

Competing interactions in the low-dimensional quantum magnet TiOCl

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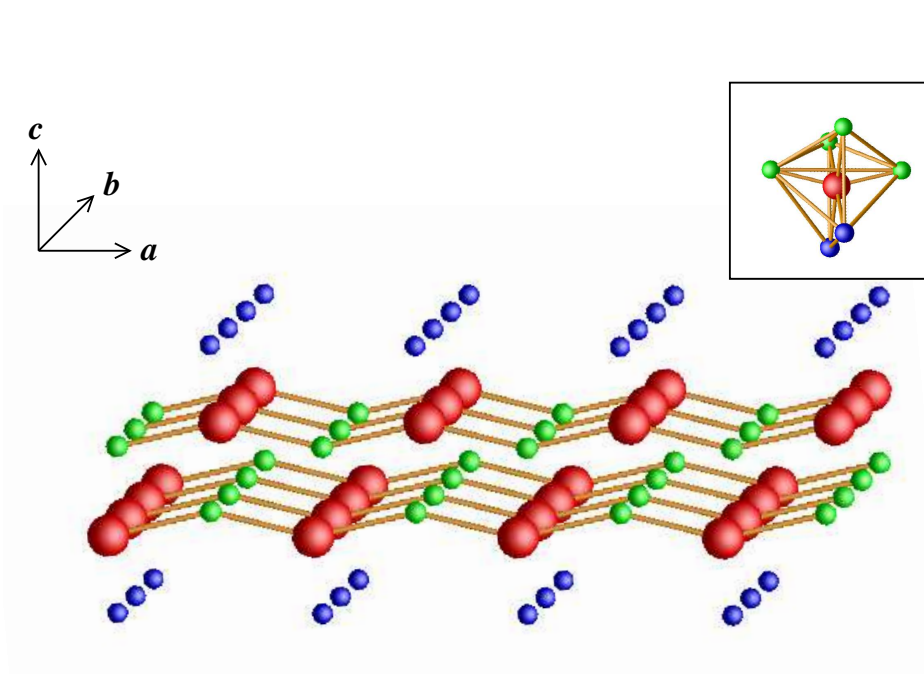
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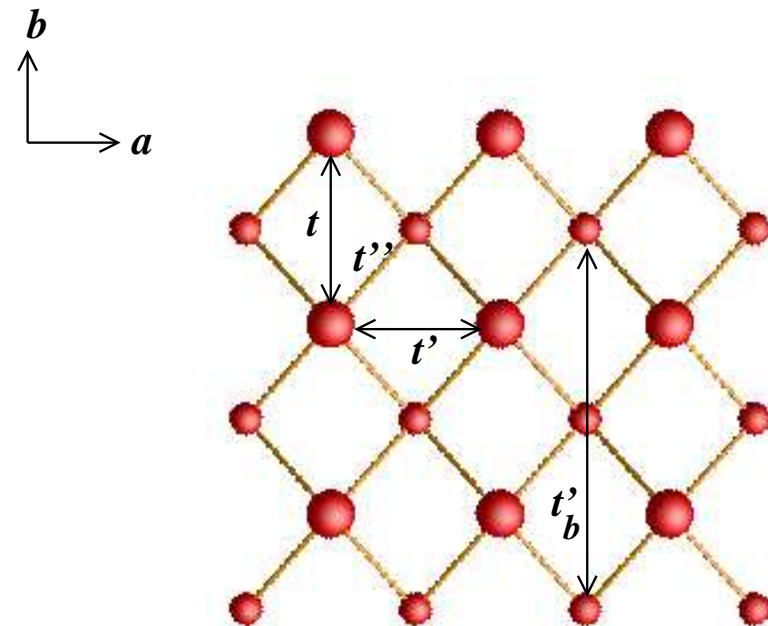
TiOCl, a layered quantum spin system

- bilayers of Ti^{3+} and O^{2-} parallel to the ab plane separated by layers of Cl^- .
- Orthorhombic space group $Pmmn$. TiCl_2O_4 octahedron



● Ti ● O ● Cl

insulator Ti^{3+} : $3d^1$ spin=1/2, multiorbital t_{2g}



Competing degrees of freedom:

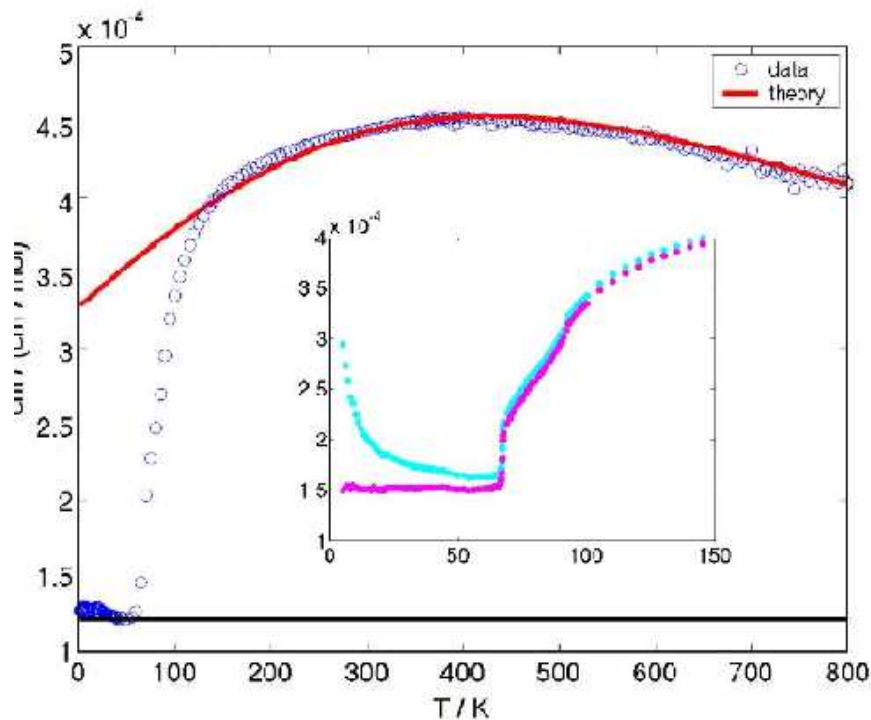
- spin
- lattice
- orbital

TiOCl, susceptibility

- kink at $T_{c_2}=94\text{K}$
- sharp drop at $T_{c_1}=66\text{K}$
opening of a **spin gap**.

A. Seidel *et al.*, PRB (2003)

P. Lemmens *et al.*, PRB (2004)



Theory: ($T > 94\text{K}$)

Fit to a spin-1/2 Heisenberg chain

$$H_{Heis} = J \sum_{i,j} \mathbf{S}_i \mathbf{S}_j$$

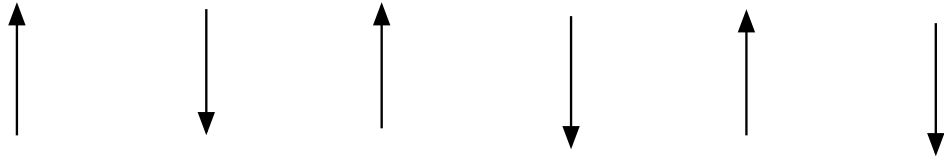
$$J=660\text{K}$$

($T < 94\text{K}$)

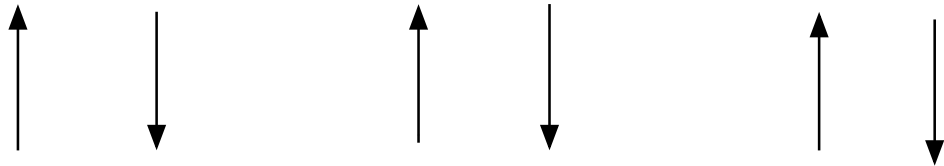
Anomalous spin-Peierls phase transition

Spin-Peierls phase transition

spin-1/2 chain:

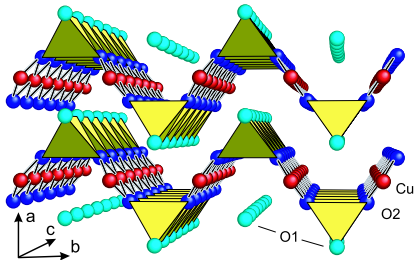


magnetoelastic coupling (spin-phonon):



- chain dimerization
- singlet-triplet spin gap

well known example: CuGeO_3



- First **inorganic** system with **Spin-Peierls** phase transition at $T=14$ K
- **Frustrated** $s=1/2$ Cu - chains

→ **BUT TiOCl shows two phase transitions!**

Microscopic description

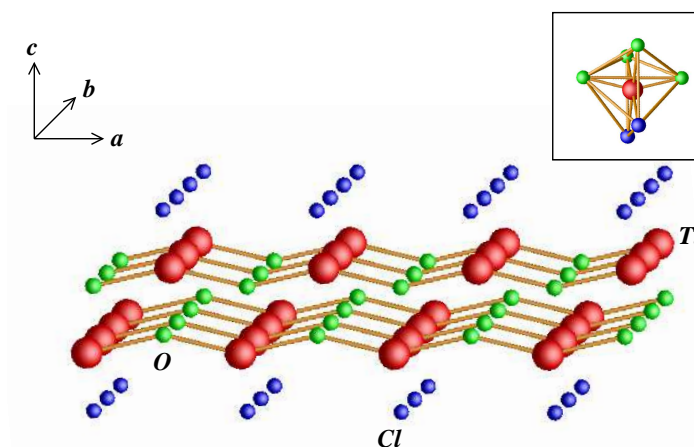
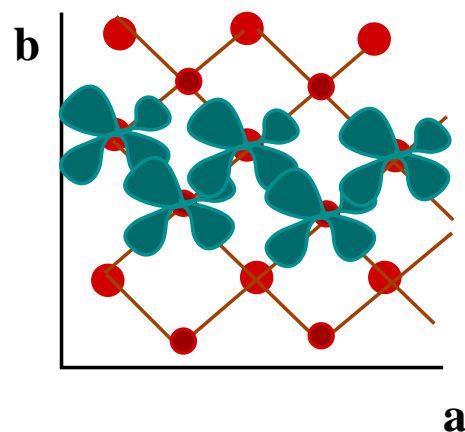
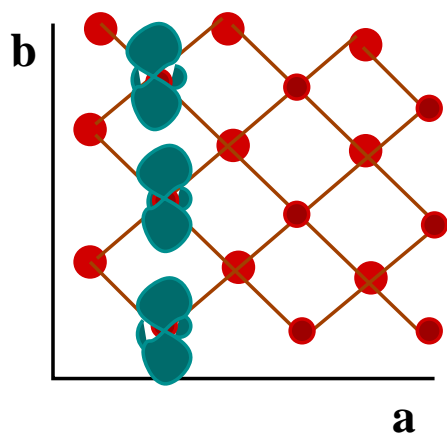
$T > 94\text{K}$

Saha-Dasgupta, Valentí, Rosner, Gros EPL (2004)

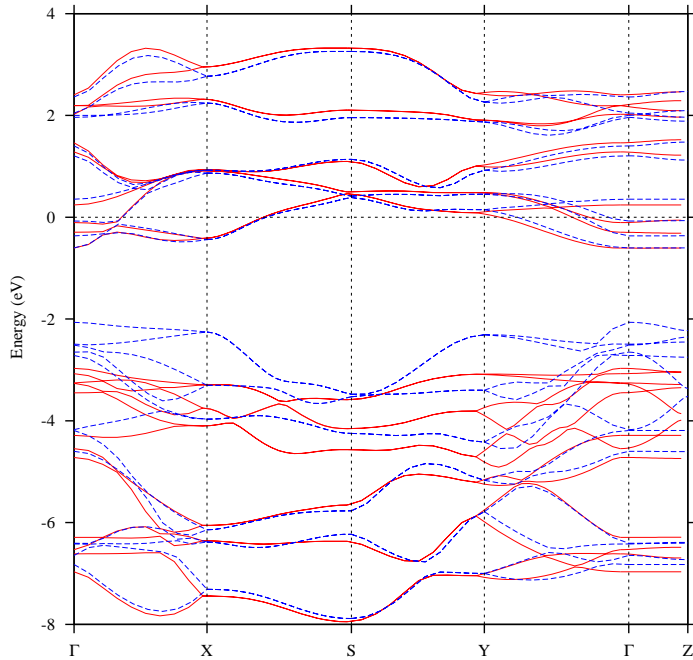
multiorbital t_{2g} , two scenarios:

linear chain along b : **Ti** d_{xy}

zig-zag chain along a : **Ti** d_{xz} , **Ti** d_{yz}



Electronic Bandstructure: **TiOCl** **TiOBr** (LMTO Basis)



NMTO-downfolding on the LDA-BS:

Andersen, Saha-Dasgupta PRB '00

Saha-Dasgupta, Valentí, Rosner, Gros EPL '04

$$H_{TB} = - \sum_{\langle i,j \rangle} t_{ij} (c_j^\dagger c_i + c_i^\dagger c_j)$$

TiOCl

TiOBr

t = -0.21 eV

-0.17 eV

t'' = 0.03 eV

0.04 eV

t' = 0.04 eV

0.06 eV

t_b = -0.03 eV

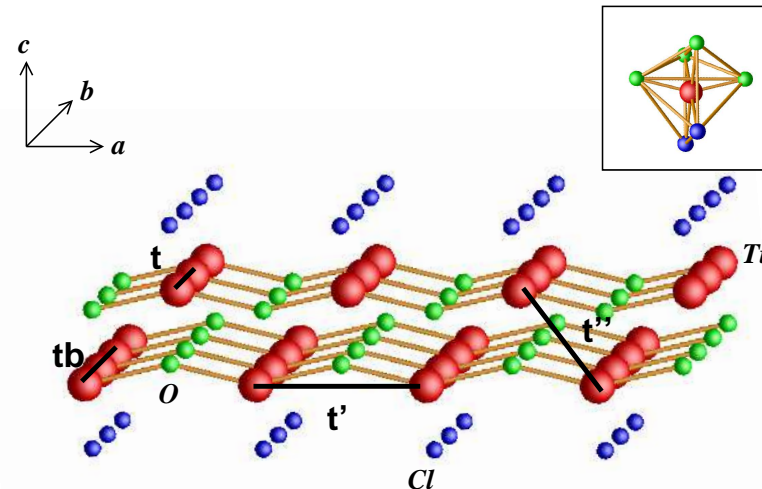
-0.04 eV

Biggest hopping

in the chain direction

Estimate: $J = \frac{4t^2}{U}$, U = 3-4 eV,

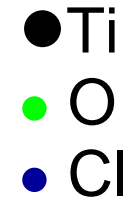
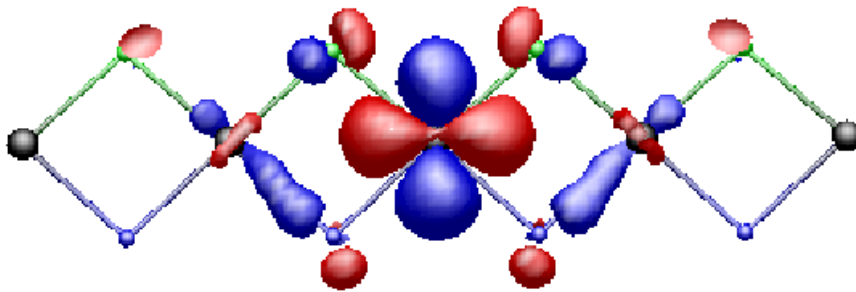
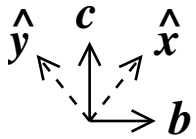
J ≈ 700K ↔ comparable: susceptibility fit



Nature of interacting pathes in TiOCl

Wannier-like wavefunctions:

Downfolded Ti- d_{xy} orbital

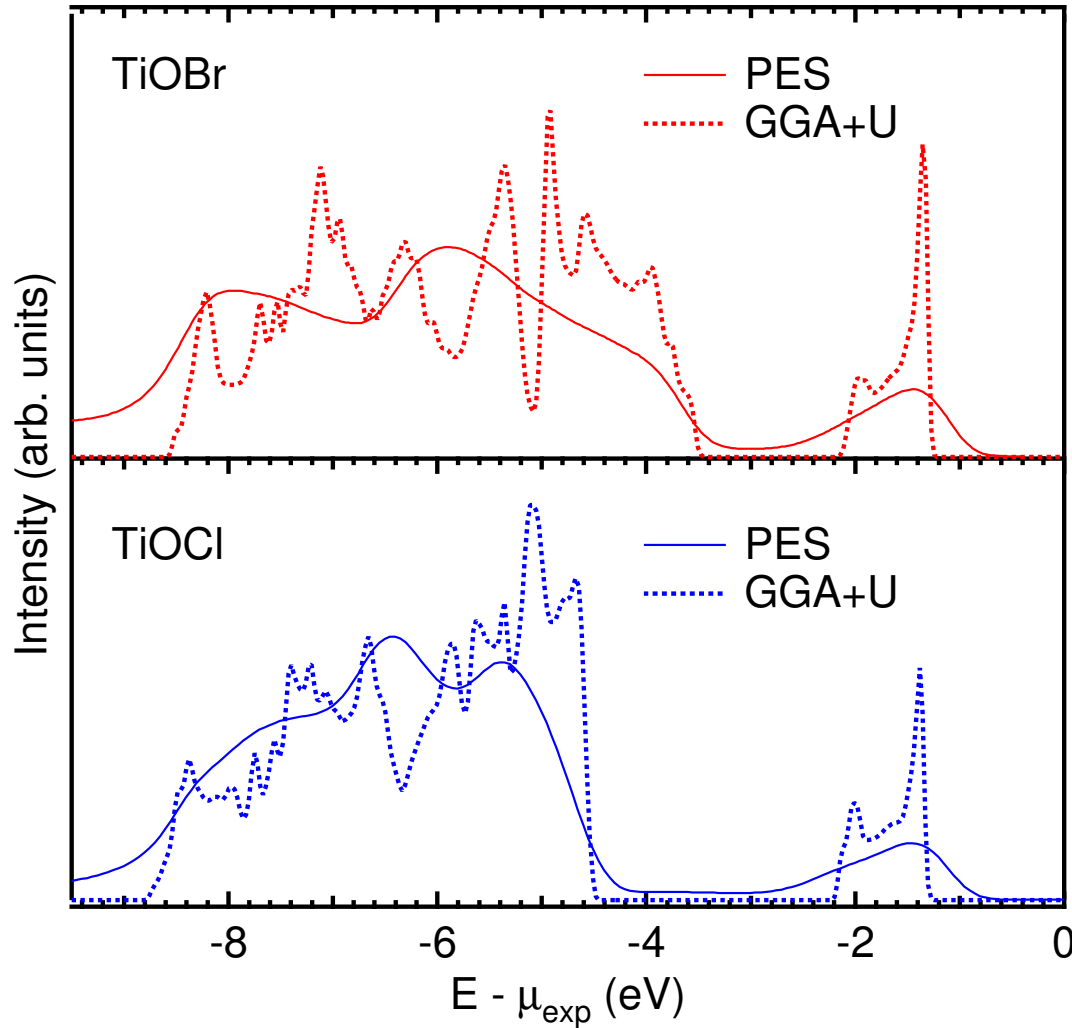


- the *central* Ti site shows the bare d_{xy} character.
- The *tail* of the orbital sitting at the O and Cl sites has appreciable weight shaped to O- p_x, p_y and Cl- p_x, p_y symmetries

→ appreciable renormalization effect in the $\text{Ti}d_{xy}\text{-Ti}d_{xy}$ path coming from $\text{O}p$ and $\text{Cl}p$

Correlation in TiOCl ($T > 94K$)

(lapw basis Wien2k)



Hoinkis *et al.* PRB '05,
Hoinkis *et al.* cond-mat/0610106

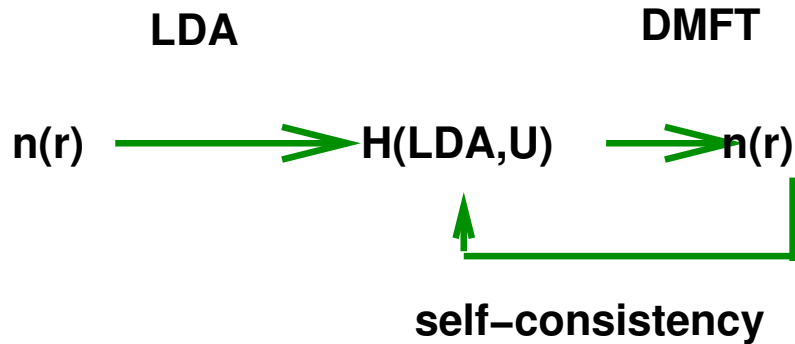
$U = 3.3\text{eV}, J = 1\text{eV}$

$$E^{LDA+U} = E^{LSDA} + \frac{1}{2} \sum_{m,m',\sigma} U (n_{m\sigma} - n_{\sigma}^0)(n_{m'-\sigma} - n_{-\sigma}^0) + \frac{1}{2} \sum_{m,m',m \neq m',\sigma} (U - J)(n_{m\sigma} - n_{\sigma}^0)(n_{m'\sigma} - n_{\sigma}^0)$$

Correlation in TiOCl ($T > 94\text{K}$)

LDA+DMFT

- Idea DMFT: substitute the lattice model by an impurity model
- Description of **local** quantum fluctuations

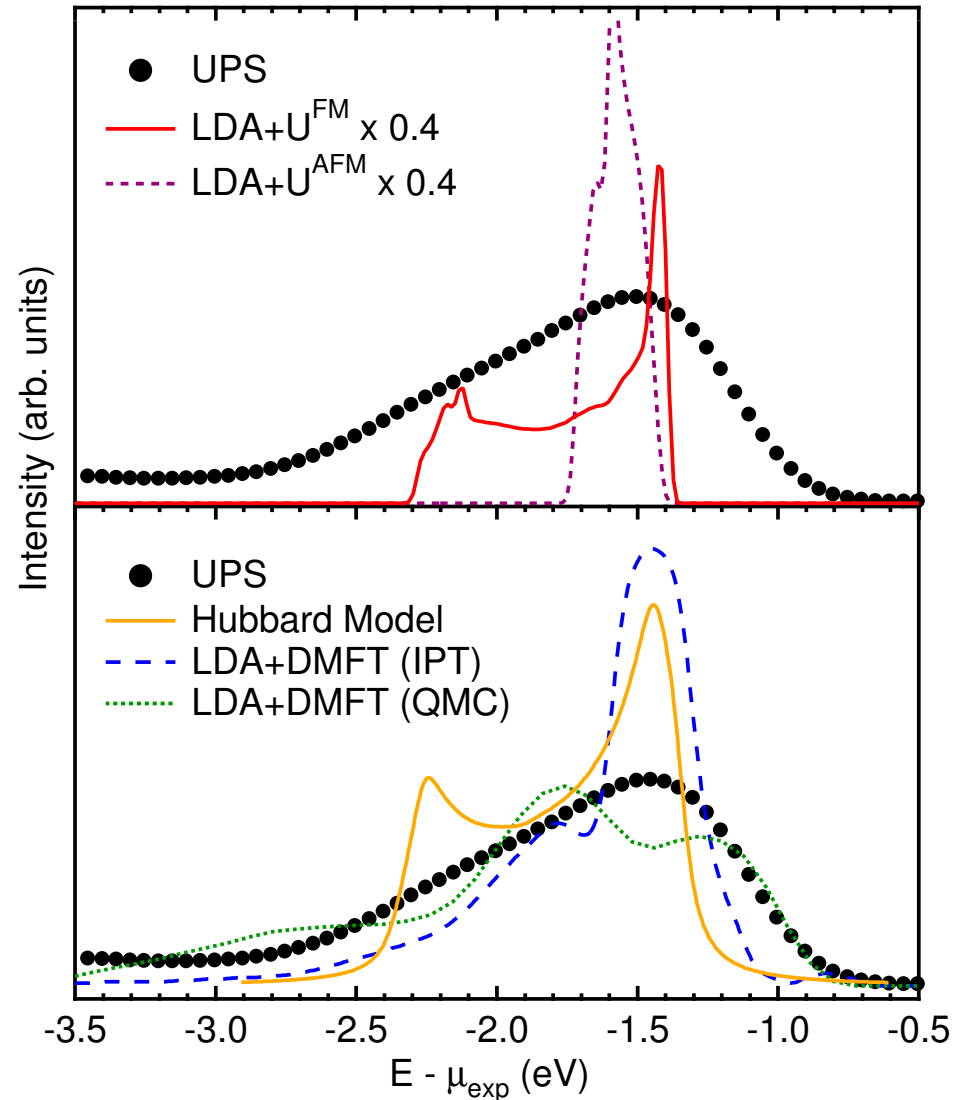


$$G(\omega_n) = \sum_k [(\omega_n + \mu)I - H^{LDA}(k) - \Sigma(\omega_n)]^{-1}$$

Hoinkis *et al.* PRB '05

Saha-Dasgupta, Lichtenstein, Valentí PRB '05

Ti d Spectral weight



Correlation in TiOCl ($T > 94\text{K}$)

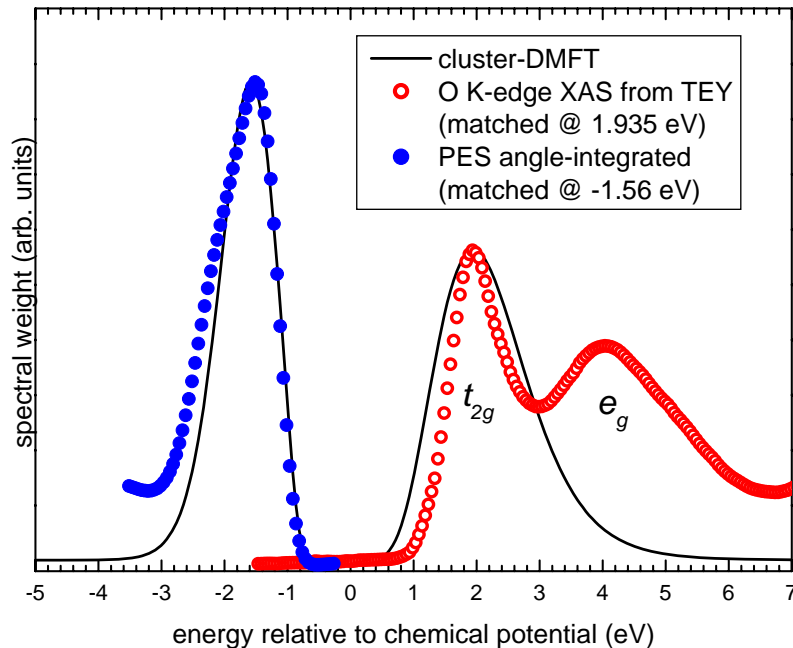
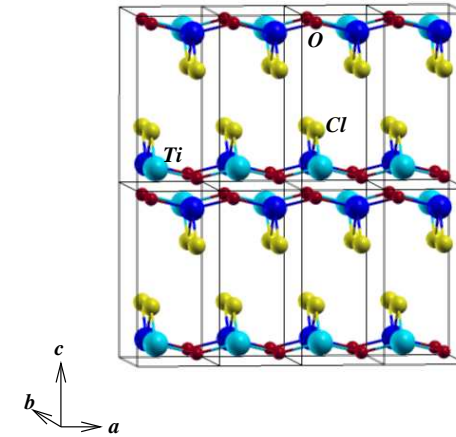
LDA+cluster-DMFT Ti-Ti two-site correlations

Saha-Dasgupta, Lichtenstein, Hoinkis, Glawion, Sing, Claessen, Valenti

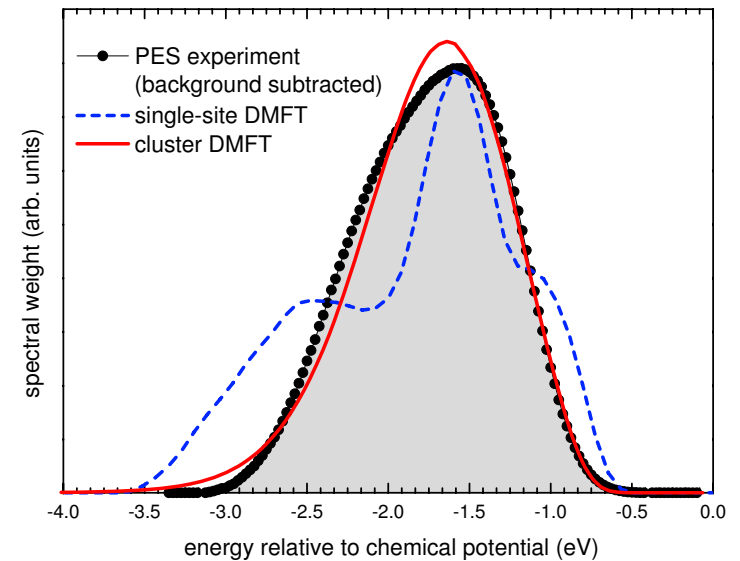
cond-mat/0612166

$$G(\omega_n) = \sum_k [(\omega_n + \mu)I - H^{LDA}(k) - \Sigma(\omega_n)]^{-1}$$

$$\Sigma = \begin{pmatrix} \hat{\Sigma}^{11} & \hat{\Sigma}^{12} & 0 & 0 \\ \hat{\Sigma}^{21} & \hat{\Sigma}^{22} & 0 & 0 \\ 0 & 0 & \hat{\Sigma}^{33} & \hat{\Sigma}^{34} \\ 0 & 0 & \hat{\Sigma}^{43} & \hat{\Sigma}^{44} \end{pmatrix}$$

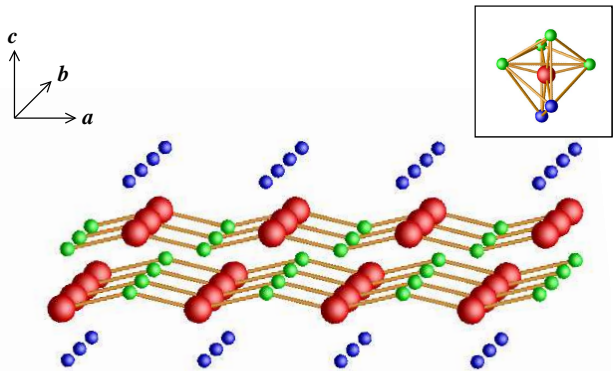
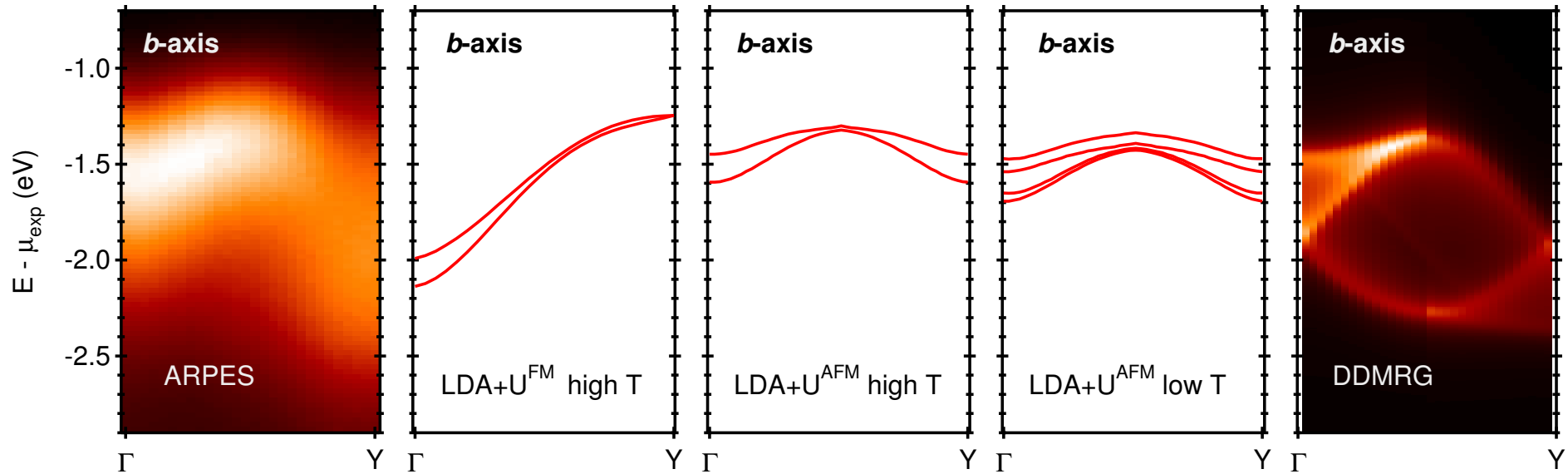


Comparison: cluster ↔ onsite DMFT



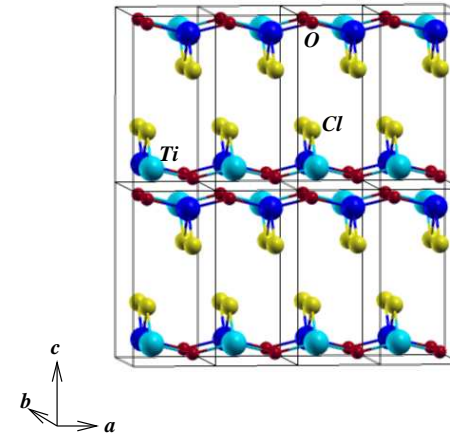
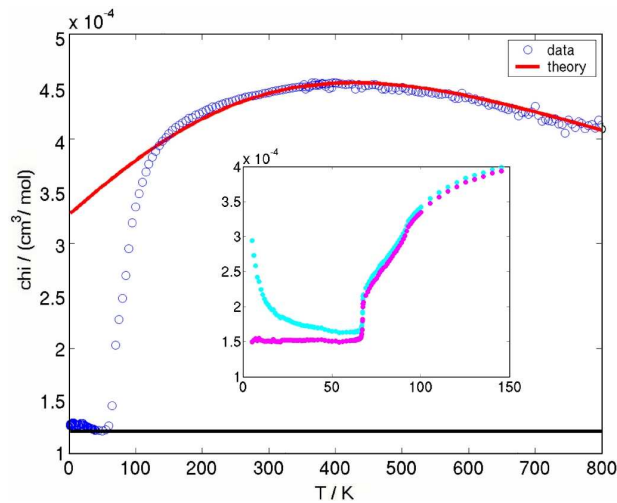
Comparison with ARPES TiOCl ($T > 94\text{K}$)

ARPES $I(\mathbf{k}, E)$ M. Hoinkis, Sing, Klemm, Horn, Benthien, Jeckelmann, Saha-Dasgupta, Pisani, Valenti, Claessen PRB (2005)



● one-particle spectral function (DDMRG)

TiOCl, spin-Peierls? $66 \text{ K} < T < 94 \text{ K}$

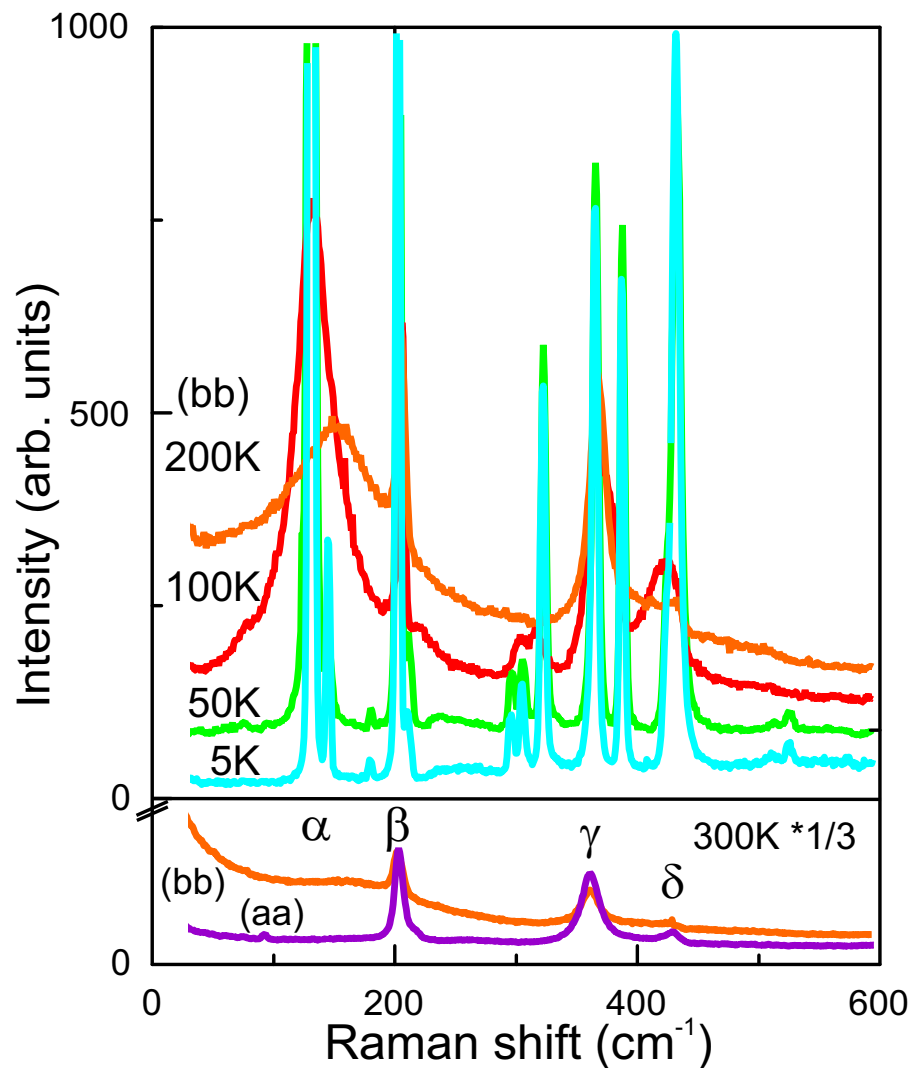


→ **Competition Spin-Peierls dimerization between chains** → **frustration**

- Incommensurate Structure modulation in X-Rays
van Smaalen et al. PRB '05, Krimmel et al. PRB '06, Rückamp et al. PRL '05
- non-negligible interchain interaction
ab initio-downfolding: $t'/t, t''/t$ 8-10 %
- Phonon instabilities?
Pisani, Valentí PRB '05 *ab initio* Phonons

Raman spectroscopy

Peter Lemmens (TU Braunschweig)



P. Lemmens *et al.*,
PRB (2004),
J. Phys.: Condens. Matter (2004)

TiOCl₂, Phonons

Pisani, Valentí PRB(RC) (2005)

- First principles frozen phonon approach:

Calculation of the dynamical matrix with LAPW Wien2k (LDA, LDA+U)

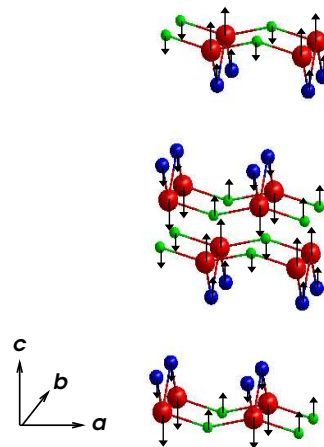
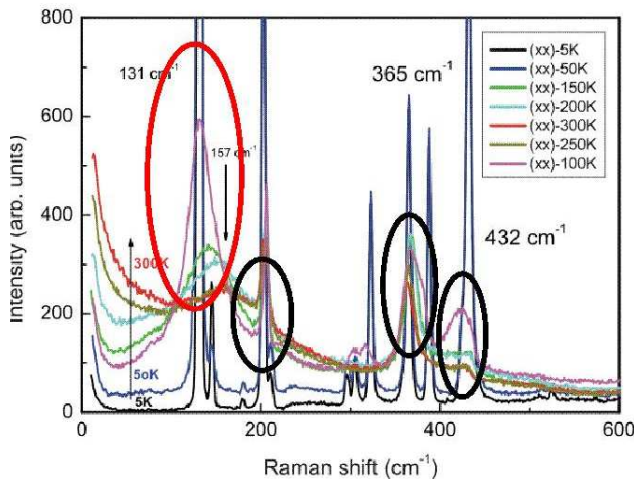
- zone-center A_{1g} modes

LDA

Expt.	Theory	Ti	O	Cl
203	154	0.909	-0.157	1.000
365	351	0.822	0.311	-1.000
430	424	-0.025	1.000	0.104

LDA+U

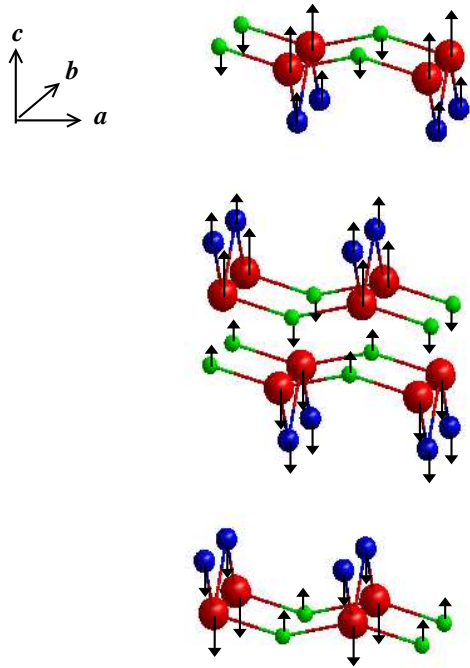
Expt.	Theory	Ti	O	Cl
203	192	0.557	-0.048	1.000
365	336	0.307	1.000	-0.213
430	407	-0.775	1.000	0.614



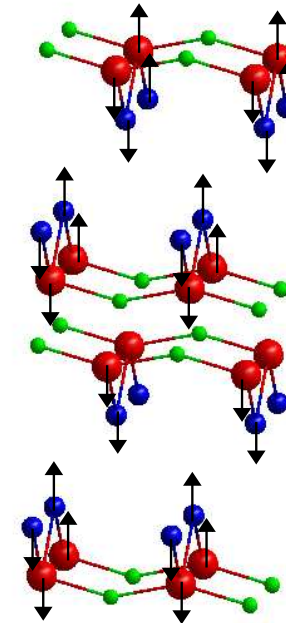
203cm⁻¹ (Ti-Cl in phase)

TiOCl, Phonons

- anomalous phonon (zone boundary) **Ti-Cl** in phase



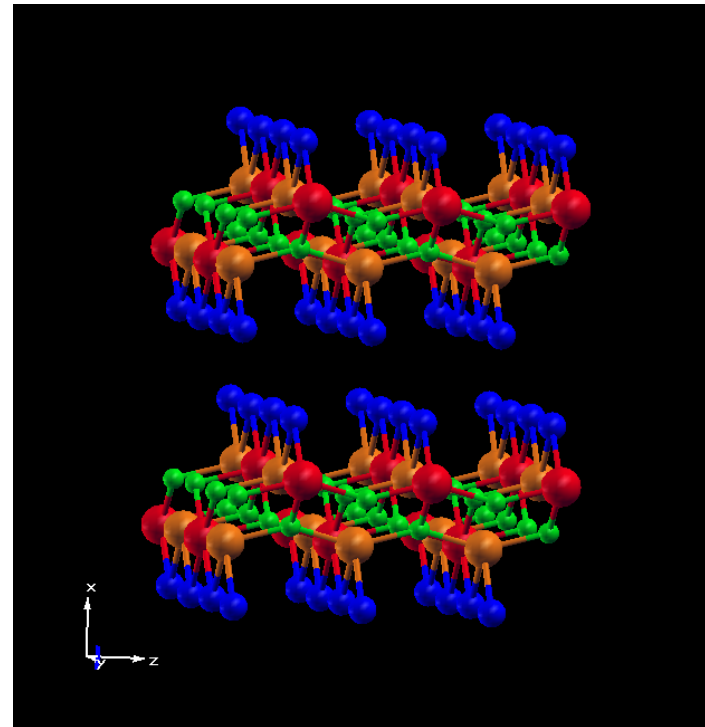
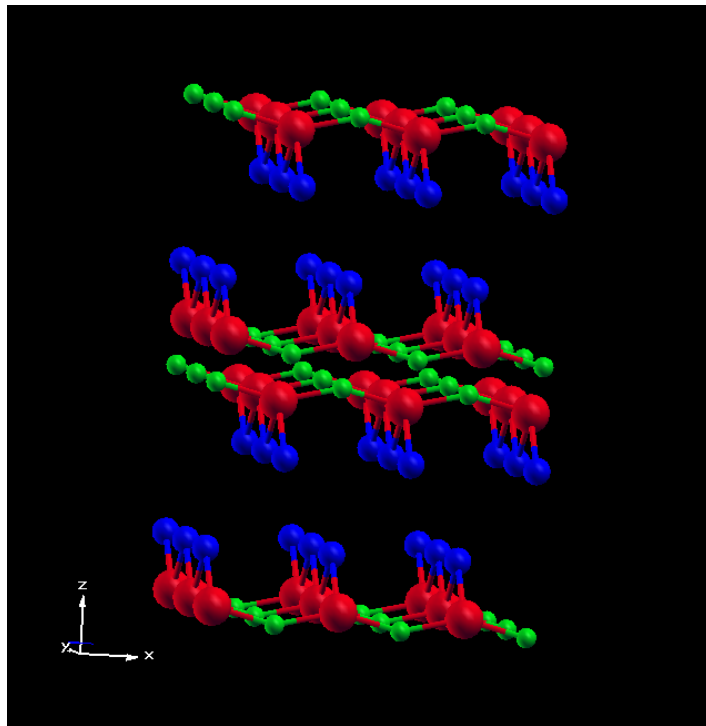
- unit-cell doubled along c
 a few % distortion \rightarrow
 occupation Ti d_{xz}, d_{yz}
 hint of orbital fluctuations only at very high T
T > 700K



- unit-cell doubled along b
 occupation of Ti d_{xy}

TiOCl, $T < 66$ K

- **magnetoelastic coupling** \rightarrow **spin-Peierls**
- crystal structure determined by van Smaalen's group M. Shaz *et al.* PRB (2004)
- Monoclinic space group $P2_1/m$.
- doubling of the unit cell along b



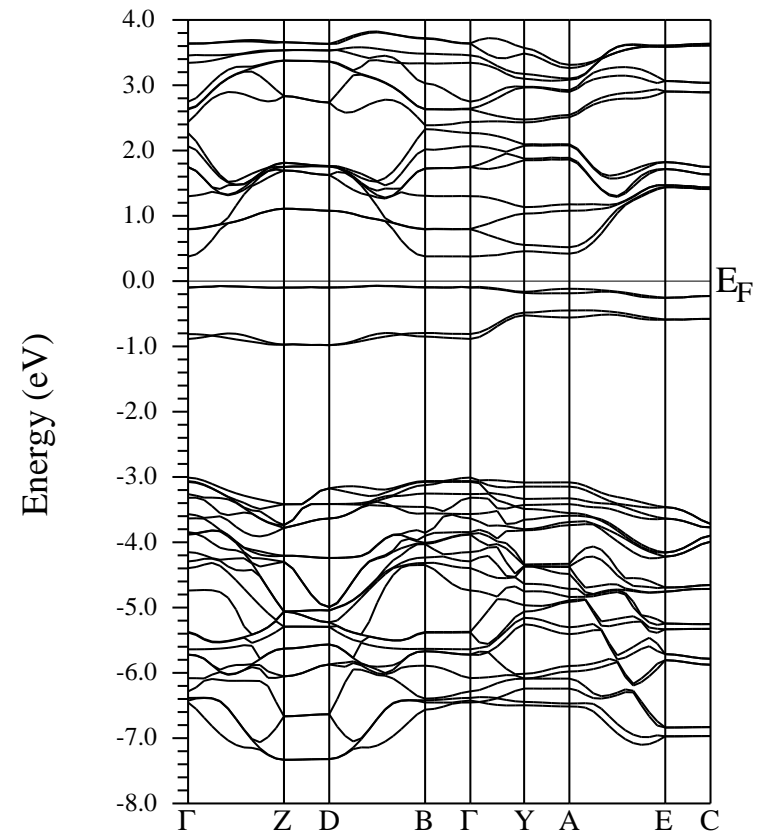
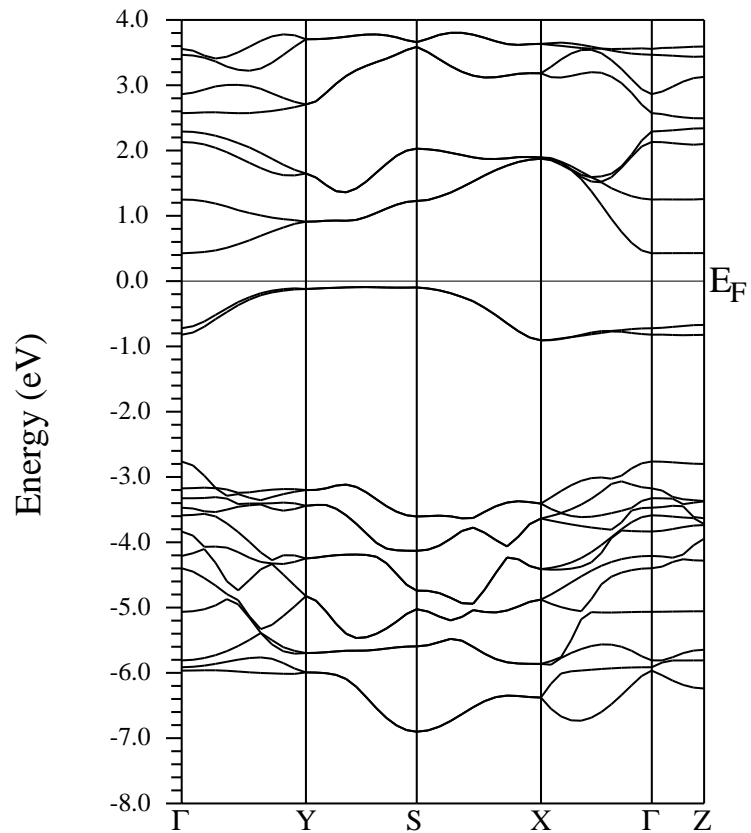
- $T > 100$ K uniform structure $T < 66$ K dimerized structure along b

TiOCl₂, comparison electronic structure

LDA+U

T > 94 K

T < 66 K



TiOCl:

- low-dimensional spin-1/2 quantum magnet
- Competing spin, orbital, lattice degrees of freedom
- anomalous spin-Peierls phase transition
- Analysis of the electronic structure, phonons:
 - ▶ orbital degrees of freedom quenched, occupation of Ti $3d_{xy}$ in the groundstate
 - ▶ electron correlation important: LDA+U, LDA+DMFT, LDA+c-DMFT
 - ▶ Mott insulator
- anomalous spin-Peierls → frustrated 2D lattice

ongoing work

- → Pressure-induced insulator-to-metal transition (Kuntscher *et al.* PRB '06)
- → doping effects