Spin-singlet nature of various dimerized cuprates. From *ab-initio* to experiment.

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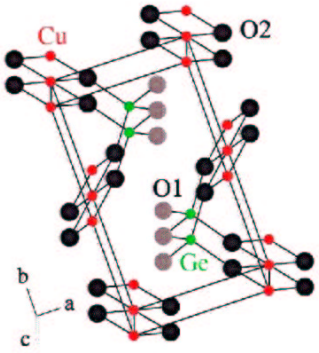
Outline

- **Motivation - Systems**
- **Dimerized-cuprates, why are they interesting?**
  - $CaCuGe_2O_6$ -related to $CuGeO_3$-
  - $KCuCl_3$ and $TlCuCl_3$
- **Microscopic description:** *ab-initio* **+ QMC**
- **Summary and Conclusions**

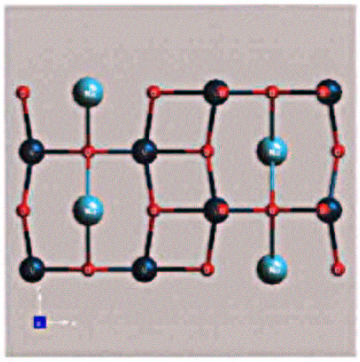
Low-dimensional transition-metal compounds

- Cuprates:



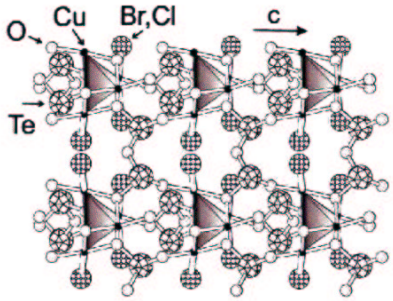
$CuGeO_3$

- Vanadates:



NaV_2O_5

- Tellurates:



$Cu_2Te_2O_5Br_2$

Properties: Spin-Peierls phase transition, Frustration, Charge-ordering, Quantum-critical behavior, superconductivity, ...

– **Electron correlation important** –

Methods

- **Density Functional Theory**.- Electronic Structure

↓ + Electron correlation

Effective Model Hubbard, Heisenberg, t-J,..

↓

- **Many-Body techniques**.- Bond-Operator Theory, Variational Ansätze, DMRG, QMC, ...

↓

Physical Picture

Dimerized Cuprates, why are they interesting?

Quantum spin systems with a singlet-triplet gap
in the spin excitation spectrum

- close gap by a strong enough H.
  Some dimers are promoted to triplets.
  These triplets behave as a gas of quantum particles.
  They can undergo different kinds of phase transitions
  as a function of H or T depending on topology, dimension, ...

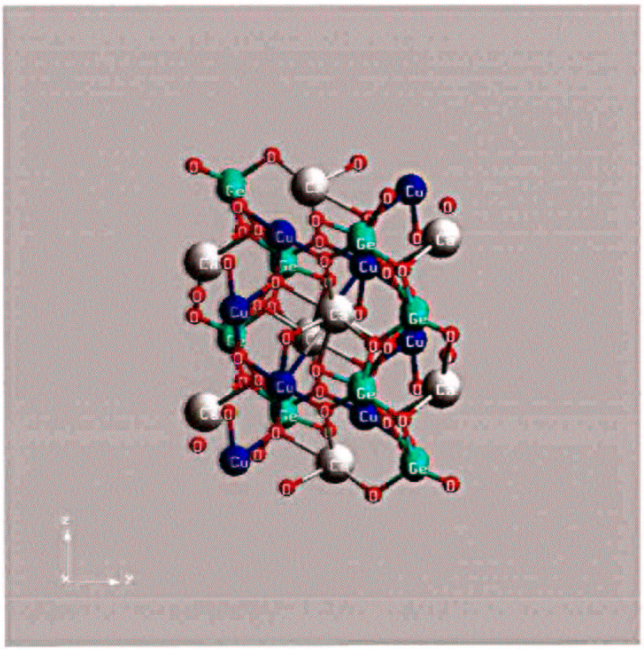
→ **rich physics!**

... often true nature of the exchange networks,
not expected from the crystal structure...

→ **microscopic investigation** *ab-initio* **+ QMC**

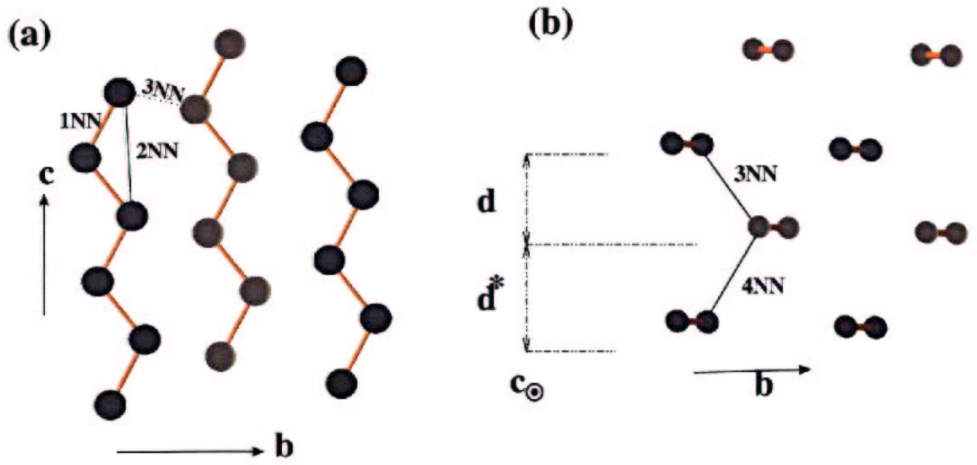
Examples: $CaCuGe_2O_6$, $TlCuCl_3$ and $KCuCl_3$

$CaCuGe_2O_6$ - Structure



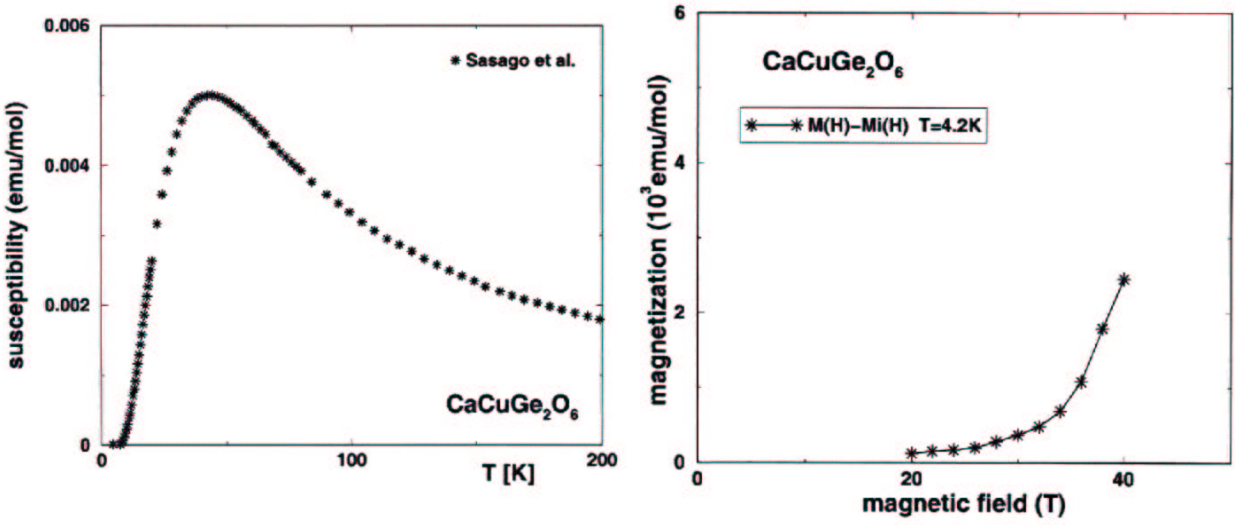
- space group $P2_1/c$
- CuO_6-zigzag chains along c

$CaCuGe_2O_6$ - Structure



- Cu^{2+}-chains alternate between two neighboring *bc* planes (black and grey)
- dist(1NN)=3.07Å, d=4.46Å, d*=5.35Å

$CaCuGe_2O_6$- Magnetism



- spin-singlet ground state with an energy gap
- INS (Zheludev *et al.*) energy gap $\sim$ 6 meV
- no spin-Peierls phase transition

Microscopic model?

Which Cu-pairs can constitute AF dimers?

$\longrightarrow$ *ab-initio*

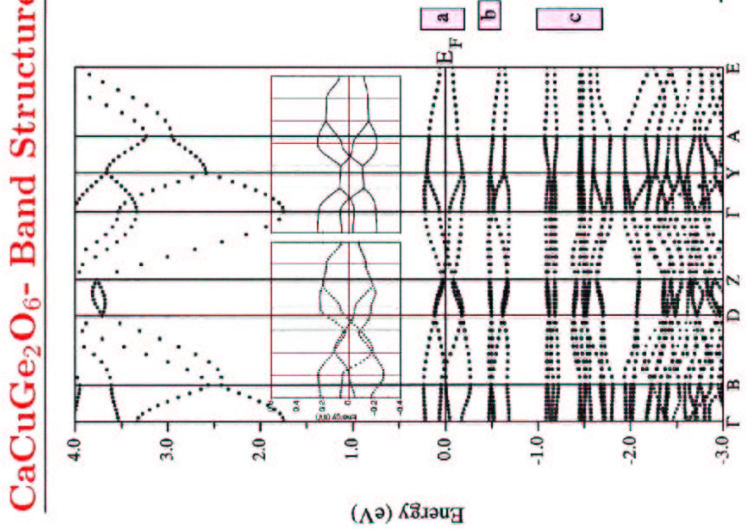
$\downarrow$

Effective Model

$\downarrow$

Thermodynamic properties

$CaCuGe_2O_6$- Band Structure



LAPW and LMTO scheme (GGA)

- a= Cu $3d_{x^2-y^2}$
- b= Cu $3d_{3z^2-1}$
- c=Cu $3d_{xy}$, $3d_{xz}$, $3d_{yz}$

- *downfolded*-TB Model:

$H_{TB} = \sum_{(i,j)} t_{ij}(c_i^\dagger c_j + H.c.)$

t_{1NN}= 68meV, t_{2NN}= 8meV

t_{3NN}= **88meV**, t_{4NN}= 4meV

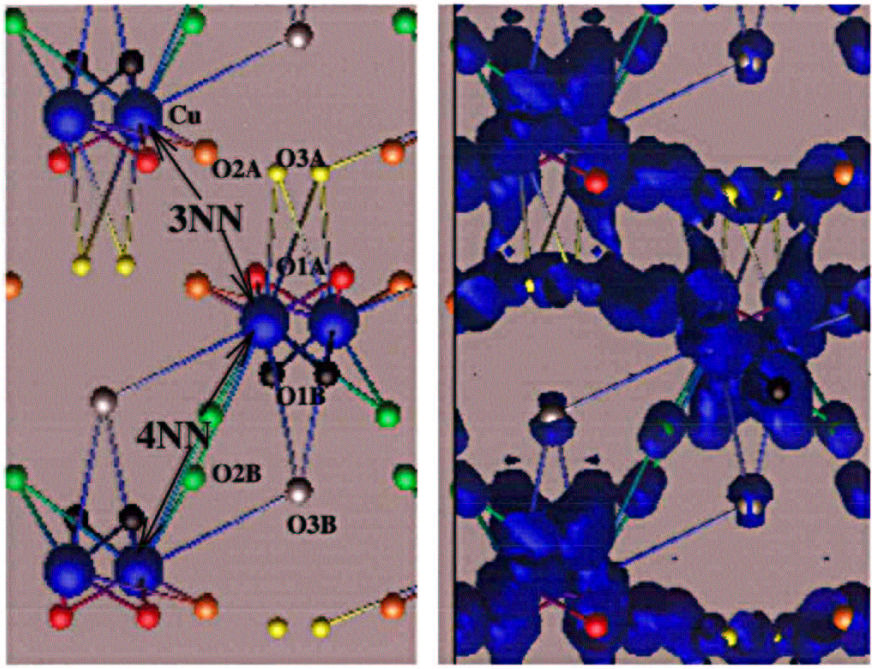
-system of interacting dimers -

dimers: $J_3 \sim 4\frac{t_{3NN}^2}{U}$, $U \sim 4.2$eV,

$J_3 \sim$ **85K** $\sim$ **7mev**

- *longer-ranged* magnetic interactions dominate over *short-ranged* interactions -

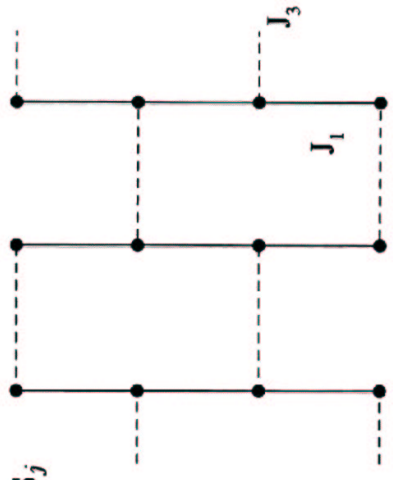
$CaCuGe_2O_6$- Electron Density



$CaCuGe_2O_6$- Spin-Model

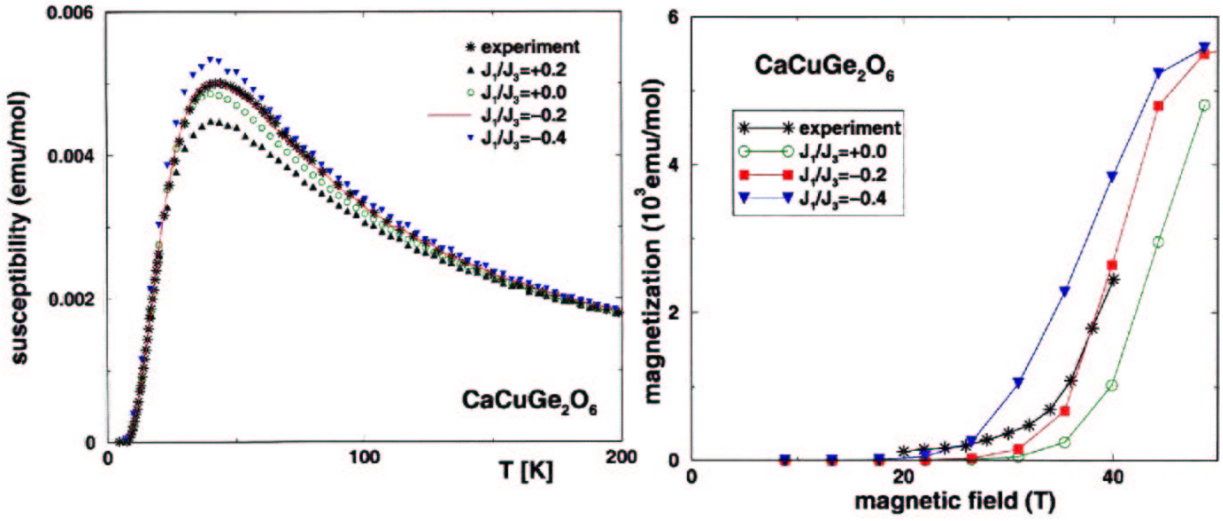
System of interacting dimers

$$H_{eff} = J_3 \sum_{<i,j>} \mathbf{S}_i\mathbf{S}_j + J_1 \sum_{(i,j)} \mathbf{S}_i\mathbf{S}_j$$



→ calculation of thermodynamic properties
by QMC (stochastic series expansion)

$CaCuGe_2O_6$- Magnetism



- Optimal value J_1/J_3= -0.2, J_3= 67K= 5.8meV ⇒
  - weak ferromagnetic interdimer coupling $J_1 < 0$ -
- The model has two quantum critical points $J_1 \simeq 0.55 J_3$, $J_1 \simeq$ -$0.9 J_3$

Order of Magnitude - Comparison with $CuGeO_3$

$CaCuGe_2O_6$:

ab-initio + Examination of χ and M by QMC ⇒

- system of dimers formed by 3NN s=$\frac{1}{2}$ Cu^{2+} with FM 1NN interdimer couplings $\mathbf{J_1/J_3} \sim$ -0.2.

  $\mathbf{J_3}$(*ab-initio*) ∼7meV, $\mathbf{J_3}$(QMC) =5.8meV

  FM $\mathbf{J_1}$ $\alpha_{Cu-O-Cu}$=92^o, $\beta_{Cu-O-Cu}$=98^o

- no spin-Peierls phase transition

$CuGeO_3$:

- Frustrated $\mathbf{J_1}$-$\mathbf{J_2}$ system + spin-Peierls phase transition

  $\mathbf{J_1}$ ∼10.3meV, $\mathbf{J_2/J_1}$∼0.24-0.34

Spin-gap systems $KCuCl_3$ and $TlCuCl_3$

- Isostructural $P2_1/c$
- **INS** (Cavadini *et al.* ('00) Tanaka *et al.* ('01) Oosawa *et al.* ('02)):

$TlCuCl_3$:

- spin excitation gap $\Delta \sim 0.65$meV
- *strongly*-coupled spin-dimer system
- Néel ordering for H > $H_g = \Delta/g\mu_B \sim 6$T BEC of magnons

$KCuCl_3$:

- spin excitation gap $\Delta \sim 2.6$meV
- *weakly*-coupled spin-dimer system
- Néel ordering for H > $H_g = \Delta/g\mu_B \sim 22$T

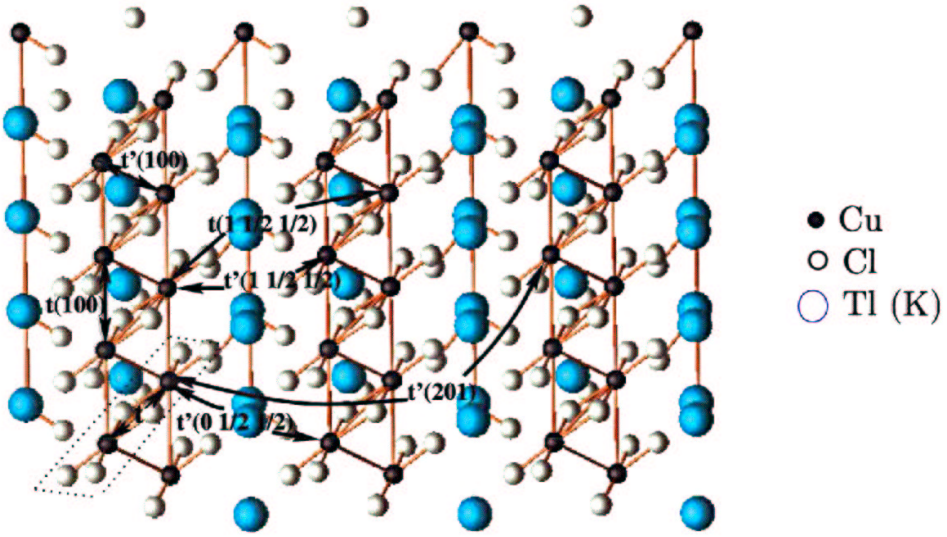
- What determines their different behavior?

- structural differences?
- role Tl $\leftrightarrow$ K ?

$\rightarrow$ *ab-initio*

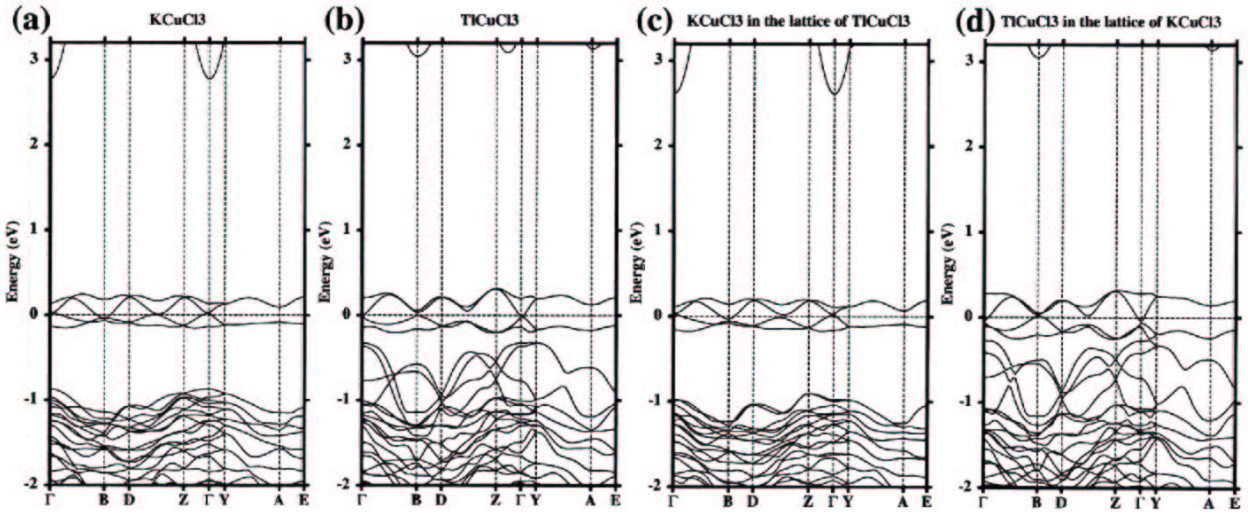
$KCuCl_3$ and $TlCuCl_3$ - Structure

Coupled two-leg s=1/2 Cu^{2+} ladders separated by Tl^+ (K^+) ions



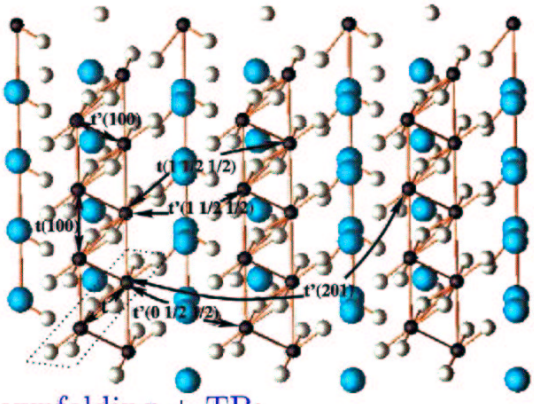
$KCuCl_3$ and $TlCuCl_3$ - Band Structure

- Four narrow bands close to EF formed by Cu $d_{x^2-y^2}$ orbitals admixed with Cl p.



- Change of lattice parameters has a minor effect on the band structure ((a) ↔ (c))
- Substitution of K^+ by Tl^+ in the same lattice has a significant effect ((a) ↔ (d))

$KCuCl_3$ and $TlCuCl_3$ - Effective Model



Downfolding + TB:

$TlCuCl_3$: **t=134 meV, t'$_{2,0,1}$=65 meV**, $t_{1,-1/2,1/2}$=32 meV, $t_{0,1/2,1/2}$= 8 meV

$KCuCl_3$: **t=116 meV, t'$_{2,0,1}$=37 meV**, $t_{1,-1/2,1/2}$= 4 meV, $t_{0,1/2,1/2}$= 5 meV

Comparison with INS analysis (Cavadini et al. ('01), Oosawa et al. ('02)):

$TlCuCl_3$: **J=5.7 meV, J$_{2,0,1}$=-1.5 meV**, $J_{1,-1/2,1/2}$=0.5 meV, $J_{0,1/2,1/2}$=-0.06 meV

$KCuCl_3$: **J=4.3 meV, J$_{2,0,1}$=-0.4 meV**, $J_{1,-1/2,1/2}$=0.3 meV, $J_{0,1/2,1/2}$=-0.003 meV

$KCuCl_3$ and $TlCuCl_3$ - Comparison

ab-initio:

- Structural differences minor effect.

  $TlCuCl_3$ lattice is compressed along a and
  enlarged in the bc plane with respect to $KCuCl_3$.

- Evident role of Tl^+ in Cu^{2+} - Cu^{2+} path.
  i.e
  larger hybridization effect between Cu $3d_{x^2-y^2}$ and
  Tl 6s and 6p energy states

- $TlCuCl_3$ stronger interdimer couplings than in $KCuCl_3$
  in agreement with predictions from **INS** experiments.

Summary and Conclusions

- Microscopic investigation (*ab-initio* + QMC) of $CaCuGe_2O_6$:

  - system with *longer-ranged* dominated exchange
  couplings (3NN) with ferromagnetic (1NN) interdimer couplings.

  - other examples: CaV_4O_9, $(VO)_2P_2O_7$

- Microscopic investigation (*ab-initio*) of $TlCuCl_3$ and $KCuCl_3$:

  - corroborates the coupled dimer behavior predicted by INS.

  - differences in the interdimer coupling related to contribution
  of Tl^+ to the chemical bonding between two Cu^{2+} ions.