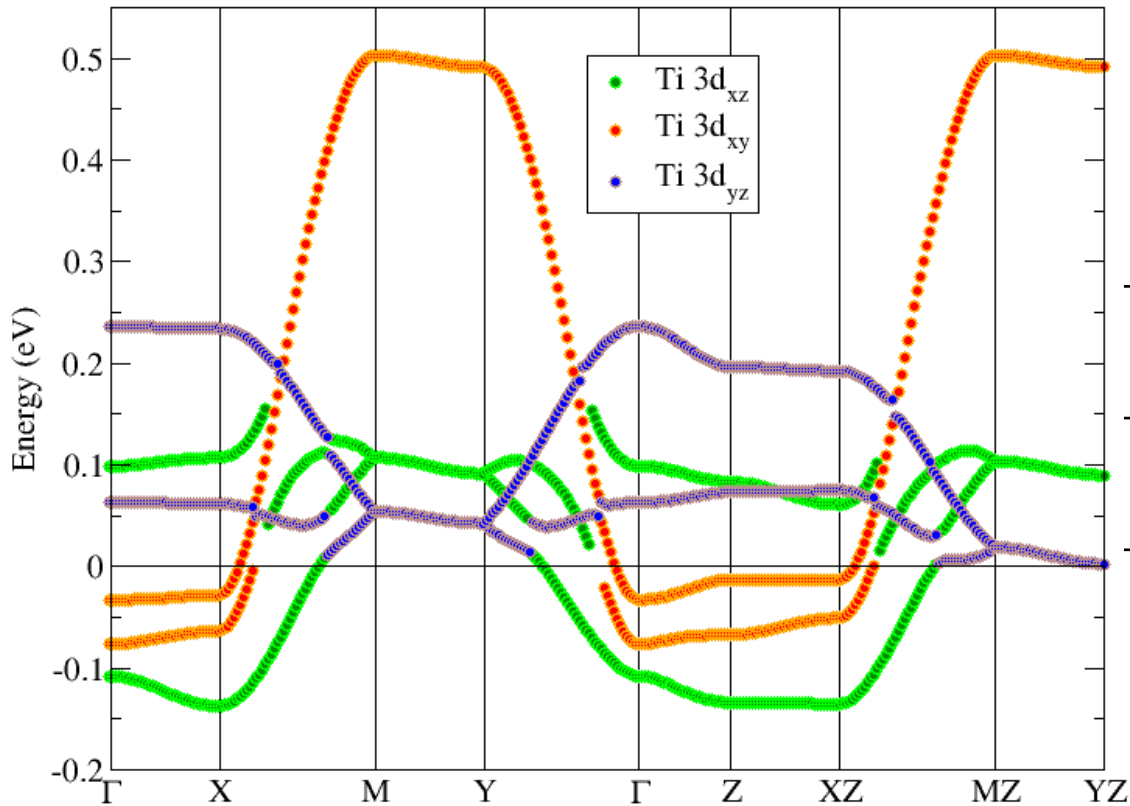
1D nature of the bands  $\rightarrow$  dispersion along the chain (X-M &  $\Gamma$ -Y) and rather flat along other directions

# Tight-binding model



- Effective one-band tight-binding model (TBM)
- For  $U_{\text{eff}} > t$ ,  $J^{\text{AFM}} = 4t^2/U_{\text{eff}}$  with  $U_{\text{eff}} = 3 \text{ eV}$

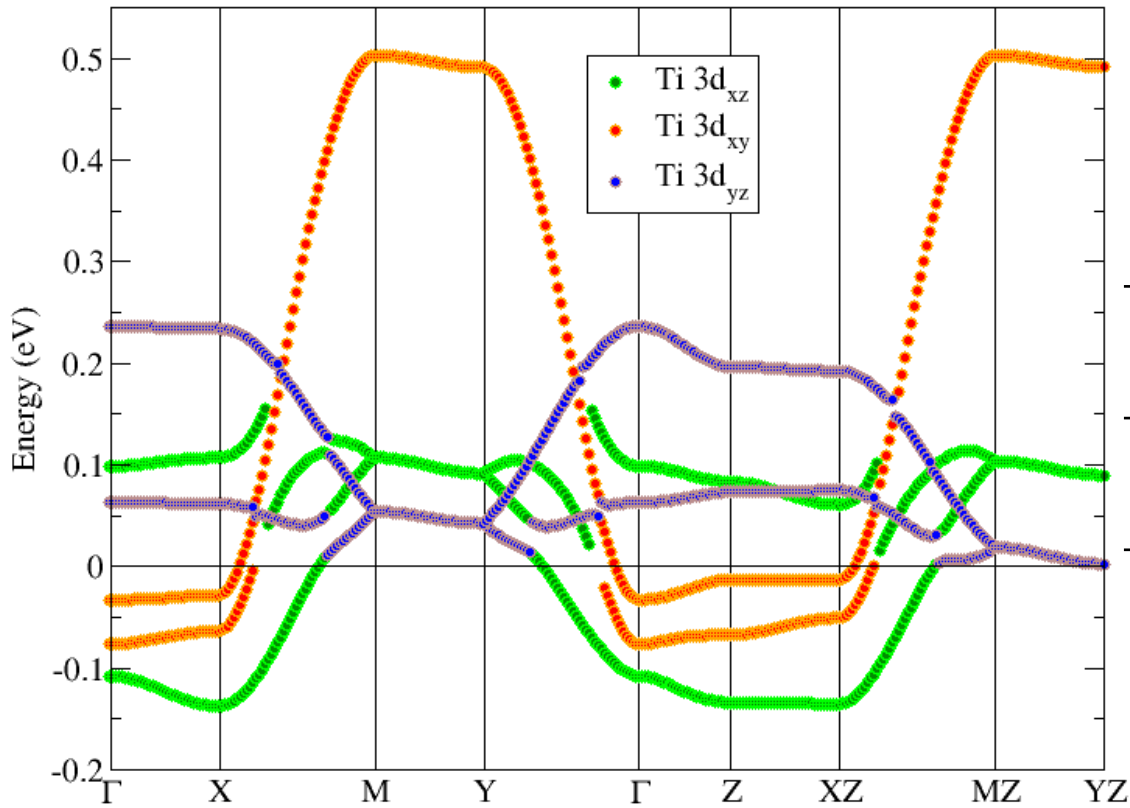
# Exchange parameters



(K)	$J_1$	$J_2$	$\alpha$
$d_{xz}$	34	13	0.39
$d_{xy}$	101	281	2.78
$d_{yz}$	21	12.5	0.59

$$J_1^{\text{exp}} = 9.5\text{K}, \quad \alpha^{\text{exp}} = 0.29$$

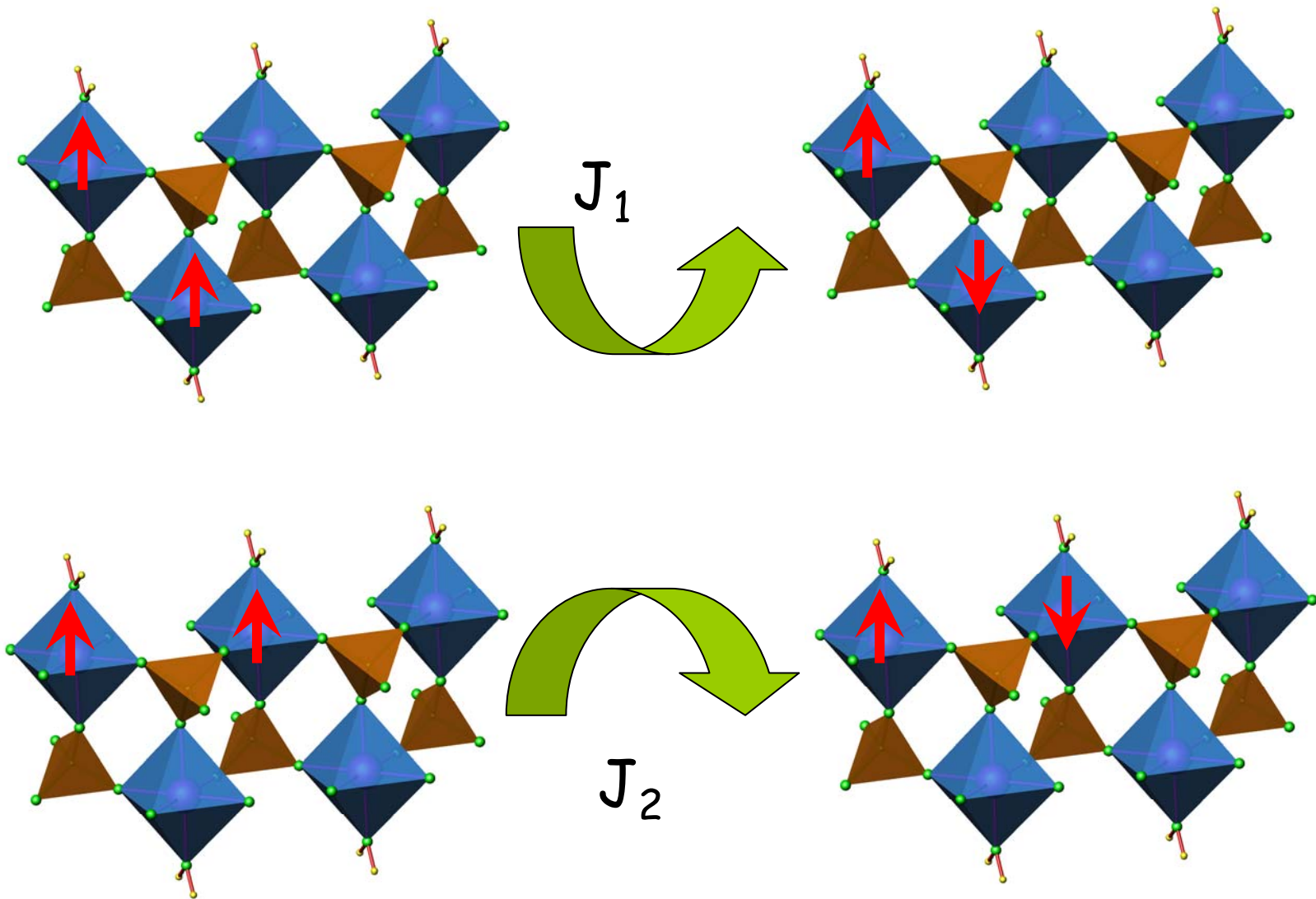
# Exchange parameters



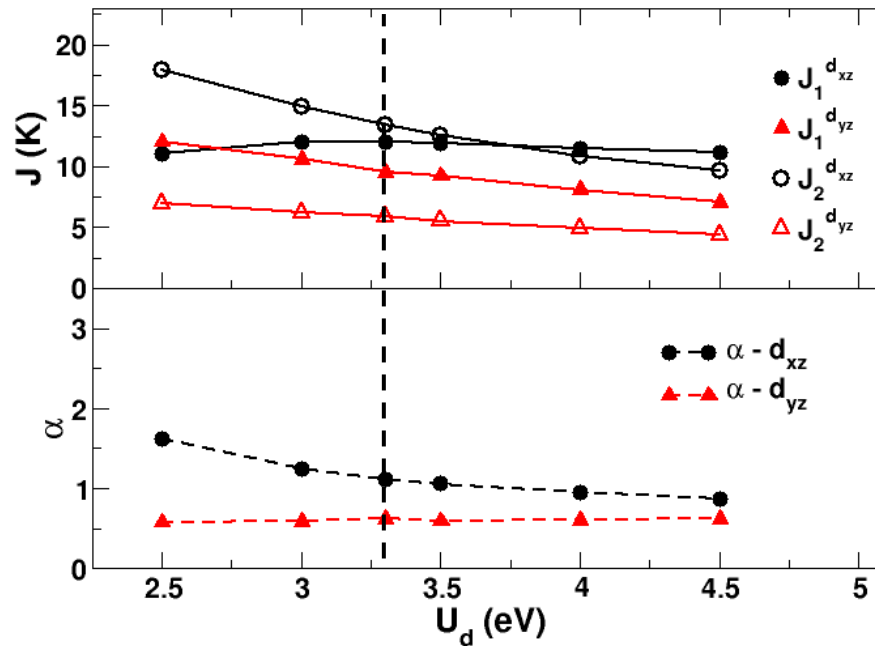
(K)	$J_1$	$J_2$	$\alpha$
$d_{xz}$	34	13	0.39
<del><math>d_{xy}</math></del>	<del>101</del>	<del>281</del>	<del>2.78</del>
$d_{yz}$	21	12.5	0.59

$$J_1^{\text{exp}} = 9.5\text{K}, \quad \alpha^{\text{exp}} = 0.29$$

# LSDA+U



# LSDA+U



- J's do not vary much for the range of U values
- $\alpha \rightarrow$  comparable to experiments for both  $d_{xz}$  and  $d_{yz}$  ( $\alpha^{\text{exp}} = 0.29$ )
- The dashed line represents  $U = 3.3\text{eV}$ . [ref. TiOCl]
- In  $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , the octahedra is made up of only oxygens (no chlorine!) - therefore the value of U for our compound should be larger than 3.3eV.
- Lowest energy  $\rightarrow d_{xz}$  orbital is spin polarized  $\rightarrow$  magnetically active orbital

## LSDA+U

1 electron in  $d_{xy}$  - could not be stabilized (consistent with the TBM)



1 electron in  $d_{yz}$  - 0.7eV

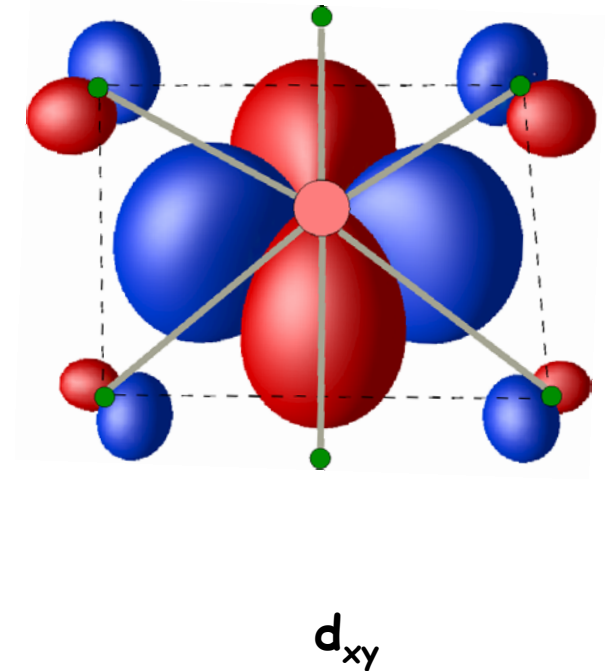
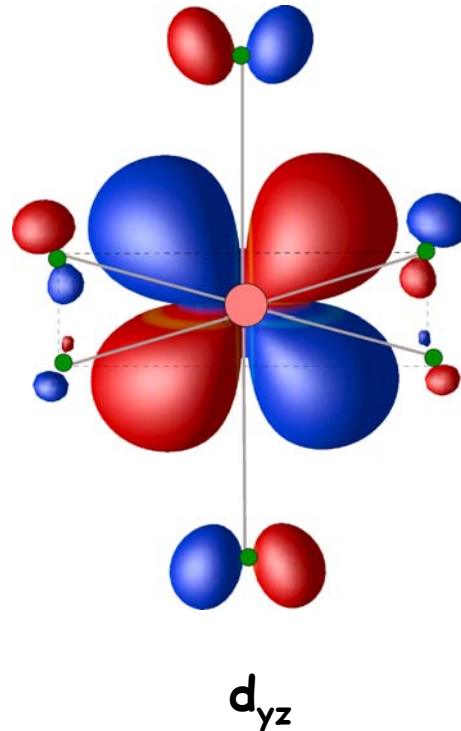
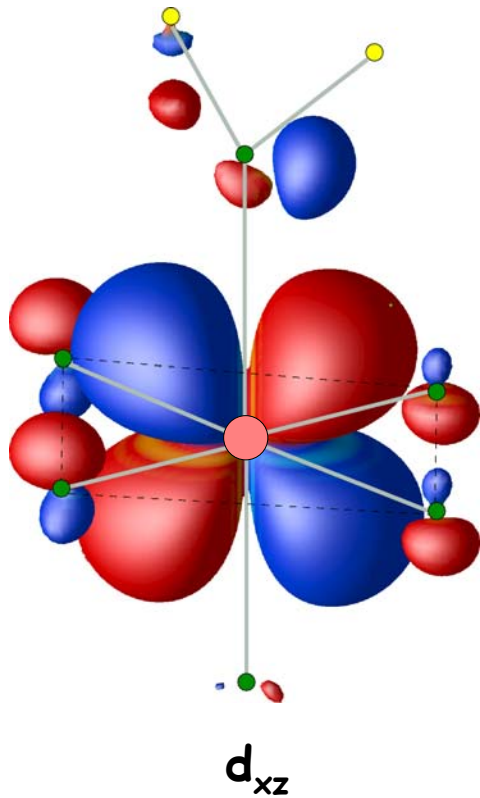


1 electron in  $d_{xz}$  - 0 eV

The magnetic interaction is via the Ti  $3d_{xz}$  orbital !

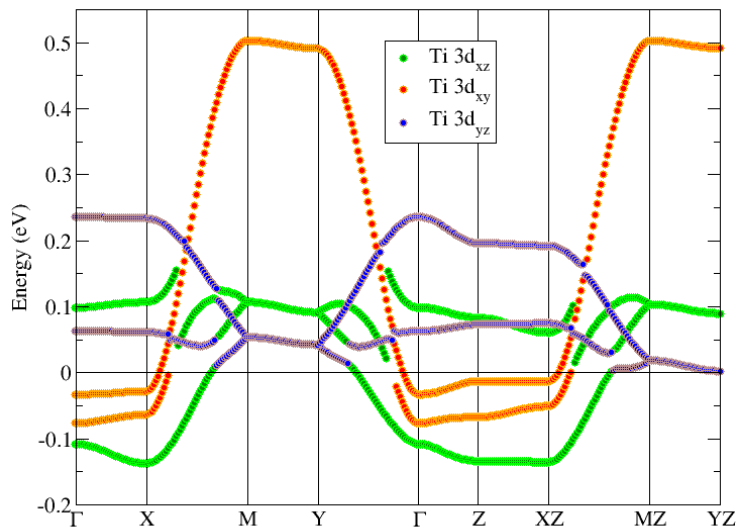
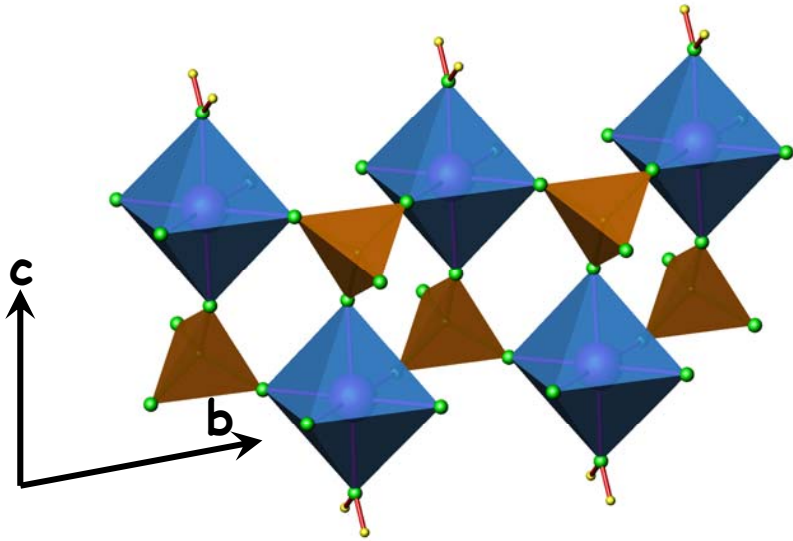
(different from that of TiOCl, where the Ti  $3d_{xy}$  orbital determines the ground state !)

## Effect of crystal water: Wannier functions

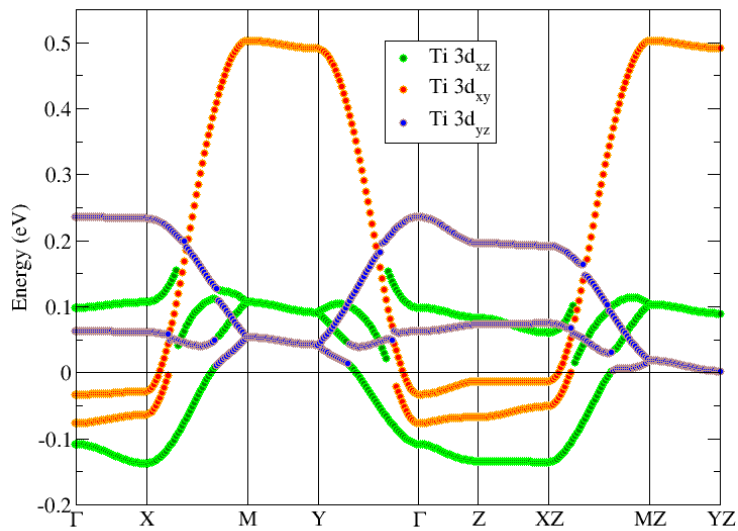
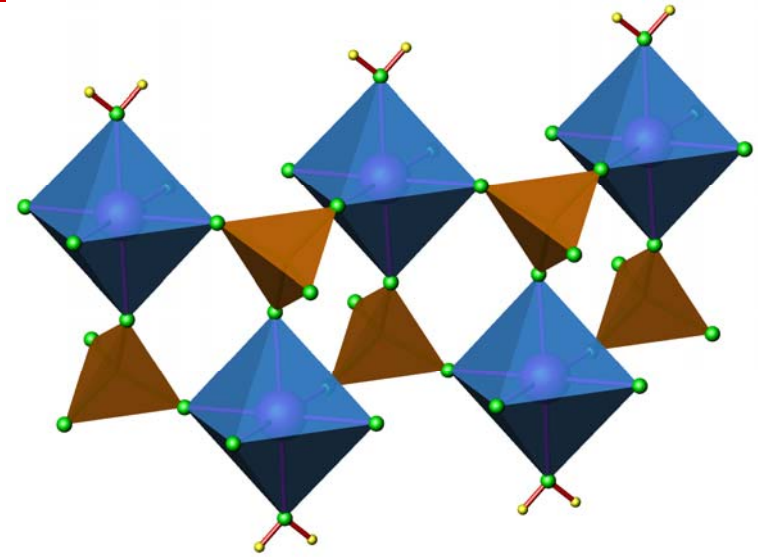
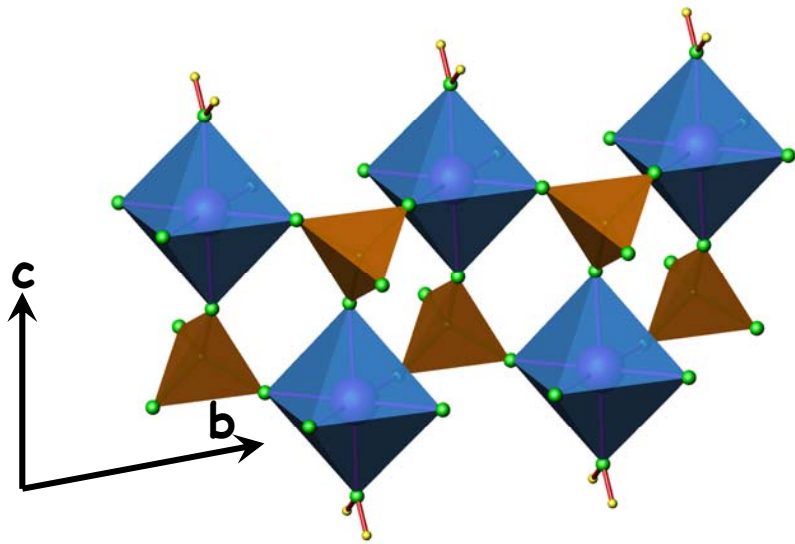


Wannier functions for the  $d_{xz}$  orbital shows extended tails pointing towards hydrogen → Orientation of water molecule plays an important role in deciding the magnetically active orbital

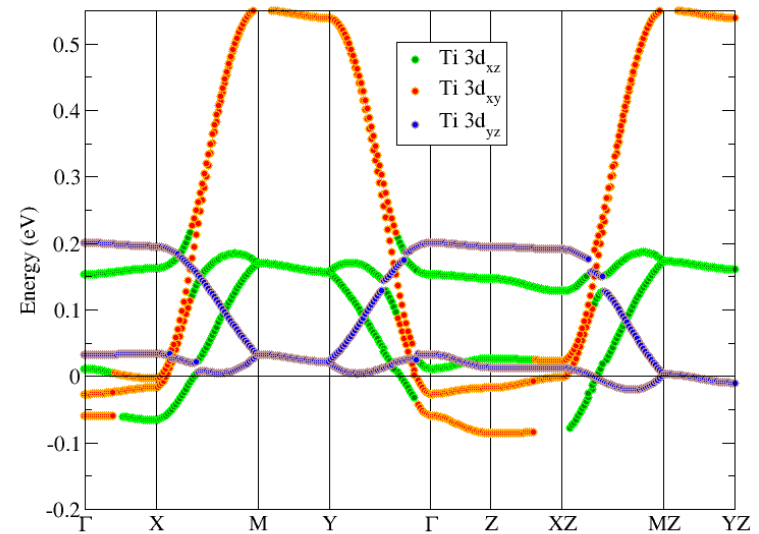
# Effect of crystal water



# Effect of crystal water



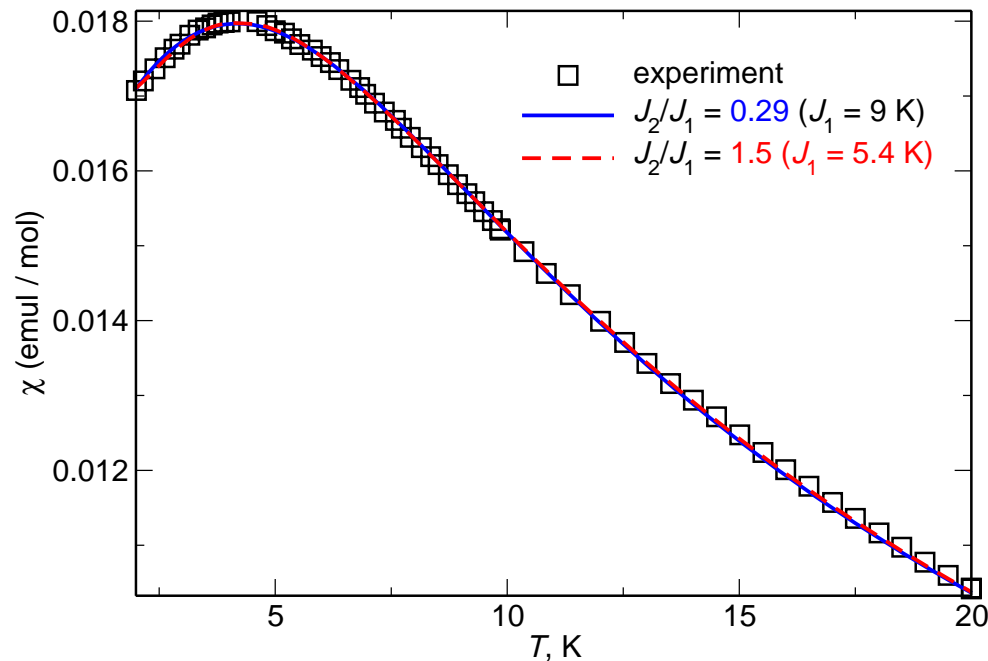
$$\alpha^{xz} = 0.39, \alpha^{yz} = 0.59$$



$$\alpha^{xz} = 1.11, \alpha^{yz} = 0.36$$

# Transfer Matrix Renormalization Group calculations

Magnetic susceptibility as a function of temperature using TMRG  
Two possible fits to the experimental data (due to inner symmetry of  $J_1$ - $J_2$  Heisenberg chain):



Ambiguity can be resolved by comparing high field magnetization curves from TMRG and expt:

Shape of the curve and saturation fields vary for different a values

## Conclusions

- $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  → DFT confirms that both  $J_1$  &  $J_2$  are AFM
  - Ti  $3d_{xz}$  orbital is the magnetically active orbital
  - TMRG → two possible fits to experimental data → ambiguity resolved by high field magnetization measurements
  - Crystal water plays an important role in deciding the choice of orbital for the magnetic ground state.
-