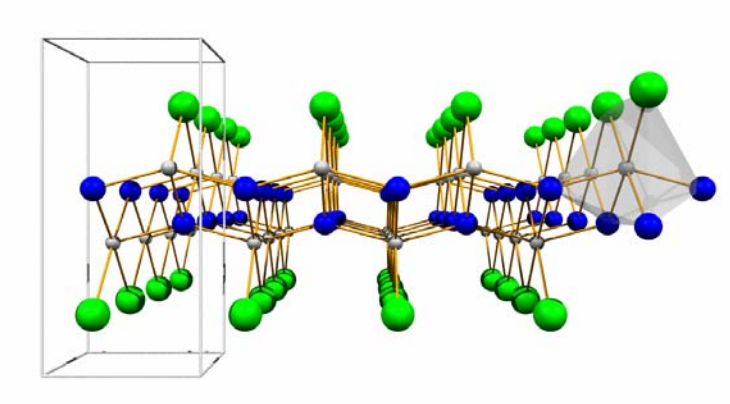
Unusual Spin-Peierls Physics in Oxyhalides

Michael Sing (U Würzburg)



M. Hoinkis (U Würzburg) S. Glawion M. Schlachter R. Claessen M. Klemm (U Augsburg) S. Horn	photoemission & crystals
H. Benthien (U Marburg) E. Jeckelmann (U Hannover)	DDMRG
T. Saha-Dasgupta (S. N. Bose Centre, Kolkata, India) L. Pisani (Imperial College, London, UK) R. Valenti (U Frankfurt/M)	LDA+U/LDA+DMFT
S. van Smaalen (U Bayreuth) A. Krimmel (U Augsburg)	structure
J. Deisenhofer (U Augsburg) J. Hemberger A. Loidl	ESR, specific heat
C. Kuntscher (U Augsburg)	optics under pressure

Outline:

- TiOCl(Br): a low-dimensional Mott insulator with magnetic frustrations
- phase transitions and unusual spin-Peierls scenario

  valence band DOS

  dispersions and anisotropy

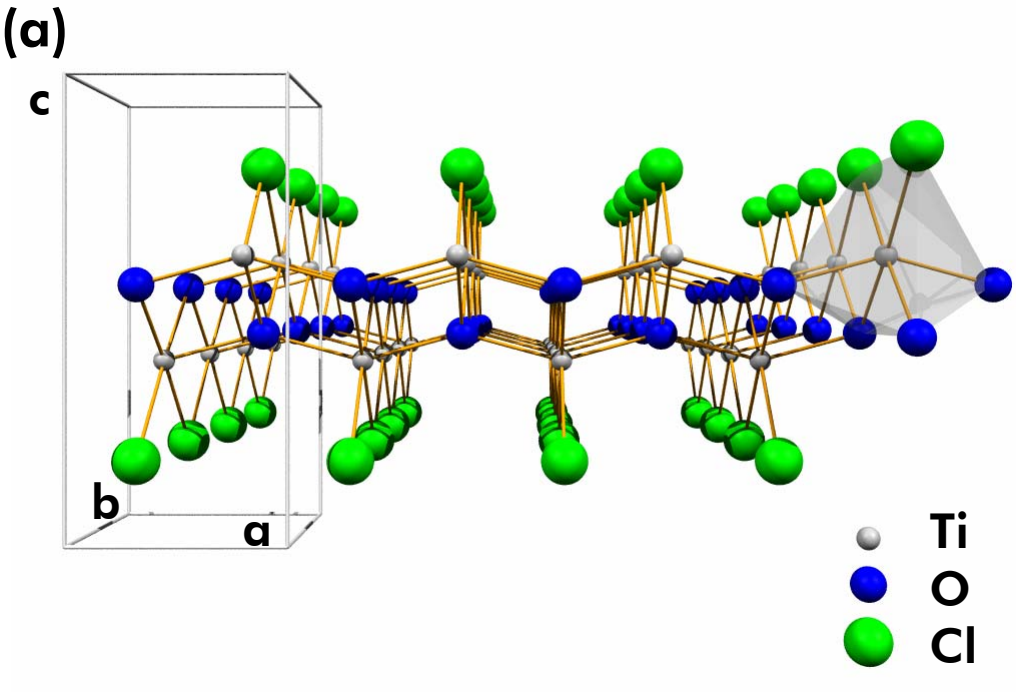
  orbital symmetry and fluctuations

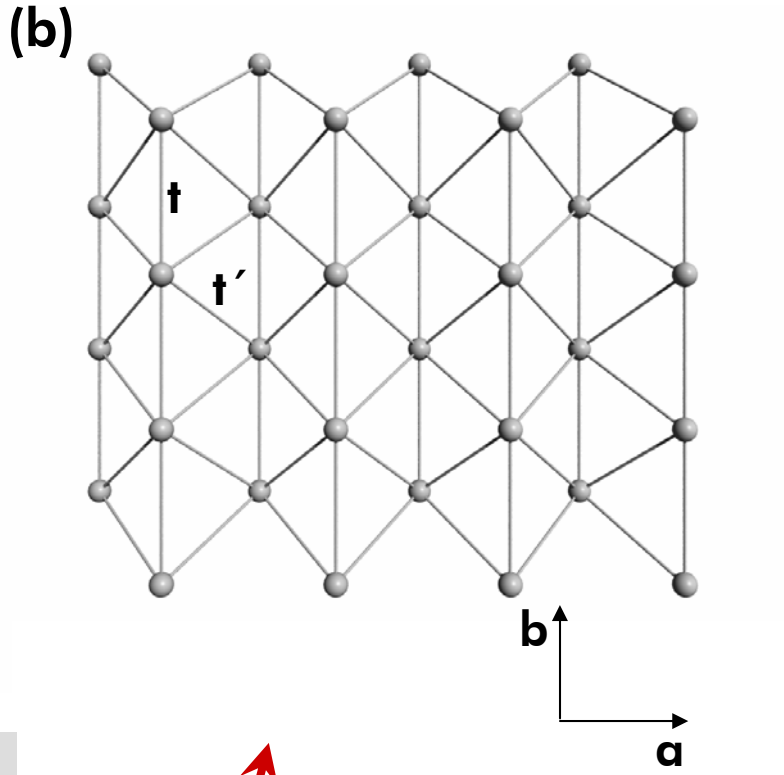
  n-type doping

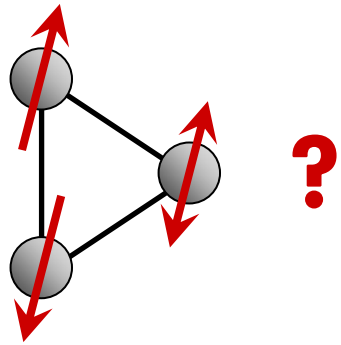
  } probed by photoemission

- summary

TiOCl: A low-dimensional Mott insulator







configuration: Ti $3d^1$

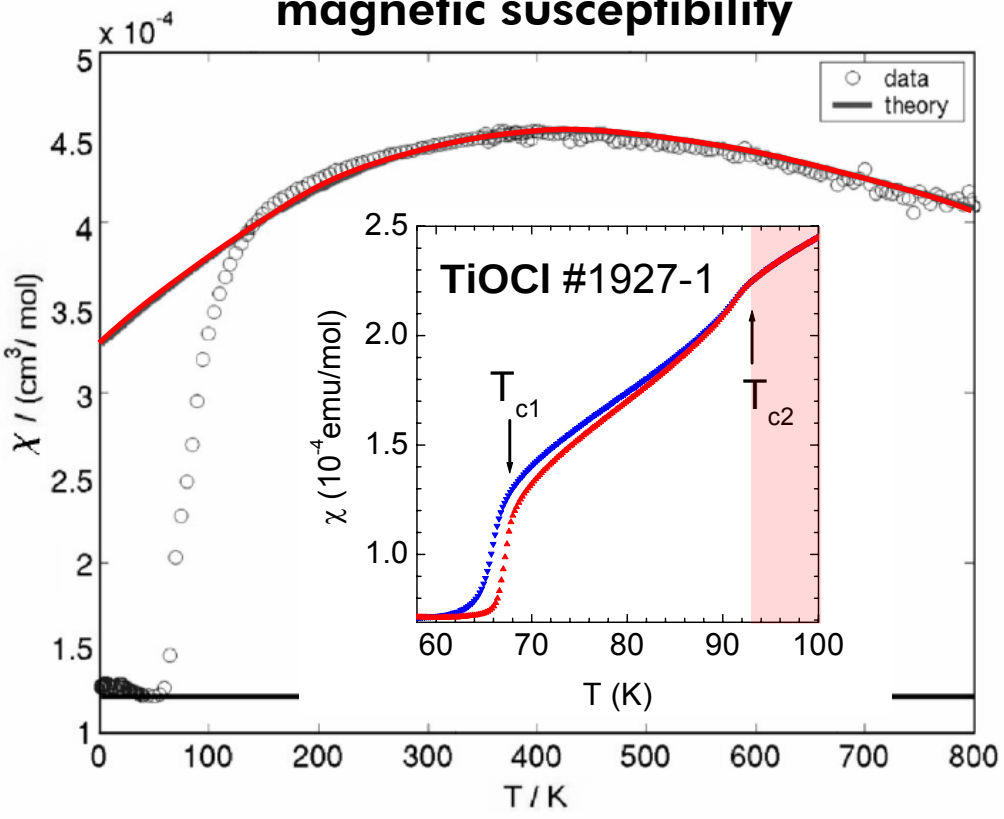
→ $1e^-$/atom: Mott insulator

→ local spin s=1/2

→ frustrated magnetism,
resonating valence bond (RVB) physics?

TiOCl: High temperature phase

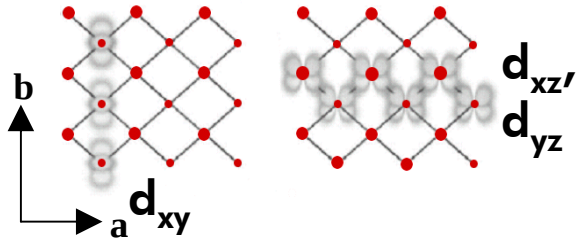
magnetic susceptibility



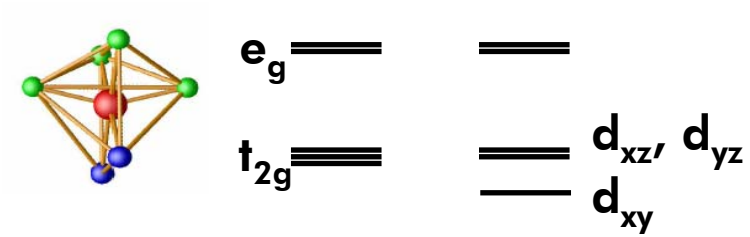
→ susceptibility of a 1D spin-1/2 chain

→ exchange constant: J ~ 660 K

electronic origin of 1D behavior?



band theory (LDA+U)

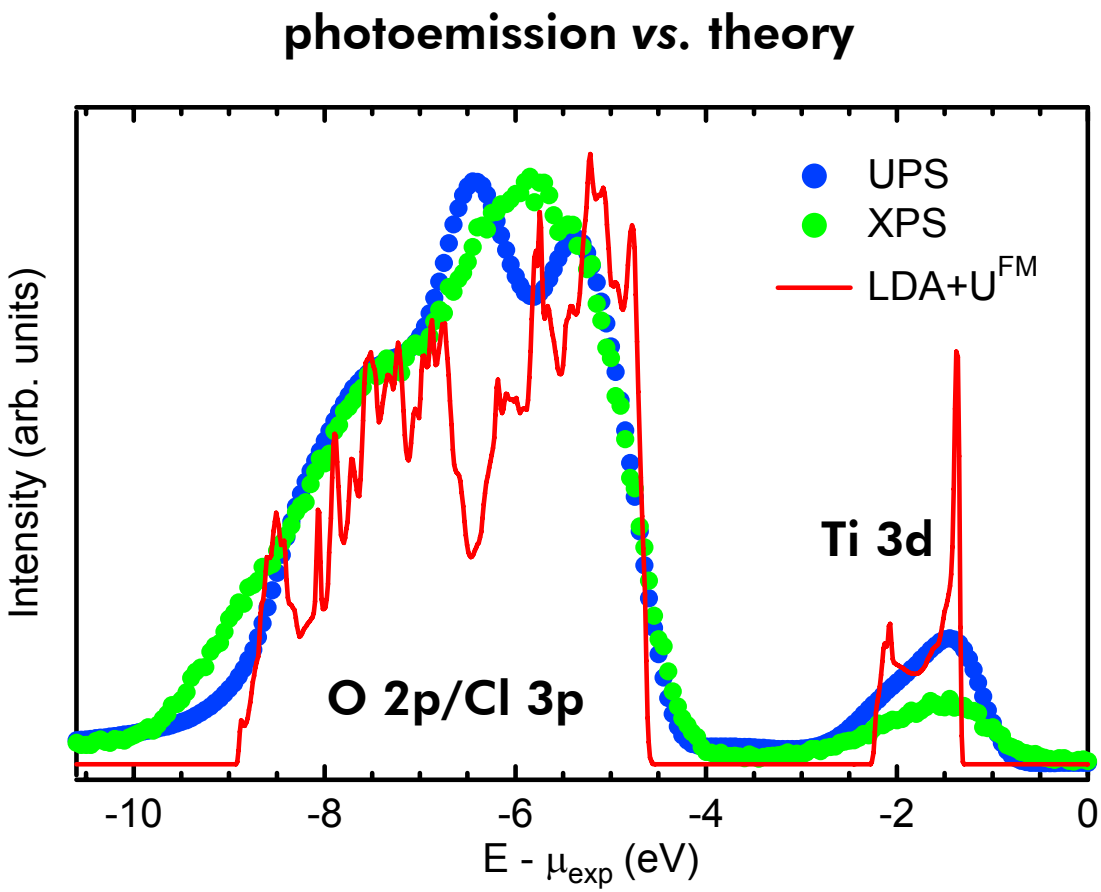


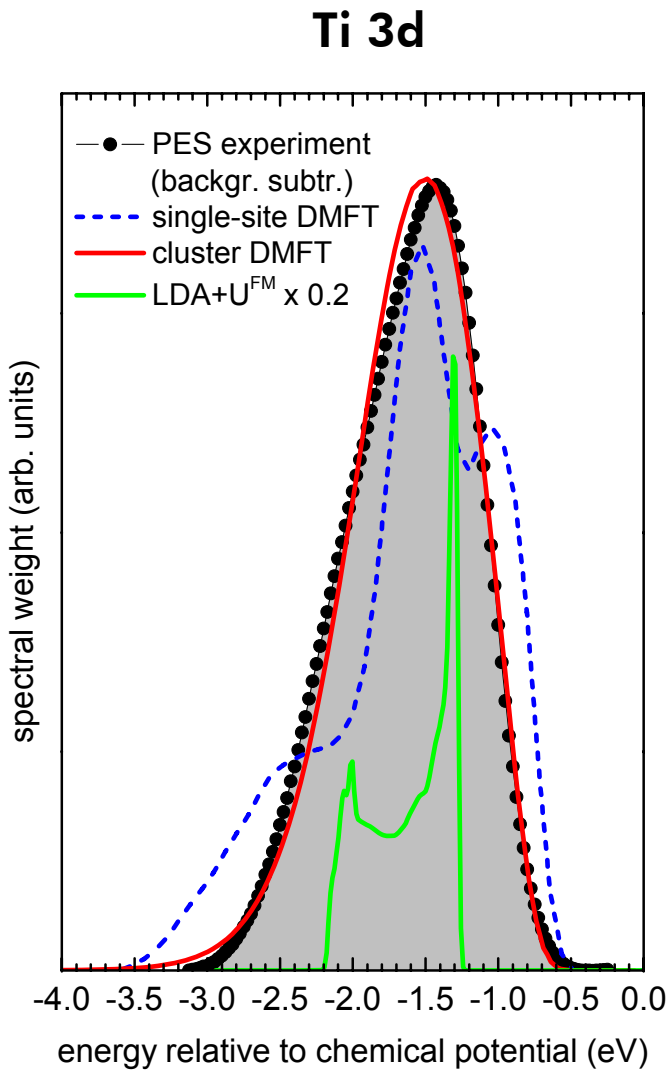
Seidel et al. (2003)
Valenti et al. (2004)

TiOCl: Electronic structure

*PRB **72**, 125127 (2005)*

with R. Valenti et al.



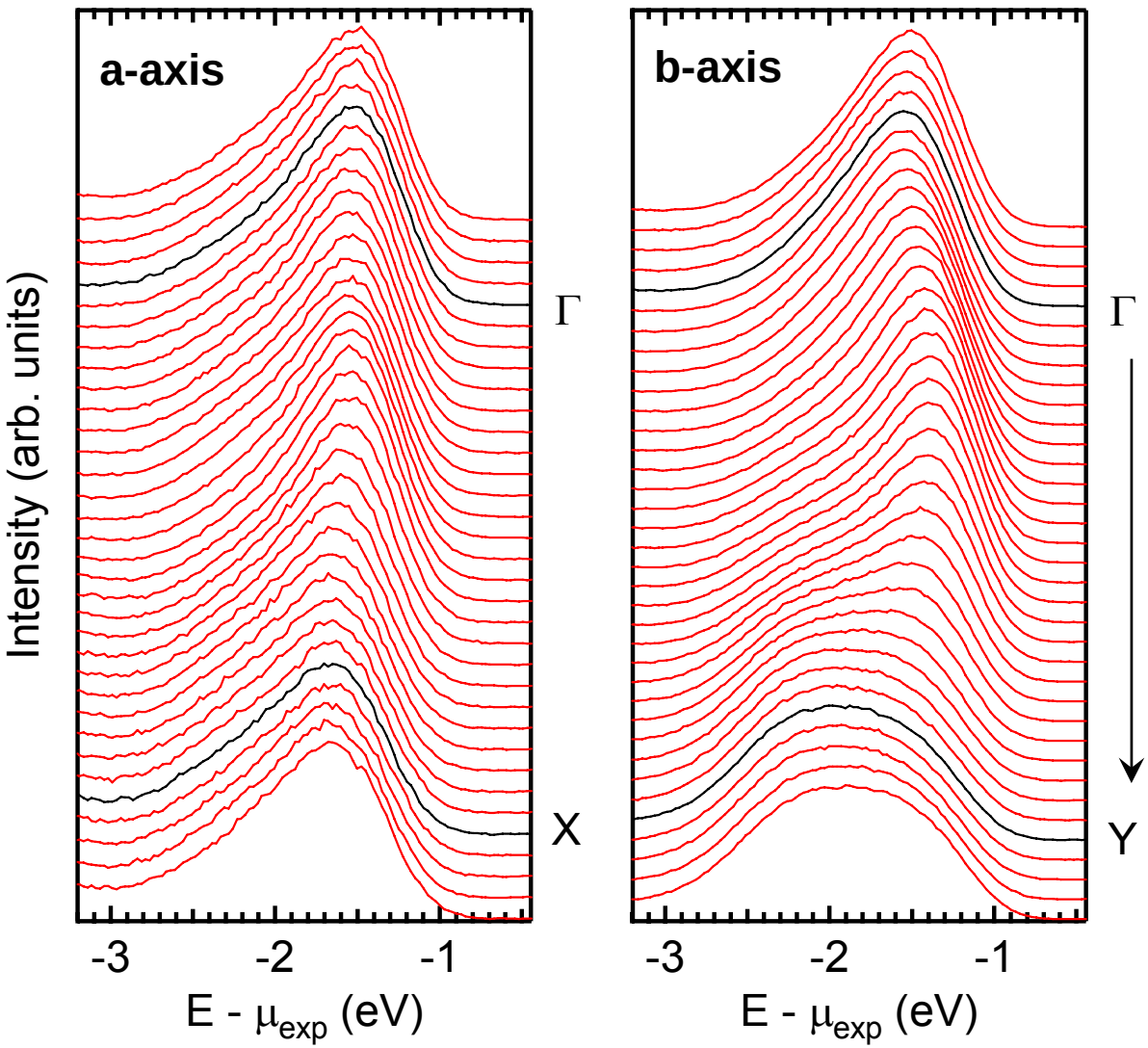


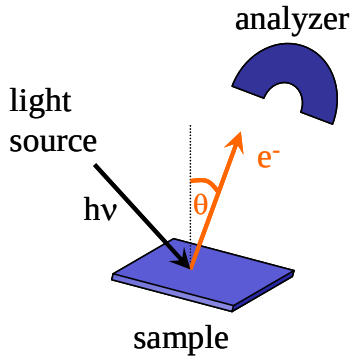
Cluster-DMFT

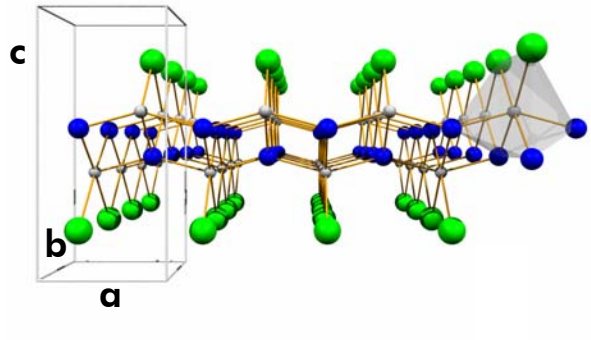
T. Saha-Dasgupta, A. Lichtenstein, R. Valenti et al. (2006)

TiOCl: ARPES on Ti 3d band

PRB ***72****, 125127 (2005)*







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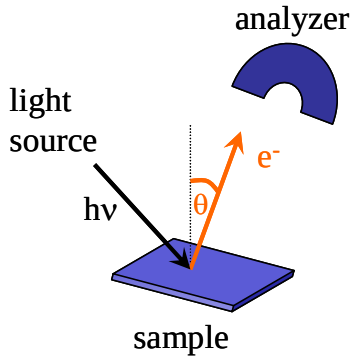
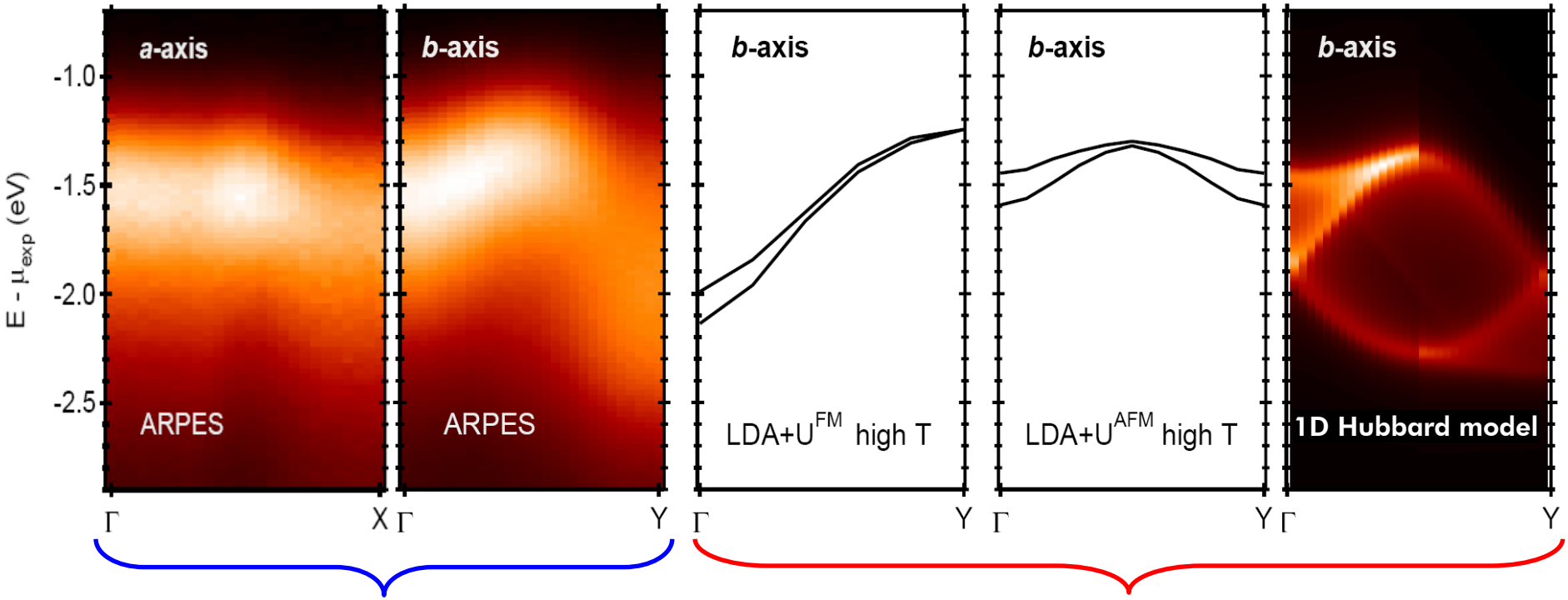
PRB ***72****, 125127 (2005)*

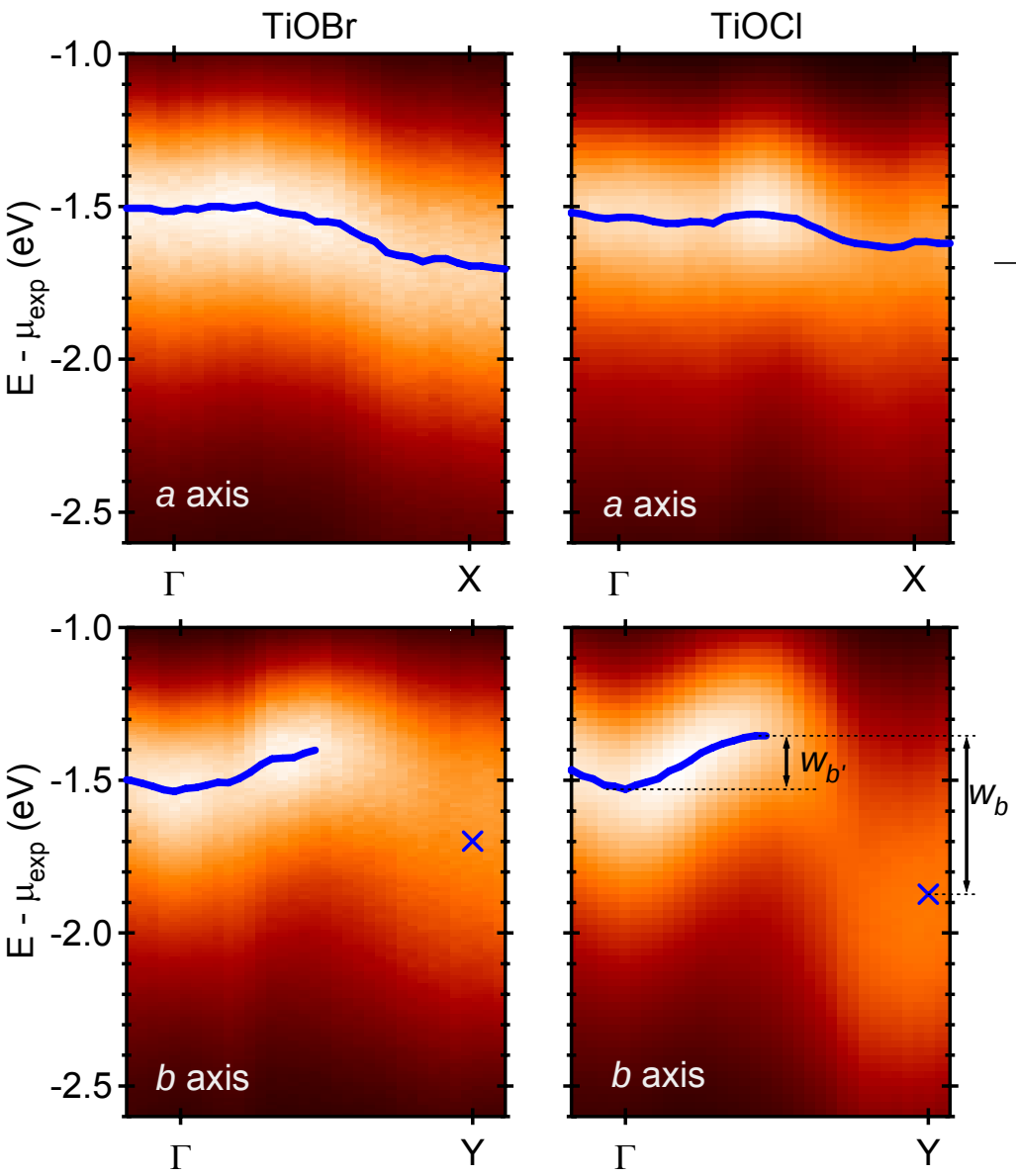




quasi-1D dispersion along b-axis

cannot explain experimental dispersion! (WHAT IS MISSING??)

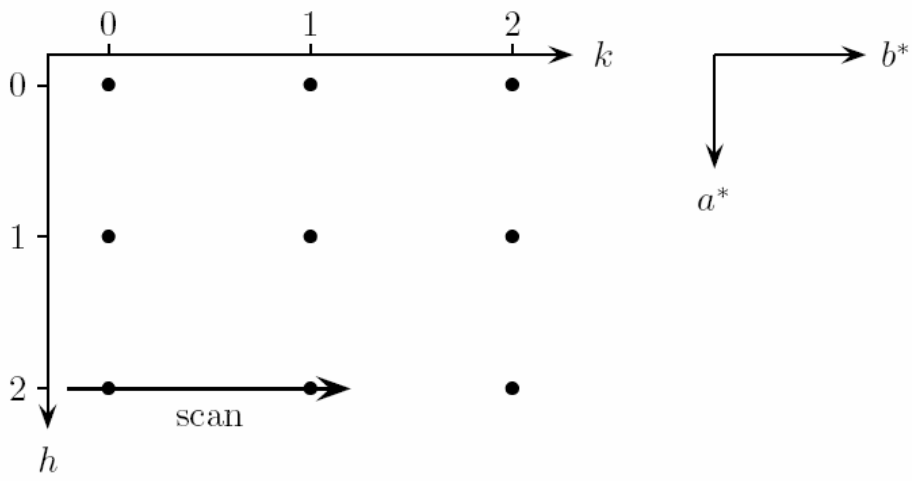
1D vs. 2D correlations

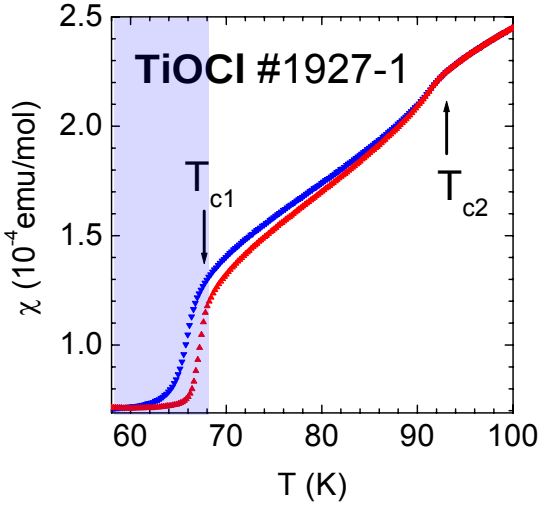


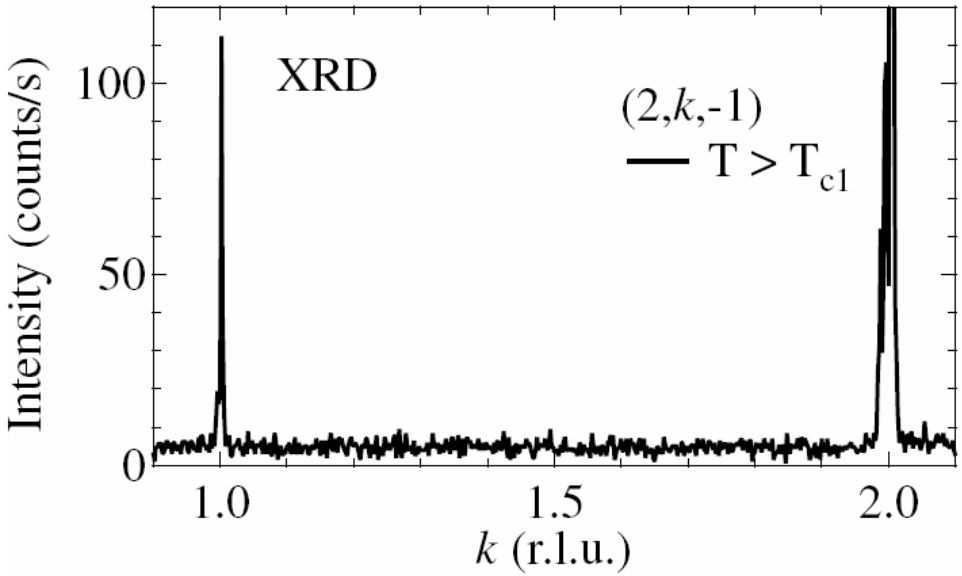
width	TiOBr	TiOCl
w_a	0.27(3) eV	0.12(3) eV
w_b	0.26(5) eV	0.47(5) eV
w_b'	0.13(1) eV	0.17(1) eV

- **TiOBr much less one-dimensional than TiOCl (cf. also susceptibility)**
- **dispersions around Γ scale with $\sqrt{J}$, *i*.e. the hopping probability *t* $\Rightarrow$ no generic 1D behavior**

TiOCl: Low temperature phase







*S. van Smaalen et al., PRB **71**, 100405(R) (2005)*

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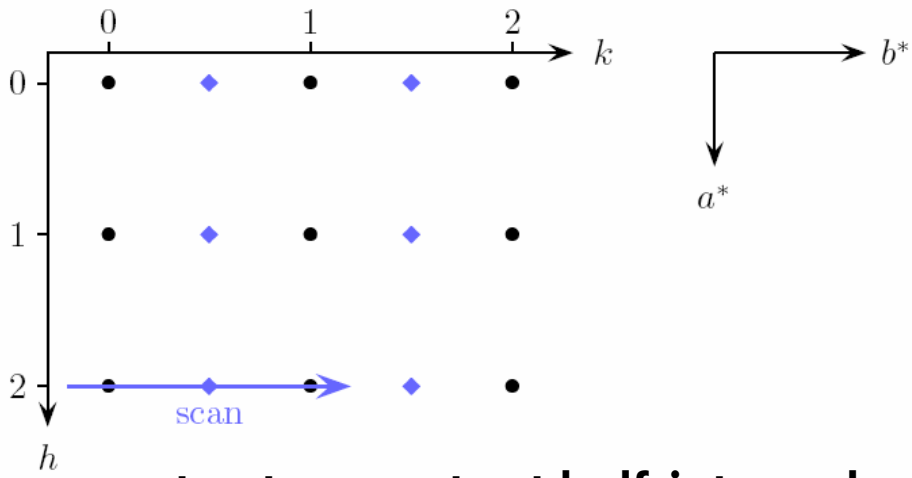
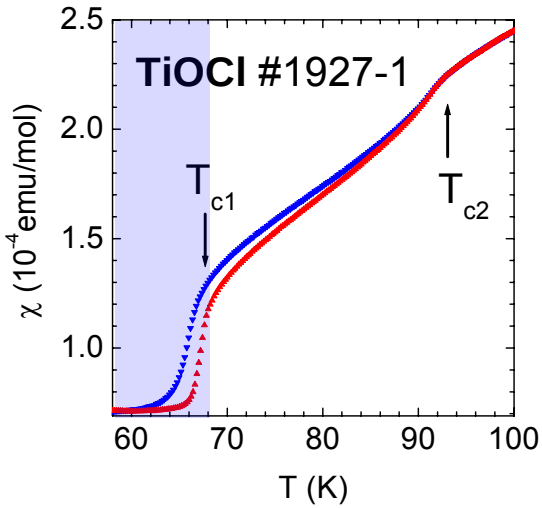
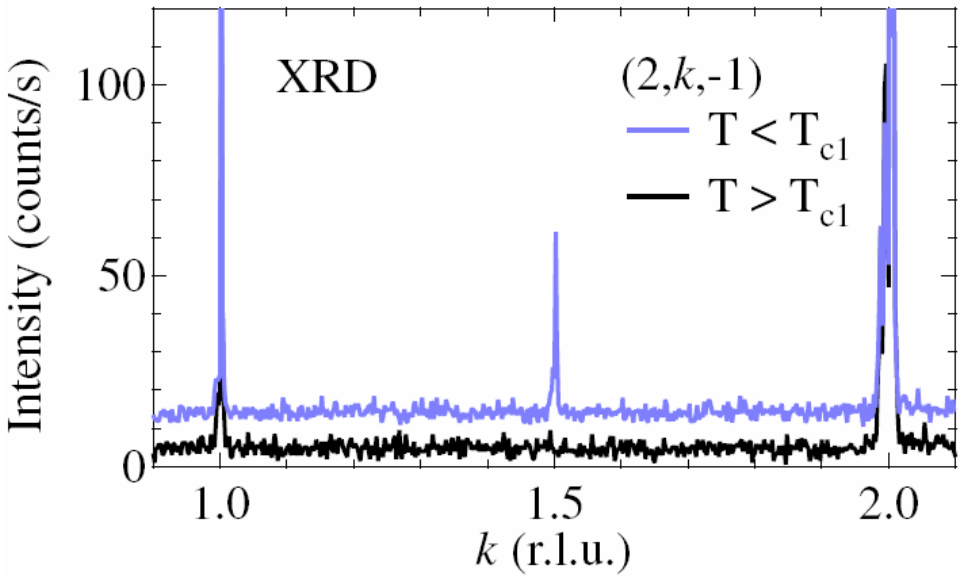
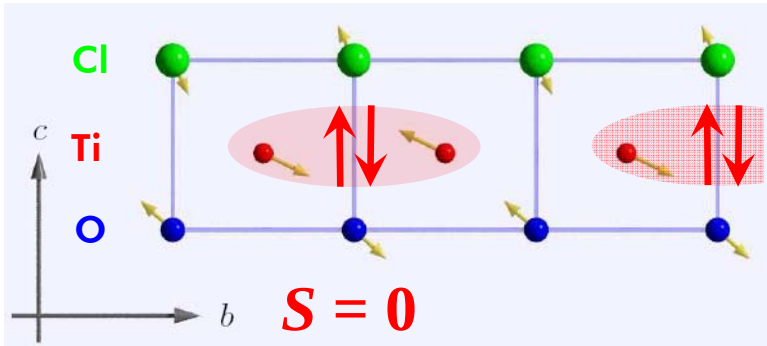


superstructure spots at half-integer k



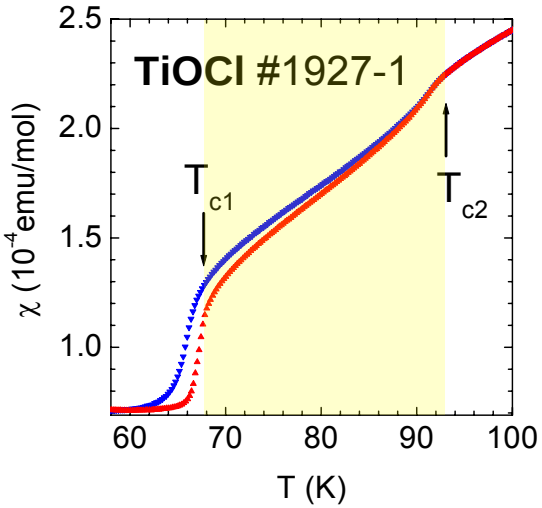




⇒ **dimerization and magneto-elastic coupling: spin-Peierls instability**

*S. van Smaalen et al., PRB **71**, 100405(R) (2005)*

TiOCl: Intermediate phase



(orbital) fluctuations?

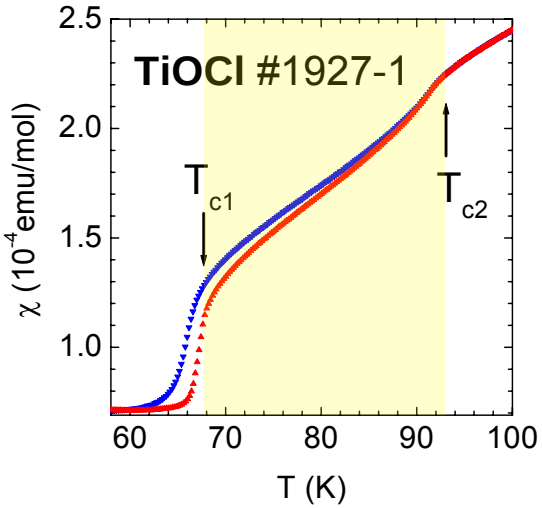
Raman scattering: anomalous phonon line broadening

NMR: pseudogap in spin excitation spectrum

specific heat: entropy at T_{c1} not fully released

LDA+U: phonon-induced admixture of d_{xz}/d_{yz} to d_{xy} ground state?

TiOCl: Intermediate phase



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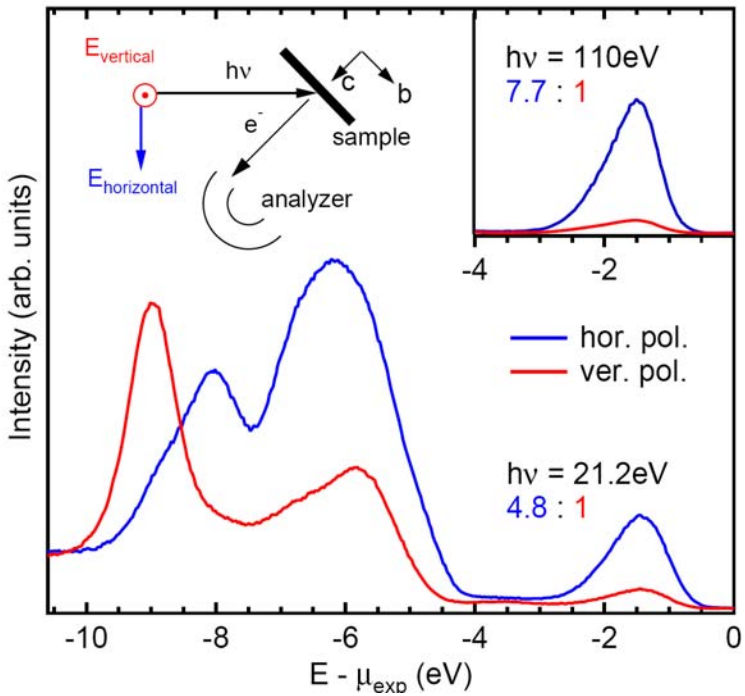
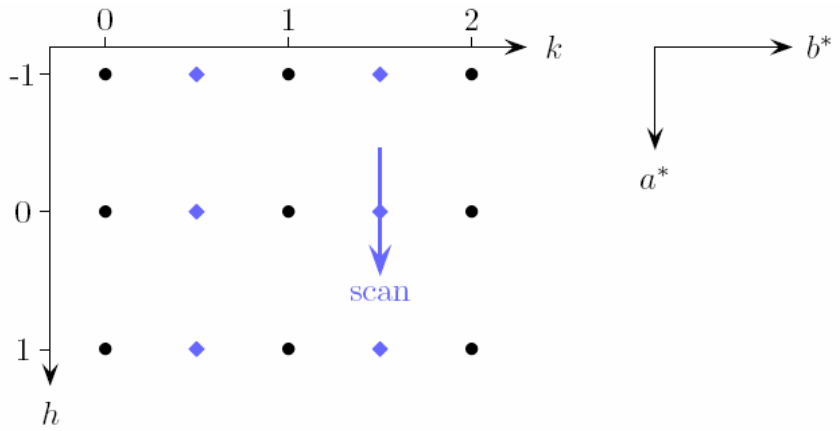


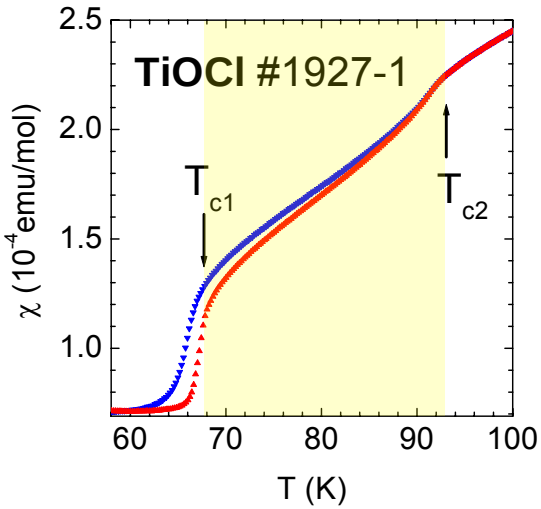
most likely not orbitals!

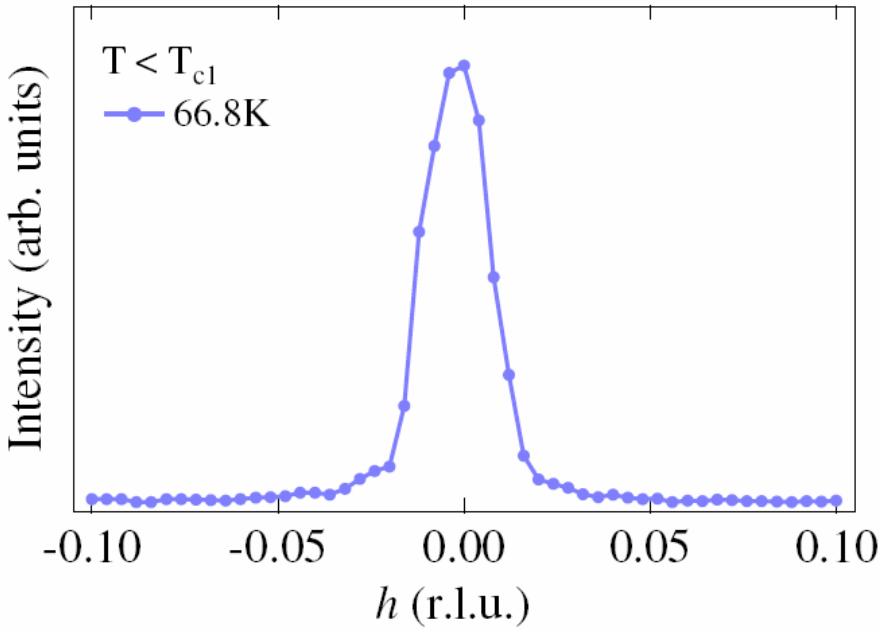
photoemission:
no admixture from other d-orbitals @ 300 K
PRB ***72****, 125127 (2005)*

optical spectroscopy+cluster calc:
pure d_{xy} ground state up to 100 K
Rückkamp et al., PRL ***95****, 097203 (2005)*

TiOCl: Intermediate phase

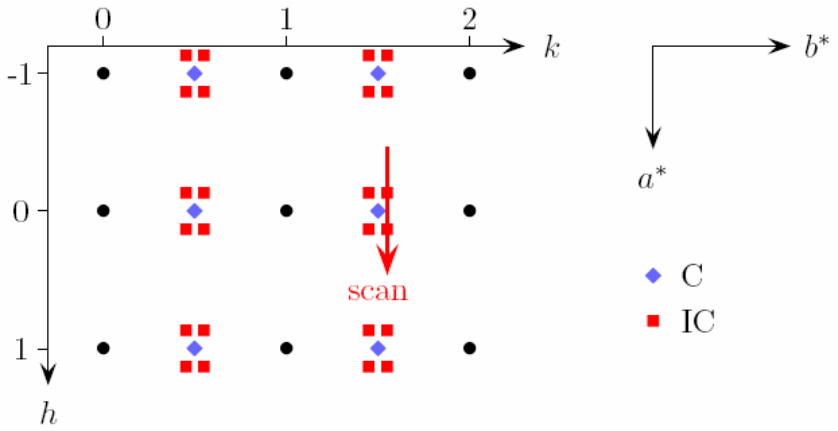


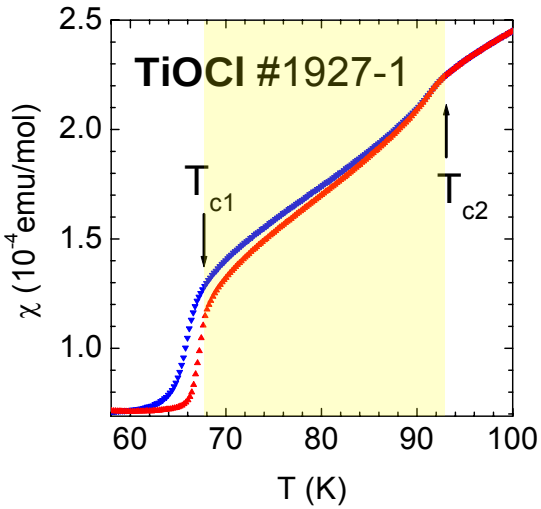




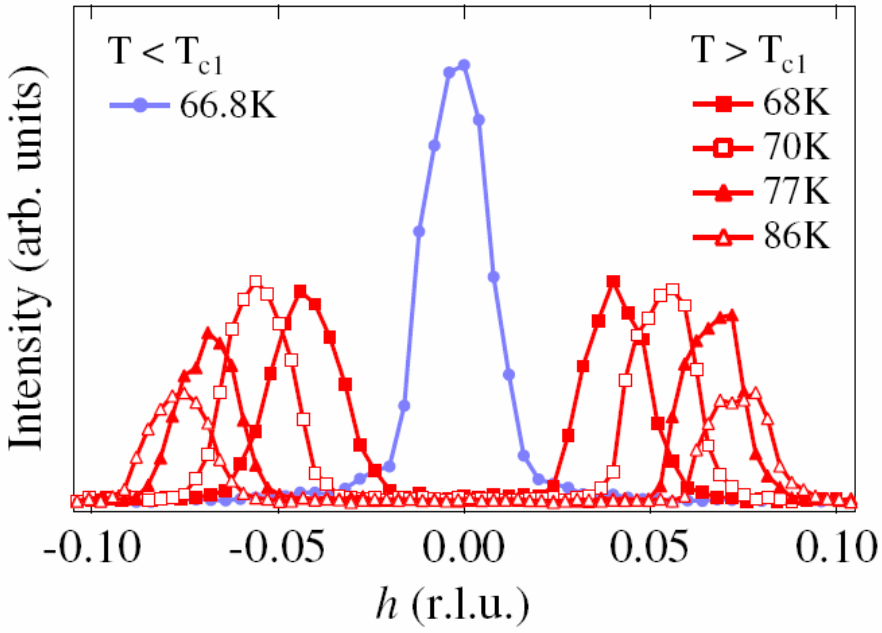
*A. Krimmel et al., PRB **73**, 172413 (2006)*

TiOCl: Intermediate phase





Incommensurate superstructure spots at $(\pm\delta, \frac{1}{2} \pm \epsilon, 0)$



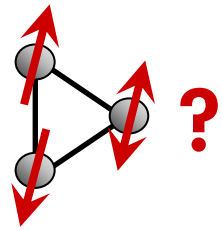
A. Krimmel et al., PRB ***73****, 172413 (2006)*

incommensurate spin-Peierls phase induced by frustrated interchain interaction?

Rückamp et al., PRL ***95****, 097203 (2005)*

⇒ (partial) restoration of RVB physics?

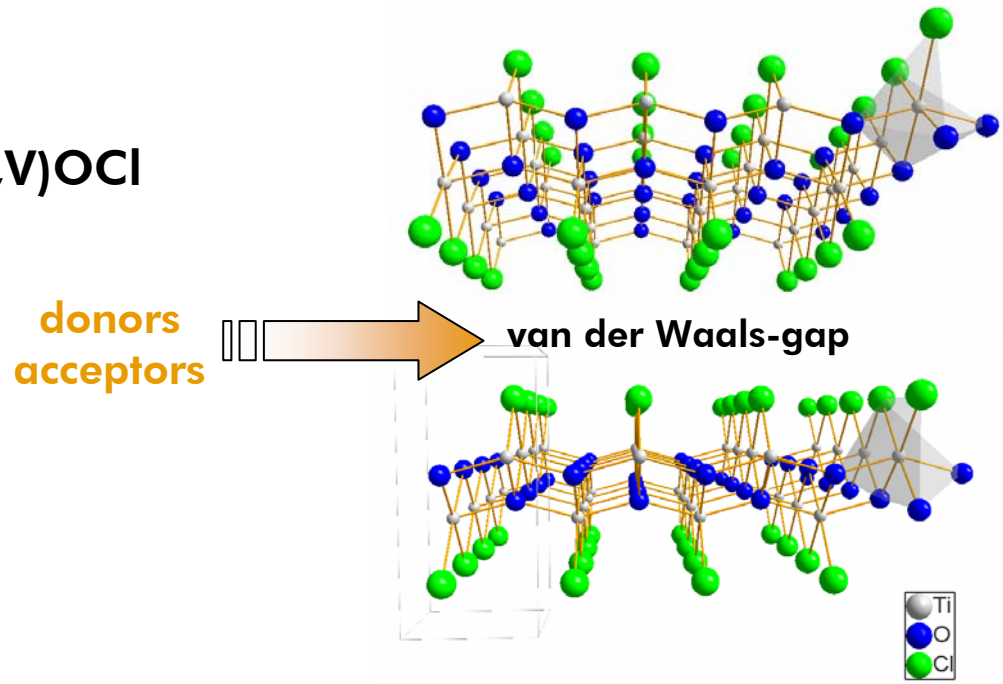
⇒ exotic supercon-ductivity, if driven into metallic state?



TiOCl: Doping and exotic superconductivity?

various routes towards doping:

- cation substitution: (Ti,Sc)OCl, (Ti,V)OCl
- anion substitution: Ti(O,N)Cl
- intercalation (electrochemically, wet-chemically, alkali metal evaporation)

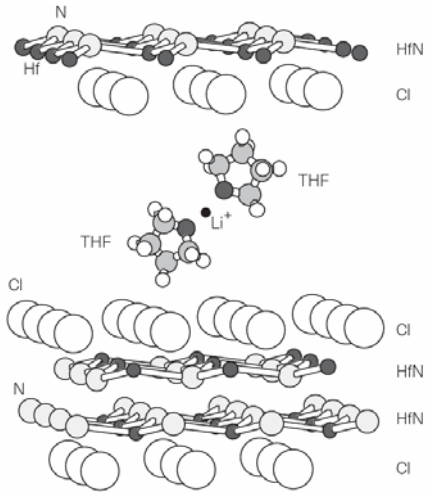


letters to nature

Superconductivity at 25.5 K in electron-doped layered hafnium nitride

Shoji Yamanaka*†, Ken-ichi Hotehama* & Hitoshi Kawaji*

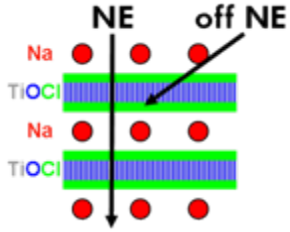
Nature **392**, 580 (1998)

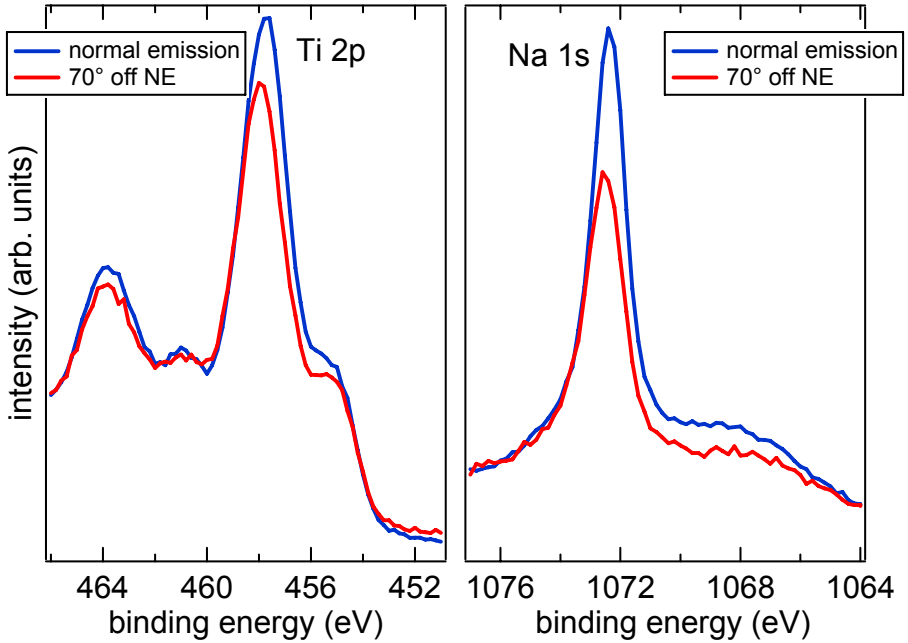


$Li_x(THF)_yHfNCl$

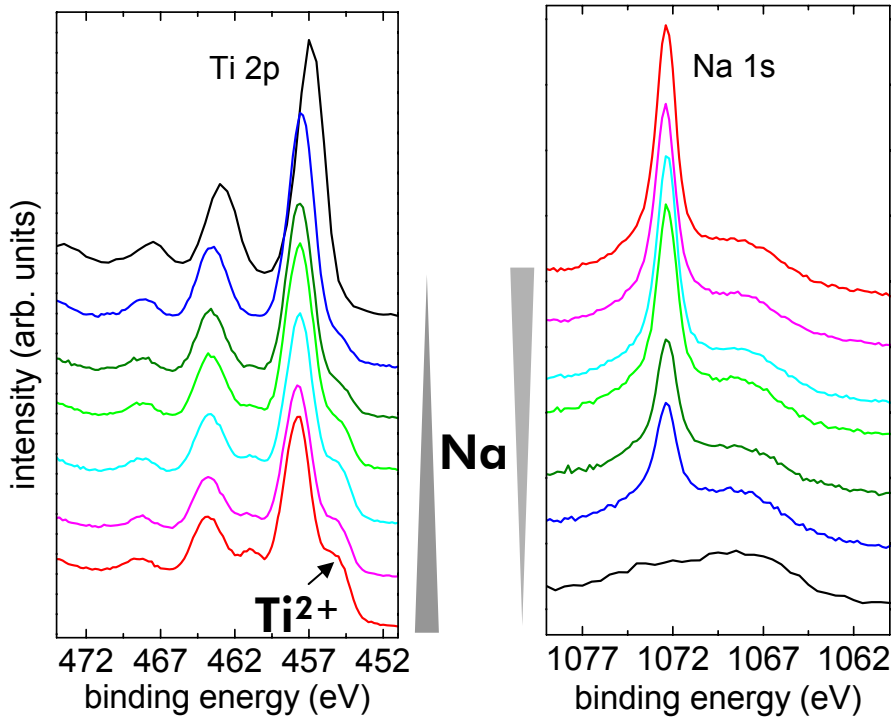
n-doping: Na surface layer?

angle-dependent XPS:





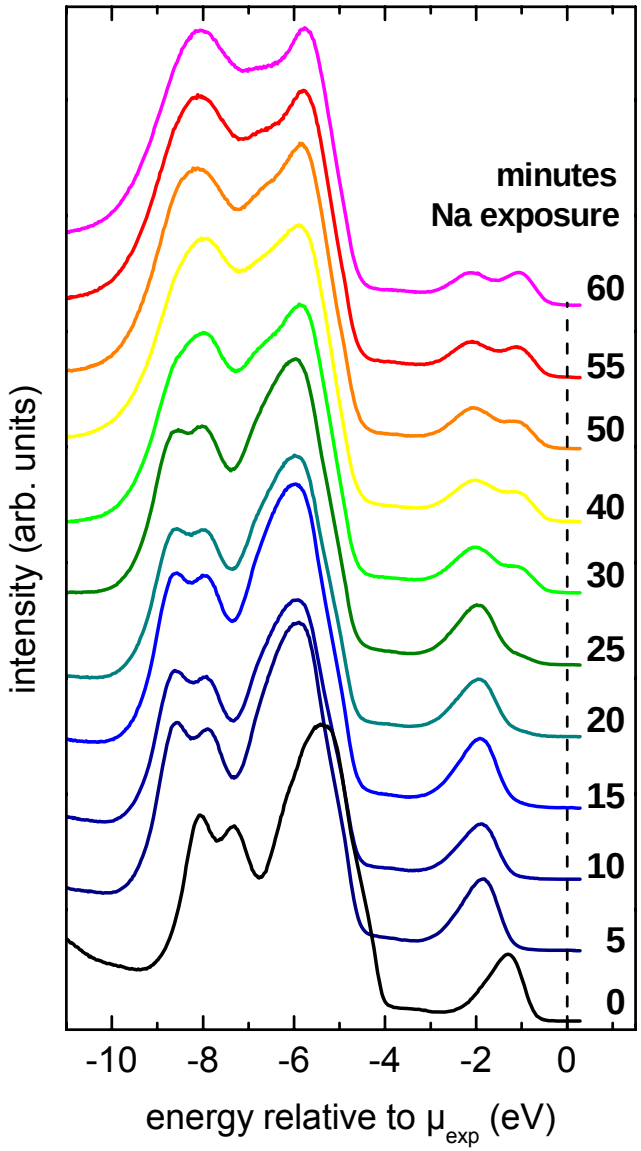
Ti^{2+}/Ti^{3+} vs. Na content



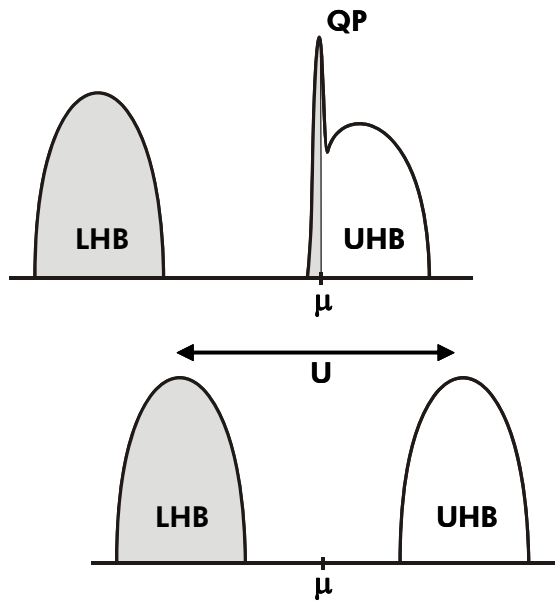
⇒ **no Na surface layer: Na atoms intercalate in van der Waals-gaps**

⇒ **Ti^{2+}/Ti^{3+} scales with Na content: charge transfer Na → Ti**

Intercalation with alkaline metals: ARPES



most simple picture

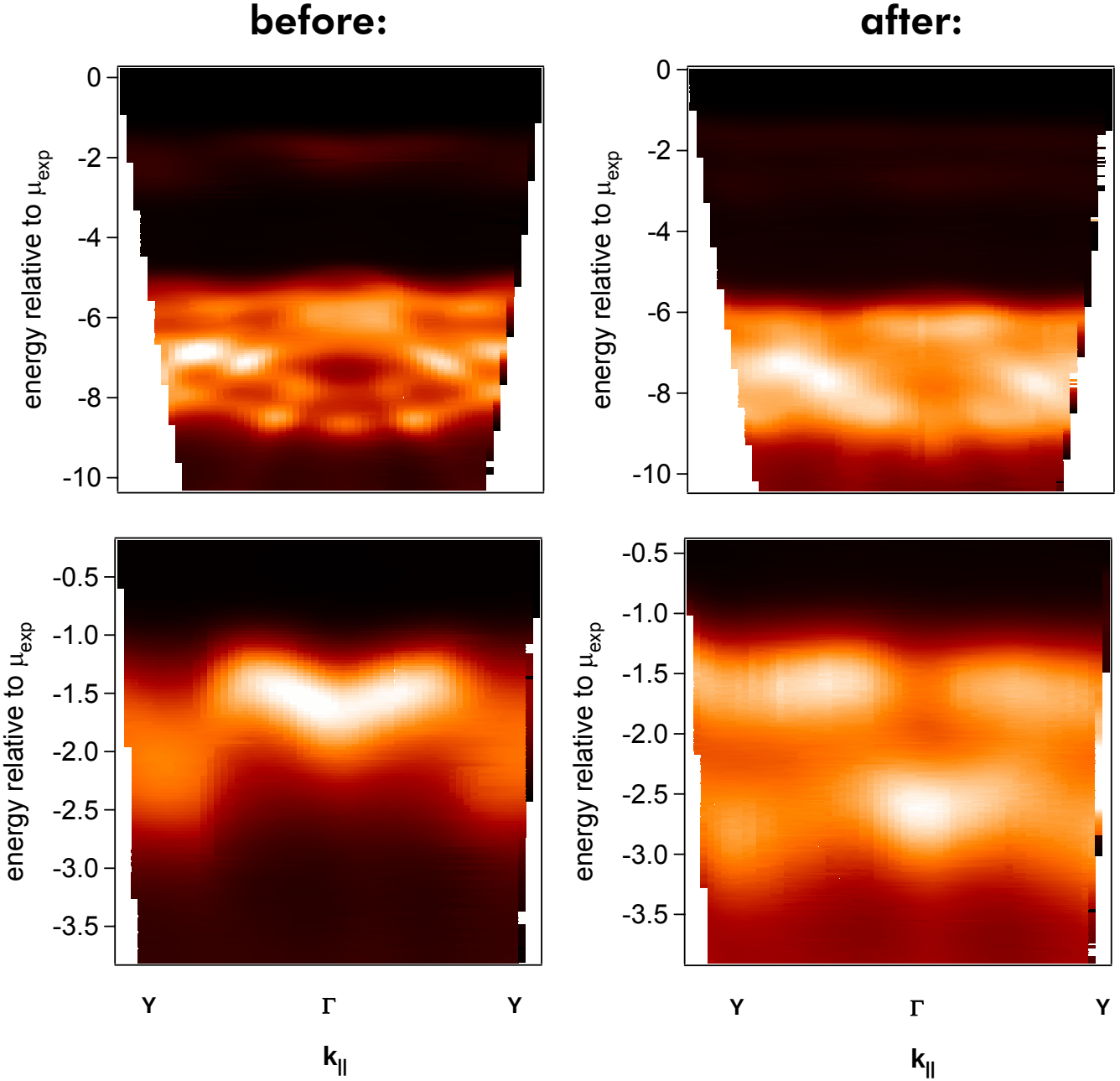


but:

- μ not pinned at about half the charge gap
- no spectral weight at μ (no QP)
- complex scaling of Ti 3d components upon doping (transfer of spectral weight?)

⇒ **multiorbital/multiplet effects important**

n-doping: effects on dispersion



- dispersions preserved
- emergence of new states in gap region: origin? incipient MIT?

Summary

Unusual Spin-Peierls Physics in Oxyhalides

- magnetoelastic coupling in 1D
- ARPES data mysterious (not generic 1D)
- incommensurable phase due to frustrated interchain coupling
- exotic superconductivity in doped spin liquid?
  n-doping not successful so far (multiplet effects)
  physics upon p-doping probably simpler